Integrated Science Assessment for Oxides of Nitrogen and Sulfur — Ecological Criteria

🌱EPA

United States
Environmental Protection
Agency

EPA/600/R-08/082F
December 2008

Integrated Science Assessment for Oxides of Nitrogen and Sulfur – Ecological Criteria

Disclaimer

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Executive Summary

Introduction

This Integrated Science Assessment (ISA) is a synthesis and evaluation of the most policy-relevant science that forms the scientific foundation for the review of the secondary (welfare-based) national ambient air quality standards (NAAQS) for oxides of nitrogen (NO_X) and oxides of sulfur (SO_X). The Clean Air Act definition of welfare effects includes, but is not limited to, effects on soils, water, wildlife, vegetation, visibility, weather, and climate, as well as effects on man-made materials, economic values, and personal comfort and well-being. The current secondary NAAQS for SO_X, set in 1973, is a 3-hour average of 0.5 ppm[1] sulfur dioxide (SO_2), not to be exceeded more than once per year. The secondary NAAQS for NO_X is identical to the primary standard set in 1971: an annual average not to exceed 0.053 ppm nitrogen dioxide (NO_2). The current secondary NAAQS were set to protect against direct damage to vegetation by exposure to gas-phase SO_X or NO_X.

[1] 1ppm= 1000 ppb

Scope

This ISA is focused on ecological effects resulting from current deposition of compounds containing nitrogen (N) and sulfur (S). Acidification, N nutrient enrichment and effects of sulfate (SO_4^{2-}) on methylation of mercury (Hg) are highlighted in the document. The following figure illustrates the scope of the document.
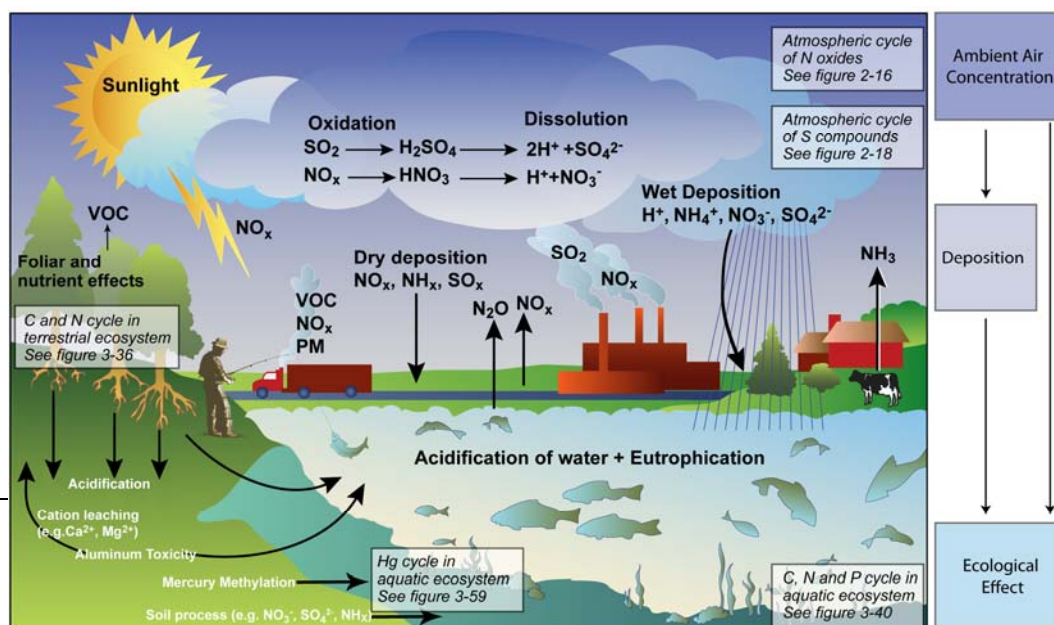
Both N and S contribute to acidification of ecosystems. This ISA considers several chemical forms that contribute to acidifying deposition, including gases and particles derived from SO_X, NO_X, and reduced nitrogen (NH_X).

Deposition of N contributes to N-nutrient enrichment and eutrophication. An assessment of the complex ecological effects of atmospheric N deposition requires consideration of many different chemical forms of reactive N (Nr). For this reason, the ISA includes evaluation of data on the most common reduced inorganic forms of N,

ammonia (NH_3) and ammonium (NH_4^+); on oxidized inorganic forms including nitric oxide (NO) and NO_2, nitrate (NO_3^-), nitric acid (HNO_3), and nitrous oxide (N_2O); and on organic N compounds including peroxyacetyl nitrate (PAN).

Other welfare effects addressed in the ISA include effects of SO_4^{2-} deposition on Hg methylation, along with evidence related to direct exposure to gas-phase NO_X and SO_X. The key conclusions of the ISA follow.

Current concentrations and deposition

Ambient annual NO_X and SO_X concentrations as reported in the routine national networks have decreased substantially owing to controls enacted since the 1970s. NO_X decreased ~35% in the period 1990-2005, to current annual average concentrations of ~15 ppb. Emissions of SO_X have been substantially reduced in recent years: annual average ambient SO_X concentrations have decreased ~50% in the period 1990–2005 and now stand at ~4 ppb for both aggregate annual and 24-hour average concentrations nation-wide.

Emitted NO_X, SO_X, NH_X and other pollutants can be transported vertically by convection into the upper part of the mixed layer on one day, then transported overnight in a layer of high concentrations. Once pollutants are lofted to the middle and upper troposphere, they typically have a much longer lifetime and, with the generally stronger winds at these altitudes, can be transported long distances from their source regions. The length scale of this transport is highly variable owing to differing chemical and meteorological conditions encountered along the transport path.

Numerical chemical-transport models (CTMs) are the prime tools for computing emissions and interactions among pollutants like NO_X, SO_X, and NH_X, their transport and transformation including production of secondary aerosols like ammonium nitrate and ammonium sulfate, the evolution of particle size distributions, the resulting atmospheric concentrations and the deposition of these pollutants to the surface. CTMs are driven by calculated emissions for primary species such as NO_X, SO_X, NH_3, and primary particulate matter, and by the meteorological fields produced by other numerical prediction models. As such, CTMs are the chief means of relating emitted pollutants with deposited ones.

The emitted, transported, and transformed pollutants reach the surface where they can have ecological effects largely through deposition. Direct and indirect wet and dry deposition to specific locations like watersheds depend on air pollutant emissions and concentrations in the airshed above the watershed, but the shape and areal extent of the airshed is quite different from that of the watershed owing to the transport and transformation of emitted pollutants described above.

Deposition is spatially heterogeneous across the U.S. In the years 2004-2006, routine na-

tional monitoring networks reported mean S deposition in the U.S. highest east of the Mississippi River with the highest reported deposition, 21 kg S/ha/yr, in the Ohio River Valley where most recording stations reported three-year averages for this period of more than 10 kg S/ha/yr. Numerous other stations in the eastern U.S. reported S deposition greater than 5 kg S/ha/yr. Data are sparse for the central U.S. between the 100th meridian and the Mississippi River; but, where available, deposition values there were lower than in most of the eastern U.S., ranging from 4 to over 5 kg S/ha/yr. Total S deposition in the U.S. west of the 100th meridian is lower than in the East or upper Midwest, owing to lower densities of high-emitting sources in the West. In the years 2004-2006, all routine recording stations in the West reported less than 2 kg S/ha/yr and many reported less than 1 kg S/ha/yr. S was primarily deposited in the form of wet SO_4^{2-}, followed by a smaller proportion of dry SO_2, and a much smaller proportion of dry SO_4^{2-}.

Expanding urbanization, agricultural intensification, and industrial production during the previous 100 years have produced a nearly 10-fold increase in total N deposited from the atmosphere compared to pre-industrial levels. NO_X, chiefly from fossil fuel combustion, often dominates total N pollution in the U.S. and comprises from 50 to 75% of current

4

total N atmospheric deposition. This wet and dry atmospheric N deposition is spatially heterogeneous, too, owing to the influence of meteorology, transport, precipitation patterns and land use.

For 2004–2006, routine national monitoring networks reported the highest mean N deposition totals in the U.S. in the Ohio River Valley, specifically in the states of Indiana and Ohio, with values greater than 9 kg N/ha/yr. N deposition was lower in other parts of the East, including the Southeast and in northern New England. In the central U.S., the highest N annual average deposition totals were on the order of 6 to 7 kg N/ha/yr. Measured concentrations and inferred deposition totals were dominated by wet NO_3^- and NH_4^+ species, followed by dry HNO_3, dry NH_4^+, and dry NO_3^-. NH_3 is not yet measured routinely in any national networks; however, smaller-scale intensive monitoring and numerical air quality modeling both indicate that it may account for more than 80% of the dry reduced N deposition total.

Although S and N deposition in most areas of the U.S. occurred as wet deposition, there were some exceptions, including parts of California where N deposition was primarily dry.

The thin coverage of monitoring sites in many locations, especially in the rural West, means that limited data exist on deposition totals in a large number of potentially sensitive places. Numerical modeling experiments can help fill in these data gaps and suggest that local and even regional areas of high ambient concentration and deposition exist where measured data are unavailable. Model-predicted values for N deposition in some regions of the Adirondacks in New York are greater than 20 kg N/ha/yr; other model estimates as high as 32 kg N/ha/yr have been made for a region of southern California, where more than half of that total was predicted to come from NO and NO_2.

The ISA concludes that the national-scale networks routinely monitoring N deposition are inadequate to characterize both the full range of reduced and oxidized forms of N deposition and the substantial regional heterogeneity across the landscape of the U.S.

Ecological effects of acidification

The effects of acidifying deposition on ecosystems have been well studied over the past several decades and vulnerable areas have been identified in the U.S. The wealth of data has led to the development of widely used ecological models for predicting soil and surface water acidification. Regional and ecosystem vulnerability to acidification results from inherent sensitivity and exposure to acidifying deposition.

Sensitivity of terrestrial and aquatic ecosystems to acidification from S and N deposition is regional and predominantly governed by surficial geology. Other factors contributing to the sensitivity of soils and surface waters to acidifying deposition include topography, vegetation, soil chemistry, land use, and hydrologic flowpath.

Soil acidification is a natural process, but is often accelerated by acidifying deposition, which can decrease concentrations of exchangeable base cations in soils. Biological effects of acidification on terrestrial ecosystems are generally attributable to Al toxicity and decreased ability of plant roots to take up base cations. Areas

most sensitive to terrestrial effects from acidifying deposition include forests in the Adirondack Mountains of New York, the Green Mountains of Vermont, the White Mountains of New Hampshire, the Allegheny Plateau of Pennsylvania, and high-elevation forest ecosystems in the central and southern Appalachians. While studies show some recovery of surface waters, there are widespread areas of ongoing depletion of exchangeable base cations in forest soils in the northeastern U.S., despite recent decreases in acidifying deposition.

In aquatic systems, consistent and coherent evidence from multiple studies of many species shows that acidification can cause the loss of acid-sensitive species, and that more species are lost with greater acidification. These effects are linked to changes in

The evidence is sufficient to infer a causal relationship between acidifying deposition and effects on:

(1) biogeochemistry related to terrestrial and aquatic ecosystems;

(2) biota in terrestrial and aquatic ecosystems.

surface water chemistry, including concentrations of SO_4^{2-}, NO_3^-, inorganic Al, and calcium (Ca^{2+}), surface water pH, sum of base cations, acid neutralizing capacity (ANC),

Examples of biogeochemical indicators of effects from acidifying deposition on ecosystems	
Ecosystem	Biogeochemical Indicator
Terrestrial	• Soil base saturation • Inorganic Aluminum concentration in soil water • Soil carbon-to-nitrogen ratio
Aquatic	• Sulfate • Nitrate • Base cations • Acid neutralizing capacity • Surface water inorganic Aluminum • pH

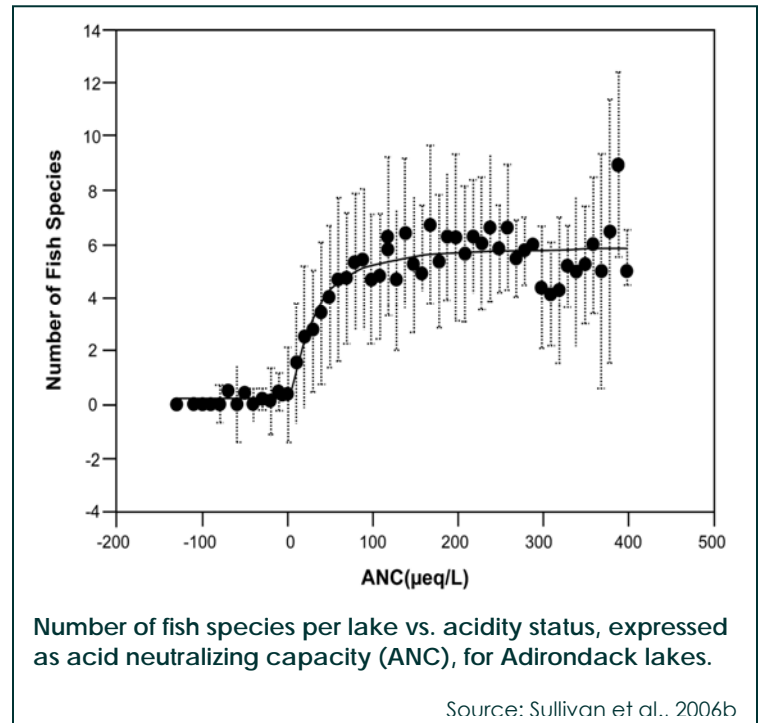| Examples of biological indicators of effects from acidifying deposition on ecosystems	
Indicator	Measure
Terrestrial Ecosystems	
Red Spruce	• Percent dieback of canopy trees
Sugar Maple	• Dead basal area, crown vigor index, fine twig dieback
Aquatic Ecosystems	
Fishes, zooplankton, crustaceans, rotifers	• Presence/absence • Fish condition factor • Biodiversity

and base cation surplus. These effects are also influenced by historical inputs to these systems. Decreases in ANC and pH and increases in inorganic Al concentration contribute to declines in zooplankton, macroin-

vertebrates, and fish species richness. These effects on species richness may also affect ecosystem services, such as biodiversity and cultural services such as fishing and tourism.

Although both N and S deposition can cause terrestrial and aquatic acidification, S deposition is generally the primary cause of chronic acidification, with secondary contributions from N deposition. Following decreases in S deposition in the 1980s and 1990s, one quarter to one third of the chronically acidic lakes and streams in the U.S. were no longer acidic during baseflow in the year 2000. A number of lakes and streams, however, remain acidic even though wet SO_4^{2-} deposition has decreased by as much as 30% since 1989. N deposition, which has also decreased in the years since 1990 in most places in the U.S. with routine monitoring, is the primary cause of episodic acidification which, despite its short duration, has been shown to cause long-term biological effects.

Many of the surface waters most sensitive to acidification in the U.S. are found in the

Northeast, the Southeast, and the mountainous West. In the West, acidic surface waters are rare and the extent of chronic surface water acidification that has occurred to date has been limited. However, episodic acidification does occur. In both the mountainous West and the Northeast, the most severe acidification of surface waters generally occurs during spring snowmelt. The ISA highlights evidence from two well-studied areas to provide more detail on how acidification affects ecosystems: The Adirondacks (NY) and Shenandoah National Park (VA). In the Adirondacks, the current rates of N and S deposition exceed the amount that would allow recovery of the most acid sensitive lakes. In the Shenandoah, past SO_4^{2-} has accumulated in the soil and is slowly released from the soil into stream water where it causes acidification, making parts of this region sensitive to even the current lower deposition loadings. Numerical models specifically calibrated to these locations and conditions suggest that the number of acidic streams will increase even under current deposition loads.

Number of fish species per lake vs. acidity status, expressed as acid neutralizing capacity (ANC), for Adirondack lakes.

Source: Sullivan et al., 2006b

Regions of the northern and eastern U.S. that contain appreciable numbers of lakes and streams sensitive to deleterious effects from acidifying deposition.

Source: Stoddard et al., 2003

Ecological effects of nitrogen deposition

There are many well-studied effects of N deposition on ecosystems and some vulnerable areas have been identified in the U.S. However, the full extent of ecosystem vulnerability is still unknown. Substantial empirical information from specific ecosystems and for specific endpoints is available, but given the complexity of the N cycle, a broadly applicable and well-tested predictive model of the ecological effects of N deposition is not yet available. Though the sensitivity of ecosystems to N deposition across the U.S. varies, a large body of evidence clearly demonstrates a relationship between N deposition and a broad range of ecological effects.

The contribution of N deposition to total N load varies among ecosystems. Atmospheric N deposition is the main source of new N to most headwater streams, high elevation lakes, and low-order streams. Atmospheric N deposition contributes to the total N load in terrestrial, wetland, freshwater, and estuarine ecosystems that receive N through multiple pathways (i.e. biological N-fixation, agricultural land runoff and waste water effluent). There are multiple biogeochemical indicators of N deposition effects.

The evidence is sufficient to infer a causal relationship between N deposition, to which NO_X and NH_X contribute, and the alteration of the following:

(1) biogeochemical cycling of N and carbon (C) in terrestrial, wetland, freshwater aquatic, and coastal marine ecosystems;

(2) biogenic flux of methane (CH_4), and N_2O in terrestrial and wetland ecosystems;

(3) species richness, species composition, and biodiversity in terrestrial, wetland, freshwater aquatic and coastal marine ecosystems.

Examples of biogeochemical indicators of effects from reactive N deposition on ecosystems	
Ecosystem	**Biogeochemical Indicator**
Terrestrial and Wetland	• NO_3^- leaching • Nitrification • Denitrification • N_2O emissions • CH_4 emissions • Soil C:N ratio • Foliar / plant tissue [N], C:N, N:magnesium, N:phosphorus • Soil water [NO_3^-] and [NH_4^+]
Freshwater and Estuarine	• Chlorophyll *a* • Water [NO_3^-] • Dissolved inorganic N • Dissolved oxygen • N:P

In terrestrial ecosystems, the onset of NO_3^- leaching is one of the best documented biogeochemical indicators that an ecosystem receives more N than it uses and is able to retain. N removal by ecosystems is a valuable ecosystem service regulating water quality. When atmospheric deposition of N impairs the ability of terrestrial and aquatic ecosystems to retain and remove N, NO_3^- leaching occurs and the degradation of water quality can occur. The onset of leaching was calculated to occur with deposition levels between 5.5 and 10 kg N/ha/yr for sensitive eastern forests. In the mixed conifer forests of the Sierra Nevada and San Bernardino mountains, the onset of increased NO_3^- leaching was calculated to be 17 kg N/ha/yr. Several studies in the Rocky Mountains indicate that the capacity of alpine catchments to retain N was exceeded at levels greater than 5-10 kg N/ha/yr.

N deposition alters the biogenic sources and sinks of two greenhouse gases (GHGs), CH_4 and N_2O, in terrestrial and wetland ecosystems, resulting in increased emissions to the atmosphere. Non-flooded upland soil is the largest biological sink and takes up about 6% of atmospheric CH_4. N addition decreases CH_4 uptake in coniferous and deciduous forests, and N addition increases

CH_4 production in wetlands. Soil is the largest source of N_2O, accounting for 60% of global emissions. N deposition increases the biogenic emission of N_2O in coniferous forest, deciduous forests, grasslands, and wetlands. Although N addition can cause a general stimulation of biogenic CH_4 and N_2O emissions from soils, it is difficult to generalize a dose-response relationship between the amount of N addition and the changes in GHG flux on a large heterogeneous landscape. This is because GHG production is influenced by multiple environmental factors (e.g., soil, vegetation and climate), which vary greatly over small spatial and temporal scales.

N is often the most limiting nutrient to growth in ecosystems. N deposition thus often increases primary productivity, thereby altering the biogeochemical cycling of C. N

Examples of biological indicators of effects from N deposition on ecosystems	
Ecosystem	Biological Indicators
Terrestrial and Wetlands	• Altered community composition, biodiversity and/or population decline. Taxa affected include: diatoms, lichen, mycorrhizae, moss, grasses and other herbaceous plants • Plant root: shoot ratio • Terrestrial plant biomass/production
Freshwater and Estuarine	• Phytoplankton biomass/production • Toxic or nuisance algae blooms • Submerged aquatic vegetation • Fauna from higher trophic levels

deposition can cause changes in ecosystem C budgets. However, whether N deposition increases or decreases ecosystem C-sequestration remains unclear. A limited number of studies suggest that N deposition may increase C-sequestration in some forests, but has no apparent effect on C-sequestration in non-forest ecosystems.

In terrestrial ecosystems, N deposition can accelerate plant growth and change C allocation patterns (e.g. shoot:root ratio), which can increase susceptibility to severe fires, drought, and wind damage. These effects have been shown in studies conducted in the western U.S. and Europe. The alteration of primary productivity can also alter competitive interactions among plant species. The increase in growth is greater for some species than others, leading to possible shifts in population dynamics, species composition, community structure, and in few instances, ecosystem type.

There are numerous sensitive terrestrial biota and ecosystems that are affected by N deposition. Acidophytic lichens are among the most sensitive terrestrial taxa to N deposition, with adverse effects occurring with exposures as low as 3 kg N/ha/yr in the Pacific Northwest and southern California. The onset of declining biodiversity in grass-lands has been estimated to be 5 kg N/ha/yr in Minnesota and the European Union. Altered community composition of alpine ecosystems in the Rocky Mountains and forest encroachment into temperate grasslands in Southern Canada is estimated to be 10 kg N/ha/yr.

The productivity of many freshwater ecosystems is N-limited. N deposition can alter species assemblages and cause eutrophication of aquatic ecosystems to the extent that N is the growth-limiting nutrient. In the Rocky Mountains, deposition loads of approximately 1.5-2 kg N/ha/yr are reported to alter species composition in the diatom communities in some freshwater lakes, an indicator of impaired water quality.

In estuarine ecosystems, N from atmospheric and non-atmospheric sources contributes to increased phytoplankton and algal productivity, leading to eutrophication. Estuary eutrophication is an ecological problem indicated by water quality deterioration, resulting in numerous adverse effects including hypoxic zones, species mortality, and harmful algal blooms. The calculated contribution of atmospheric deposition to total N loads can be as high as 72% in estuaries. The Chesapeake Bay is an example of a large, well-studied, and severely eutrophic estuary that is calculated to receive as much as 30% of its total N load from the atmosphere.

Examples of quantified relationships between deposition levels and ecological effects	
Kg N/ha/yr	Ecological effect
~1.5	Altered diatom communities in high elevation freshwater lakes and elevated N in tree leaf tissue high elevation forests in the western U.S.
3.1	Decline of some lichen species in the western U.S.
4	Altered growth and coverage of alpine plant species in the western U.S.
5	Onset of decline of species richness in grasslands of the U.S. and U.K.
5.5 - 10	Onset of nitrate leaching in Eastern forests of the U.S.
5-10	Multiple effects in tundra, bogs and freshwater lakes in Europe
5-15	Multiple effects in arctic, alpine, subalpine and scrub habitats in Europe

Other welfare effects: Mercury methylation

Hg is highly neurotoxic and once methylated, principally by S-reducing bacteria, it can be taken up by microorganisms, zooplankton and macroinvertebrates, and concentrated in higher trophic levels, including fish eaten by humans. In 2006, 3,080 fish consumption advisories were issued because of methylmercury (MeHg), and as of July 2007, 23 states had issued statewide advisories. The production of meaningful amounts of MeHg requires the presence of SO_4^{2-} and Hg, and where Hg is present, increased availability of SO_4^{2-} results in increased production of MeHg. The amount of MeHg produced varies with

The evidence is sufficient to infer a causal relationship between S deposition and increased Hg methylation in wetlands and aquatic environments.

oxygen content, temperature, pH, and supply of labile organic C. Watersheds with conditions known to be conducive to Hg methylation can be found in the northeastern U.S. and southeastern Canada, but biotic Hg accumulation has been widely observed in other regions that have not been studied as extensively, and where a different set of conditions may exist.

Other welfare effects: Direct phytotoxic

Acute and chronic exposures to SO_2 have phytotoxic effects on vegetation which include foliar injury, decreased photosynthesis, and decreased growth. Acute exposures to NO_2, NO, PAN, and HNO_3 cause plant foliar injury and decreased growth. However, the majority of studies have been performed at concentrations of these gas-phase species above current ambient conditions observed in the U.S. Consequently, there is little evidence that current concentrations of gas-phase S or N oxides are high enough to cause phytotoxic effects. One exception is that some studies indicate that current

> *The evidence is sufficient to infer a causal relationship between exposure to SO_2, NO, NO_2, PAN, and HNO_3 and injury to vegetation.*

HNO_3 concentrations may be contributing to the decline in lichen species in the Los Angeles basin.

Conclusion

The main effects of N and S pollution assessed in the ISA are acidification, N enrichment, and Hg methylation. Acidification of ecosystems is driven primarily by deposition resulting from SO_X, NO_X, and NH_X pollution. Acidification from the deposition resulting from current emission levels causes a cascade of effects that harm susceptible aquatic and terrestrial ecosystems, including slower growth and injury to forests and localized extinction of fishes and other aquatic species. In addition to acidification, atmospheric deposition of reactive N resulting from current NO_X and NH_X emissions along with other non-atmospheric sources (e.g., fertilizers and wastewater), causes a suite of ecological changes within sensitive ecosystems. These include increased primary productivity in most N-limited ecosystems, biodiversity losses, changes in C cycling, and eutrophication and harmful algal blooms in freshwater, estuarine, and ocean ecosystems. In some watersheds, additional SO_4^{2-} from atmospheric deposition increases Hg methylation rates by increasing both the number and activity of S-reducing bacteria. Methylmercury is a powerful toxin that can bioaccumulate to toxic amounts in food webs at higher trophic levels (e.g. bass, perch, otters, or kingfishers).

Contents

List of Tables

List of Figures

Acronyms and Abbreviations

ACCENT	Atmospheric Composition Change: the European Network of excellence
AIRMoN	Atmospheric Integrated Research Monitoring Network
AIRS	Atmospheric Infrared Sounder (instrument)
Al	aluminum
Al^{3+}	aluminum ion
Ali	inorganic aluminum
Al^{n+}	aluminum ion
Alo	organic aluminum
$Al(OH)_3$	aluminum hydroxide
ALSC	Adirondack Lake Survey Corporation
ALTM	Adirondack Long Term Monitoring
AMD	acid mine drainage
ANC	acid neutralizing capacity
AOD	aerosol optical depth
AQCD	Air Quality Criteria Document
AQEG	Air Quality Expert Group
AQI	Air Quality Index
AQS	Air Quality System (database)
Ar	argon
ARS	Agricultural Research Service
As	arsenic
ASI	Acid Stress Index
asl	above sea level
ATMOS	Atmospheric Trace Molecule Spectroscopy
ATTILA	type of Lagrangian model
AUSPEX	Atmospheric Utility Signatures, Predictions, and Experiments
AVIRIS	Airborne Visible and Infrared Imaging Spectrometer
Ba	barium
BBW	Bear Brook Watershed
BBWM	Bear Brook Watershed, Maine
BC	black carbon
BCS	base-cation surplus
BGC	Biogeochemical (model)
B-IBI	benthic index of biological integrity
BMPs	best management practices
BNF	bacterial nitrogen fertilization
Br	bromine
Br^-	bromine ion
Br_2	molecular bromine
BrCl	bromine chloride
BrO	bromine oxide
BUV	Backscatter Ultraviolet Spectrometer
BUVD	Beneficial Use Values Database
C	carbon; concentration

^{12}C	carbon-12, stable isotope of carbon
^{13}C	carbon-13, stable isotope of carbon
C_a	ambient air concentration
Ca	calcium
Ca^{2+}	calcium ion
CAA	Clean Air Act
CAAA	Amendments to the Clean Air Act
CAAAC	Clean Air Act Advisory Committee
$CaCl_2$	calcium chloride
$CaCO_3$	calcium carbonate
CALIPSO	Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (satellite)
$Ca(NO_3)_2$	calcium nitrate
$Ca(OH)_2$	calcium hydroxide
CAPMoN	Canadian Air and Precipitation Monitoring Network
$CaSO_4 \cdot 2H_2O$	gypsum
CASTNet	Clean Air Status and Trends Network
CB4	Carbon Bond 4 (model)
Cd	cadmium
CEC	cation exchange capacity
CENTURY	model that simulates carbon, nitrogen, phosphorus, sulfur, and water dynamics in the soil-plant system at monthly intervals over time scales of centuries and millennia
CFCs	chlorinated fluorocarbons
CG	cloud-to-ground (lightning flash)
Chl a	chlorophyll a
CH_4	methane
C_2H_4	ethene
C_2H_6	ethane
C_5H_8	isoprene
CH_3CHO	acetaldehyde
$CH_3C(O)$	acetyl radical
$CH_3C(O)OO$	acetyl peroxy radical
CH_2I_2	diiodomethane
CH_2O	formaldehyde
CH_3OOH	methyl hydroperoxide
CH_3-S-CH_3	dimethylsulfide, DMS
CH_3-S-H	methyl mercaptan
$(CH_3)_2SO$	dimethyl sulfoxide, DMSO
CH_3SO_3H	methanesulfonic acid
CH_3-S-S-CH_3	dimethyl disulfide, DMDS
C_i	interstitial air concentration
CL	critical load
Cl	chlorine
Cl^-	chlorine ion
Cl_2	molecular chlorine

CLaMS	type of Lagrangian model	EPT	Ephemeroptera-Plecoptera-Tricoptera (index)
CloudSat	NASA Earth observation satellite	ERP	Episodic Response Project
ClNO$_2$	nitryl chloride	ESA	European Space Agency
CMAQ	Community Multiscale Air Quality (modeling system)	EVRI	Environmental Valuation Reference Inventory
CMSA	consolidated metropolitan statistical area	F	flux
CO	carbon monoxide	F$^-$	fluorine ion
CO$_2$	carbon dioxide	FAB	First-order Acidity Balance model
CO$_3^-$	carbonate	FACE	free-air CO$_2$ enrichment (studies)
CONUS	continental U.S.	Fe	iron
CPUE	catch per unit effort	FePO$_4$	iron phosphate
CRREL	U.S. Army Cold Regions Research and Engineering Laboratory	FeS	iron sulfide
		F-factor	fraction of the change in mineral acid anions that is neutralized by base cation release
CS	Consumer surplus		
CS$_2$	carbon disulfide	FHM	Forest Health Monitoring
CSS	coastal sage scrub (ecosystem)	FIA	Forest Inventory and Analysis (program)
CTM	chemical transport model	FISH	Fish in Sensitive Habitats (project)
Cu	copper	FLEXPART	type of Lagrangian model
CV	contingent valuation	ForSAFE	three-component model using nitrogen, carbon cycling, and soil chemistry
CVM	contingent valuation method		
Δ, δ	delta, difference; change	FRM	Federal Reference Method
DayCent	model for daily biogeochemistry for forest, grassland, cropland, and savanna systems	FTIR	Fourier Transform Infrared Spectroscopy
		FW2	black carbon soot
DayCent-Chem	combination of DayCent-Chem and PHREEQC models	F$_x$	flux
		γN$_2$O$_5$	reaction potential coefficient for N$_2$O$_5$
DC	dichotomous choice	GAW	Global Atmospheric Watch (program)
DDRP	Direct Delayed Response Project	GCE	Goddard Cumulus Ensemble (model)
DDT	Damage Delay Time	GDP	gross domestic product
DECOMP	decomposition model based on soil-plant system dynamics	GEOS	Goddard Earth Observing System
		GEOS-Chem	Goddard Earth Observing System (with global chemical transport model)
DEP	Department of Environmental Protection		
DIC	dissolved inorganic carbon	GEOS-1DAS	Goddard Earth Observing System Data Assimilation System
DIN	dissolved inorganic nitrogen		
DMDS	dimethyl disulfide, CH3-S-S-CH3	GFED	Global Fire Emissions Database
DMS	dimethyl sulfide, CH3-S-CH3	GHG	greenhouse gas
DMSO	dimethylsulfoxide	GOES	Geostationary Operational Environmental Satellites
DNDC	Denitrification-Decomposition (model)		
DO	dissolved oxygen	GOME	Global Ozone Monitoring Experiment
DOC	dissolved organic carbon	g$_s$	stomatal conductance
DON	dissolved organic nitrogen	GtC	global ton carbon
EBB	East Bear Brook	Gton	global ton
EC	elemental carbon	GWP	global warming potential
EEAs	Essential Ecological Attributes	H	hydrogen; hydrogen atom
ELA	Experimental Lakes Area	^{2}H	hydrogen-2, deuterium, stable isotope of hydrogen
ELS	Eastern Lakes Survey		
EMAP	Environmental Monitoring and Assessment Program	H$^+$	proton, hydrogen ion; relative acidity
		ha	hectare
EMEFS	Eulerian Model Evaluation Field Study	HAPs	hazardous air pollutants
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe	HBEF	Hubbard Brook Experimental Forest
		HBES	Hubbard Brook Ecosystem Study
		HBN	Hydrologic Benchmark Network
EMF	ectomycorrhizal fungi	HC	hydrocarbon
EOS	Earth Observation System	HCHO	formaldehyde
EPA	U.S. Environmental Protection Agency	HCl	hydrochloric acid

Hg	mercury
HNO$_2$, HONO	nitrous acid
HNO$_3$, HOONO	nitric acid
HNO$_4$	pernitric acid
HO$_2$	hydroperoxyl radical
H$_2$O$_2$	hydrogen peroxide
HO$_2$NO$_2$	peroxynitric acid
HOBr	hypobromous acid
HOCl	hypochlorous acid
HOX	hypohalous acid
HP	hedonic pricing
HSO$_3^-$	bisulfate ion
HSO$_4^-$	sulfuric acid ion
H$_2$S	hydrogen sulfide
H$_2$SO$_3$	sulfurous acid
H$_2$SO$_4$	sulfuric acid
hν	photon with energy at wavelength ν
I	iodine
I$_2$	molecular iodine
IA	Integrated Assessment
IADN	Integrated Atmospheric Monitoring Deposition Network
IC	intracloud (lightning flash)
ILWAS	Integrated Lake-Watershed Acidification Study
IPC	International Cooperative Programme
IEc	Industrial Economicsym
IIASA	International Institute for Applied Systems Analysis
IMPROVE	Interagency Monitoring of Protected Visual Environments
INO$_3$	iodine nitrate
INTEX-NA	Intercontinental Chemical Transport Experiment - North America
IO	iodine oxide
IPCC	Intergovernmental Panel on Climate Change
IPCC-AR4	Intergovernmental Panel on Climate Change 4th Assessment Report
IPCC-TAR	Intergovernmental Panel on Climate Change 3rd Assessment Report
IQR	interquartile range
IR	infrared
ISA	Integrated Science Assessment
J	flux from a leaf, deposition flux (g/cm/second)
JPL	Jet Propulsion Laboratory
JRGCE	Jasper Ridge Global Climate Change Experiment
K	potassium
K$^+$	potassium ion
Ka	dissociation constant
Kb	dissociation constant
KH	Henry's Law constant in M/atm (M•atm^{-1})
KNO$_3$	potassium nitrate
K$_w$	ion product of water

LAF	Lake Acidification and Fisheries
LAR	leaf-area ratio
LB	laboratory bioassay
LC$_{0.01}$	lethal concentration at which 0.01% of exposed animals die
LD$_{33}$	lethal dose at which 33% of exposed animals die
LDH	lactic acid dehydrogenase
LIDAR	Light Detection and Ranging (remote sensing system)
LIF	laser-induced fluorescence
LIMS	Limb Infrared Monitor of the Stratosphere
LOD	limit of detection
LP	long-path
LRTAP	Long Range Transport of Air Pollution
LTER	Long-Term Ecological Research (program)
LTM	Long-Term Monitoring (project)
M	air molecule
MA	Millennium Ecosystem Assessment
MAGIC	Model of Acidification of Groundwater in Catchments (model)
MAHA	Mid-Atlantic Highlands Assessment of streams
MAQSIP	Multiscale Air Quality Simulation Platform (model)
MAT	moist acidic tundra
MAX-DOAS	multiple axis differential optical absorption spectroscopy
MBL	marine boundary layer
MDN	Mercury Deposition Network
MeHg	methylmercury
MEM	model ensemble mean
µeq	microequivalent
Mg	magnesium
Mg^{2+}	magnesium ion
MIMS	membrane inlet mass spectrometry
MM5	National Center for Atmospheric Research/Penn State Mesoscale Model, version 5
Mn	manganese
MOBILE6	Highway Vehicle Emission Factor Model
MODIS	Moderate Resolution Imaging Spectroradiometer
MOPITT	Measurement of Pollution in the Troposphere
MOZAIC	Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft
MOZART	Model for Ozone and Related Chemical Tracers
MPAN	peroxymethacrylic nitrate
MSA	metropolitan statistical area
Mt	million tons
N	nitrogen
N, n	number of observations
^{14}N	nitrogen-14, stable isotope of nitrogen
^{15}N	nitrogen-15, stable isotope of nitrogen

N_2	molecular nitrogen; nonreactive nitrogen
NA	not available; insufficient data
Na	sodium
Na^+	sodium ion
NAAQS	National Ambient Air Quality Standards
NaCl	sodium chloride
NADP	National Atmospheric Deposition Program
Na_2MoO_4	sodium molybdate
NAMS	National Air Monitoring Stations
NANI	Net anthropogenic nitrogen inputs
NAPAP	National Acid Precipitation Assessment Program
NASQAN	National Stream Quality Accounting Network
NARSTO	program formerly known as North American Regional Strategy for Atmospheric Ozone
NAS	National Academy of Sciences
NASA	National Aeronautics and Space Administration
Na_2SO_4	sodium sulfate
NASQAN	National Stream Quality Accounting Network
NATTS	National Air Toxics Trends (network)
NAWQA	National Water Quality Assessment (program)
NCore	National Core Monitoring Network
NEE	net ecosystem exchange
NEG/ECP	New England Governors and Eastern Canadian Premiers
NEI	National Emissions Inventory
NEON	National Ecological Observatory Network
NEP	net ecosystem productivity
NFI	net factor income
NH_3	ammonia
NH_2	amino (chemical group)
NH_4^+	ammonium ion
NH_4Cl	ammonium chloride
NH_4NO_3	ammonium nitrate
$(NH_4)_2SO_4$	ammonium sulfate
NH_X	category label for NH_3 plus NH_4^+
NH_Y	total reduced nitrogen
Ni	nickel
NILU	Norwegian Institute for Air Research
NITREX	Nitrogen saturation Experiments
nitro-PAH	nitro-polycyclic aromatic hydrocarbon
NLCD	National Land Cover Data
NMOC	nonmethane organic compound
NO	nitric oxide
NO_2	nitrogen dioxide
NO_2^-	nitrite
NO_3^-	nitrate
N_2O	nitrous oxide
N_2O_5	dinitrogen pentoxide
NOAA	U.S. National Oceanic and Atmospheric Administration
NOAA-ARL	U.S. National Oceanic and Atmospheric Administration Air Resources Laboratory
NOAEL	no-observed-adverse-effect level
NOEC	no-observed-effect concentration
NO_X	sum of NO and NO_2
NO_Y	sum of NO_X and NO_Z; odd nitrogen species; total oxidized nitrogen
NO_Z	sum of all inorganic and organic reaction products of NO_X (HONO, HNO_3, HNO_4, organic nitrates, particulate nitrate, nitro-PAHs, etc.)
NPOESS	National Polar-orbiting Operational Environmental Satellite System
NPP	net primary production
NPS	National Park Service
N_r	reactive nitrogen
NRC	National Research Council
NS	nonsignificant
NSF	National Science Foundation
NSS	National Stream Survey
nss	non-sea salt
NSTC	National Science and Technology Council
NSWS	National Surface Water Survey
NTN	National Trends Network
NuCM	nutrient cycling model
O_2	molecular oxygen
O_3	ozone
^{16}O	oxygen-16, stable isotope of oxygen
^{18}O	oxygen-18, stable isotope of oxygen
^{19}O	oxygen-19, radioactive isotope of oxygen
OC	organic carbon
OCO	Orbiting Carbon Observatory
OCS	carbonyl sulfide
$O(^1D)$	electronically excited oxygen atom
OH	hydroxyl radical
OMI	Ozone Monitoring Instrument
$O(^3P)$	ground-state oxygen atom
P	phosphorus
P, p	probability value
P_1	1st percentile
P_5	5th percentile
P_{95}	95th percentile
P_{99}	99th percentile
PAHs	polycyclic aromatic hydrocarbons
PAMS	Photochemical Assessment Monitoring Stations
PAN	peroxyacetyl nitrate
PANs	peroxyacyl nitrates
PARASOL	Polarization and Anisotropy of Reflectances for Atmospheric Sciences coupled with Observations from a Lidar (satellite)
Pb	lead
PBL	planetary boundary layer
PC	payment card
PCBs	polychlorinated biphenyl compounds
pH	relative acidity

$P(HNO_3)$	production of nitric acid
PHREEQC	model for soil and water geochemical equilibrium
PIRLA	Paleoecological Investigation of Recent Lake Acidification (projects)
pK_a	dissociation constant
PM	particulate matter
$PM_{2.5}$	particulate matter with aerodynamic diameter of #2.5 μm
PM_{10}	particulate matter with aerodynamic diameter #10 μm
$PM_{10-2.5}$	particulate matter with aerodynamic diameter between 10 and 2.5 μm
PM-CAMx	Comprehensive Air Quality Model with extensions and with particulate matter chemistry
PnET	Photosynthesis and EvapoTranspiration (model)
PnET-BGC	Photosynthesis and EvapoTranspiration-Biogeochemical (model)
PnET-CN	Photosynthesis and EvapoTranspiration model of C, water, and N balances
PnET-N-DNDC	Photosynthesis and EvapoTranspiration-Denitrification-Decomposition (model)
pNO_3^-	particulate nitrate
$P(O_3)$	production of O_3
PO_4^-, PO_4^{3-}	phosphate
POPs	persistent organic pollutants
ppb	parts per billion
PPN	peroxypropionyl nitrate
ppt	parts per trillion
PRB	policy relevant background
PRE-STORM	Preliminary Regional Experiment for STORM
PROFILE	model using soil mineralogy as input
PS	producer surplus
pSO_4^{2-}	particulate sulfate
$P(SO_4^{2-})$	production of sulfate
Q	flow rate; discharge
Q_{10}	temperature coefficient
QAPP	Quality Assurance Project Plan
R	generic organic group attached to a molecule
R^2	coefficient of determination
r^2	correlation coefficient
Ra	aerodynamic resistance
Rb	boundary layer resistance
Rc	internal resistance
RADM	Regional Acid Deposition Model
RAMS	Regional Atmospheric Modeling System
RAPS	Regional Air Pollution Study
RCOO-s	strongly acidic organic anions
RC(O)OO	organic peroxy radical
RDT	Recovery Delay Time
REMAP	Regional Environmental Monitoring and Assessment Program
RH	relative humidity
RLTM	Regional Long-Term Monitoring
RMCC	Research and Monitoring Coordinating Committee
RMSE	root mean squared error
RO_2	organic peroxyl; organic peroxy
$RONO_2$	organic nitrate
RO_2NO_2	peroxynitrate
RP	revealed preferences
RR_x	lognormal-transformed response ratio
RuBisCO	ribulose-1,5-bisphosphate carboxylase/oxygenase
s	second
S	sulfur
^{32}S	sulfur-32, stable isotope of sulfur
^{34}S	sulfur-34, stable isotope of sulfur
^{35}S	sulfur-35, radioactive isotope of sulfur
SAA	sum of mineral acid anion concentrations
SAFE	Soil Acidification in Forest Ecosystems (model)
SAMAB	Southern Appalachian Man and the Biosphere (program)
SAMI	Southern Appalachian Mountains Initiative
SAO	Smithsonian Astrophysical Observatory
SAPRAC	Statewide Air Pollution Research Center
SBC	sum of base cation concentrations
SBUV	Solar Backscatter Ultraviolet Spectrometer
SC	safe concentration
SCAQS	Southern California Air Quality Study
SCIAMACHY	Scanning Imaging Absorption Spectrometer for Atmospheric Chartography
Se	selenium; standard error
SEARCH	Southeastern Aerosol Research and Characterization Study (monitoring program)
Si	silicon
SIP	State Implementation Plan
SJAQS	San Joaquin Valley Air Quality Study
SLA	specific leaf area
SLAMS	State and Local Air Monitoring Stations
SMART	Simulation Model for Acidification's Regional Trends (model)
SMB	Simple Mass Balance (model)
SO	sulfur monoxide
SO_2	sulfur dioxide
SO_3	sulfur trioxide
SO_3^{2-}	sulfite
SO_4^{2-}	sulfate ion
S_2O	disulfur monoxide
SONEX	Subsonics Assessment Ozone and Nitrogen Oxides Experiment
SOS	Southern Oxidant Study
SOS/T	State of Science/Technology (report)
SO_X	sulfur oxides
SP	stated preferences

SPARROW	SPAtially Referenced Regressions on Watershed Attributes (model)		WATERSN	Watershed Assessment Tool for Evaluating Reduction Scenarios for Nitrogen
Sr	strontium		WBB	West Bear Brook
^{86}Sr	strontium-86, stable isotope of strontium		WEBB	Water, Energy, and Biogeochemical Budgets
^{87}Sr	strontium-87, stable isotope of strontium		WFPS	water-filled pore space
SRB	sulfate-reducing bacteria		WGE	Working Group on Effects
SRP	soluble reactive phosphorus		WLS	Western Lakes Survey
SSWC	Steady State Water Chemistry (model)		WMO	World Meteorological Organization
STE	stratospheric-tropospheric exchange		WMP	Watershed Manipulation Project
STN	Speciation Trends Network		WSA	Wadeable Stream Assessment (survey)
SUM06	seasonal sum of all hourly average concentrations ≥ 0.06 ppm		wt %	percent by weight
SVOC	semivolatile organic compound		WTA	willingness-to-accept
SWAS	Shenandoah Watershed Study		WTP	willingness-to-pay
T, τ	tau, atmospheric lifetime		XNO_3	nitrate halogen-X salt
T	time; duration of exposure		XO	halogen-X oxide
TAF	Tracking and Analysis Framework (model)		Zn	zinc
T_{air}	air temperature		ZnO	zinc oxide
TAMM	Timber Assessment Market Model			
TAR	Third Assessment Report			
TC	total carbon; travel cost			
TCM	travel cost method			
TDLAS	Tunable Diode Laser Absorption Spectrometer			
Tg	teragram			
TIME	Temporally Integrated Monitoring of Ecosystems (program)			
TN	total nitrogen			
TOMS	Total Ozone Mapping Spectrometer			
TOR	tropospheric ozone residual			
TP	total phosphorus			
TRACE-P	Transport and Chemical Evolution over the Pacific			
TSI	timber-stand improvement			
TSS	total suspended solids			
T_{water}	water temperature			
UMD-CTM	University of Maryland Chemical Transport Model			
UNECE	United Nations Economic Commission for Europe			
USDA	U.S. Department of Agriculture			
USFS	U.S. Forest Service			
USGS	U.S. Geological Survey			
UV	ultraviolet			
UV-A	ultraviolet radiation of wavelengths from 320 to 400 nm			
UV-B	ultraviolet radiation of wavelengths from 280 to 320 nm			
V_d	deposition rate, deposition velocity (cm/s)			
VOC	volatile organic compound			
VSD	Very Simple Dynamic (soil acidification model)			
VTSSS	Virginia Trout Stream Sensitivity Study			
WARMS	Waterfowl Acidification Response Modeling System			

Authors, Contributors, Reviewers

Authors

Dr. Tara Greaver (NO_X and SO_X Project Manager)—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Jeffrey R. Arnold—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Jill S. Baron—U.S. Geological Survey, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins CO

Dr. Jana Compton—National Health and Environmental Effects Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Corvallis, OR

Dr. Bernard J. Cosby, Jr.—Department of Environmental Sciences, University of Virginia, Charlottesville, VA

Dr. Ila Cote—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Ms. Rebecca Daniels— National Health and Environmental Effects Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Jean-Jacques B. Dubois—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Christine L. Goodale—Department of Ecology and Evolutionary Biology, Cornell University, Ithaca, NY

Dr. Alan T. Herlihy—Department of Fisheries & Wildlife, Oregon State University, Corvallis, OR

Dr. Jeffrey D. Herrick—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Alan J. Krupnick—Resources for the Future, Washington, DC

Dr. Kathleen Fallon Lambert—Ecologic: Analysis and Communications, Woodstock, VT

Dr. Gregory B. Lawrence—U.S. Geological Survey Troy, NY

Dr. Lingli Liu—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Todd C. McDonnell—E&S Environmental Chemistry, Inc., Corvallis, OR

Dr. Kristopher Novak—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Joseph Pinto—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Mary A. Ross—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Mr. Rich Scheffe—Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Juha Siikamaki—Resources for the Future, Washington, DC

Dr. Timothy J. Sullivan—E&S Environmental Chemistry, Inc., Corvallis, OR

Dr. Helga Van Miegroet—Department of Wildland Resources, Department of Watershed Sciences, Utah State University, Logan, UT

Dr. Paul F. Wagner—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Contributors

Dr. Robin L. Dennis—National Effects Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Russell Dickerson—Dept. of Atmospheric and Oceanic Sciences, University of Maryland, College Park, MD

Dr. Tina Fan— Environmental and Occupational Health Sciences Institute/ University of Medicine and Dentistry: New Jersey, Piscataway, NJ

Dr. Arlene Fiore—Geophysical Fluid Dynamics Laboratory/NOAA, Princeton, NJ

Dr. Larry Horowitz—Geophysical Fluid Dynamics Laboratory/NOAA, Princeton, NJ

Dr. William Keene—Dept. of Environmental Sciences, University of Virginia, Charlottesville, VA

Dr. Randall Martin—Dept. of Physics, Dalhousie University, Halifax, Nova Scotia, Canada

Dr. William Munger—Center for Earth and Planetary Physics, Harvard University, Cambridge, MA

Dr. Sandy Sillman—Dept. of Atmospheric and Oceanic Sciences, University of Michigan, Ann Arbor, MI

Dr. John T. Walker—National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Reviewers

Dr. Lawrence Band—Department of Geography, UNC Chapel Hill, Chapel Hill, NC

Dr. Tamara Blett—National Park Service, Lakewood, CO

Dr. Jana Compton—National Health and Environmental Effects Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Corvallis, OR

Dr. Russell Dickerson—Department of Chemistry & Chemical Physics, University or Maryland, College Park, MD

Dr. Dave A. Evans—Office of Policy, Economics, and Innovation, Washington, DC

Dr. Dale Evarts—Office of Air and Radiation, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Jacqueline Geoghegan—Department of Economics, Clark University, Worcester, MA

Dr. D. Alan Hansen—Electric Power Research Institute, Palo Alto, CA

Dr. Brooke Hemming—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Brian Heninger—Office of Policy, Economics, and Innovation, Washington, DC

Dr. William Hogsett—National Health and Environmental Effects Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Corvallis, OR

Dr. Bryan Hubbell—Office of Air and Radiation, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Gary Lear—Office of Air and Radiation, Office of Atmospheric Programs Washington, DC

Dr. John Lehrter—National Health and Environmental Effects Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Gulf Breeze, FL

Dr. Jason Lynch—Office of Air and Radiation, Office of Atmospheric Programs, U.S. Environmental Protection Agency, Washington, DC

Dr. William Malm—National Park Service, Fort Collins, CO

Dr. Steve McNulty—USDA Forest Service, Raleigh, NC

Ms. Connie Meacham—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Mr. Greg Miller—Office of Policy, Economics, and Innovation, Washington, DC

Dr. James Morris—Belle W. Baruch Institute for Marine & Coastal Sciences, University of South Carolina, Columbia, SC

Dr. William Munger—School of Engineering and Applied Science Harvard University, Cambridge, MA

Dr. Knute Nadelhoffer—University of Michigan Biological Station, Pellston, MI

Dr. Christine Negra—The Heinz Center, Washington, DC

Dr. William Orem—U.S. Geological Survey, Reston, VA

Dr. Ellen Porter—National Park Service, Denver, CO

Dr. Anne Rea—Office of Air and Radiation, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Paul Ringold—National Health and Environmental Effects Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Corvallis, OR

Ms. Vicki Sandiford—Office of Air and Radiation, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. William Showers—Dept. of Marine, Earth and Atmospheric Sciences, North Carolina State University, Raleigh, NC

Dr. Gail Tonnesen—University of California, Denver, CO

Dr. John Vandenberg (Division Director) —National Center for Environmental Assessment-RTP Division, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Lisa Wainger—TN and Associates, Hollywood, MD

Mr. Randy Waite—Office of Air and Radiation, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC

Ms. Debra Walsh (Deputy Division Director)— National Center for Environmental Assessment-RTP Division, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Shaun Watmough—Dept. of Environmental and Resource Studies, Trent University, Peterborough, Ontario

Ms. Lydia Wegman—Office of Air and Radiation, Office of Air Quality Planning and Standards U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Jason West—Dept. of Environmental Sciences & Engineering, University of North Carolina, Chapel Hill, NC

Dr. William Wilson—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Project Team

Executive Direction

Dr. Ila Cote (Acting Division Director)—National Center for Environmental Assessment-RTP Division, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. John Vandenberg (Division Director) —National Center for Environmental Assessment-RTP Division, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Ms. Debra Walsh (Deputy Division Director)— National Center for Environmental Assessment-RTP Division, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Mary A. Ross (Branch Chief)—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Scientific Staff

Dr. Tara Greaver (NO_X and SO_X Project Manager)—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Jeffrey R. Arnold—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Jean-Jacques Dubois—Oak Ridge Institute for Science and Education, Postdoctoral Research Fellow to National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Jeffrey D. Herrick—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Lingli Liu— Oak Ridge Institute for Science and Education, Postdoctoral Research Fellow to National Center for National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Kristopher Novak—National Center for Environmental Assessment, U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Paul F. Wagner—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Technical Support Staff

Ms. Ellen Lorang—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Ms. Connie Meacham—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Ms. Deborah Wales—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Mr. Richard Wilson—National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC

Clean Air Scientific Advisory Committee
NO_X and SO_X Secondary NAAQS Review Panel

Dr. Armistead (Ted) Russell* (Chair)—Georgia Power Distinguished Professor of Environmental Engineering, Environmental Engineering Group, School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA

Dr. Praveen Amar, Director, Science and Policy, Northeast States for Coordinated Air Use Management, Boston, MA

Dr. Andrzej Bytnerowicz, Senior Scientist, Pacific Southwest Research Station, USDA Forest Service, Riverside, CA

Ms. Lauraine Chestnut, Managing Economist, Stratus Consulting Inc., Boulder, CO

Dr. Ellis B. Cowling*, Emeritus Professor, Colleges of Natural Resources and Agriculture and Life Sciences, North Carolina State University, Raleigh, NC

Dr. Douglas Crawford-Brown*, Professor and Director, Department of Environmental Sciences and Engineering, Carolina Environmental Program, University of North Carolina at Chapel Hill, Chapel Hill, NC

Dr. Charles T. Driscoll, Jr., Professor, Environmental Systems Engineering, College of Engineering and Computer Science, Syracuse University, Syracuse, NY

Dr. Paul J. Hanson, Distinguished R&D Staff Member, Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN

Dr. Rudolf Husar, Professor and Director, Mechanical Engineering, Engineering and Applied Science, Center for Air Pollution Impact and Trend Analysis, Washington University, St. Louis, MO

Dr. Dale Johnson, Professor, Department of Environmental and Resource Sciences, College of Agriculture, University of Nevada, Reno, NV

Dr. Donna Kenski*, Director, Lake Michigan Air Directors Consortium, Rosemont, IL

Dr. Naresh Kumar, Senior Program Manager, Environment Division, Electric Power Research Institute, Palo Alto, CA

Dr. Myron Mitchell, Distinguished Professor and Director of Council on Hydrologic Systems Science, College of Environmental and Forestry, State University of New York, Syracuse, NY

Mr. Richard L. Poirot, Environmental Analyst, Air Pollution Control Division, Department of Environmental Conservation, Vermont Agency of Natural Resources, Waterbury, VT

Mr. David J. Shaw, Director, Division of Air Resources, New York State Department of Environmental Conservation, Albany, NY

Dr. Kathleen Weathers, Senior Scientist, Cary Institute of Ecosystem Studies, Millbrook, NY

* Members of the statutory Clean Air Scientific Advisory committee (CASAC) appointed by the United States (U.S.) Environmental Protection Agency (EPA) Administrator

Chapter 1. Introduction

This Integrated Science Assessment (ISA) synthesizes and evaluates the most policy-relevant science to help form the scientific foundation for the review of the secondary (welfare-based) National Ambient Air Quality Standards (NAAQS) for oxides of nitrogen (NO_X) and sulfur oxides (SO_X). The Clean Air Act (CAA) definition of welfare effects includes, but is not limited to, effects on soils, water, wildlife, vegetation, visibility, weather, and climate, as well as effects on materials, economic values, and personal comfort and well-being.

The intent of the ISA, according to the CAA, is to "accurately reflect the latest scientific knowledge expected from the presence of [a] pollutant in ambient air" (U.S. Code, 1970a, 1970b). It includes scientific research from atmospheric sciences, exposure and deposition, biogeochemistry, hydrology, soil science, marine science, plant physiology, animal physiology, and ecology conducted at multiple scales (e.g., population, community, ecosystem, landscape levels). Key information and judgments formerly found in the Air Quality Criteria Documents (AQCDs) for NO_X and SO_X are included; Annexes provide a more detailed discussion of the most pertinent scientific literature. Together, the ISA and Annexes serve to update and revise the last NO_X and SO_X AQCDs that were published in 1993 and 1982, respectively.

As discussed in the *Integrated Plan for the Review of the Secondary NAAQS for Nitrogen Dioxide and Sulfur Dioxide* (U.S. EPA, 2007a) a series of policy-relevant questions frames this review of the scientific evidence used to provide a scientific basis for evaluation of the secondary NAAQS for NO_2 (0.053 parts per million [ppm], annual average) and SO_2 (0.5 ppm, 3-h average). The framing questions considered are:

1. What are the known or anticipated welfare effects influenced by ambient NO_X and SO_X? For which effects is there sufficient information available to be useful as a basis for considering distinct secondary standards?

2. What is the nature and magnitude of ecosystem responses to NO_X and SO_X that are understood to have known or anticipated adverse effects? What is the variability associated with these responses (including ecosystem type, climatic conditions, environmental effects, and interactions with other environmental factors and pollutants)?

3. To what extent do the current standards provide the requisite protection for the public welfare effects associated with NO_X and SO_X?

4. Which biotic species are most vulnerable to the adverse effects of NO_X and SO_X air pollution? How is adversity defined?

5. What ecosystems are most sensitive to NO_X and SO_X pollution?

6. How does NO_X and SO_X pollution impact ecosystem services?

7. What are the most appropriate spatial and temporal scales to evaluate impacts on ecosystems?

8. What is the relationship between ecological vulnerability to NO_X and SO_X pollution and variations in current meteorology or gradients in climate?

1.1. Scope

The U.S. EPA is integrating the science assessment for these two criteria air pollutants due to their combined effects on atmospheric chemistry, deposition processes, and public welfare effects. The focus of

this assessment is primarily on effects related to the deposition of nitrogen (N)- and sulfur (S)-containing compounds. Ecological effects from acidification and N-nutrient enrichment have been studied most extensively in the ecological literature. An assessment of the complex ecological effects of N deposition requires consideration of multiple forms of N. Thus, this assessment includes evaluation of data on inorganic reduced forms of N (e.g., ammonia [NH_3] and ammonium ion [NH_4^+]), inorganic oxidized forms (e.g., NO_X, nitric acid [HNO_3], nitrous oxide [N_2O], nitrate [NO_3^-]), and organic N compounds (e.g., urea, amines, proteins, nucleic acids). In addition to acidification and N-nutrient enrichment, other welfare effects related to deposition of N- and S-containing compounds are discussed, such as SO_X interactions with mercury (Hg) methylation. In addition, this assessment includes evidence related to direct ecological effects of gas-phase NO_X and SO_X since the direct effects of gas-phase SO_X on vegetation formed a primary basis for the initial establishment of the secondary NAAQS for SO_2. The contribution of gas-phase NO_X as greenhouse gases (GHG), particularly N_2O, is considered, chiefly in the response of soils to reactive nitrogen (N_r) enrichment.

A review of the particulate matter (PM) NAAQS is underway. Recent data on the welfare effects of airborne particulate NO_X and SO_X in the ambient air will be evaluated in the PM ISA. These effects include visibility impairment, soiling and damage to materials, and effects of ambient PM on climate. (For more information, see http://www.epa.gov/ttn/naaqs/standards/pm/s_pm_index.html.)

Gas-phase and particulate NO_X and SO_X compounds can affect ecosystems and alter numerous linked biogeochemical cycles. A simplified diagram of the combined NO_X and SO_X cycle is presented in Figure 1-1. The ISA includes additional figures that provide more detail on the interactions among biogeochemical cycles, and the locations of those figures are indicated in the diagram. These figures include atmospheric cycling, interactions between the N cycle and carbon (C), the N cycle and phosphorous (P), and the S cycle and Hg.
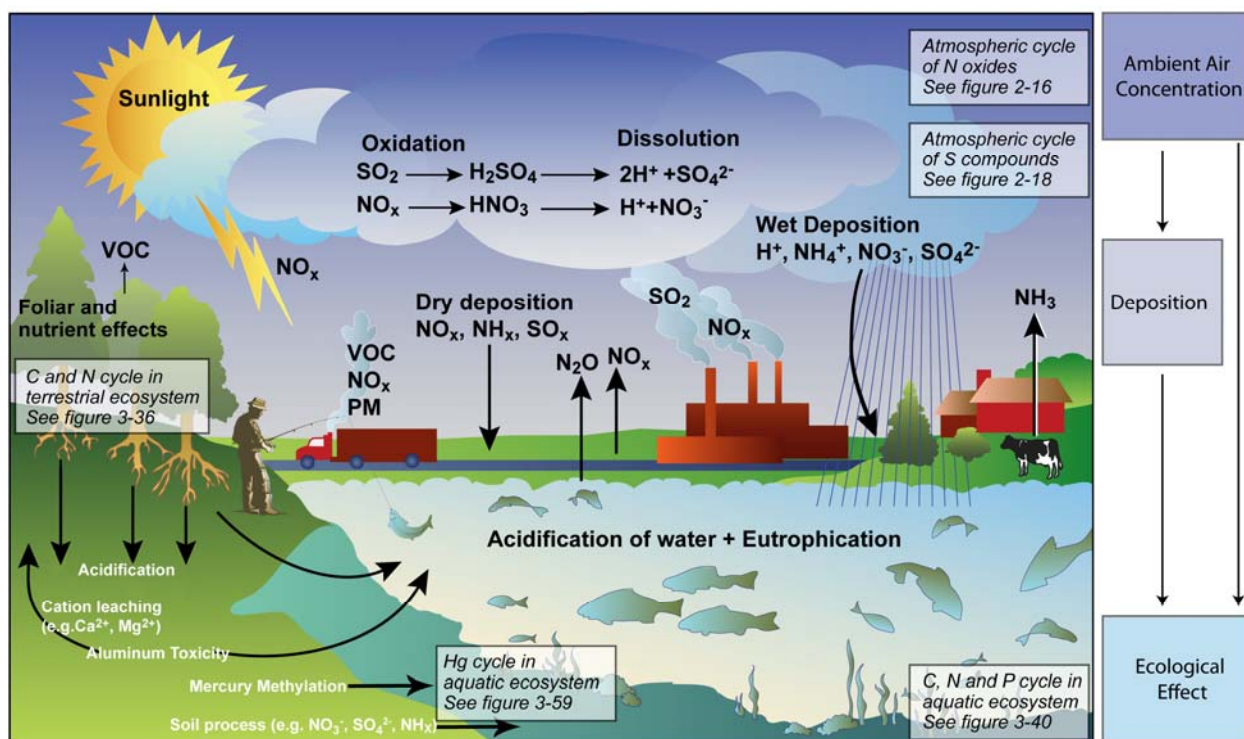
Figure 1-1. Biogeochemical cycles of NO_X and SO_X.

1.2. History of the NO$_X$ and SO$_X$ Review

Nitrogen Oxides

In 1971, U.S. EPA promulgated identical primary and secondary NAAQS for NO$_2$: 0.053 ppm as an annual average (36 FR 8186). The scientific bases for these NAAQS were provided in the AQCD for NO$_X$ (U.S. EPA, 1971).

In 1984, U.S. EPA proposed to retain these standards (49 FR 6866), and after the public comment period, finalized that decision in 1985 (50 FR 25532); the scientific basis for this review was provided by the 1982 AQCD for NO$_X$ (U.S. EPA, 1982a).

In 1991, U.S. EPA released an updated draft AQCD for the Clean Air Scientific Advisory Committee (CASAC) and public review and comment (56 FR 59285). CASAC reviewed the document and concluded it "provides a scientifically balanced and defensible summary of current knowledge of the effects of this pollutant and provides an adequate basis for U.S. EPA to make a decision as to the appropriate NAAQS for NO$_2$" (Wolff, 1993).

The U.S. EPA also prepared a draft Staff Paper that summarized and integrated the key studies and scientific evidence contained in the revised AQCD and identified the critical elements to be considered in the review of the NO$_2$ NAAQS. In September 1995, U.S. EPA finalized the Staff Paper, *Review of the National Ambient Air Quality Standards for Nitrogen Dioxide: Assessment of Scientific and Technical Information* (U.S. EPA, 1995b). The Administrator made a final determination that no revisions to the primary and secondary NAAQS for NO$_2$ were appropriate at that time (61 FR 52852, October 8, 1996). The level for both the existing primary and secondary NAAQS for NO$_2$ remains 0.053 ppm (equivalent to 100 micrograms per cubic meter of air [μg/m^3]) in annual arithmetic average, calculated as the arithmetic mean of the 1-h NO$_2$ concentrations.

Sulfur Oxides

Based on the 1970 SO$_X$ AQCD (U.S. Department of Health, Education and Welfare, 1970), U.S. EPA promulgated primary and secondary NAAQS for SO$_2$, under Section 109 of the CAA on April 30, 1971 (36 FR 8186). The secondary standard was set at 0.02 ppm in an annual arithmetic mean and a 3-h average of 0.5 ppm, not to be exceeded more than once per year. These standards were established solely based on vegetation effects evidence. In 1973, revisions made to Chapter 5 "Effects of Sulfur Oxide in the Atmosphere on Vegetation" of the SO$_X$ AQCD (U.S. EPA, 1973), indicated that it could not properly be concluded that the reported vegetation injury resulted from the average SO$_2$ exposure over the growing season rather than from short-term peak concentrations. U.S. EPA, therefore, proposed (38 FR 11355) and then finalized a revocation of the annual mean secondary standard (38 FR 25678).

In 1979, U.S. EPA announced that it was revising the SO$_X$ AQCD concurrently with the PM review and would produce a combined PM SO$_X$ AQCD. Following review of the draft revised criteria document in August 1980, CASAC concluded acidic deposition was a topic of extreme scientific complexity because of the difficulty in establishing firm quantitative relationships among (a) emissions of relevant pollutants (e.g., SO$_2$ and NO$_X$), (b) formation of acidic wet and dry deposition products, and (c) effects on terrestrial and aquatic ecosystems. CASAC also noted that acidic deposition involves, at a minimum, several different criteria pollutants (i.e., SO$_X$, NO$_X$, and the fine particulate fraction of suspended particles). CASAC recommended that any document on this subject should address both wet and dry deposition, because dry deposition was believed to account for at least half of the total acid deposition problem.

The U.S. EPA proposed not to revise the existing primary and secondary standards on April 26, 1988 (53 FR 14926). Regarding the secondary SO$_2$ NAAQS, the U.S. EPA Administrator concluded that based upon then-current scientific understanding of the acidic deposition problem, it would be premature and unwise to prescribe any regulatory control program at that time, and when the fundamental scientific uncertainties had been reduced through ongoing research efforts, U.S. EPA would draft and support an

appropriate set of control measures. On May 22, 1996, U.S. EPA's final decision, that revisions of the NAAQS for SO$_X$ were not appropriate at that time, was announced in the Federal Register (61 FR 25566).

Acidic Deposition Assessments

Based upon their conclusions from the AQCD review discussed above, CASAC recommended that a separate, comprehensive document on acidic deposition be prepared before any regulatory consideration for the control of acidic deposition. CASAC also suggested that a discussion of acidic deposition be included in the AQCDs for both NO$_X$ and PM-SO$_X$. Following CASAC closure on the criteria document for SO$_2$ in 1981, U.S. EPA's Office of Air Quality Planning and Standards (OAQPS) published a Staff Paper (U.S. EPA, 1982c); it did not, however, directly address this issue. U.S. EPA followed CASAC guidance and subsequently prepared the following documents: *The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Review Papers, Volumes I and II* (U.S. EPA, 1984a, 1984b) and *The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Document* (U.S. EPA, 1985). These documents, though they were not considered criteria documents and did not undergo CASAC review, represented the most comprehensive summary of relevant scientific information completed by the U.S. EPA at that point.

Assessment of the ecological effects of NO$_X$ and SO$_X$ has been conducted under the U.S. EPA acid precipitation control program. In the 1990 CAA Amendments (CAAA), Title IV was to reduce emissions of SO$_2$ and NO$_X$ from fossil fuel-burning power plants to protect ecosystems suffering damage from acid deposition and to improve air quality. The National Acid Precipitation Assessment Program (NAPAP) has periodically assessed and reported to Congress on the implementation of the Acid Rain Program, recent scientific knowledge surrounding acid deposition and its effects, and the reduction in acid deposition necessary to prevent adverse ecological effects. These assessments were to be reported to Congress quadrennially, beginning in 1996. The most recent in this series of reports is the *National Acid Precipitation Assessment Program Report to Congress: An Integrated Assessment* that was submitted to Congress in 2005 (NAPAP, 2005).

The 1990 CAAA also required U.S. EPA to conduct a study on the feasibility and effectiveness of an acid deposition standard or standards to protect "sensitive and critically sensitive aquatic and terrestrial resources." In 1995, the U.S. EPA submitted to Congress its report titled *Acid Deposition Standard Feasibility Study: Report to Congress* (U.S. EPA, 1995a) in fulfillment of this requirement. The Acid Deposition Standard Feasibility Study Report to Congress concluded establishing acid deposition standards for S and N deposition may at some point in the future be technically feasible although appropriate deposition loads for these acidifying chemicals could not defined with reasonable certainty at that time.

1.3. History of the Current Review

U.S. EPA's National Center for Environmental Assessment in Research Triangle Park, NC announced the official initiation of the current periodic review of air quality criteria for NO$_X$ on December 9, 2005 (70 FR 73236), and for SO$_X$ on May 15, 2006 (71 FR 28023), with a call for information. A workshop to inform the Agency's review of the secondary standards for these two pollutants was held on July 17-19, 2007 (72 FR 11960). The first ISA external review draft was published in December 2007 (72 FR 72719) and reviewed by CASAC at a public meeting on April 2-3, 2008. The second ISA external review draft was published in August 2008 (73 FR 46908) and reviewed by the CASAC at a public meeting on October 1-2, 2008. This final ISA (December 2008) includes revisions to address comments from CASAC and the public.

1.4. Development of the Integrated Science Assessment

An extensive search and review of the literature is the initial step in preparing the ISA. Additional publications were identified by U.S. EPA scientists in a variety of disciplines. In addition to peer-reviewed literature, previous U.S. EPA reports and materials identified in reviewing reference lists were examined. Further publications have been identified through the peer review process by CASAC, other experts, and the public. The focus of this ISA is on literature published since the 1993 NO_X AQCD and the 1982 SO_X AQCD. Key findings and conclusions from the 1993 and 1982 reviews are discussed in conjunction with recent studies. In addition, analyses of air quality and emissions data, and studies on atmospheric chemistry, transport, and fate of these emissions were scrutinized.

Emphasis was placed on studies that evaluated effects near ambient levels and studies that consider NO_X and SO_X as components of a complex mixture of air pollutants. Studies conducted in any country that contribute significantly to the knowledge base were considered for inclusion. In evaluating quantitative exposure-response relationships, emphasis was placed on findings from studies conducted in the U.S. and Canada as having ecological and climatic conditions most relevant for review of the NAAQS. In assessing the relative scientific quality of studies reviewed here and to assist in interpreting the findings, the following were considered:

1. To what extent are the aerometric data/exposure metrics of adequate quality and sufficiently representative to serve as credible exposure indicators?

2. Were the study populations well-defined and adequately selected to allow for meaningful comparisons between study groups?

3. Were the ecological assessment endpoints reliable and policy-relevant?

4. Were the statistical analyses used appropriately and properly performed and interpreted?

5. Were likely important covariates (e.g., potential confounders or effect modifiers) adequately controlled or taken into account in the study design and statistical analyses?

6. Were the reported findings consistent, biologically plausible, and coherent in terms of consistency with other known facts?

These guidelines provide benchmarks for evaluating various studies and for focusing on the highest quality studies in assessing the body of environmental effects evidence. Detailed critical analysis of all NO_X and SO_X environmental effects studies, especially in relation to the above considerations, is beyond the scope of the ISA and Annexes. Studies providing qualitative or quantitative information on exposure-response relationships for the environmental effects associated with current ambient air concentrations of NO_X and SO_X or deposition levels likely to be encountered in the U.S. were considered most relevant.

1.5. Organization of the Integrated Science Assessment

This ISA has four chapters. Chapter 1 provides background information on the purpose of the document, explains how policy-relevant scientific studies are identified and selected for inclusion, and introduces the causality framework used in U.S. EPA's assessments. Chapter 2 presents fundamental and applied atmospheric science data to support assessing the environmental exposures and effects associated with N and S oxides. Information relevant to the review of the welfare effects of NO_X and SO_X is integrated and evaluated in Chapter 3. Findings are organized into three categories: ecological effects of acidification, ecological effects of N nutrient pollution, and other welfare effects, which address several minor welfare effects, including gas-phase foliar toxicity and the role of S in Hg methylation. Finally, summary and conclusions are found in Chapter 4. Supplementary Annexes provide additional details.

1.6. Causality Framework

U.S. EPA uses a two-step approach to evaluate the scientific evidence on welfare effects of criteria pollutants, similar to the approach it uses for health effects. The steps address two general policy-relevant questions:

1. Given the total body of evidence, what, if any, are the welfare effects of NO_X and SO_X?

2. Can levels of exposure at which welfare effects of concern occur be defined?

The first step determines the weight of evidence in support of causation, and characterizes the strength of any resulting causal classification. The second step includes further evaluation of the quantitative evidence with respect to concentration-response relationships and the levels, duration, and pattern of exposures at which effects are observed.

The most widely cited aspects of causality in public health were articulated by Sir Austin Bradford Hill (1965), and have been widely used (e.g., IARC, 2006; Samet and Bodurow, 2008). Several adaptations of the Hill aspects have been used in aiding causality judgments in the ecological sciences (Adams, 2003; Buck et al., 2000; Collier, 2003; Fox, 1991; Gerritsen et al., 1998). Based on these adaptations, the U.S. EPA uses eight aspects in judging causality (see Table 1-1). The broad national scale of this assessment differs from the site-specific scale of ecological assessment for which applications of the Hill aspects have been published. The following aspects were developed to meet the scope of this ISA:

Table 1-1.   Aspects to aid in judging causality.

- **CONSISTENCY of the observed association.** The inference of causality is strengthened when the same association between agent and effect is observed across similar, independent studies. The reproducibility of findings constitutes one of the strongest arguments for causality. If there are discordant results among comparable investigations, possible reasons such as differences in exposure, confounding factors, and the power of the study are considered.

- **STRENGTH of the observed association.** The finding of large, well-demarcated effects increases confidence that the association is causal. However, given a truly causal agent, a small magnitude in the effect could follow from a lower level of exposure, a lower potency, or the prevalence of other agents causing similar effects. While large effects support causality, modest effects, therefore, do not preclude it.

- **SPECIFICITY of the observed association.** The effect is only observed after exposure to that agent, and the agent produces only that effect. Hill (1965), and subsequent authors, consider specificity a weak aspect. At the scale of ecosystems, as in epidemiology, complexity is such that single agents causing single effects, and single effects following single causes, are extremely unlikely. The absence of specificity cannot be used to exclude causality, especially at those scales. However, if specificity can be demonstrated, as in some laboratory or other experimental studies, it does add strong support to causality.

- **TEMPORALITY of the observed association.** Evidence of a temporal sequence between the introduction of an agent and appearance of the effect constitutes another argument in favor of causality.

- **GRADIENT.** A clear exposure-response relationship (e.g., increasing effects associated with greater exposure) strongly suggests cause and effect.

- **PLAUSIBILITY.** A credible ecological basis for the observed association adds strength to an inference of causality. A proposed mechanistic linking between an effect, and exposure to the agent, is an important source of support for causality, especially when data establishing the existence and functioning of those mechanistic links are available. A lack of biological understanding, however, is not sufficient reason to reject causality.

- **EXPERIMENTAL evidence.** Controlled exposure to the agents provides results that support the proposed causal relationship. The practical limits on control as the number of potential interacting factors increases are such that the most compelling experiments can only be conducted at the scale of a laboratory, growth chamber, or, at most, mesocosm. Therefore, since a judgment of causality derived from experimental evidence often cannot be extended very far beyond the scale at which the experiment was conducted, experimental evidence is generally only one element of the information that comes to bear in determining causality at the ecosystem, regional, or greater scales.

- **COHERENCE.** Given the scale and complexity of the environment and of ecosystems, determinations of causality are usually based on many lines of evidence, considered jointly. Evidence may be drawn from a variety of experimental approaches (e.g., greenhouse, laboratory, field) and subdisciplines of ecology (e.g., community ecology, biogeochemistry, paleological/historical reconstructions). The coherence of the available sources is a critical aspect of assessing the strength of a causal association. The coherence of evidence from various fields, and at various scales, greatly adds to the strength of an inference of causality.

While these aspects provide a framework for assessing the evidence, they are not simple formulas or fixed rules of evidence leading to conclusions about causality (Hill, 1965). The aspects in Table 1-1 cannot be used as a strict checklist, but rather to determine the weight of the evidence for inferring causality. In particular, the absence of one or more of the aspects does not automatically exclude a study from consideration (e.g., see discussion in CDC, 2004). For example, one cannot simply count the number of studies reporting statistically significant or nonsignificant results, and reach credible conclusions about the relative weight of the evidence and the likelihood of causality. Rather, the aspects are an important part of the assessment, whose goal is to produce an objective appraisal of the evidence, and is informed by peer and public comment and advice, including weighing of alternative views on controversial issues.

1.6.1. First Step: Determination of Causality

In this ISA, U.S. EPA evaluated publications available since the previous NAAQS reviews. This evaluation builds upon evidence available and conclusions drawn in the previous reviews to draw conclusions on the causal relationships between relevant pollutant exposures and welfare outcomes. A five-level hierarchy is used to classify the weight of evidence for causation, as assessed by the reviewing group with input from peers, CASAC, and the public. After integration of the evidence from all relevant disciplines or types of studies (laboratory studies, ecosystem experiments, simulation models and observational studies), the weight of evidence in support of causality is expressed using one of the five descriptors (see Table 1-2). In this multi-pollutant assessment, the effects may be due to a combination of pollutants (e.g., in acidifying deposition or N deposition). To the extent possible, U.S. EPA will identify the pollutants that are "significant contributing factors" to the relationship being evaluated.

Table 1-2.   Weight of evidence for causal determination.

Relationship	Description
Causal relationship	Evidence is sufficient to conclude that there is a causal relationship between relevant pollutant exposure and the outcome. Causality is supported when an association has been observed between the pollutant and the outcome in studies in which chance, bias, and confounding could be ruled out with reasonable confidence. Controlled exposure (laboratory or small- to medium-scale field studies) provides the strongest evidence for causality, but the scope of inference may be limited. Generally, determination is based on multiple studies conducted by multiple research groups, and evidence that is considered sufficient to infer a causal relationship is usually obtained from the joint consideration of many lines of evidence that reinforce each other.
Likely to be a causal relationship	Evidence is sufficient to conclude that there is a likely causal association between relevant pollutant exposures and the outcome. That is, an association has been observed between the pollutant and the outcome in studies in which chance, bias and confounding are minimized, but uncertainties remain. For example, field studies show a relationship, but suspected interacting factors cannot be controlled, and other lines of evidence are limited or inconsistent. Generally, determination is based on multiple studies in multiple research groups.
Suggestive of a causal relationship	Evidence is suggestive of an association between relevant pollutant exposures and the outcome, but chance, bias and confounding cannot be ruled out. For example, at least one high-quality study shows an association, but the results of other studies are inconsistent.
Inadequate to infer a causal relationship	The available studies are of insufficient quality, consistency or statistical power to permit a conclusion regarding the presence or absence of an association between relevant pollutant exposure and the outcome.
Suggestive of no causal relationship	Several adequate studies, examining relationships between relevant exposures and outcomes, are consistent in failing to show an association between exposure and the outcome at any level of exposure.

1.6.2. Second Step: Evaluation of Ecological Response

Beyond judgments regarding causality are questions relevant to characterizing exposure concentration response and risk to ecosystems (e.g., the levels and loads of pollution at which ecological effects occur). Such questions include:

1. What elements of the ecosystem (e.g., types, regions, taxonomic groups, populations, functions) appear to be affected, and/or are more susceptible to effects?

2. Under what exposure conditions (amount or concentration, duration and pattern) are effects seen?

3. What is the shape of the concentration-response or exposure-response relationship?

Causal and likely causal claims typically characterize how the probability of ecological effects changes in response to exposure. The ecological scale at which those quantitative considerations are valid is a concern. Initially, responses are evaluated within the range of observation, but ecological data for concentration-response analyses are often not available at the national or even regional scale. They are, therefore, typically presented site by site. Where greenhouse or animal ecotoxicological studies are available, they may be used to aid in characterizing concentration-response relations, particularly those relative to mechanisms of action and characteristics of sensitive biota.

Chapter 2. Source to Deposition

This chapter provides fundamental and applied atmospheric science data to support assessing the environmental exposures and effects associated with N and S oxides. More specifically, these data relate to N and S emissions sources and rates, atmospheric transformation and transport, total atmospheric loadings, measurement and modeling techniques, and deposition issues relevant to this review of the NAAQS. These data are prologue for the detailed descriptions of the evidence of environmental effects from N and S oxides that follow in Chapter 3, and a source of information to help interpret those effects when integrated with these data on atmospheric concentrations and exposures.

2.1. Introduction

As noted in Chapter 1, the definition of NO_X appearing in the NAAQS enabling legislation differs from the one used by atmospheric scientists and air quality control experts. The atmospheric sciences community defines NO_X as the sum of NO and NO_2. However, in the Federal Register Notice (FRN) (October 8, 1996) for the "National Ambient Air Quality Standards for NO_2: Final Rule" (61 FR 52852), the term "nitrogen oxides" was used to "describe the sum of NO, NO_2, and other oxides of nitrogen." This ISA uses the legal, rather than the technical definition; hence, the terms "oxides of nitrogen" and "nitrogen oxides" here refer to all forms of oxidized N compounds, including NO, NO_2, and all other oxidized N-containing compounds transformed from NO and NO_2.[1] Additionally, because some of the constituent members of the NO_X family of chemical species interact with particulate-phase chemical species and change phase themselves, the chemistry, concentrations, and deposition of particulate N compounds are also considered in this assessment.

Oxides of sulfur (SO_X) is defined here to include sulfur monoxide (SO), sulfur dioxide (SO_2 [the largest component of SO_X and the U.S. EPA Criteria Air Pollutant]), sulfur trioxide (SO_3), and disulfur monoxide (S_2O). Of these, only SO_2 is present in the lower troposphere at concentrations relevant for environmental considerations. Moreover, some gas-phase sulfur oxides interact with particles and change phase themselves, just as do some constituent members of the N family of gas-phase chemical species; hence, particulate-phase S compounds are also assessed here.

NH_3 is included in this ISA both because its oxidation can be a minor source of NO_X and because it is the precursor for ammonium ion (NH_4^+), which plays a key role in neutralizing acidity in ambient particles produced from NO_2 and SO_2 and in cloud, fog, and rain water. (NH_3 and NH_4^+ are conventionally grouped together under the category label NH_X.) Excess NH_3 is also an actor in nitrification of aqueous and terrestrial ecosystems, participating alone and together with NO_X in the N cascade (Galloway et al., 2003). Additionally, NH_3 is involved in the ternary nucleation of new particles and reacts with gas-phase HNO_3 to form ammonium nitrate (NH_4NO_3), a major component of N deposition in many areas of the contiguous U.S. (CONUS).

---

[1] This follows usage in the Clean Air Act, Section 108(c): "Such criteria [for oxides of nitrogen] shall include a discussion of nitric and nitrous acids, nitrites, nitrates, nitrosamines, and other carcinogenic and potentially carcinogenic derivatives of oxides of nitrogen." (U.S. Code 1970a) By contrast, within the air pollution research and control communities, the terms "oxides of nitrogen" and "nitrogen oxides" are restricted to refer only to the sum of NO and NO_2, and this sum is commonly abbreviated as NO_X. The category label used by this air pollution research and control community for the sum of all oxidized N compounds, including those listed in Section 108(c), is NO_Y.

2.2. Sources and Emissions of Tropospheric NO_X

Tropospheric NO_X emissions sources can be anthropogenic, resulting from human activity, or biogenic and natural, resulting from the activity of non-human organisms, though sometimes with the addition of human activities, as with production from livestock or agriculture, and from other smaller miscellaneous non-biological sources. However, anthropogenic sources contribute substantially more mass than biogenic ones. The anthropogenic and biogenic sources of NO_X are described in detail and their emissions totals are provided below.

2.2.1. Major Anthropogenic Sources

Anthropogenic NO_X emissions are dominated by fossil fuel combustion sources that release NO_X predominantly in the form of NO with variable amounts of NO_2. In 2002, anthropogenic NO_X emissions in the U.S. totaled 23.19 teragram/year (Tg/yr). Table 2-1 lists fractions and totals from anthropogenic NO_X sources collected for the 2002 National Emissions Inventory (NEI) (U.S. EPA, 2006a).

Table 2-1. Emissions of NO_X, NH_3, and SO_2 in the U.S. by source and category, 2002.

2002 Emissions (Tg/yr)	NO_X[1]	NH_3	SO_2	2002 Emissions (Tg/yr)	NO_X[1]	NH_3	SO_2
Total All Sources	23.19	4.08	16.87	Liquid Waste	0.01		
Fuel Combustion Total	9.11	0.02	14.47	Other	0.04		
Fuel Combustion Electrical Utilities	5.16	<0.01	11.31	Internal Combustion	1.15	<0.01	0.01
Coal	4.50	<0.01	10.70	Fuel Combustion Other	0.80	<0.01	0.63
Bituminous	2.90		8.04	Commercial / Institutional Coal	0.04	<0.01	0.16
Subbituminous	1.42		2.14	Commercial / Institutional Oil	0.08	<0.01	0.28
Anthracite & Lignite	0.18		0.51	Commercial / Institutional Gas	0.25	<0.01	0.02
Other	<0.01			Misc. Fuel Combust. (Exc. Resident.)	0.03	<0.01	0.01
Oil	0.14	<0.01	0.38	Residential Wood	0.03		<0.01
Residual	0.13		0.36	Residential Other	0.36		0.16
Distillate	0.01		0.01	Distillate Oil	0.06		0.15
Gas	0.30	<0.01	0.01	Bituminous/Subbituminous	0.26		<0.01
Natural	0.29			Other	0.04		<0.01
Process	0.01			Industrial Process Total	1.10	0.21	1.54
Other	0.05	<0.01	0.21	Chemical & Allied Product Mfg	0.12	0.02	0.36
Internal Combustion	0.17	<0.01	0.01	Organic Chemical Mfg	0.02	<0.01	0.01
Fuel Combustion Industrial	3.15	<0.01	2.53	Inorganic Chemical Mfg	0.01	<0.01	0.18
Coal	0.49	<0.01	1.26	Sulfur Compounds			0.17
Bituminous	0.25		0.70	Other			0.02
Subbituminous	0.07		0.10	Polymer & Resin Mfg	<0.01	<0.01	<0.01
Anthracite & Lignite	0.04		0.13	Agricultural Chemical Mfg	0.05	0.02	0.05
Other	0.13		0.33	Ammonium Nitrate/Urea Mfg.		<0.01	
Oil	0.19	<0.01	0.59	Other		0.02	
Residual	0.09		0.40	Paint, Varnish, Lacquer, Enamel Mfg	0.00		0.00
Distillate	0.09		0.16	Pharmaceutical Mfg	0.00		0.00
Other	0.01		0.02	Other Chemical Mfg	0.03	<0.01	0.12
Gas	1.16	<0.01	0.52	Metals Processing	0.09	<0.01	0.30
Natural	0.92			Non-Ferrous Metals Processing	0.01	<0.01	0.17
Process	0.24			Copper			0.04
Other	<0.01			Lead			0.07
Other	0.16	<0.01	0.15	Zinc			0.01
Wood/Bark Waste	0.11			Other			<0.01

2002 Emissions (Tg/yr)	NO_x[1]	NH_3	SO_2
Ferrous Metals Processing	0.07	<0.01	0.11
Metals Processing	0.01	<0.01	0.02
Petroleum & Related Industries	0.16	<0.01	0.38
Oil & Gas Production	0.07	<0.01	0.11
Natural Gas			0.11
Other			0.01
Petrol. Refineries & Related Industries	0.05	<0.01	0.26
Fluid Catalytic Cracking Units		<0.01	0.16
Other		<0.01	0.07
Asphalt Manufacturing	0.04		0.01
Other Industrial Processes	0.54	0.05	0.46
Agriculture, Food, & Kindred Products	0.01	<0.01	0.01
Textiles, Leather, & Apparel Products	<0.01	<0.01	<0.01
Wood, Pulp & Paper, Publish. Prods.	0.09	<0.01	0.10
Rubber & Misc. Plastic Products	<0.01	<0.01	<0.01
Mineral Products	0.42	<0.01	0.33
Cement Mfg	0.24		0.19
Glass Mfg	0.01		
Other	0.10		0.09
Machinery Products	<0.01	<0.01	<0.01
Electronic Equipment	<0.01	<0.01	<0.01
Transportation Equipment	<0.01		<0.01
Miscellaneous Industrial Processes	0.01	0.05	0.02
Solvent Utilization	0.01	<0.01	<0.01
Degreasing	<0.01	<0.01	<0.01
Graphic Arts	<0.01	<0.01	<0.01
Dry Cleaning	<0.01	<0.01	<0.01
Surface Coating	<0.01	<0.01	<0.01
Other Industrial	<0.01	<0.01	<0.01
Nonindustrial	<0.01		
Solvent Utilization	<0.01		
Storage & Transport	<0.01	<0.01	0.01
Bulk Terminals & Plants	<0.01	<0.01	<0.01
Petrol. & Petrol. Product Storage	<0.01	<0.01	<0.01
Petrol. & Petrol. Product Transport	<0.01	<0.01	<0.01
Service Stations: Stage II	<0.01		<0.01
Organic Chemical Storage	<0.01	<0.01	<0.01
Organic Chemical Transport	0.01		<0.01
Inorganic Chemical Storage	<0.01	<0.01	<0.01
Inorganic Chemical Transport	<0.01		<0.01
Bulk Materials Storage	0.01	<0.01	<0.01
Waste Disposal & Recycling	0.17	0.14	0.03
Incineration	0.06	<0.01	0.02
Industrial			
Other			<0.01
Open Burning	0.10	<0.01	<0.01
Industrial			<0.01
Land Clearing Debris			
Other			<0.01
Public Operating Treatment Works	<0.01	0.14	<0.01
Industrial Waste Water	<0.01	<0.01	<0.01
Treatment, Storage, Disposal Facility	<0.01	<0.01	<0.01
Landfills	<0.01	<0.01	<0.01
Industrial			<0.01
Other			<0.01
Other	<0.01	<0.01	<0.01
Transportation Total	12.58	0.32	0.76

2002 Emissions (Tg/yr)	NO_x[1]	NH_3	SO_2
Highway Vehicles	8.09	0.32	0.30
Light-Duty Gas Vehicles & Motorcycles	2.38	0.20	0.10
Light-Duty Gas Vehicles	2.36		0.10
Motorcycles	0.02		0.00
Light-Duty Gas Trucks	1.54	0.10	0.07
Light-Duty Gas Trucks 1	1.07		0.05
Light-Duty Gas Trucks 2	0.47		0.02
Heavy-Duty Gas Vehicles	0.44	<0.01	0.01
Diesels	3.73	<0.01	0.12
Heavy-Duty Diesel Vehicles	3.71		
Light-Duty Diesel Trucks	0.01		
Light-Duty Diesel Vehicles	0.01		
Off-Highway	4.49	<0.01	0.46
Non-Road Gasoline	0.23	<0.01	0.01
Recreational	0.01		
Construction	0.01		
Industrial	0.01		
Lawn & Garden	0.10		
Farm	0.01		
Light Commercial	0.04		
Logging	<0.01		
Airport Service	<0.01		
Railway Maintenance	<0.01		
Recreational Marine Vessels	0.05		
Non-Road Diesel	1.76	<0.01	0.22
Recreational	0.00		
Construction	0.84		
Industrial	0.15		
Lawn & Garden	0.05		
Farm	0.57		
Light Commercial	0.08		
Logging	0.02		
Airport Service	0.01		
Railway Maintenance	<0.01		
Recreational Marine Vessels	0.03		
Aircraft	0.09		0.01
Marine Vessels	1.11		0.18
Diesel	1.11		
Residual Oil			
Other			
Railroads	0.98		0.05
Other	0.32	<0.01	0.00
Liquefied Petroleum Gas	0.29		
Compressed Natural Gas	0.04		
Miscellaneous	0.39	3.53	0.10
Agriculture & Forestry	<0.01	3.45	<0.01
Agricultural Crops		<0.01	
Agricultural Livestock		2.66	
Other Combustion		0.08	0.10
Health Services			
Cooling Towers			
Fugitive Dust			
Other			
Natural Sources	3.10	0.03	

[1] Emissions are expressed in terms of NO_2. Note: Subcategory values may not sum to category totals due to rounding. Source: U.S. EPA (2006a)

Of this total, emissions from all types of transportation accounted for ~56% of NO_X, or 12.58 Tg, with on-road highway vehicles representing the major mobile source component, 8.09 Tg. Roughly one-half of these on-road emissions have diesel engine sources and one-half have gasoline engine sources. (Sawyer et al. [2000] reviewed in detail the factors associated with NO_X emissions by mobile sources.) The next largest source category, electric-generating utilities (EGUs), accounted for ~22%, or 5.16 Tg of total NO_X in 2002. Stationary engines, non-road vehicles, and industrial facilities also emit NO_X, but because they are fewer in number or burn less fuel, their mass contributions to total NO_X are less than transportation and EGUs.

The values in Table 2-1 are U.S. national averages and so may not reflect differences in the relative contributions of NO_X sources to ambient mass loadings at any particular location; hence, these values are not likely to be useful predictors of any particular localized environmental exposures to NO_X. As a partial refinement of scale, county-level NO_X emissions are depicted in Figure 2-1.[1] A further refinement appears in Figure 2-2, where the same 2001 NO_X emissions data are plotted as area-normalized intensities in tons per square mile. This normalized emissions intensity base is also used to show the separate contributions from EGUs and on-road mobile sources in Figures 2-3 and 2-4, respectively.
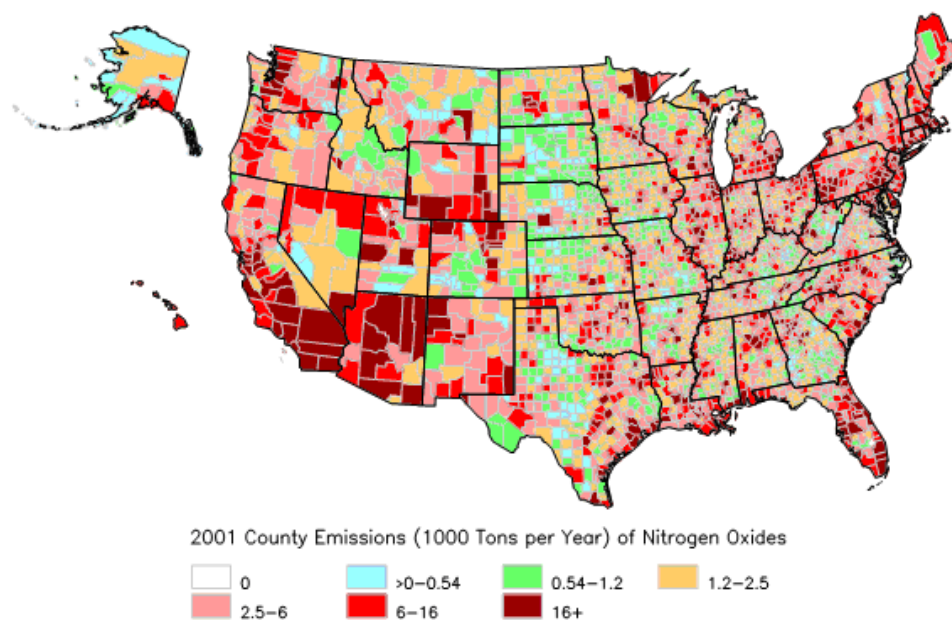
Source: U.S. EPA (2006a)

Figure 2-1.   2001 county-level total U.S. NO_X (NO and NO_2) emissions.[1]

---

[1] Range values: White, 0 or no reported value; Blue, from the smallest non-zero to the 10th percentile value; Green, from above the 10th to the 25th percentile; Yellow, from above the 25th to the 50th percentile; Pink, from above the 50th to the 75th percentile; Red, from above the 75th to the 90th percentile; Brown, from above the 90th percentile to the highest reported value.

2001 County Emissions Density (Tons per sq.mi.) of Nitrogen Oxides

☐ 0	>0–0.79	0.79–1.8	1.8–4.1
4.1–10	10–30	30+	
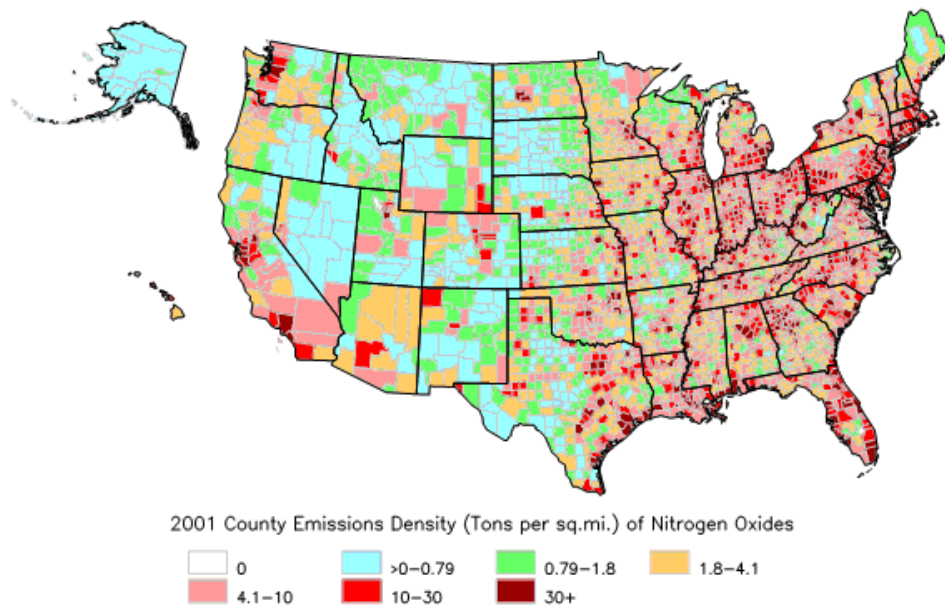
Source: US EPA Office of Air and Radiation, NEI Database

Thursday, July 10, 2008

Source: U.S. EPA (2006a)

Figure 2-2. **2001 county-level total U.S. NO$_X$ (NO and NO$_2$) emissions densities (tons per square mile).** [1]

2001 County Emissions Density (Tons per sq.mi.) of Nitrogen Oxides

☐ 0	>0–0.0022	0.0022–0.025	0.025–0.3
0.3–5.4	5.4–25	25+	
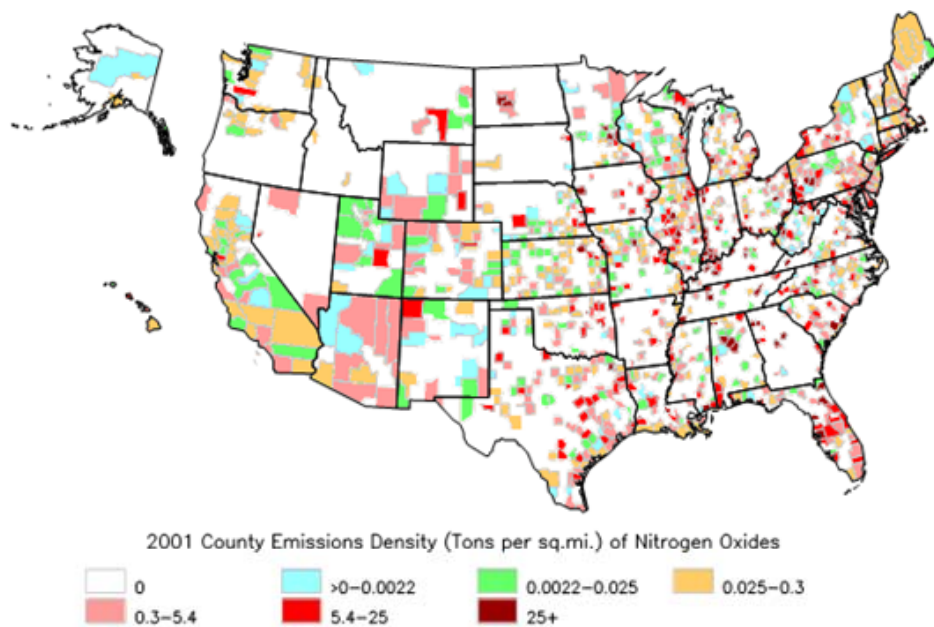
Source: U.S. EPA (2006a)

Figure 2-3. **2001 county-level total U.S. NO$_X$ (NO and NO$_2$) emissions densities (tons per square mile) from electric-generating utilities (EGUs).** [1]

---

[1] Range values: White, 0 or no reported value; Blue, from the smallest non-zero to the 10th percentile value; Green, from above the 10th to the 25th percentile; Yellow, from above the 25th to the 50th percentile; Pink, from above the 50th to the 75th percentile; Red, from above the 75th to the 90th percentile; Brown, from above the 90th percentile to the highest reported value.

2001 County Emissions Density (Tons per sq.mi.) of Nitrogen Oxides

☐ 0	▨ >0–0.2 ▨ 0.2–0.65 ▨ 0.65–1.7
▨ 1.7–4.1	▨ 4.1–10 ▨ 10+
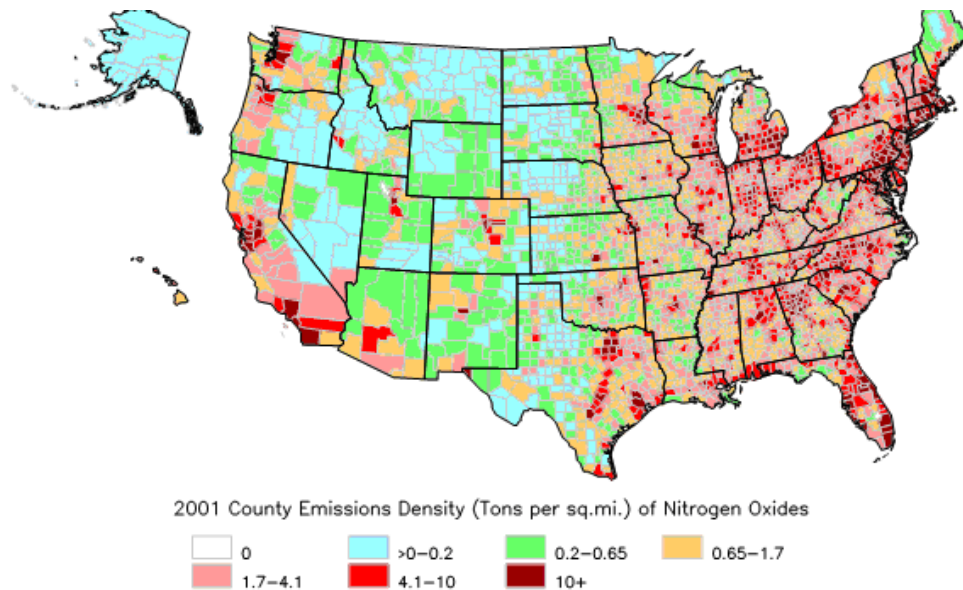
Figure 2-4. **2001 county-level total U.S. NO$_X$ (NO and NO$_2$) emissions densities (tons per square mile) from on-road mobile sources. [1]**

Emissions of NO$_X$ from combustion are derived from both fuel N and atmospheric N. Combustion-zone temperatures >~1300 K are required to fix atmospheric N$_2$ by the reaction.

$$N_2 + O_2 \longrightarrow 2NO$$
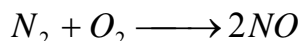
Reaction 1

Below this temperature, NO can be formed from fuel N by the reaction

$$C_a H_b O_c N_d \ + \ O_2 \ \longrightarrow \ xCO_2 \ + \ yH_2O \ + \ zNO$$
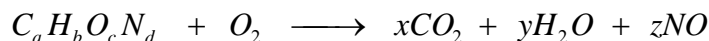
Reaction 2

Both Reaction 1 and Reaction 2 have temperature dependencies and vary with concentrations of hydroxyl radical (OH), hydroperoxy radical (HO$_2$), and O$_2$.

The N content in fossil fuels and its specific chemical form vary strongly with source type, fuel, engine emissions controls, and running conditions. N content in fuel stocks ranges from 0.05% by weight (wt %) in light distillates such as diesel fuel (Samet and Bodurow, 2008) to 1.5 wt % in heavy fuel oils, and from 0.5 to 2.0 wt % in coal, as surveyed by the United Kingdom (U.K. AQEG, 2004) Air Quality Expert Group.

On-road mobile source emissions constitute the largest type of emissions from all transportation sources. Significant variability attaches to these emissions. For example, the ratio of NO$_2$ to total NO$_X$ in

---

[1] Range values: White, 0 or no reported value; Blue, from the smallest non-zero to the 10th percentile value; Green, from above the 10th to the 25th percentile; Yellow, from above the 25th to the 50th percentile; Pink, from above the 50th to the 75th percentile; Red, from above the 75th to the 90th percentile; Brown, from above the 90th percentile to the highest reported value.

exhaust gases in primary emissions ranges from 1 to 3% from gasoline engines tested on dynamometers (Heeb et al., 2008; Hilliard and Wheeler, 1979). On the other hand, some European studies have reported NO_2-to-NO_X ratios ≥ 15% from gasoline vehicles based on integrated measurements from Tedlar bags (Lenner, 1987; Soltic and Weilenmann, 2003). However, subsequent studies suggesting that NO-to-NO_2 conversion will occur within a bag sample of diluted exhaust if not properly handled have led groups performing these measurements to revise their measurement techniques to avoid use of Tedlar bag samples (Alvarez et al., 2008). As a result, dynamometer-based measurements generally indicate that in the absence of post-tailpipe transformation, NO_2 comprises, at most, only a few percent of the total NO_X in current-generation gasoline engine exhaust.

The emissions ratio of NO_2 to NO_X ranges between 5 and 12% from heavy-duty diesel truck engines, although some emission control devices used for diesel engines in Europe increase the fraction of exhaust NO_X emitted as NO_2 to >20% (Carslaw and Beevers, 2005; Carslaw, 2005; Carslaw and Carslaw, 2007; Kessler et al., 2006). In the U.S., on-road experiments with diesel engines propelling heavy buses in congested urban areas like New York City have shown that engines equipped with emissions control devices similar to those in the European studies increased the NO_2-to-NO_X ratio from ~10% before addition of the new controls to ~30% after controls were added (Shorter et al., 2005). In a second type of experiment in a different setting, Kittelson et al. (2006) used an on-road laboratory to sample exhaust plumes of a truck equipped with the European-style emissions control device under highway cruise conditions and found the NO_2-to-NO_X ratios for this exhaust under highway cruise conditions ranged from 59 to 70%. The wide range revealed by comparing these two studies illustrates the significant differences in NO_X exhaust under different conditions of engine load and ambient temperature.

As for other combustion sources, NO_2-to-NO_X emissions ratios for compressed natural gas engines range between 5 and 10%, and between 5 and 10% from most stationary sources. The NO_2-to-NO_X ratios in emissions from turbine jet engines are as high as 35% during taxi and takeoff (U.S. EPA, 2006a).

In addition to NO and NO_2, mobile sources emit other forms of oxidized N including nitrous acid (HNO_2); measured ratios of HNO_2 to NO_X range from a low of 0.3% in the Caldecott Tunnel, San Francisco, CA (Kirchstetter and Harley, 1996), up to as much as 0.5 and 1.0% in studies in the U.K. (U.K. AQEG, 2004).

Marine transport represents an additional source of NO_X in the U.S., especially for coastal cities with large ports, but constitutes a larger source in Europe where it is expected to represent more than 60% of land-based NO_X sources (U.K. AQEG, 2004).

The anthropogenic sources of NO_X are distributed with height such that some, like on-road mobile sources, are nearer to ground level than others, like the emissions stacks from EGUs and some industrial emitters. Emissions height is an important consideration because the prevailing winds aloft are generally stronger than those at the surface. The result is that emissions from elevated sources can be distributed over a wider area than those emitted at the surface and hence can be diluted to lower mixing ratios than those emitted nearer their sources.

2.2.2. Major Biogenic Sources

2.2.2.1. Soils

Nitrification and denitrification processes in soils produce two gas-phase intermediates, NO and N_2O, which can evolve from soil microbes before reaching their reaction endpoint, N_2. N_2O is not among the nitrogen oxides important for urban and regional air quality either for human health concerns or environmental effects because its reaction potential on these spatio-temporal scales in the troposphere is insignificant. As a result, NO from soil metabolism is the prime, but not exclusive, form of atmospheric NO_X from the biosphere relevant to this ISA.

Biogenic NO_X emissions are predominately the result of incomplete bacterial denitrification and nitrification processes, as described above. Denitrification is a reduction process performed by particular groups of heterotrophic bacteria having the ability to use nitrate ion (NO_3^-) as an electron acceptor during anaerobic respiration, thereby converting NO_3^- in soils and water to gas-phase forms (Firestone and Davidson, 1989). At low O_2 concentrations, these microbial communities may use NO_3^-, nitrite (NO_2^-), or N_2O as alternative electron acceptors to O_2 (Davidson and Schimel, 1995).

The basic outlines of these reaction pathways are known, but uncertainty remains concerning the conditions favoring production of the various products of the NO_3^- transformations. Groups of aerobic bacteria use most NH_4^+ in soils as an energy source, oxidizing it to NO_2 and then NO_3^-. Oxidized N products from nitrification may undergo denitrification and thus also drive production of NO_X. Some bacteria are known to be nitrifiers and denitrifiers and can change depending on environmental conditions, including high loadings of exogenous N.

Soil emissions of NO_X can be increased by agricultural practices and activities, including the use of synthetic and organic fertilizers, production of N-fixing crops, cultivation of soils with high organic content, and the application of livestock manure to croplands and pasture. All of these practices directly add exogenous N to soils, of which a portion will then be converted to NO or N_2O on the pathway to full conversion to N_2. Additionally, indirect additions of N to soils can also result in NO_X emissions from agricultural and non-agricultural systems. Indirect additions include processes by which atmospheric NO_X is deposited directly to a region or N from applied fertilizer or manure volatilizes to NH_3 and is oxidized to NO_X and then is ultimately re-deposited onto soils as NH_4NO_3, HNO_3, or NO_X (U.S. EPA, 2006c).

N metabolism in soils is strongly dependent on soil substrate concentrations and physical conditions. Where N is limiting, it is efficiently retained and little gas-phase N is released; where N is in excess of demand, N emissions increase. As a consequence, soil NO emissions are highest from fertilized agricultural lands and tropical soils (Davidson and Kingerlee, 1997; Williams et al., 1992). In addition, temperature, soil moisture, and O_2 concentrations control both the rates of reaction and the partitioning between NO and N_2O. In flooded soils where O_2 concentrations are low, N_2O is the dominant soil N gas; as soils dry, more O_2 diffuses in and NO emissions increase. In very dry soils, microbial activity is inhibited and emissions of both N_2O and NO decrease.

Emission rates of NO from cultivated soils depend largely on fertilization levels and soil temperature. Production of NO from agriculture results from the oxidation of NH_3 emitted both by livestock and by soils after fertilization with NH_4NO_3. Estimates of biogenic N emissions are far less certain than those of anthropogenic emissions sources. Uncertainty on the order of a factor of 3 or more is introduced by the variation within biomes to which fertilizer is applied, such as between shortgrass and tallgrass prairie for example (Davidson and Kingerlee, 1997; Williams et al., 1992; Yienger and Levy, 1995). The contribution of soil emissions to the global NO_X budget is approximately 10% (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 1998; Van Aardenne et al., 2001), but NO_X emissions from fertilized fields are highly variable. Soil NO emissions can be estimated from the fraction of the applied fertilizer N emitted as NO_X, for example, but the flux depends strongly on land use type and temperature. Estimates of globally averaged fractional-applied N lost as NO vary from a low of 0.3% (Skiba et al., 1997) up to 2.5% (Yienger and Levy, 1995).

The spatial scales of these N fluxes are also significant. Local contributions to soil NO_X can be much greater than the global average, particularly in summer, and especially where corn is grown extensively. Approximately 60% of total NO_X emitted by soils in the U.S. occurs in the central corn belt. Nitrification of fertilizer NH_3 to NO_3^- in aerobic soils appears to be the dominant pathway to soil NO_X emissions, but the mass and chemical form of N applied to soils, the vegetative cover, the temperature and soil moisture characteristics, and the agricultural practices such as tillage all influence the amount of fertilizer N converted and released as NO_X. On sub-national scales these emissions can be large and highly variable. Williams et al. (1992) estimated that NO_X from soils in Illinois was ~25% of the total NO_X emissions from industrial and commercial processes in that state. In Iowa, Kansas, Minnesota, Nebraska, and South Dakota—states with smaller human populations than Illinois—soil emissions may, in fact, dominate the NO_X budget.

Emissions of NO_X from soils often peak in summer when ozone (O_3) formation is also at a maximum. The significance of agricultural emission sources of NO and NH_3 among other air pollutants was described in detail in a recent National Research Council report (NRC, 2002). That report recommended immediate implementation of best management practices to control these emissions, and called for additional research to quantify the magnitude of emissions and the effects of agriculture on air quality. The effects of such changes in management practice can be dramatic: Civerolo and Dickerson (1998) reported that the use of no-till cultivation techniques on a fertilized cornfield in Maryland reduced NO emissions by a factor of 7.

2.2.2.2. Live Vegetation

Extensive work on N inputs from the atmosphere to forests was conducted in the 1980s as part of the Integrated Forest Study, summarized by Johnson and Lindberg (1992b). As noted below and in Chapter 4, our understanding of NO_2 exchange with vegetation suggests that NO_2 should be emitted from foliage when ambient concentrations are below the compensation point of ~1 ppb. However, Lerdau et al. (2000) noted that current understanding of the global distribution of NO_X is not consistent with the large source that would be expected in remote forests if NO_2 emissions were significant when atmospheric concentrations were below the 1 ppb compensation point.

2.2.2.3. Biomass Burning

During biomass burning, N is derived mainly from fuel N and not from atmospheric N_2, since temperatures required to fix atmospheric N_2 are likely to be found only in the flaming crowns of the most intense boreal forest fires. N is present in plants mostly as amine (NH_2) groups in amino acids. During combustion, N is released in many forms, mostly unidentified and presumably as N_2, leaving very little N remaining in the fuel ash. Emissions of NO_X are estimated to be ~0.2 to 0.3% of the total biomass burned (e.g., Andreae, 1991; Radke et al., 1991). The most abundant NO_X species in biomass burning plumes is NO, emissions of which account for ~10 to 20% of the total fuel N loadings (Lobert et al., 1991); other N-containing species such as NO_2, nitriles, and NH_3 together account for a similar amount. Westerling et al. (2006) noted that the frequency and intensity of wildfires in the western U.S. increased substantially since 1970, lending added importance to consideration of all NO_X emissions from this sector.

2.2.2.4. Lightning

Annual global production of NO by lightning is the most uncertain source of atmospheric N. In the last decade, literature values of the global average production rate ranged from 2 to 20 Tg N/yr. Most recent estimates, however, are in the range of 3 to 8 Tg N/yr. This large and persistent uncertainty stems from several factors: a wide range of as much as two orders of magnitude in NO production rates per meter of flash length; uncertainty over whether cloud-to-ground (CG) and intracloud (IC) flashes produce substantially different NO levels; the global average flash rate; and the ratio of IC to CG flashes.

Estimates of the NO concentration produced per flash have been made from theoretical considerations (e.g., Price et al., 1997), laboratory experiments (e.g., Wang et al., 1998), and field experiments (Huntrieser et al., 2002, 2007; Stith et al., 1999), and with a hybrid method of cloud-resolving model simulations, observed lightning flash rates, and measurements of NO concentrations in cloud anvils (DeCaria et al., 2000, 2005; Ott et al., 2007). A series of midlatitude and subtropical thunderstorm events were simulated with the model of DeCaria et al. (2005) and the derived NO production per CG flash was, on average, 500 moles/flash, while production per IC flash was 425 moles/flash on average (Ott et al., 2007). The hybrid method had earlier been used by Pickering et al. (1998) who showed that only ~5 to 20% of the total NO produced by lightning in a given storm exists in

the planetary boundary layer (PBL) at the end of a thunderstorm event, thereby reducing its importance as a direct emissions source to the urban and regional troposphere.

2.2.3. Anthropogenic and Biogenic Sources of N_2O

N_2O has an atmospheric lifetime (τ) of ~114 years, resulting from its having effectively no chemistry in the lower troposphere on urban and regional scales. The chief N_2O loss pathway with a quantum yield of ~1 is the photodissociation process

$$N_2O \longrightarrow N_2 \ + \ O(^1D)$$
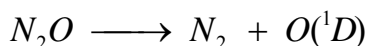
<div align="right">Reaction 3</div>

driven by the short wavelength UV present only in the stratosphere.

However, N_2O is also a GHG with a global warming potential (GWP) on the conventional 100–year time horizon of ~296; i.e., 1 molecule of N_2O is nearly 300 times more effective at trapping heat in the atmosphere than 1 molecule of carbon dioxide (CO_2) over a 100–year period (IPCC, 2001b). The high GWP of N_2O results from its combination of direct and indirect radiative forcing climate effects in the stratosphere. By comparison, the primary climate effects of NO and NO_2 are indirect and result from their role in promoting the production of O_3 ($P(O_3)$) in the troposphere and, to a lesser degree, in the lower stratosphere where NO_X has positive radiative forcing effects. Additional complications for calculating NO_X GWPs ensue owing to the fact that NO_X emissions from high-altitude aircraft are also likely to decrease methane (CH_4) concentrations, a negative radiative forcing effect (IPCC, 1996), and that particulate nitrate (pNO_3^-) transformed from NO_X also has negative radiative forcing effects. U.S. EPA does not calculate GWPs for total NO_X or for SO_X or for the other atmospheric constituents for which no agreed-upon method exists to estimate the contributions from these gases that are short-lived in the atmosphere, have strong spatial variability, or have only indirect effects on radiative forcing.

Thus, because there are no tropospheric reactions or effects to consider, N_2O is not a significant component of NO_X for this ISA review of the NO_X and SO_X secondary effects related to the NAAQS. However, the role of N_2O as an intermediate product along with NO from the complex soil metabolism described in Section 2.2.2.1 means that a brief description of its emissions strengths and its component part of the total budget of U.S. GHGs will be useful, and so appears just below.

N_2O is a contributor to the total U.S. GHG budget, with 6.5% of total GHG on a Tg CO_2 equivalents basis (CO_2e) in 2005 (U.S. EPA, 2007b). CO_2, by comparison, accounted for 83.9% in the same year, and CH_4 for 7.4% (U.S. EPA, 2007b). Although atmospheric concentrations of N_2O have increased globally by ~18% to a current value of ~315 ppb due to western industrialization since the year 1750 C.E. (Hofmann et al., 2004), there is considerable interannual variation in N_2O emissions which remains largely unexplained (IPCC, 2001a). N_2O emissions in the U.S., for example, decreased by 2.8%, or 13.4 Tg CO_2e, between 1990 and 2005 (U.S. EPA, 2007a).

N_2O is produced by biological processes occurring in the soil and water, as described in Section 2.2.2 above, and by a variety of anthropogenic activities in the agricultural, energy, industrial, and waste management sectors. The chief anthropogenic activities producing N_2O in the U.S. are agricultural soil management, fuel combustion in motor vehicles, manure management, production of adipic acid (nylon) and HNO_3, wastewater treatment, and stationary fuel combustion.

N_2O emissions from anthropogenic activities in the U.S. were 386.7 Tg CO_2e/yr between 1990 and 2004 (U.S. EPA, 2007a). These emissions resulted from the fuel combustion, industrial practices, and stimulation of biogenic sources through agricultural practices listed above. In 2005, N_2O emissions from mobile sources were 38.0 Tg CO_2e, or ~8% of the U.S. N_2O emissions total (U.S. EPA, 2007a). In the period between 1990 and 1998, control technologies on mobile sources reduced on-road vehicle NO and NO_2 emissions at the expense of increasing N_2O emissions by 10%. The overall reduction in N_2O mobile

source emissions between 1998 and 2005 (when totals were last available), however, has been 13% owing to more efficient controls used after 1998.

Biogenic production of N_2O stimulated through soil management accounted for >75% of all U.S. N_2O emissions in 2005 (U.S. EPA, 2007a). N_2O emissions from these sources have shown no significant long-term trend because the biogenic emitters are highly sensitive to the concentrations and forms of N applied to soils, and these applications have been largely constant (U.S. EPA, 2007a).

Aquatic sources of N_2O may also be stimulated by environmental conditions. In some ocean areas, large areas of surface water can become depleted in O_2, allowing active denitrification in open water, and potentially increasing N_2O emissions as described in Section 2.2.2. In addition, oceanic N_2O can also arise from denitrification in marine sediments, particularly in nutrient-rich areas like estuaries.

2.3. Sources and Emissions of Tropospheric SO_X

Emissions of SO_2, the chief component of SO_X, are due mostly to combustion of fossil fuels by EGUs and industrial processes, with transportation-related sources making smaller but significant contributions.

2.3.1. Major Anthropogenic Sources

Table 2-1 shows that for 2002, fossil fuel combustion at EGUs accounted for ~66% of total SO_2 emissions in the U.S., or 11.31 Tg of the total 16.87 Tg. All transportation sources accounted for ~5% of the total U.S. SO_2 emissions in 2002, or 0.76 Tg. On-road vehicles produced ~40% of the transportation-related total SO_2 emissions in 2002, with off-road diesel and marine traffic together accounting for the remainder. Thus, most SO_2 emissions originate from point sources having well-known locations and identifiable fuel streams.

Since nearly all S in fuels is released in volatile components, either SO_2 or SO_3, during combustion, total S emissions from these point sources can be computed from the known S content in fuel stocks with greater accuracy than can total NO_X emissions from point sources. However, just as for the NO_X emissions totals described above, total SO_X emissions estimates are national-scale averages and so cannot accurately reflect the contribution of local sources to selected environmental exposures to SO_X at specific locations and times. To refine those national estimates, county-level average SO_2 emissions for 2001 are shown in Figure 2-5; and normalized emissions intensities per square mile like those shown above for NO_X are shown for SO_2 in Figure 2-6.

Figure 2-6 illustrates the west-to-east increasing gradient in SO_2 emissions densities, with most counties east of the Mississippi River in warmer colors (greater emissions densities) than most counties in the West. The upper end of the SO_2 emissions density distribution represented here includes many counties in the eastern U.S.—primarily in the Ohio River Valley—with 2001 SO_2 emissions densities significantly greater than 20. Examples of these high densities (in tons per square mile) are Hillsborough County, FL, 80; Grant County, WV, 156; Indiana County, PA, 190; Washington County, OH, 273; and Armstrong County, PA, 292. In these counties, SO_2 emissions were due mostly to EGU fuel combustion, as shown in Table 2-2. For the non-EGU emissions densities and the total SO_2 densities in Figure 2-6, the upper end of the density distribution compresses a wide range; see Table 2-2. Thus, for the five counties considered above, non-EGU emissions were <5% of total SO_2 emissions in Washington County, OH, and <1% in Indiana County, PA, Armstrong County, PA, and Grant County, WV. Hillsborough County, FL, is an exception, where 17% of the 2001 SO_2 emissions density came from non-EGU sources, the largest of which was chemical and allied product manufacturing.

2001 County Emissions (1000 Tons per Year) of Sulfur Dioxide

☐ 0	☐ >0–0.05	☐ 0.05–0.11	☐ 0.11–0.31
☐ 0.31–1.5	☐ 1.5–12	☐ 12+	
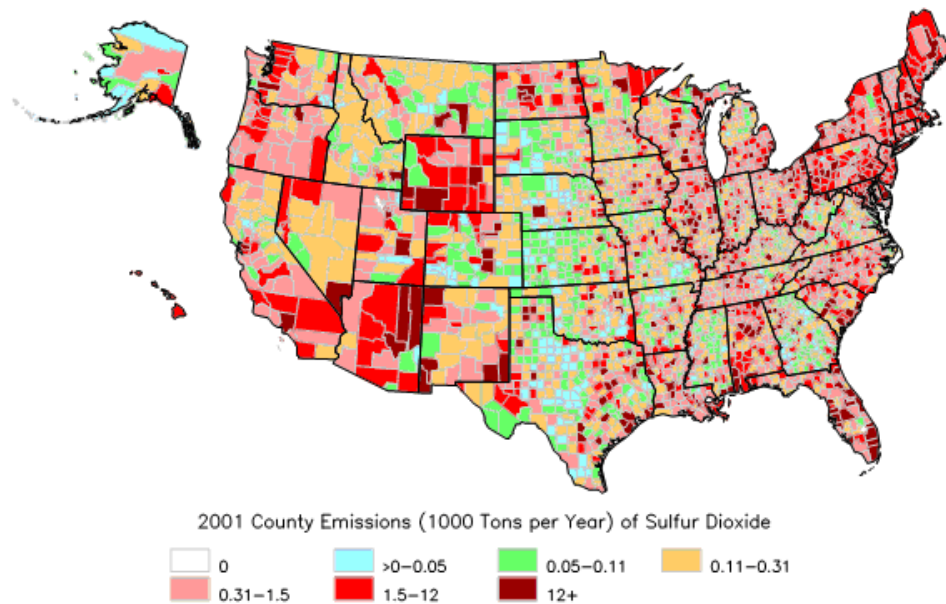
Figure 2-5. **2001 county-level total U.S. SO$_2$ emissions.[1]**

2001 County Emissions Density (Tons per sq.mi.) of Sulfur Dioxide

☐ 0	☐ >0–0.069	☐ 0.069–0.17	☐ 0.17–0.54
☐ 0.54–2.7	☐ 2.7–20	☐ 20+	
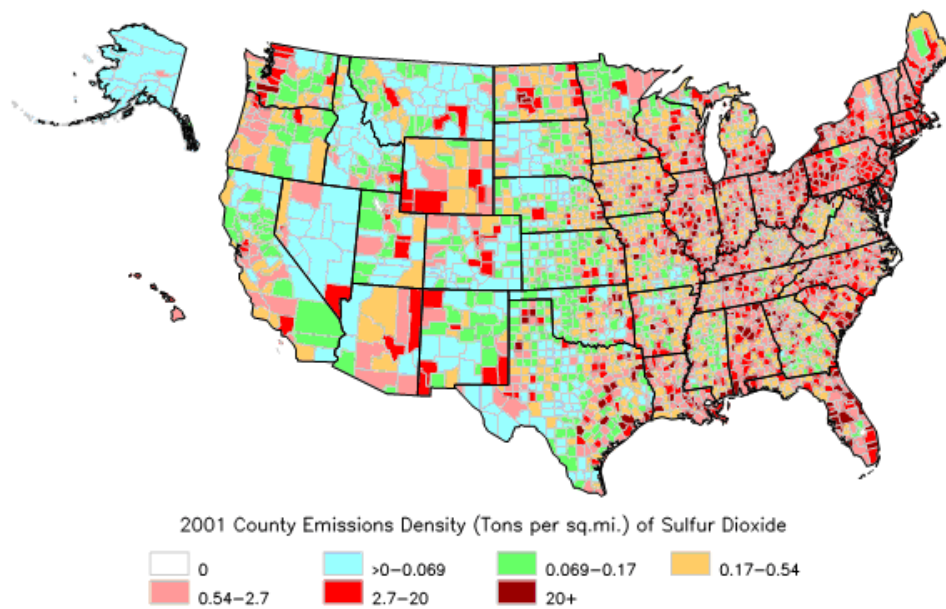
Figure 2-6. **2001 county-level total U.S. SO$_2$ emissions densities (tons per square mile).[1]**

---

[1]Range values: White, 0 or no reported value; Blue, from the smallest non-zero to the 10th percentile value; Green, from above the 10th to the 25th percentile; Yellow, from above the 25th to the 50th percentile; Pink, from above the 50th to the 75th percentile; Red, from above the 75th to the 90th percentile; Brown, from above the 90th percentile to the highest reported value.

2001 County Emissions Density (Tons per sq.mi.) of Sulfur Dioxide

☐ 0	☐ >0–0.000098	☐ 0.000098–0.0011	☐ 0.0011–0.045
☐ 0.045–13	☐ 13–57	☐ 57+
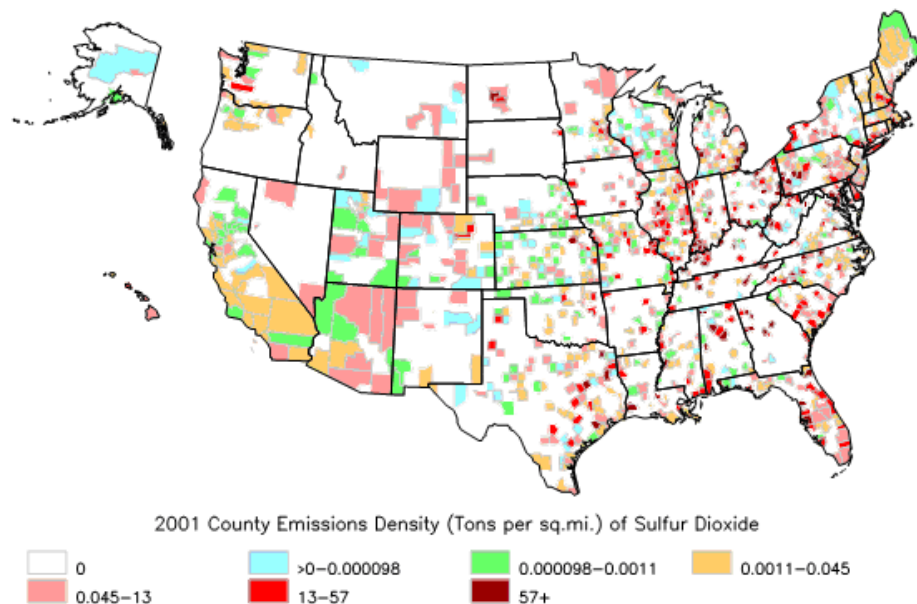
Figure 2-7.   2001 county-level SO$_2$ emissions densities (tons per square mile) from EGUs. [1]

Although on-road mobile sources in 2001 contributed <5% to SO$_2$ emissions totals on the national scale, their fraction of county-level emissions densities varies widely. Generally, however, on-road mobile source SO$_2$ emissions reflect the west-to-east increasing gradient in the densities of both total SO$_2$ emissions and U.S. population, as shown in Figure 2-8. In areas such as Wayne County, MI, and Bronx County, NY, for example, 2001 SO$_2$ emissions densities from on-road mobile sources were 3 and 8.8 tons per square mile out of totals of 98 and 160 tons per square mile, total SO$_2$, respectively. In other areas like Dallas County, TX, and DeKalb County, GA, however, the on-road fraction of total SO$_2$ emissions densities in 2001 was substantially greater: 1.5 out of the total 4.1 tons per square mile in Dallas County, and 3.5 out of the total 6.5 tons per square mile in DeKalb County.

Table 2-2.   Total and non-EGU SO$_2$ emissions densities for selected U.S. counties, 2001.

County	SO$_2$ Emissions Density (tons/mile^2)	Non-EGU Emissions Density Fraction (%)
Hillsborough, FL	80	17
Grant, WV	156	<1
Indiana, PA	190	<1
Washington, OH	273	<5
Armstrong, PA	292	<1

[1]Range values: White, 0 or no reported value; Blue, from the smallest non-zero to the 10th percentile value; Green, from above the 10th to the 25th percentile; Yellow, from above the 25th to the 50th percentile; Pink, from above the 50th to the 75th percentile; Red, from above the 75th to the 90th percentile; Brown, from above the 90th percentile to the highest reported value.

2001 County Emissions Density (Tons per sq.mi.) of Sulfur Dioxide

☐ 0	☐ >0–0.0065	☐ 0.0065–0.022	☐ 0.022–0.057
☐ 0.057–0.14	☐ 0.14–0.32	☐ 0.32+	
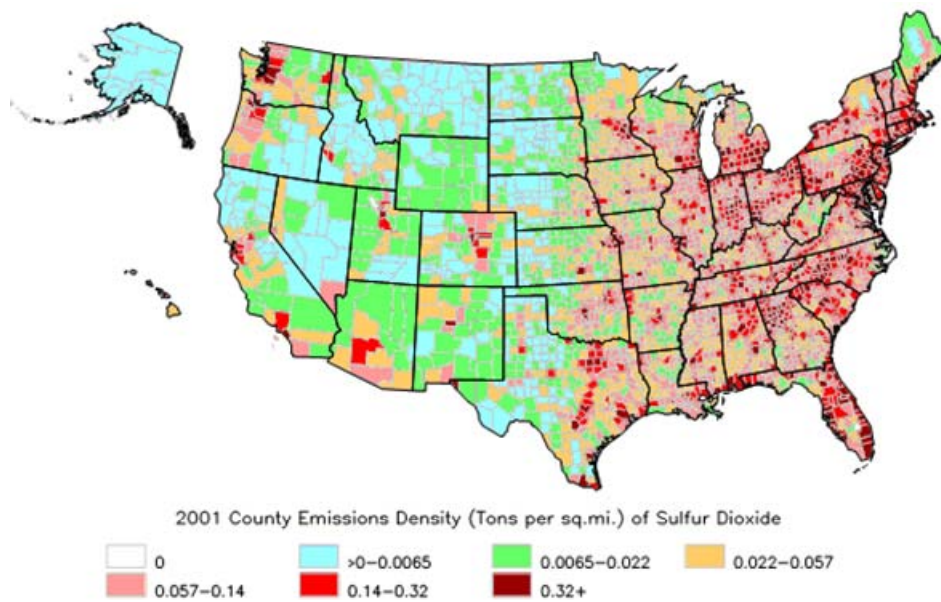
Source: U.S. EPA (2006a)

Figure 2-8.   2001 county-level SO₂ emissions densities (tons per square mile) from on-road mobile sources.[1]

2001 County Emissions Density (Tons per sq.mi.) of Sulfur Dioxide

☐ 0	☐ >0–0.016	☐ 0.016–0.041	☐ 0.041–0.087
☐ 0.087–0.18	☐ 0.18–0.5	☐ 0.5+	
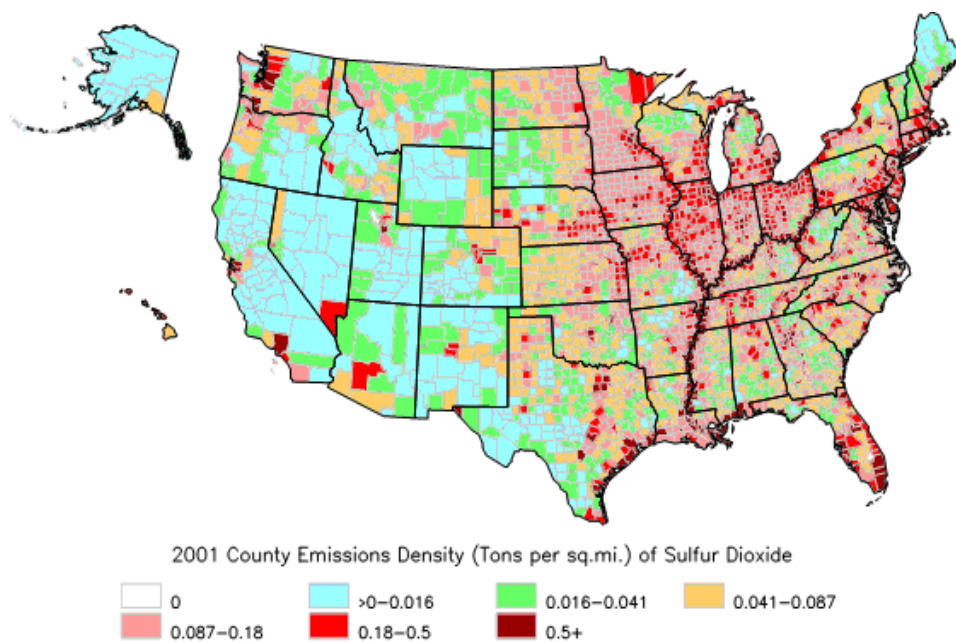
Source: U.S. EPA (2006a)

Figure 2-9.   2001 county-level SO₂ emissions densities (tons per square mile) from off-road mobile and other transportation sources. [1]

---

[1]Range values: White, 0 or no reported value; Blue, from the smallest non-zero to the 10th percentile value; Green, from above the 10th to the 25th percentile; Yellow, from above the 25th to the 50th percentile; Pink, from above the 50th to the 75th percentile; Red, from above the 75th to the 90th percentile; Brown, from above the 90th percentile to the highest reported value.

An additional source of SO_2 emissions of concern in particular locations not immediately obvious from national-scale averages and totals are transit and in-port activities in areas with substantial shipping traffic (Wang et al., 2007). Because of the importance of these SO_2 emissions, the ports of Long Beach and Los Angeles, CA, for example, are part of a Sulfur Emissions Control Area in which S contents of fuels are not to exceed 1.5%. Figure 2-9 shows SO_2 emissions densities combined for all non-road transportation-related emitters in which coastal areas with ports and shipping routes, such as the Mississippi River, are easily discerned. In Los Angeles County, CA, for example, off-road transportation including shipping and port traffic contributed 1.4 of the total 4.1 tons of SO_2 per square mile in 2001; in King County (including the city of Seattle), WA, the off-road transportation fraction was 42% of the total SO_2 emissions density, or 1.2 of the total 2.8 tons per square mile. Emissions density data at finer scales more specific to the ports are not available in the routine emissions inventories and some confusion attends estimates of the actual SO_2 loads from these sources. Modeling studies by Vutukuru and Dabdub (2008) for southern California ports, for example, have shown that ships contribute <2 ppb to the 24-h average SO_2 concentration in Long Beach, CA, in 2002 and <0.5 ppb farther inland.

SO_2 data collected from the State and Local Air Monitoring Stations (SLAMS) and National Air Monitoring Stations (NAMS) networks show that the decline in SO_2 emissions following controls placed on electric generating utilities in the previous 15 years has improved air quality. There has not been a single monitored exceedance of the SO_2 annual ambient air quality standard in the U.S. since 2000, (U.S. EPA, 2006e). U.S. EPA trends data (www.epa.gov/airtrends) reveal that the national composite average SO_2 annual mean ambient concentration decreased by ~48% from 1990 to 2005, with the largest single-year reduction coming in 1994-1995, the Acid Rain Program's (ARP) first operating year (U.S. EPA, 2006e). Figure 2-10 depicts data for SO_2 emissions in the CONUS in these years that reflect this reduction using individual state-level totals. Note that SO_X emissions have changed over this period both temporally and spatially, with some areas in the southeast U.S. such as North Carolina and Georgia realizing increased SO_X emissions since 2000. SO_X emissions from the largest emitters in the states of the Ohio River Valley, however, have mostly decreased, in some cases by very large fractions.
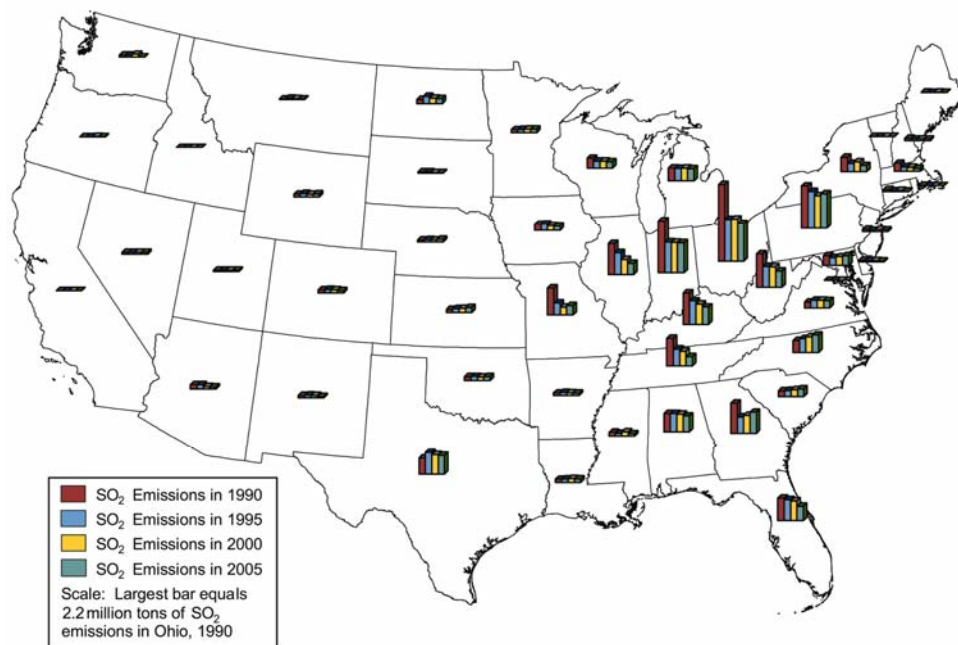
Figure 2-10.   State-level SO$_2$ emissions, 1990-2005.

These trends in emissions data are consistent with the trends in the observed ambient concentrations from the Clean Air Status and Trends Network (CASTNet). Following implementation of the Phase I controls on ARP sources between 1995 and 2000, significant reductions in SO_2 concentrations and ambient SO_4^{2-} concentrations were observed at CASTNet sites throughout the eastern U.S.

2.3.2. Major Biogenic Sources

Emissions of SO_X from natural sources are small compared to industrial emissions within the U.S. (see Table 2-1). However, important exceptions occur locally as the result of volcanic activity, wildfires, and in certain coastal zones as described above.

The major biogenic sources of SO_2 are volcanoes, biomass burning, wildfires, and dimethylsulfide (DMS) oxidation over the oceans. Although SO_2 constitutes a relatively minor fraction of 0.005% by volume of total volcanic emissions (Holland, 1978), concentrations in volcanic plumes can range from several to tens of ppm. The ratio of hydrogen sulfide (H_2S) to SO_2 is highly variable in volcanic gases, typically <1, as in the Mount St. Helens eruption in the Washington Cascade Range (46º20'N, 122º18'W, summit 2549 m asl) (Turco et al., 1983). However, in addition to being degassed from magma, H_2S can be produced if ground waters, especially those containing organic matter, come into contact with volcanic gases. In this case, the ratio of H_2S to SO_2 can be >1. H_2S produced this way would more likely be emitted through side vents than through eruption columns (Pinto et al., 1989). Primary particulate sulfate (pSO_4) is a component of marine aerosol and is also produced by wind erosion of surface soils.

Since 1980, the Mount St. Helens volcano has been a variable source of SO_2. Its major effects came in the explosive eruptions of 1980, which primarily affected the northern part of the mountainous western half of the U.S. The Augustine volcano near the mouth of the Cook Inlet in southwestern Alaska (59º36'N, 153º43'W, summit 1252 m asl) has had variable SO_2 emissions since its last major eruptions in 1986. Volcanoes in the Kamchatka peninsula of the eastern region of Siberian Russia do not significantly affect surface SO_2 concentrations in northwestern North America. The most serious effects from volcanic SO_2 in the U.S. occur on the island of Hawaii. Nearly continuous venting of SO_2 from Mauna Loa and Kilauea produces SO_2 in such large amounts that >100 km downwind of the island, levels of SO_2 can exceed 30 ppb (Thornton and Bandy, 1993).

Emissions of SO_2 from burning vegetation are generally in the range of 1 to 2% of the biomass burned (see e.g., Levine et al., 1999). S is bound in amino acids in vegetation, and ~50% of this organically–bound S is released during combustion, leaving the remainder in the ash (Delmas, 1982). Gas-phase emissions are mainly in the form of SO_2, with much smaller amounts of H_2S and carbonyl sulfide (OCS). The ratio of reduced S species such as H_2S to more oxidized forms such as SO_2, increases as the fire conditions change from flaming to smoldering phases of combustion because emissions of reduced species are favored by lower temperatures and decreased O_2 availability.

SO_2 is also produced by the photochemical oxidation of reduced S compounds such as DMS, H_2S, carbon disulfide (CS_2), OCS, methyl mercaptan (CH_3-S-H), and dimethyl disulfide (CH_3-S-S-CH_3). The sources for these compounds are mainly biogenic (see Table 2-1). Emissions of reduced S species are associated typically with marine organisms living either in pelagic or coastal zones and with anaerobic bacteria in marshes and estuaries. Emissions of DMS from marine plankton represent the largest single source of reduced S species to the atmosphere (Berresheim et al., 1995). Other sources such as wetlands and terrestrial plants and soils account for <5% of the DMS global flux, with most of this coming from wetlands.

Other than OCS, which is lost mainly by photolysis with a τ of ~6 months, SO_X species are lost mainly by reaction with OH and NO_3^- and are relatively short-lived, with τ ranging from a few hours to a few days. Reaction with NO_3^- at night most likely represents the major loss process for DMS and methyl mercaptan. Although the mechanisms for the oxidation of DMS are not known with certainty, excess SO_4^{2-} in marine aerosol appears related mainly to production of SO_2 from the oxidation of DMS. Because

OCS is relatively long-lived, it can survive oxidation in the troposphere and be transported upward into the stratosphere. Crutzen (1976) proposed that its oxidation to SO_4^{2-} in the stratosphere serves as the major source of the stratospheric aerosol layer. However, Myhre et al. (2004) proposed that SO_2 transported upward from the troposphere by deep convection is the most likely source, since the flux of OCS is too small to account for current atmospheric loadings. In addition, in situ measurements of the isotopic composition of S in stratospheric SO_4^{2-} do not match those of OCS (Leung et al., 2002). Thus, in addition to biogenic OCS, anthropogenic SO_2 emissions could be important precursors to the formation of the stratospheric aerosol layer.

The coastal and wetland sources of DMS have a dormant period in the fall and winter from plant senescence. Marshes die back in fall and winter, so DMS emissions from them are lower, and lower light levels in winter at mid-to-high latitudes lessen phytoplankton growth also tend to lower DMS emissions. Western coasts at mid-to-high latitudes have lower actinic flux to drive photochemical production and oxidation of DMS. Freezing at mid and high latitudes affects the release of biogenic S gases, particularly in the nutrient-rich regions around Alaska. Transport of SO_2 from regions of biomass burning seems to be limited by heterogeneous losses that accompany convective processes that ventilate the surface layer and the lower boundary layer (Thornton et al., 1996).

Reduced S species are also produced by several anthropogenic industrial sources: DMS is used in petroleum refining; and in petrochemical production processes to control the formation of coke and CO; to control dusting in steel mills; in a range of organic syntheses; as a food flavoring component; and can also be oxidized by natural or artificial means to dimethyl sulfoxide, a widely-used industrial solvent.

2.4. NH$_X$ Emissions

NH$_3$ can be emitted from or deposited to soils, water, or vegetation depending on the ratio of the atmospheric NH$_3$ concentration to the compensation point of the underlying surface. The compensation point, χ, generally is governed by the form, concentration, and acidity of N at the surface of exchange, and hence changes over time as these variables change. For most of the year, large areas of the U.S. are very near the nominal χ of 1 $\mu g/m^3$, with the result that the NH$_3$ air-surface flux is very often highly dynamic. Figure 2-11 and Figure 2-12 show county-level annual total NH$_3$ emissions for 2001 in tons, and the spatially normalized county-level emissions in tons per square mile, respectively.

Total emissions of NH$_3$ on a national scale show a strikingly different pattern from those of NO$_X$ or SO$_2$ as comparison of these figures to their NO$_X$ and SO$_X$ analogs above illustrates. Anthropogenic NH$_3$ emissions from mobile sources are small since the three-way catalysts used in motor vehicles emit only small amounts of NH$_3$ as a byproduct during the reduction of NO$_X$; in 2002, this totaled ~8% of the national NH$_3$ total of ~3.7 metric short tons. Stationary combustion sources including EGUs make even smaller contributions to emissions of NH$_3$ because their efficient combustion favors NO$_X$ formation and NH$_3$ is produced during combustion largely by inefficient, low-temperature burning. In 2002, the total from all stationary source fuel combustion processes amounted to <2% of total NH$_3$ emissions and chemical production added only ~0.7% more. Hence, NH$_3$ emissions totals are dominated by biogenic production from agriculture, chiefly from livestock management and fertilizer applications to soils. In 2002, these sources accounted for ~86% of U.S. total emissions.

As with NO$_X$ and SO$_X$ emissions, however, these national-scale emissions totals obscure important variability at finer scales. To illustrate this point, Figures 2-13 through 2-15 show county-level NH$_3$ emissions densities separately for emissions from on-road mobile sources, EGUs, and miscellaneous and biogenics, respectively.

2001 County Emissions (Tons per Year) of Ammonia

☐ 0	☐ >0−120	☐ 120−320	☐ 320−690
☐ 690−1300	☐ 1300−2400	☐ 2400+	
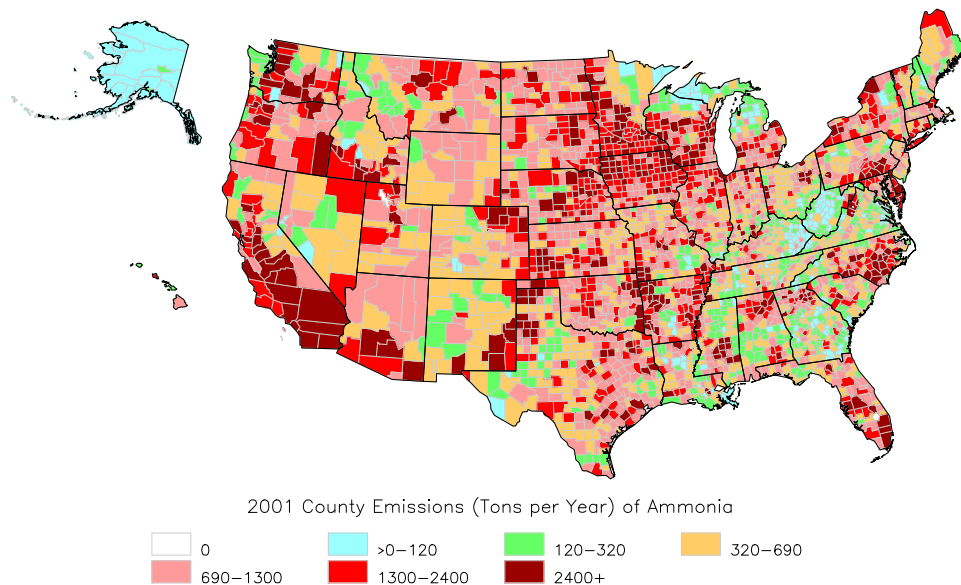
Source: U.S. EPA (2006a)

Figure 2-11.   2001 county-level total U.S. NH$_3$ emissions.[1]

2001 County Emissions Density (Tons per sq.mi.) of Ammonia

☐ 0	☐ >0−0.18	☐ 0.18−0.46	☐ 0.46−1.1
☐ 1.1−2.1	☐ 2.1−3.7	☐ 3.7+	
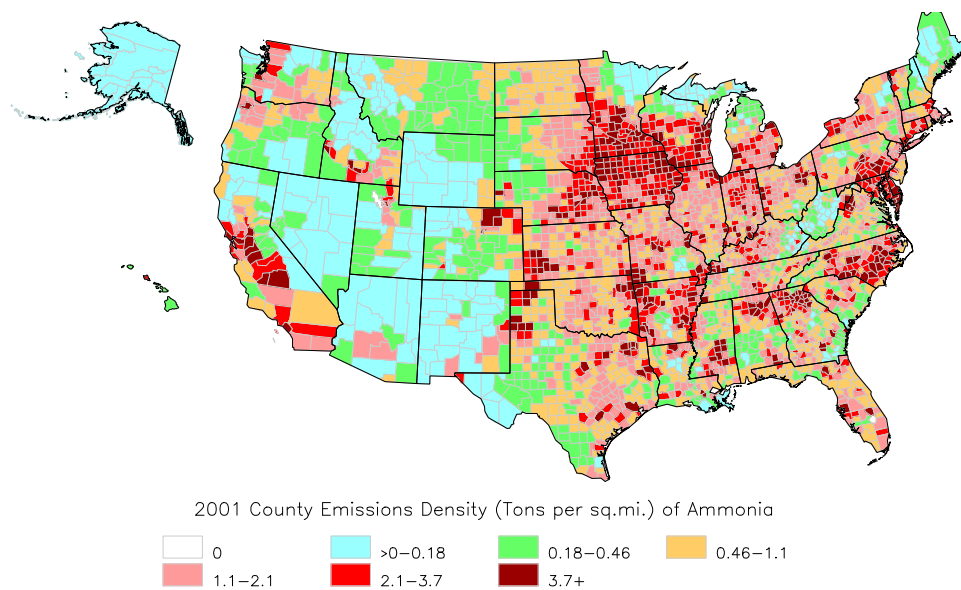
Source: U.S. EPA (2006a)

Figure 2-12.   2001 county-level total U.S. NH$_3$ emissions densities.[1]

---

[1] Range values: White, 0 or no reported value; Blue, from the smallest non-zero to the 10th percentile value; Green, from above the 10th to the 25th percentile; Yellow, from above the 25th to the 50th percentile; Pink, from above the 50th to the 75th percentile; Red, from above the 75th to the 90th percentile; Brown, from above the 90th percentile to the highest reported value.

2001 County Emissions Density (Tons per sq.mi.) of Ammonia

☐ 0	>0−0.0057	0.0057−0.019	0.019−0.05
0.05−0.12	0.12−0.34	0.34+	
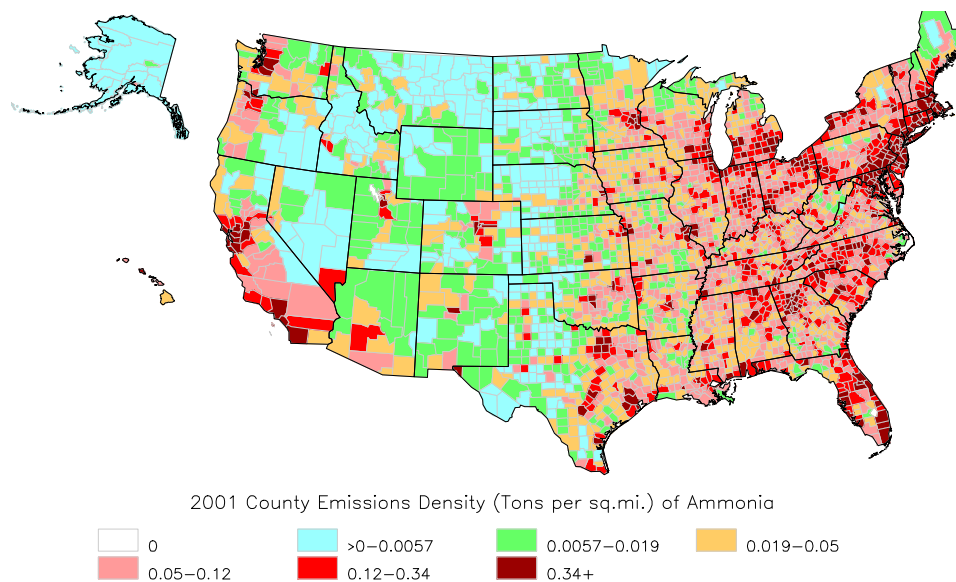
Figure 2-13.   2001 county-level NH$_3$ emissions densities from on-road mobile sources.

2001 County Emissions Density (Tons per sq.mi.) of Ammonia

☐ 0	>0−0.00008	0.00008−0.00045	0.00045−0.0023
0.0023−0.009	0.009−0.067	0.067+	
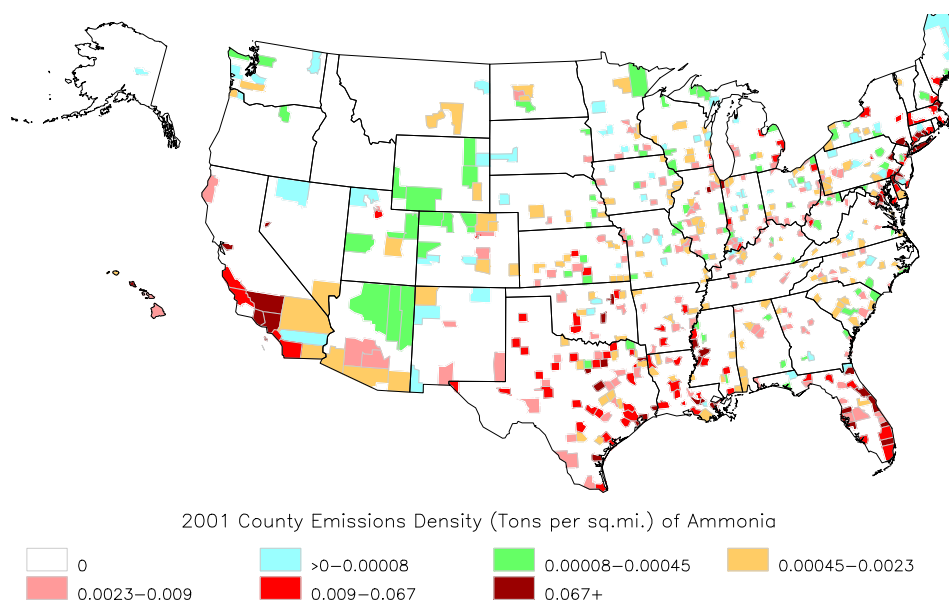
Figure 2-14.   2001 county-level NH$_3$ emissions densities from EGUs.[1]

---

[1] Range values: White, 0 or no reported value; Blue, from the smallest non-zero to the 10th percentile value; Green, from above the 10th to the 25th percentile; Yellow, from above the 25th to the 50th percentile; Pink, from above the 50th to the 75th percentile; Red, from above the 75th to the 90th percentile; Brown, from above the 90th percentile to the highest reported value.

2001 County Emissions Density (Tons per sq.mi.) of Ammonia

0	>0−0.16	0.16−0.37	0.37−0.88
0.88−1.8	1.8−3.2	3.2+	
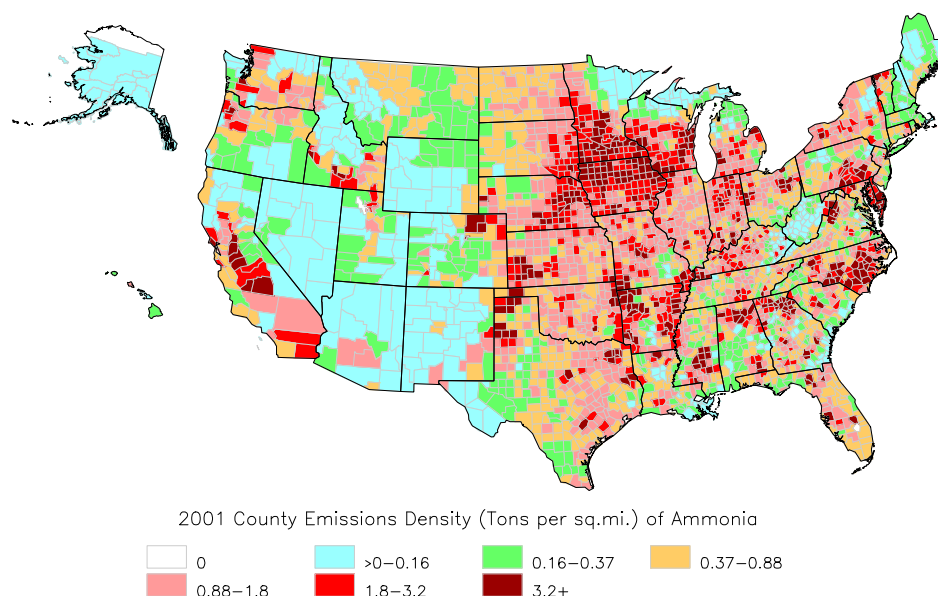
Figure 2-15.   2001 county-level NH₃ emissions densities from miscellaneous and biogenic sources. [1]

2.5. Evaluating Emissions Inventories

Emissions inventories are very complex and highly changeable conjoined forms built from measurements and production and transfer rates, some measured directly, others indirectly, and others merely assumed, combined with model predictions. National-scale emissions inventories like the ones illustrated in county-level maps here have uncertainties embedded in them owing to unknown emission factors, unknown and varying emission rates, generalized or depleted profiles, and the like. Substantial effort is applied at national, state, and local scales to test these terms in the final emissions totals, and to assure their quality.

One means for evaluating emissions inventories has been to compare predictions in the inventories to measured long-term trends or to ratios of pollutants in ambient air. Comparisons of emissions model predictions with observations have been performed in a number of environments. Very often emissions inventories for NO_X and SO_X are evaluated in relation to CO emissions because the low reactivity of CO on urban and regional scales means it can be treated as largely conserved. Using the distinction between mobile sources which emit NO_X and CO but little SO_2, and power plants which emit NO_X and SO_2 but little CO, Stehr et al. (2000) evaluated emissions estimates for the eastern U.S. Results indicated that coal combustion contributes 25 to 35% of the total area NO_X emissions in rough agreement with the U.S. EPA NEI (2006a). Studies using ratios of CO concentrations to NO_X concentrations, and concentrations of nonmethane organic compounds (NMOC) to NO_X carried out in the early 1990s in tunnels and ambient air indicated that emissions of CO and NMOC were systematically underestimated in emissions inventories at that time. More details are available in the 2000 CO AQCD (U.S. EPA, 2000a).

These reconciliation studies depend on the assumption that NO_X emissions are predicted correctly by emissions factor models which are merely mean and aggregate descriptions of the highly variable U.S.

---

[1] Range values: White, 0 or no reported value; Blue, from the smallest non-zero to the 10th percentile value; Green, from above the 10th to the 25th percentile; Yellow, from above the 25th to the 50th percentile; Pink, from above the 50th to the 75th percentile; Red, from above the 75th to the 90th percentile; Brown, from above the 90th percentile to the highest reported value.

mobile source fleet. Roadside remote sensing data have indicated that >50% of non-methane hydrocarbons (NMHC) and CO emissions are produced by less than 10% of vehicles (Stedman et al., 1991), typically the poorly maintained super-emitters.

Parrish et al. (1998) and Parrish and Fehsenfeld (2000) proposed methods to derive emission rates by examining measured ambient ratios among individual volatile organic compounds (VOCs), NO_X, and NO_Y. Typically, strong correlations exist among measured values for these species because emission sources are geographically co-located, even when individual sources are different. Correlations can be used to derive emissions ratios between species, including adjustments for the effect of photochemical aging. Examples of this type include using correlations between CO and NO_Y (e.g., Parrish et al., 1991), between individual VOC species and NO_Y (Goldan et al., 1995, 2000) and among various VOC species (McKeen and Liu, 1993; McKeen et al., 1996). Many of these studies were summarized in Parrish et al. (1998), Parrish and Fehsenfeld (2000), and Trainer et al. (2000).

Other methods for emissions evaluation exist. Buhr et al., (1992) derived emission estimates from principal component analysis (PCA) and other statistical methods. Goldstein and Schade (2000) also used species correlations to identify the relative effects of anthropogenic and biogenic emissions. Chang et al. (1996, 1997), and Mendoza-Dominguez and Russell (2000) used inverse modeling to derive emission rates in conjunction with results from chemical-transport models (CTMs).

A decadal field study of ambient CO at a rural site in the eastern U.S. (Hallock-Waters et al., 1999) indicated a downward trend consistent with the downward trend in estimated emissions over the period 1988 to 1999 (U.S. EPA, 2000e), even when the global downward trend was taken into account. Measurements at two urban areas in the U.S. confirmed the decrease in CO emissions (Parrish et al., 2002). That study also indicated that the ratio of CO to NO_X emissions decreased by approximately a factor of 3 over 12 years. NEI estimates (U.S. EPA, 1997b) indicated a much smaller decrease in this ratio, suggesting that NO_X emissions from mobile sources may have been underestimated or increasing or both. Parrish et al. (2002) concluded that O_3 photochemistry in U.S. urban areas may have become more NO_X-limited over the past decade. (See Section 2.6.2.1 for a discussion of NO_X and its role in enhancing and limiting O_3 formation.)

Results from these recent emissions evaluation studies have been mixed, with some studies showing agreement to within ± 50% (U.S. EPA, 2000e). However, Pokharel et al. (2002) employed remotely sensed emissions from on-road vehicles and fuel use data to estimate emissions in Denver. Their calculations indicated a continual decrease in CO, hydrocarbons (HC), and NO emissions from mobile sources over the 6–year study period, 1996 through 2001. Inventories based on the ambient data were 30 to 70% lower for CO, 40% higher for HC, and 40 to 80% lower for NO than those predicted by the MOBILE6 on-road mobile source emissions model. (See http://www.epa.gov/otaq/m6.htm for information on MOBILE6).

Satellite data also have proved useful for optimizing estimates of NO_2 emissions (Jaeglé et al., 2005; Leue et al., 2001; Martin et al., 2003). Satellite-borne instruments such as the Global Ozone Monitoring Experiment (GOME) (see, e.g., Martin et al., 2003, and references therein) and the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) retrieve tropospheric NO_2 columns that can be combined with model-derived τ of NO_X to yield emissions of NO_X.

Top-down inference of NO_X emission inventories from the satellite observations of NO_2 concentrations columns by mass balance requires at minimum three pieces of information: the retrieved tropospheric NO_2 column; the tropospheric NO_X-to-NO_2 ratio in the columns; and the NO_X τ against reaction losses to stable chemical reservoirs. (See the discussion of these chemical reservoirs in Section 2.6.) A photochemical model has been used to provide information on the latter two pieces of information. The method is most often applied to land surface emissions, excluding lightning. Tropospheric NO_2 columns are largely insensitive to lightning NO_X emissions since most of the lightning NO_X in the upper troposphere is present as NO at the time of the satellite measurements (Ridley et al., 1996) owing to the slower reactions of NO with O_3 at the altitude where lightning production is most prevalent.

Using satellite data, Bertram et al. (2005) found clear signals in the SCIAMACHY observations of short, intense NO_X pulses following springtime fertilizer application and subsequent precipitation over

agricultural regions of the western U.S. For the agricultural region in north-central Montana, they calculated an annual SCIAMACHY top-down estimate that is 60% greater than a commonly-used model of soil NO_X emissions by Yienger and Levy (1995).

Jaeglé et al. (2005) applied additional information on the spatial distribution of emissions and fire activity to partition NO_X emissions into sources from fossil fuel combustion, soils, and biomass burning. Global a posteriori estimates of soil NO_X emissions were 68% larger than the a priori estimates. Large increases were found for the agricultural region of the western U. S. during summer, increasing total U.S. soil NO_X emissions by a factor of 2.

Martin et al. (2006) retrieved tropospheric NO_2 columns for May 2004 to April 2005 from the SCIAMACHY satellite instrument to derive top-down NO_X emissions estimates via inverse modeling with the GEOS-Chem global chemical transport model. (See http://www.as.harvard.edu/ctm/geos/ for more information on GEOS-Chem.) The top-down emissions were combined with a priori information from a bottom-up emissions inventory with error weighting to achieve an improved a posteriori estimate of the global distribution of surface NO_X emissions. Their a posteriori inventory improved GEOS-Chem simulations of NO_X, peroxyacetyl nitrate (PAN), and HNO_3 as compared against airborne in situ measurements over and downwind of New York City. Their a posteriori inventory also showed lower NO_X emissions from the Ohio River Valley in summer than winter, reflecting recent controls on NO_X emissions from EGUs there. Their a posteriori global inventory was highly consistent with the NEI 1999 (http://www.epa.gov/ttn/chief/net/1999inventory.html) (R^2 = 0.82, bias = 3%); however, it was 68% greater than a recent inventory by Streets et al. (2003) for East Asia for the year 2000.

Significant uncertainties attach to estimates of the magnitude and spatial and temporal variability of NH_3 emissions. A strong seasonal pattern should be evident in NH_3 emissions profiles to correspond with the overwhelmingly agricultural sources of NH_3 and strong seasonal temperature differences in NH_3 volatility, for example, but this pattern has not appeared in previous emissions factors and inventories. The magnitude of these temporal differences is large: Heber et al. (2001) showed that NH_3 flux from two swine finishing buildings were ~70% higher in June than in fall and winter months, and Aneja et al. (2000) found fluxes from hog waste lagoons ~80 to 90% higher in summer as compared to winter.

The value of inverse modeling techniques using large-scale Eulerian air quality models (AQMs) has been successfully demonstrated for several aspects of emissions inventories; see, for example, Mendoza-Dominguez and Russell (2000, 2001a, b). Gilliland (2001), Gilliland et al. (2001), and Pinder et al. (2006) have worked extensively with Kalman filter inverse modeling and the U.S. EPA Community Multiscale Air Quality (CMAQ) modeling system (Byun and Ching, 1999), to reduce uncertainties specifically in NH_3 emissions. NH_3 is an especially good case for emissions estimate evaluation with inverse modeling techniques because the modeled response in NH_4^+ wet deposition is strongly linear with changes in NH_3 emissions. Correcting the NH_3 emissions estimates was also shown to be an essential step for reasonable model predictions of other N compounds (Gilliland et al., 2003). Results can be highly significant. For example, the a posteriori R value of CMAQ predictions against measured wet NH_4^+ concentrations from the National Atmospheric Deposition Program (NADP) sites in the U.S. was 0.98, increased from the a priori value of 0.12. Pinder et al. (2004) provided the first farm-level model for NH_3 emissions from dairy cattle, and this has been coupled with the seasonally varying fertilizer inventory for NH_3 from Goebes et al. (2003) and with the inverse modeling results of Gilliland et al. (2003) to correct the NEI NH_3 emissions totals. The estimate of Gilliland et al. (2003) was that the annual NEI NH_3 was ~37% too high to optimize the modeled wet NH_4^+ concentration. Following earlier work by Gilliland and others in this vein, U.S. EPA (2006a), in fact, reported its intention to decrease total NH_3 emissions in the NEI by 23% by altering emissions factors for nondairy cows and swine.

Holland et al. (2005) estimated wet and dry deposition of NH_X based on measurements over the CONUS and reported that NH_3 emissions in the 1999 NEI were underestimated by a factor of ~2 or 3. Possible reasons for this error included under-representation of deposition monitoring sites in populated areas and the neglect of offshore transport in the NEI. The use of fixed deposition velocities (V_d) not reflective of local conditions at the time of measurement introduces additional uncertainty into estimates of dry deposition to which NH_3 is particularly sensitive.

2.5.1. Emissions for Historical Modeling

Rigorous emissions inventories require careful analysis of very large data sets on fuel use and types and activity patterns for them to be a reliable basis for atmospheric concentration and deposition calculations. Sections 2.2 to 2.5 make clear that even with current best estimates for these input data, present-day emissions inventories can be substantially in error.

However, estimates of biological effects from long-term acidifying deposition require computation of historical emissions. Such historical estimates of emissions generally use some divisions of economic sectors together with estimates of fuel type and S content, for example. Schopp et al. (2003) have pursued this method for estimating acid deposition in Europe between 1880 and 2030 using the International Institute for Applied Systems Analysis (IIASA) Regional Acidification and Information System (RAINS) model; see Alcamo et al. (1990) and Asman et al. (1988) for descriptions and applications of RAINS. Mylonda (1996) used similar tools and methods to compute estimates of SO_2 emissions and atmospheric concentrations and deposition in Europe showing that emissions, which peaked in Europe in the 1960s and 1970s had increased by a factor of 10 since the 1880s. Similarly, modeled concentrations and deposition increased by factors of 2 to 6, depending on location in the same time period.

Historical emissions and concentration estimates are often not resolved to more than decadal resolution because of the very large uncertainties inherent in their computation, which very often includes no information on variability in the meteorological state of the atmosphere or its oxidizing capacity, both of which change over time. Spatial resolution, however, has extended from continental scale, like those using RAINS, up to global scale estimates and down to subregional ones. A survey of methods and cautions for interpretation was made by Galloway (1995).

Global estimates like the ones by Lefohn et al. (1999) use methods similar to those at the continental scale, though with more specific factors on S content in fuels, for example, where those are known. Lefohn et al. (1999), for example, estimated the global average anthropogenic S emissions in 1850 to be <2% of current levels. At finer scales, Driscoll et al. (2001b) used U.S. EPA (2000e) estimates of emissions trends between 1900 and 1998 together with biogeochemical modeling to estimate historical loadings to the northeast U.S. to calculate potential recovery times in affected lakes and streams.

Among the finest-scale historical estimates for N emissions and deposition are those by Bowen and Valiela (2001) for Cape Cod, MA. Bowen and Valiela (2001) computed decadal changes in several oxidized and reduced nitrogen species for the time period between 1910 and 1995 to conclude that total N deposition at Cape Cod has been increasing at the rate of 0.26 kg N/ha/decade.

2.6. NO_X-SO_X-NH_X Chemistry in the Troposphere

2.6.1. Introduction

NO_X, VOCs, and CO are precursors in the formation of O_3 and other elements of photochemical smog and PM. The role of NO_X in producing O_3, the factors controlling $P(O_3)$ efficiency and methods for calculating O_3 from its NO_X and VOC precursors were all reviewed in Section 2.2 of the 2006 O_3 AQCD (U.S. EPA, 2006b) and are available in numerous texts including Jacob, 2000; Jacobson, 2002; and Seinfeld and Pandis, 1998. More specific details on the chemistry and transformation of SO_X can be found in the 2008 SO_X ISA (U.S. EPA 2008b). Hence, those topics are only briefly recounted here with special reference to the secondary NO_X and SO_X NAAQS.

Figure 2-16. Atmospheric cycle of reactive oxidized N species. NO_Y refers to all the species shown within the inner and outer box: NO_X to NO and NO_2 (in the inner box), and NO_Z to all the species outside of the inner box. IN refers to inorganic particulate species (e.g., sodium [Na^+], calcium [Ca^{2+}]), MPP to multiphase processes, $h\nu$ to a solar photon, and R to an organic radical. Particle-phase $RONO_2$ are formed from the species shown on the right side. For the purposes of this document, "NO_X" is defined as the group of all N-containing compounds inside the large dashed-line box, the same group generally termed "NO_Y" by atmospheric scientists.

Important compounds, reactions, and cycles are schematized in Figure 2-16. Figure 2-16 also illustrates that NO_2, itself an oxidant, can react to form other photochemical oxidants including organic nitrates ($RONO_2$) like the PANs shown in Figure 2-16, and can react with toxic compounds like the polycyclic aromatic hydrocarbons (PAHs) to form nitro-PAHs, some of which demonstrate greater toxicity than either reactant alone. NO_2 can also be further transformed to HNO_3 and can contribute in that form to the acidity of cloud, fog, and rain water and can form ambient NO_3^- particles (pNO_3).

The only gas-phase forms of SO_X of interest in tropospheric chemistry are SO_2, SO_3, and H_2SO_4. SO_3 can be emitted from the stacks of power plants and factories; however, it reacts extremely rapidly with H_2O in the stacks or immediately after release into the atmosphere to form sulfuric acid (H_2SO_4). H_2SO_4 in turn mainly condenses onto existing particles when particle loadings are high, or nucleates to form new particles under lower concentration conditions. Thus, of the gas-phase SO_X species, only SO_2 is emitted in the tropospheric boundary layer at concentrations of concern for environmental exposures.

NH_3, the gas-phase precursor for NH_4^+, plays a key role in neutralizing acidity in ambient particles and in cloud, fog, and rain water. NH_3 is also involved in the ternary nucleation of new particles and reacts with gas-phase HNO_3 to form NH_4NO_3, and with SO_4^{2-} to form ammonium bisulfate (NH_4HSO_4) and ammonium sulfate (($NH_4)_2SO_4$), three significant components of N and S deposition across the landscape. The NO_X-SO_X-NH_X cycles and phase-changes are schematized in Figure 2-17.

Figure 2-17.   The combined NO$_X$ + SO$_X$ + NH$_X$ system showing how atmospheric fates and lifetimes of reduced and oxidized N components are linked.

2.6.2. NO$_X$ Chemistry

As described in Section 2.2, NO$_X$ is emitted by combustion sources mainly as NO with ~5 to 10% NO$_2$. The rapid photochemical cycle in the troposphere linking NO and NO$_2$ involves photolysis of NO$_2$ by UV-A radiation to yield NO and a ground-state oxygen atom, O(^{3}P).

$$NO_2 \; + \; h\nu \; \longrightarrow \; NO \; + \; O(^3P)$$
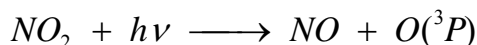
Reaction 4

This ground state oxygen atom, O(^{3}P), can then combine with molecular oxygen (O$_2$) to form O$_3$; and, colliding with M, any molecule from the surrounding air (M = N$_2$, O$_2$, etc.), the newly formed O$_3$ molecule transfers excess energy and is stabilized

$$O(^3P) \; + \; O_2 \; + \; M \; \longrightarrow \; O_3 \; + \; M$$

Reaction 5

NO and O$_3$ react to re-form NO$_2$.

$$NO + O_3 \longrightarrow NO_2 + O_2$$
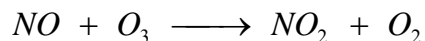
Reaction 6 is responsible for O_3 decreases and NO_2 increases found near sources of NO (like highways or power plant plumes). The falloff of NO_2 with distance from a road depends on: wind speed and direction; the local structure of turbulent mixing; temperature through the temperature dependence of Reaction 6; and the amount of UVA-flux through Reaction 4.

Oxidation of reactive VOCs leads to formation of reactive radical species that allow conversion of NO to NO_2 without participation of O_3 as in Reaction 6.

$$NO \xrightarrow{\quad HO_2, \ RO_2 \quad} NO_2$$
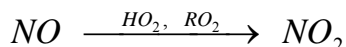
O_3, therefore, can accumulate as NO_2 photolyzes as in Reaction 4, followed by Reaction 5. Specific mechanisms for the oxidation of a number of VOCs were discussed in the 2006 O_3 AQCD (U.S. EPA, 2006b).

It is often convenient to speak about families of chemical species defined in terms of members that interconvert rapidly on time scales shorter than those for formation or destruction of the family as a whole. For example, an odd oxygen (O_X) family can be defined as

$$O_X = \sum (O(^3P) + O(^1D) + O_3 + NO_2)$$

In much the same way, NO_X is sometimes referred to as odd nitrogen. Hence, production of O_X occurs by Equation 1, while the sequence of reactions given by Reactions 4–6 represents no net production of O_X. (Definitions of species families and methods for constructing families are discussed in Jacobson [1999] and references therein). Other families including N-containing species used later in this chapter are

$$NO_Z = \sum HNO_2 + HNO_3 + HNO_4 + NO_3^- + 2N_2O_5 + PAN(CH_3CHO - OO - NO_2)$$
$$+ \ other\ organic\ nitrates + halogen\ nitrates + particulate\ nitrates$$

and

$$NO_Y = NO_X + NO_Z$$

and

$$HO_X = OH + HO_2$$

NO_Z refers to the sum of all oxidation products of NO_X without the original NO and NO_2.

The reaction of NO_2 with O_3 leads to formation of the NO_3 radical.

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$
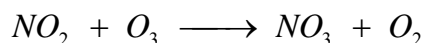
However, NO_3 radical reacts rapidly, having a τ of ~5 seconds during the photochemically most active period of the day near local solar noon, by two pathways (Atkinson et al., 1992):

$$NO_3 + h\nu \longrightarrow NO + O_{2(10\%)}$$

Reaction 9

$$NO_3 + h\nu \longrightarrow NO_2 + O(^3P)_{(90\%)}$$
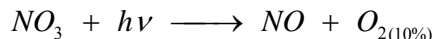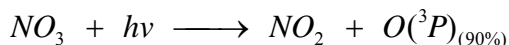
Reaction 10

Because of this, NO_3 concentrations remain low during daylight hours but can increase after sunset to nighttime concentrations of $<5 \times 10^7$ to 1×10^{10} molecules/cm^3 or <2 to 430 parts per trillion (ppt) over continental areas influenced by anthropogenic emissions of NO_X (Atkinson et al., 1986). At night, NO_3, rather than OH, is most often the primary oxidant in polluted tropospheric systems. Moreover, NO_3 can combine with NO_2 to form dinitrogen pentoxide (N_2O_5)

$$NO_3 + NO_2 \xleftrightarrow{M} N_2O_5$$
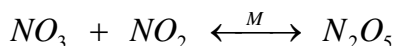
Reaction 11

and N_2O_5 then both photolyzes and thermally decomposes back to NO_2 and NO_3 during the day; however, N_2O_5 concentrations can accumulate during the night to ppb levels in polluted urban atmospheres.

The tropospheric chemical removal processes for NO_X include reaction of NO_2 with the OH radical and hydrolysis of N_2O_5 in aqueous aerosol solutions if there is no organic coating. Both of these reactions produce HNO_3

$$OH + NO_2 \xrightarrow{M} HNO_3$$

Reaction 12

$$N_2O_5 \xrightarrow{H_2O\,(1)} 2HNO_3$$
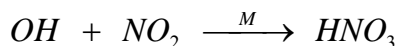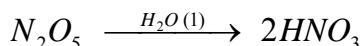
Reaction 13

The gas-phase reaction of OH with NO_2 (Reaction 12) is one of the major and ultimate removal processes for NO_X in the troposphere. This reaction removes OH and NO_2 in one step and competes with HC for OH in areas characterized by high NO_X concentrations such as urban centers. The τ for conversion of NO_X to HNO_3 in the PBL at 40ºN latitude ranges from ~4 hours in July to ~16 hours in January. The corresponding range in τ at 25ºN latitude is between 4 and 5 hours, while at 50ºN latitude, HNO_3 τ ranges from about 4 to 20 hours (Martin et al., 2003).

In addition to gas-phase HNO_3, Golden and Smith (2000) have shown on the basis of theoretical studies that pernitrous acid (HO_2NO) is also produced by the reaction of NO_2 and OH; however, this production channel most likely represents a minor yield of ~15% at the surface (JPL, 2003). Pernitrous acid will also thermally decompose and photolyze. Gas-phase HNO_3 formed from Reaction 12 and Reaction 13 undergoes wet and dry deposition to the surface and uptake by ambient aerosol particles.

In addition to uptake on particles and in cloud droplets, HNO_3, photolyzes and reacts with OH

$$HNO_3 \; + \; h\nu \; \longrightarrow \; OH \; + \; NO_2$$

Reaction 14

$$HNO_3 \; + \; h\nu \; \longrightarrow \; O \; + \; HNO_2$$

Reaction 15

$$HNO_3 \; + \; h\nu \; \longrightarrow \; H \; + \; NO_3$$

Reaction 16

and

$$HNO_3 \; + \; OH \; \longrightarrow \; NO_3 \; + \; H_2O$$
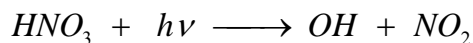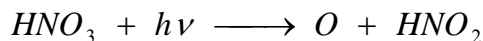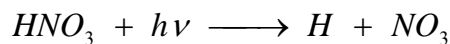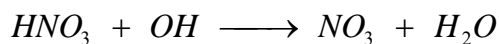
Reaction 17

Margitan and Watson (1982) established that Reaction 14 has a quantum yield of ~1, with only very small contributions from the two other possible photolytic pathways (Reactions 15 and 16). The τ of HNO_3 with respect to these two reactions is long enough for HNO_3 to act somewhat as a reservoir species for NO_X during long-range transport, contributing in this way to NO_2 levels in areas remote from the source region of the NO_X that formed this HNO_3.

The contribution of Reaction 13 to HNO_3 formation is highly uncertain during both winter and summer. The importance of Reaction 13 could be much higher during winter than during summer because of the much lower concentration of OH and the enhanced stability of N_2O_5 due to lower temperatures and UV flux. Geyer and Platt (2002) concluded that Reaction 16 constituted about 10% of the removal of NO_X at a site near Berlin, Germany during spring and summer. However, Dentener and Crutzen (1993) estimated this to be 20% in summer and 80% in winter. A modeling study by Tonnesen and Dennis (2000) reported; 16 to 31% of summer HNO_3 production from Reaction 13. Recent work in the northeastern U.S. (Brown et al., 2006a, b; Frost et al., 2006a) indicates that this reaction proceeds at a faster rate in power plant plumes than in urban plumes.

OH also reacts with NO to produce nitrous acid (HNO_2).

$$OH \; + \; NO \; \xrightarrow{\;M\;} \; HNO_2$$
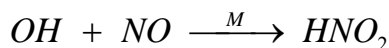
Reaction 18

In sunlight, HNO_2 is rapidly photolyzed back to the original reactants.

$$HNO_2 \; + \; h\nu \; \longrightarrow \; OH \; + \; NO$$
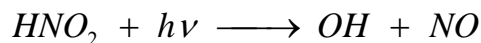
Reaction 19

Reaction 18 is, however, a negligible source of HNO_2, which is formed mainly by multiphase processes. At night, heterogeneous reactions of NO_2 in aerosols or at Earth's surface result in accumulation of HNO_2 (Harris et al., 1982; Jacob, 2000). Harris et al., (1982) suggested that photolysis of HNO_2 at sunrise could provide an important early-morning source of OH necessary to drive $P(O_3)$.

HO$_2$ can react with NO$_2$ to produce pernitric acid (HNO$_4$)

$$HO_2 + NO_2 + M \longrightarrow HNO_4 + M$$
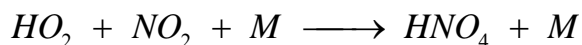
which can thermally decompose and photolyze back to its original reactants. The acids formed in these gas-phase reactions are all water soluble; thus, they can be incorporated into cloud droplets and in the aqueous phase of particles.

A broad range of organic N compounds are directly emitted by combustion sources or formed in the atmosphere from NO$_X$ emissions. Organic N compounds include the PANs, nitrosamines, nitro-PAHs, and the more recently identified nitrated quinones. Oxidation of VOCs produces organic peroxy radicals (RO$_2$). Reaction of RO$_2$ radicals with NO and NO$_2$ produces RONO$_2$ and peroxynitrates (RO$_2$NO$_2$)

$$RO_2 + NO \xrightarrow{M} RONO_2$$
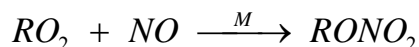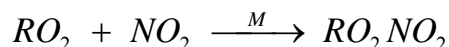
$$RO_2 + NO_2 \xrightarrow{M} RO_2NO_2$$

Reaction 21 is a minor branch for the reaction of RO$_2$ with NO; the major branch produces RO and NO$_2$ as discussed in the next section. However, the RONO$_2$ yield increases with carbon number (Atkinson, 2000).

The most important of these organic nitrates is PAN, the dominant member of the broader family of peroxyacyl nitrate species (PANs) which includes peroxypropionyl nitrate (PPN) of anthropogenic origin and peroxymethacrylic nitrate (MPAN) produced from isoprene oxidation. The PANs are formed by the combination reaction of acetyl peroxy radicals with NO$_2$

$$CH_3C(O)OO + NO_2 \longrightarrow CH_3C(O)OONO_2$$
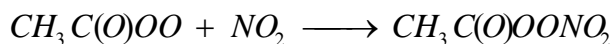
where the acetyl peroxy radicals are formed mainly during the oxidation of ethane (C$_2$H$_6$). Acetaldehyde (CH$_3$CHO) is formed as an intermediate species during the oxidation of ethane. CH$_3$CHO can be photolyzed or react with OH to yield acetyl radicals

$$CH_3C(O)H + h\nu \longrightarrow CH_3C(O) + H$$

$$CH_3C(O)H + OH \longrightarrow CH_3C(O) + H_2O$$
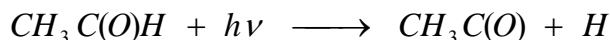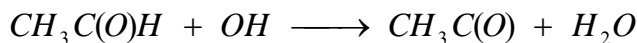
Acetyl radicals then react with O$_2$ to yield acetyl peroxy radicals.

$$CH_3C(O) + O_2 + M \longrightarrow CH_3C(O)OO + M$$
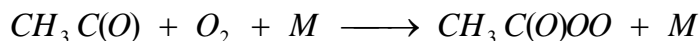
However, acetyl peroxy radicals will react with NO in areas of high NO concentrations

$$CH_3(CO)OO \; + \; NO \; \longrightarrow \; CH_3(CO)O \; + \; NO_2$$
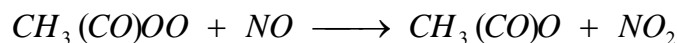
Reaction 27

and the acetyl-oxy radicals will then decompose.

$$CH_3(CO)O \; \longrightarrow \; CH_3 \; + \; CO_2$$
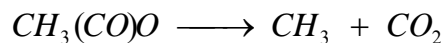
Reaction 28

Thus, formation of PAN is favored at conditions of high ratios of NO_2 to NO, which are most typically found under low total NO_X concentration conditions. The PANs both thermally decompose and photolyze back to their reactants with τ on the order of a few hours during warm sunlit conditions: τ with respect to thermal decomposition range from ~1 h at 298 K to ~2.5 days at 273 K and up to several weeks at 250 K. Thus, PANs can provide a reversible sink of NO_X at cold temperatures and high solar zenith angles, allowing release of NO_2 as air masses warm, particularly by subsidence from the free troposphere. The PANs are also removed by uptake to vegetation (Sparks et al., 2003; Teklemariam and Sparks, 2004). RO_2NO_2 produced by Reaction 22 are thermally unstable and most have very short τ of <100 seconds owing to thermal decomposition back to the original reactants. Thus they are not effective permanent sinks of NO_X, except at lower temepatures.

2.6.2.1. NO_X and Ozone Formation

O_3 is unlike most other air pollution species whose rates of formation vary directly with the emissions of their precursors in that $P(O_3)$ changes nonlinearly with the concentrations of its precursors. At the low NO_X concentrations found in most environments ranging from remote continental areas to rural and suburban areas downwind of urban centers, net $P(O_3)$ increases with increasing NO_X levels. At the high NO_X concentrations found in downtown metropolitan areas especially near busy streets and roadways and in power plant plumes, net destruction of O_3 by titration reaction with NO dominates. Between these two regimes is a transition stage in which $P(O_3)$ shows only a weak dependence on NO_X concentrations. In the high NO_X concentration regime, NO_2 scavenges OH (Reaction 12) which would otherwise oxidize VOCs to produce HO_2, which in turn would oxidize NO to NO_2 (Reaction 7). In the low NO_X concentration regime, VOC oxidation generates, or at least does not consume, free radicals, and $P(O_3)$ varies directly with NO_X levels. Sometimes the terms VOC-limited and NO_X-limited are used to describe these two regimes; also, the terms NO_X-limited and NO_X-saturated are used (see Jaeglé et al., 2001). OH chemistry initiates HC oxidation and behaves similarly to that for O_3 with respect to NO_X concentrations (Hameed et al., 1979; Pinto et al., 1993; Poppe et al., 1993; Zimmermann and Poppe, 1993). These considerations introduce a high degree of uncertainty into attempts to relate changes in O_3 concentration to precursors emissions. Note that in a NO_X-limited or NO_X-sensitive regime, $P(O_3)$ is not insensitive to radical production or the flux of solar UV photons; rather, $P(O_3)$ is simply more sensitive to the NO_X concentrations. For example, global tropospheric O_3 is sensitive to CH_4, even though the troposphere is predominantly NO_X-limited. More details on $P(O_3)$ are given in the 2008 NO_X ISA (U.S. EPA, 2008a).

2.6.2.2. Multiphase Interactions

Warneck (1999a) constructed a box model describing the chemistry of the oxidation of NO_2 including the interactions of N species and minor processes in sunlit cumulus clouds. The relative contributions of different reactions to the oxidation of NO_2 to NO_3 10 minutes after cloud formation are

given in Table 2-3 where the last two columns show the relative contributions with and without transition metal ions. Oxidation of NO_2 as delineated in Table 2-3 occurs mainly in the gas phase within clouds, implying that gas-phase oxidation of NO_2 by OH predominates.

NO_X and Halogen Chemistry Interactions

Four decades of observational data on O_3 in the troposphere have revealed numerous anomalies not fully explained by the gas-phase HO_X-NO_X photochemistry (described above). The best-known example is the dramatic decrease in ground-level O_3 concentration during polar sunrise due to multiphase catalytic cycles involving inorganic Br and Cl radicals (Barrie et al., 1988; Foster et al., 2001; Martinez et al., 1999). Other examples of anomalies in tropospheric O_3 at lower latitudes include O_3 concentrations <10 ppb in the marine boundary layer (MBL) and overlying free troposphere (FT) at times over large portions of the tropical Pacific (Kley et al., 1996), as well as post-sunrise O_3 concentration decreases over the western subtropical Pacific Ocean (Nagao et al., 1999), the temperate Southern Ocean (Galbally et al., 2000), and the tropical Indian Ocean (Dickerson et al., 1999).

Table 2-3. **Relative contributions of various gas and aqueous phase reactions to aqueous NO_3 formation within a sunlit cloud, 10 minutes after cloud formation.**

Reaction	% of Total[a]	% of Total[b]
GAS PHASE		
$OH + NO_2 + M$	57.7	67.4
AQUEOUS PHASE		
$N_2O_5(g) + H_2O$	8.1	11.2
$NO_3^- + Cl^-$	<0.1	0.1
$NO_3^- + SO_3^{2-}$	0.7	1.0
$NO_3^- + HCOO^-$	0.6	0.8
$HNO_4 + SO_3^{2-}$	31.9	20.5
$HOONO + NO_3^-$	0.8	<0.1
$O_3 + NO_2^-$	<0.1	<0.1

[a] In the absence of transition metals. [b] In the presence of iron and copper ions.
Source: Adapted from Warneck (1999a). Used with permission.

The set of N reactions with aerosol salts in marine atmospheres sketched briefly here was reviewed in detail by De Haan et al. (1999). This chemistry remains important not only for halogen cycling and atmospheric oxidation reactions (Andreae and Crutzen, 1997), but also because through them NO_3^- can be shifted from gas-phase HNO_3 or from fine-mode aerosol after dissociation of NH_4NO_3, for example, to coarse-mode particles, thereby enhancing the potential for local N deposition to coastal regions. The actual areal extent of N deposition resulting from gas-to-particle NO_3^- conversion, however, is a complex function of local wind speeds, as shown by Pryor and Sørensen (2000). With moderate winds of 3.5–10 m/s (~8 to 22 mph), gas-phase HNO_3 V_d exceeded that of an average sodium nitrate ($NaNO_3$) particle, whereas at higher and lower wind speeds the reverse was true. This means that as a result of gas-to-particle NO_3^- conversion, under commonly moderate winds, less N would be deposited locally and more would be available for transport and deposition in a larger area of extent.

2.6.3. SO$_X$ Chemistry

The only forms of monomeric SO$_X$ of interest in troposheric chemistry are SO$_2$ and SO$_3$. SO$_3$ can be emitted from the stacks of power plants and factories; however, it reacts extremely rapidly with H$_2$O in the stacks or immediately after release into the atmosphere to form H$_2$SO$_4$, which mainly condenses onto existing particles when particle loadings are high; it can nucleate to form new particles under lower concentration conditions. Thus, only SO$_2$ is present in the troposheric boundary layer at concentrations of concern for environmental exposures.

Gas phase oxidation of SO$_2$ is initiated by the reaction

$$SO_2 + OH + M \longrightarrow HSO_3 + M$$

Reaction 29

followed by

$$HSO_3 + O_2 \longrightarrow SO_3 + HO_2$$

Reaction 30

$$SO_3 + H_2O \longrightarrow H_2SO_4$$
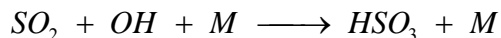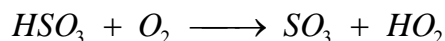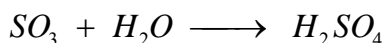
Reaction 31

Because the saturation vapor pressure of H$_2$SO$_4$ is extremely low, it will be removed rapidly by transfer to the aqueous phase of aerosol particles and cloud droplets. Depending on atmospheric conditions and the concentrations of other ambient particles and gas-phase species that can participate in new particle formation, it can also nucleate to form new particles. Rate coefficients for the reactions of SO$_2$ with either HO$_2$ or NO$_3$ (JPL, 2003) are too low to be significant.

SO$_2$ is chiefly but not exclusively primary in origin; it is also produced by the photochemical oxidation of reduced S compounds such as DMS, H$_2$S, CS$_2$, OCS, and methyl mercaptan, which are all mainly biogenic in origin (Their sources are discussed in Section 2.3.2). Table 2-4 lists the τ of reduced S species with respect to reaction with various oxidants. Except for OCS, which is lost mainly by photolysis with τ ~6 months, these species are lost mainly by reaction with OH and NO$_3^-$.

Table 2-4. **Atmospheric lifetimes (τ) of SO$_2$ and reduced S species with respect to reaction with OH, NO$_3$, and Cl radicals.**

Compound	OH		NO$_3$		Cl	
	k x 10^{12}	τ	k x 10^{12}	τ	k x 10^{12}	τ
SO$_2$	1.6	7.2 d	NA		NA	
CH$_3$−S-CH$_3$	5.0	2.3 d	1.0	1.1 h	400	29 d
H$_2$S	4.7	2.2 d	NA		74	157 d
CS$_2$	1.2	9.6 d	<0.0004	>116 day	<0.004	Nr
OCS	0.0019	17 y	<0.0001	>1.3 yr	<0.0001	Nr
CH$_3$−S-H	33	8.4 h	0.89	1.2 h	200	58 d
CH$_3$−S-S-CH$_3$	230	1.2 h	0.53	2.1 h	NA	

[1]Rate coefficients were taken from JPL Chemical Kinetics Evaluation No. 14 (JPL 2003). NA = Reaction rate coefficient not available. OH = 1 × 10^6/cm^3 . NO$_3$ = 2.5 × 10^8/cm^3
Cl = 1 × 10^8/cm^3. Nr = Rate coefficient too low to be relevant as an atmospheric loss mechanism. Rate coefficients were calculated at 298 K and 1 atmosphere.
Source: Seinfeld and Pandis (1998)

Because OCS is relatively long-lived in the troposphere, it can be transported upwards into the stratosphere. Crutzen (1976) proposed that its oxidation serves as the major source of SO$_4^{2-}$ in the stratospheric Junge layer during periods when volcanic plumes do not reach the stratosphere. However, the flux of OCS into the stratosphere is probably not sufficient to maintain this stratospheric aerosol layer. Myhre et al. (2004) proposed instead that SO$_2$ transported upwards from the troposphere is the most likely source since the upward flux of OCS is too small to sustain observed SO$_4^{2-}$ loadings in the Junge layer. In addition, in situ measurements of the isotopic composition of S do not match those of OCS (Leung et al., 2002).

Reaction with NO$_3$ at night most likely represents the major loss process for DMS and methyl mercaptan, although the mechanisms are not well understood. Initial attack by NO$_3$ and OH involves H$^+$ abstraction, with a smaller branch leading to OH addition to the S atom. The OH addition branch increases in importance as temperatures decrease, becoming the major pathway below temperatures of 285 K (Ravishankara, 1997). The adduct may either decompose to form methanesulfonic acid (MSA) or undergo further reactions in the main pathway to yield DMS (Barnes et al., 1991). Following H$^+$ abstraction from DMS, the main reaction products include MSA and SO$_2$. The ratio of MSA to SO$_2$ is strongly temperature dependent, varying from 0.1 in tropical waters to 0.4 in Antarctic waters (Seinfeld and Pandis, 1998). SO$_4^{2-}$ in excess of that expected from sea salt aerosols is related mainly to production of SO$_2$ from the oxidation of DMS. These transformations among atmospheric S compounds are summarized in Figure 2-18.
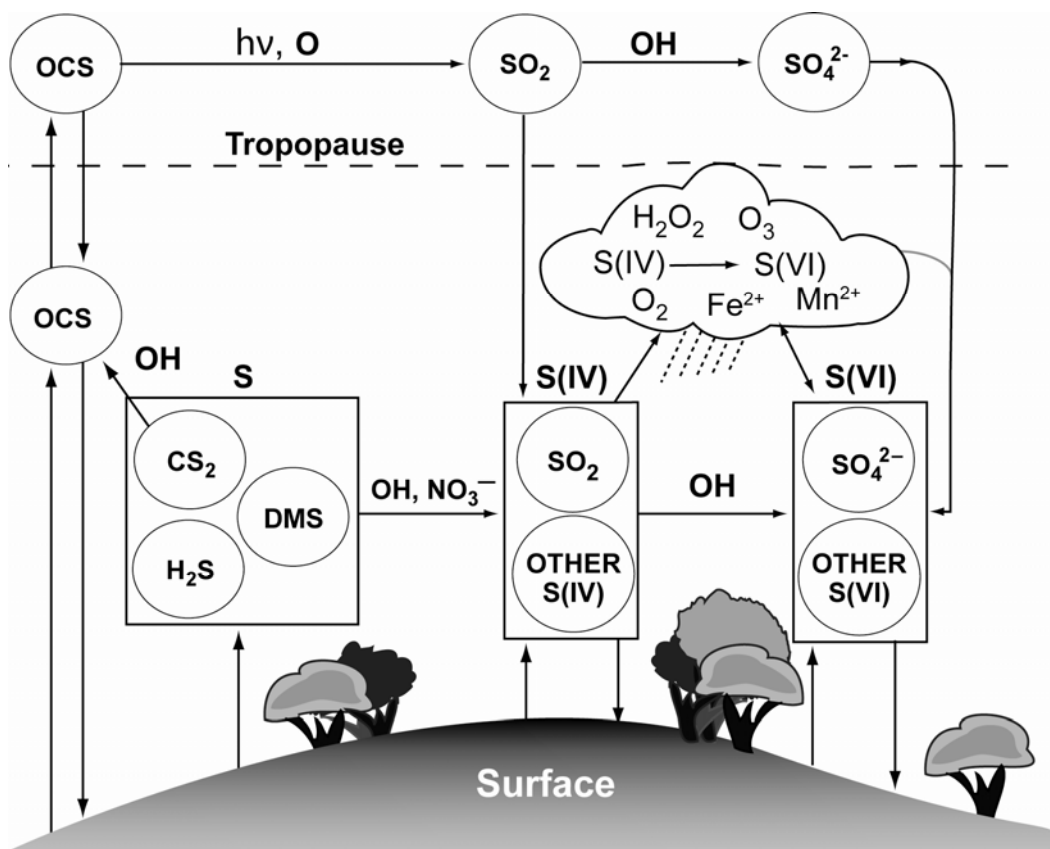
Figure 2-18.   Atmospheric cycle of S compounds.

2.6.3.1. Multi-Phase SO_X Chemistry

The major S species in clouds are hydrogen sulfite (HSO_3^-) and the sulfite ion (SO_3^{2-}). Both are derived from the dissolution of SO_2 in water and are grouped together as S(IV); bisulfate ion (HSO_4^-) and SO_4^{2-} are grouped together as S(VI). The chief species capable of oxidizing S(IV) to S(VI) in cloud water are O_3, H_2O_2 or organic peroxides, OH, and ions of transition metals such as iron (Fe), manganese (Mn) and copper (Cu) in the presence of O_2. The basic mechanism of aqueous-phase oxidation of SO_2 has long been studied and can be found in numerous texts on atmospheric chemistry; see for example, Finlayson-Pitts and Pitts (2000), Jacob (1999), Jacobson (2002), and Seinfeld and Pandis (1998). Following Jacobson (2002), the steps involved in aqueous-phase oxidation of SO_2 can be summarized as: dissolution of SO_2

$$SO_2(g) \longleftrightarrow SO_2(aq)$$
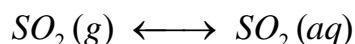
Reaction 32

and formation and dissociation of H_2SO_3.

$$SO_2(aq) + H_2O(aq) \longleftrightarrow H_2SO_3 \longleftrightarrow H^+ + HSO_3^- \longleftrightarrow 2H^+ + SO_3^{2-}$$
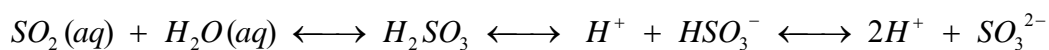
Reaction 33

In the pH range commonly found in rainwater, pH 2 to 6, the most important reaction converting S(IV) to S(VI) is

$$HSO_3^- + H_2O + H^+ \longleftrightarrow SO_4^{2-} + H_2O + 2H^+$$
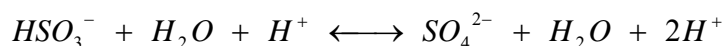
Reaction 34

as SO_3^{2-} is much less abundant than HSO_3^-.

Another pathway to aqueous-phase oxidation of S(IV) is reaction with O_3

$$HSO_3^- + O_3 + OH \longrightarrow SO_4^{2-} + H_2O + O_2$$
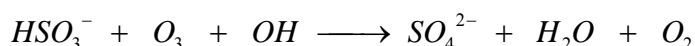
Reaction 35

But while the gas-phase reaction of SO_2 with O_3 is slow, the aqueous phase analog of Reaction 35 is rapid, with rate coefficient increases up to a value of $\sim 5 \times 10^{-3}$ with increasing pH between 1 and 3 (Finlayson-Pitts and Pitts, 2000).

Major pathways for the aqueous-phase oxidation of S(IV) to S(VI) as a function of pH are shown in Figure 2-19. For pH up to about 5.3, H_2O_2 is the dominant oxidant converting S(IV) to S(VI), while at pH >5.3, O_3 becomes dominant, followed by Fe(III), using the characteristic values found in Seinfeld and Pandis (1998). However, differences in concentrations of oxidants result in differences in the pH at which this transition occurs. Note that oxidation of SO_2 by O_3 and O_2 tends to be self-limiting: as SO_4^{2-} is formed, pH decreases and rates of these reactions decrease. Higher pH levels are expected to be found mainly in marine aerosols; however, in marine aerosols, the Cl-catalyzed oxidation of S(IV) may be more important (Hoppel and Caffrey, 2005; Zhang and Millero, 1991). Because NH_4^+ is so effective in neutralizing acidity, it, too, affects the rate of oxidation of S(IV) to S(VI) and the rate of dissolution of SO_2 in particles and cloud droplets.

Comparison of the relative rates of oxidation by gas-and-aqueous phase reactions by Warneck (1999b) indicated that, on average, only $\sim 20\%$ of SO_2 is oxidized by gas-phase reactions; the remainder is oxidized by aqueous-phase reactions. Warneck's box model (1999a) describing the chemistry of the oxidation of SO_2 and NO_2 included interactions of S species and minor processes in sunlit cumulus clouds. The relative contributions of different reactions to the oxidation of S(IV) species to S(VI) 10 minutes after cloud formation are given in Table 2-5 with the last two columns showing the relative contributions with and without transition metal ions. As can be seen from Table 2-5, SO_2 within a cloud (gas + cloud droplets) is oxidized mainly by H_2O_2 in the aqueous phase, while gas-phase oxidation by OH is small by comparison. A much smaller contribution in the aqueous phase is made by methyl hydroperoxide (CH_3OOH) because it is formed mainly in the gas phase and its Henry's Law constant is several orders of magnitude smaller that of H_2O_2. After H_2O_2, HNO_4 is the major contributor to S(IV) oxidation.

The values shown in Table 2-5 here and Table 2-3 above for NO_3 indicate that gas-phase oxidation accounts for only $\sim 20\%$ of SO_2 oxidation but $\sim 90\%$ of NO_2 oxidation.
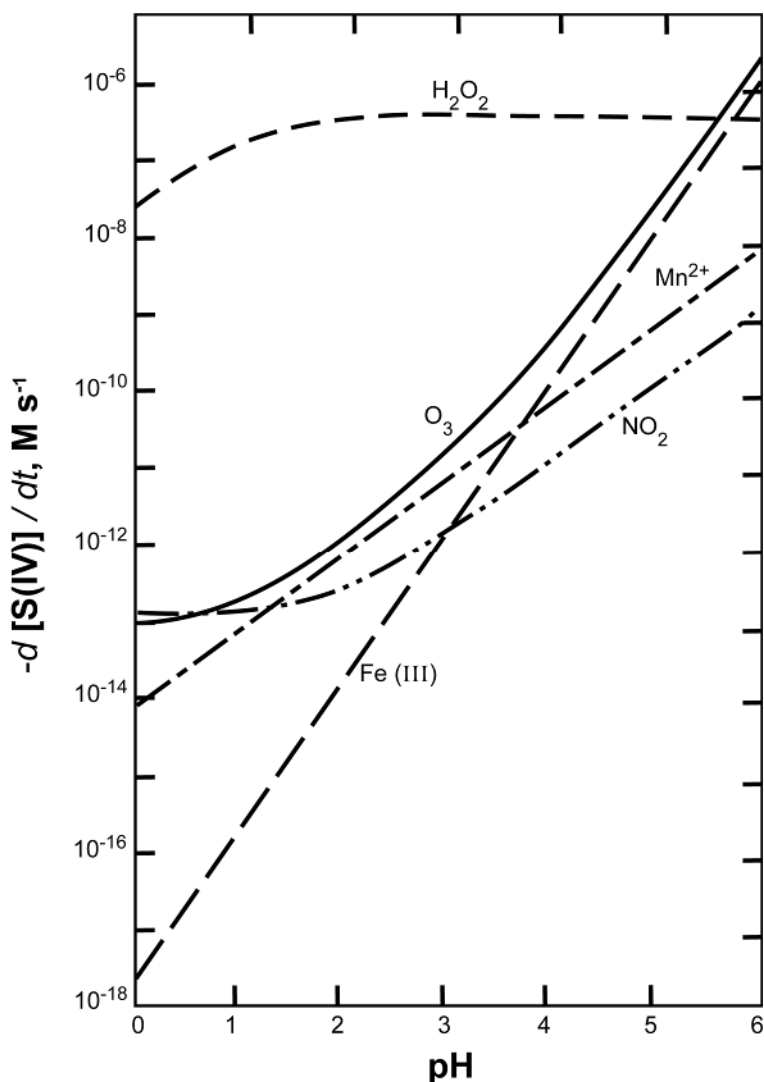
Figure 2-19. Comparison of aqueous-phase oxidation paths. The rate of conversion of S(IV) to S(VI) is shown as a function of pH. Concentrations assumed are: $[SO_2(g)] = 5$ ppb; $[NO_2(g)] = 1$ ppb; $[H_2O_2(g)] = 1$ ppb; $[O_3(g)] = 50$ ppb; $[Fe(III)(aq)] = 0.3$ μM; $[Mn(II)(aq)] = 0.3$ μM.

In areas away from strong pollution sources, the SO_2 τ is ~7 days, based on measurements of the rate constant for Reaction 29 (JPL, 2003) and a nominal OH concentration of 10^6 molecules/cm^3. However, the mechanism of SO_2 oxidation at a particular location depends on local environmental conditions. For example, near stacks, oxidants such as OH are depleted and almost no SO_2 is oxidized in the gas phase. Farther downwind, as the plume is diluted with background air, the gas phase oxidation of SO_2 increases in importance. Finally, even farther downwind when conditions in the plume can become more oxidizing than in background air, the SO_2 oxidation rate can exceed that in background air.

SO_2 in the PBL is also removed from the atmosphere by dry deposition to moist surfaces, resulting in an atmospheric τ with respect to dry deposition of ~1 day to 1 week. Wet deposition of S naturally depends on the variable nature of rainfall, but in general results in a τ of ~7 days, too. These two processes, oxidation and deposition, lead to an overall τ of SO_2 in the atmosphere of 3 to 4 days.

Table 2-5. Relative contributions of various reactions to the total S(IV) oxidation rate within a sunlit cloud, 10 minutes after cloud formation.

Reaction	% of Total[a]	% of Total[b]
GAS PHASE		
$OH + SO_2$	3.5	3.1
AQUEOUS PHASE		
$O_3 + HSO_3^-$	0.6	0.7
$O_3 + SO_3^{2-}$	7.0	8.2
$H_2O_2 + SO_3^{2-}$	78.4	82.1
$CH_3OOH + HSO_3^-$	0.1	0.1
$HNO_4 + HSO_3^-$	9.0	4.4
$HOONO + HSO_3^-$	<0.1	<0.1
$HSO_5^- + HSO_3^-$	1.2	<0.1
$SO_5^- + SO_3^{2-}$	<0.1	<0.1
$HSO_5^- + Fe^{2+}$		0.6

[a]In the absence of transition metals. [b]In the presence of iron and copper ions.
Source: Adapted from Warneck (1999a). Used with permission.

Multiphase chemical transformations involving inorganic halogenated compounds effect changes in the multiphase cycling of SO_X in ways analogous to their effects on NO_X. Oxidation of DMS by BrO produces dimethyl sulfoxide (DMSO) (Barnes et al., 1991; Toumi, 1994), and oxidation by Cl leads to formation of SO_2 (Keene et al., 1996). DMSO and SO_2 are precursors for MSA and H_2SO_4. In the MBL, virtually all H_2SO_4 and MSA vapor condenses onto existing aerosols or cloud droplets, which subsequently evaporate thereby contributing to aerosol growth and acidification. Unlike MSA, H_2SO_4 also has the potential to produce new particles (Korhonen et al., 1999; Kulmala et al., 2000) which in marine regions is thought to occur primarily in the free troposphere.

Excepting H_2SO_4, inorganic particles are solid at low relative humidity (RH), and their composition determines their deliquescence thresholds for forming saturated aqueous solutions. Crystallization is not simply the reverse of deliquescence but is a process subject to hysteresis; see the sodium chloride (NaCl) + Na_2SO_4 example in Figure 2-20, and Tang and Munkelwitz (1993) for deliquescence RH points of other inorganic particles.

Particles with several components behave similarly to the example of Na_2SO_4 but with more complex curves and generally have deliquescence RH points below those of their constituent components (Wexler and Seinfeld, 1991).

Saiz-Lopez et al. (2004) estimated that observed levels of BrO at Mace Head Atmospheric Research Station in Ireland would oxidize $(CH_3)_2S$ ~6 times faster than OH and thereby substantially increase $P(H_2SO_4)$ and other condensable S species in the MBL. SO_2 is also scavenged by deliquesced aerosols and oxidized to H_2SO_4 in the aqueous phase by several strongly pH-dependent pathways (Chameides and Stelson, 1992; Keene and Savoie, 1998; Vogt et al., 1996). Model calculations indicate that oxidation of S(IV) by O_3 dominates in fresh, alkaline sea salt aerosols, whereas oxidation by hypohalous acids, primarily HOCl, dominates in moderately acidic solutions.
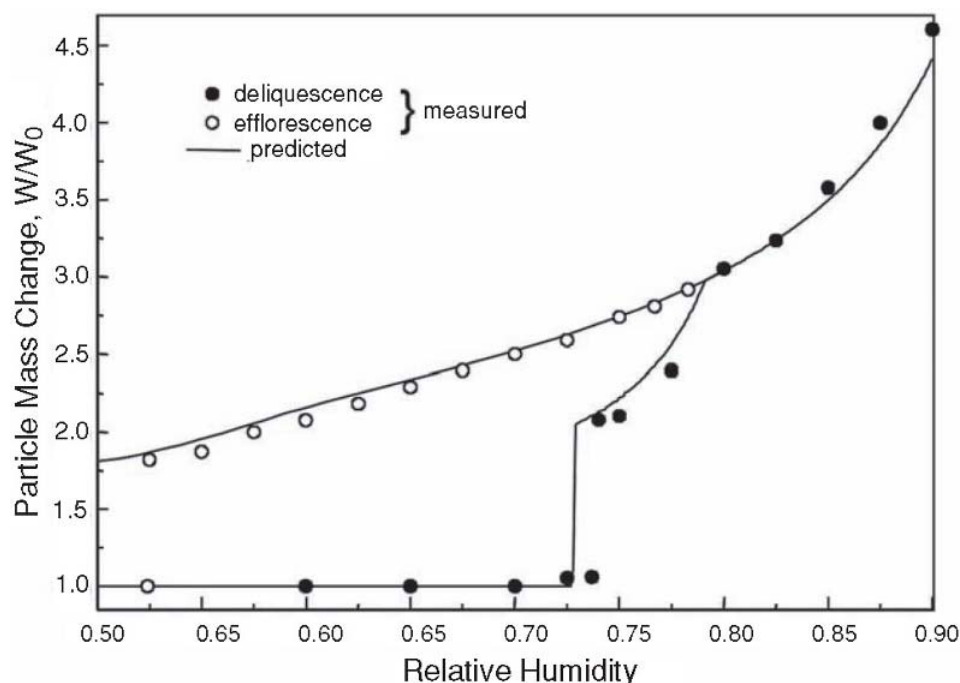
Figure 2-20. **RH effects on deliquescence and efflorescence points for a NaCl+ Na₂SO₄ particle, indicating deliquescence at ~72% relative humidity and re-crystallization at ~52% RH. Points are measurements from Tang et al., (1997); solid line is aerosol thermodynamic model prediction of Ansari and Pandis (2000).**

Additional non-sea salt (nss) pSO_4 is generated by SO_2 oxidation in cloud droplets (Clegg and Toumi, 1998). Ion-balance calculations indicate that most of the nss pSO_4 in short-lived sea salt size fractions accumulates in acidic aerosol solutions or in acidic aerosols processed through clouds or both (see, e.g., Keene et al., 2004). The production, cycling, and associated radiative effects of S-containing aerosols in marine and coastal air are regulated in part by chemical transformations involving inorganic halogens (Von Glasow et al., 2002b). These transformations include: dry-deposition fluxes of nss pSO_4 in marine air dominated, naturally, by the sea salt size fractions (Huebert et al., 1996; Turekian et al., 2001); HCl phase partitioning that regulates sea salt pH and associated pH-dependent pathways for S(IV) oxidation (Keene et al., 2002; Pszenny et al., 2004); and potentially important oxidative reactions with reactive halogens for $(CH_3)_2S$ and S(IV). However, both the absolute magnitudes and relative importance of these processes in MBL S cycling are poorly understood.

2.6.4. Multiphase NO_X, SO_X, and NH_X Interactions

Figure 2-17 above illustrated the central role NH_3 can play in the atmospheric chemistry of NO_X and SO_X. This results in part from its being the most common soluble base in the atmosphere and from a range of its possible chemical reactions. OH attack on NH_3 proceeds by

$$NH_3 + OH \longrightarrow NH_2 + H_2O$$
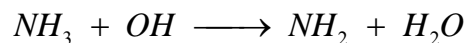
Reaction 36

The fate of the NH_2 radical is not known with certainty, but in polluted atmospheres can be

$$NH_2 + O_3 \longrightarrow NH, NHO, NO$$

$$NH_2 + NO_2 \longrightarrow N_2$$

$$NH_2 + NO_2 \longrightarrow N_2O + H_2O$$
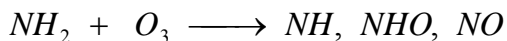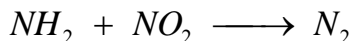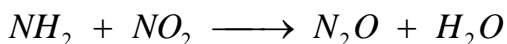
However, with typical OH concentrations of 1 to 2 x 10^6 molecules/cm^3, the τ of NH_3 against the initial reaction is ~30 to 70 days, sufficiently long that this is a small sink compared to NH_3 uptake by cloud droplets where it is reduced to NH4+

$$NH_3(g) + H_2O \longleftrightarrow NH_3 \cdot H_2O(aq) \longleftrightarrow NH_4^+ + OH$$
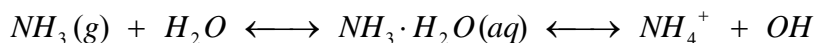
Gas-phase NH_3 also reacts with gas-phase HNO_3 to form particulate NH_4NO_3

$$NH_3 + HNO_3 \longleftrightarrow NH_4NO_3$$
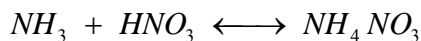
and with aqueous-phase H_2SO_4 to form particulate and aqueous-phase NH_4HSO_4 and $(NH_4)_2SO_4$.

$$NH_3(g) + H_2SO_4(l) \longrightarrow NH_4HSO_4(s,l)$$

$$NH_3(g) + NH_4HSO_4(l) \longrightarrow (NH_4)_2SO_4(s,l)$$
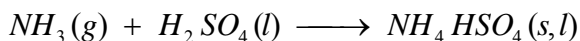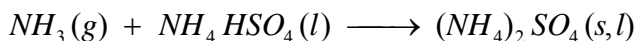
These products are of special note because submicron NH_4HSO_4 and $(NH_4)_2SO_4$ can act as cloud condensation nuclei, but the $H_2SO_4 + H_2O$ system does not readily undergo nucleation without addition of NH_4^+ (Coffman and Hegg, 1995; Kulmala et al., 2007). These two product species are also of interest because Reaction 42 and Reaction 43 are not reversible under typical ambient conditions, while Reaction 41, resulting in creation of NH_4NO_3, is reversible. The NH_4NO_3 is in a thermodynamic equilibrium with NH_4^+ and HNO_3 in the gas phase such that lower temperatures shift the equilibrium toward greater production of NH_4NO_3. Higher RH also shifts the equilibrium toward liquid-phase NH_4NO_3. For these reasons, and because gas-phase NH_3 will neutralize SO_4^{2-} preferentially first, NH_4NO_3 can only form when an excess of gas-phase NH_3 first exists.

Along with HNO_3 and H_2SO_4, NH_3 can be limiting in the formation of secondary atmospheric particles containing NO_3 and SO_4^{2-}. Measurements and thermodynamic models of free and condensed-phase precursors have been used to predict the limiting reactant under different atmospheric conditions (Blanchard et al., 2000; Dennis et al., 2001; Watson et al., 1994). Figure 2-21 shows results from one application of this technique from Blanchard et al. (2000) with isopleths of NO_3^- concentrations as predicted from total HNO_3 and NH_3 with 25 µg/m^3 SO_4^{2-} and 2 µg/m^3 total Cl$^-$. Formation of pNO3 is limited by total NH_3 availability, but not HNO_3, where isolines are vertical. NO_3^- exists predominately in

the condensed phase where isolines are horizontal and formation is not limited by NH_3 there. These relationships have been confirmed in field measurements like those reported for NO_3^- aloft in Arnold and Luke (2007).
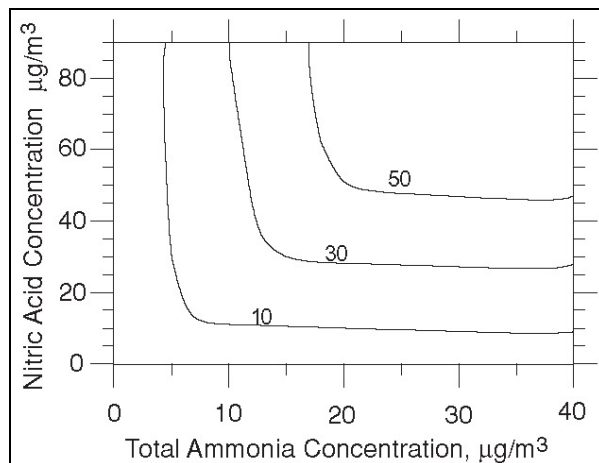
Figure 2-21. Predicted isolines of particulate NO$_3$ concentrations (µg/m³) as a function of total HNO$_3$ and NH$_3$ at 293 K and 80% relative humidity, and with 25 µg/m³ SO$_4^{2-}$ and 2 µg/m³ total Cl⁻.
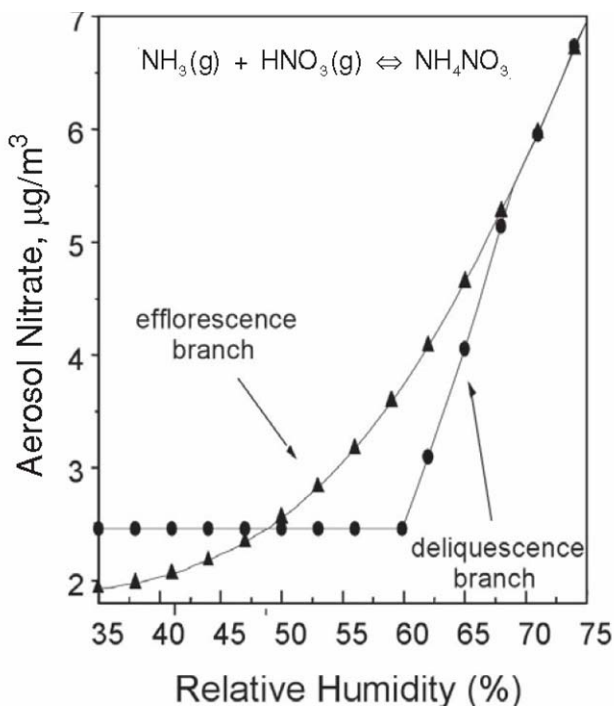
Figure 2-22. Predicted particulate NO$_3$ concentration as a function of RH for a typical environment. Actual measured values depend on aging characteristics of the particle.

Changing RH and particle water content also change the partitioning between gas and condensed phases for semivolatile species like NO_3^-; see Figure 2-22 for the example of NH_4NO_3.

The phase partitioning of NH_3 with deliquesced aerosol solutions is controlled primarily by the thermodynamic properties of the system

$$NH_3(\,g\,) \xleftrightarrow{\;K_H\;} [\,NH_3(\,aq\,)] \xleftrightarrow{\;K_b\;} [\,NH_4^+\,] + K_w/[\,H^+\,]$$
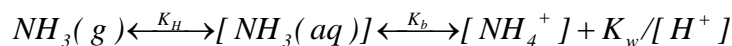
<div align="right">Reaction 44</div>

where K_H and K_b are the temperature-dependent Henry's Law and dissociation constants 62 M/atm, 1.8×10^{-5} M, respectively, for NH_3; and K_w is the ion product of water, 1.0×10^{-14} M (Chameides, 1984). For a given NH_X concentration, increasing aqueous concentrations of particulate H^+ will shift the partitioning of NH_3 towards the condensed phase. Consequently, under the more polluted conditions characterized by higher pSO_4 concentration, ratios of gas-phase NH_3 to particulate NH_4^+ decrease (Smith et al., 2007). It also follows that in marine air, where aerosol acidity varies substantially as a function of particle size, NH_3 partitions preferentially to the more acidic submicron size fractions (Keene et al., 2004; Smith et al., 2007).

Because the dry V_d of gas-phase NH_3 to the surface is substantially greater than that for the submicron pSO_4 fractions with which most NH_4^+ is associated, dry deposition fluxes of total NH_3 are dominated by the gas-phase fraction (Russell et al., 2003; Smith et al., 2007). Consequently, partitioning with acidic pSO_4 effectively increases the τ of total NH_3 against dry deposition.

This shift has important consequences for NH_3 cycling in the atmosphere and potential ecological effects. In coastal New England during summer, air transported from rural eastern Canada contains relatively low concentrations of nss pSO_4 and total NH_3 (Smith et al., 2007). Under these conditions, the roughly equal partitioning of total NH_3 between gas and particulate phases sustains substantial dry deposition fluxes to the coastal ocean of total NH_3 with a median value of 10.7 $\mu M/m^2$/day. In contrast, heavily polluted air transported from the industrialized midwestern U.S. contains median concentrations of nss pSO_4 and total NH_3, which are a factor of ~3 or greater more than that median value for clean air. Under these conditions, >85% of the total NH_3 partitions to the acidic pSO_4 size fractions, and, consequently, the median dry-deposition flux of total NH_3 is 30% lower than that under the cleaner, northerly flow regime. The relatively longer atmospheric τ of total NH_3 against dry deposition under more polluted conditions implies that, on average, total NH_3 would accumulate to higher atmospheric concentrations under these conditions and also be subject to atmospheric transport over longer distances. Consequently, the importance of NH_X removal via wet deposition would also increase. Because of the inherently sporadic character of precipitation, greater heterogeneity may exist in NH_3 deposition fields leading to similar heterogeneity in any potential responses in sensitive ecosystems downwind of major S emissions regions.

2.6.5. Transport-Related Effects on Chemistry

Convective processes and small-scale turbulence transport pollutants both upward and downward throughout the PBL and the FT. NO_X, SO_X, and NH_X can be transported vertically by convection into the upper part of the mixed layer on one day, then transported overnight as a layer of elevated mixing ratios, sometimes by a nocturnal low-level jet, and then entrained into a growing convective boundary layer downwind and brought back to the surface.

Because NO and NO_2 are only slightly soluble, they can be transported over longer distances in the gas phase than can more soluble species which are depleted by deposition to moist surfaces or taken up more readily on aqueous surfaces of particles. During transport, emitted N species can be transformed into reservoir species such as HNO_3, PANs, and N_2O_5. These species can then contribute to local NO_X concentrations in remote areas. For example, it is now well established that PAN decomposition provides

a major source of NO_X in the remote troposphere (Staudt et al., 2003). PAN decomposition in subsiding air masses from Asia over the eastern Pacific could make an important contribution to O_3 and NO_X enhancement in the U.S. (Hudman et al., 2004; Kotchenruther et al., 2001). Further details about mechanisms for transporting O_3 and its precursors were described at length in 2006 O_3 AQCD (U.S. EPA, 2006b).

Major episodes of high pollution concentrations in the eastern U.S. and in Europe are often associated with slow-moving high-pressure systems. High-pressure systems during the warmer seasons are associated with subsidence, resulting in warm, generally cloudless conditions with light winds. The subsidence results in stable conditions near the surface, which inhibit or reduce the vertical mixing of primary and secondary pollutants. Photochemical activity is enhanced under these conditions because of higher temperatures and the availability of sunlight.

Crutzen and Gidel (1983), Gidel (1983), and Chatfield and Crutzen (1984) hypothesized that convective clouds played an important role in rapid atmospheric vertical transport of trace species and first tested simple parameterizations of convective transport in atmospheric chemical models. At nearly the same time, evidence was shown of venting the boundary layer by shallow, fair weather cumulus clouds (see, e.g., Greenhut et al., 1984; Greenhut, 1986). Field experiments were conducted in 1985, which resulted in verification of the hypothesis that deep convective clouds are instrumental in atmospheric transport of trace constituents (Dickerson et al., 1987). Once pollutants are lofted to the middle and upper troposphere, they typically have a much longer chemical τ and, with the generally stronger winds at these altitudes, can be transported long distances from their source regions. Transport of NO_X from the boundary layer to the upper troposphere by convection tends to dilute concentrations and extend the NO_X τ from <24 h to several days. Photochemical reactions occur during this long-range transport. Pickering et al. (1990) demonstrated that venting of boundary layer NO_X by convective clouds (shallow and deep) causes enhanced $P(O_3)$ in the FT. NO_X at the surface can often increase $P(O_3)$ efficiency. Therefore, convection aids in the transformation of local pollution into a contribution to global atmospheric pollution. Downdrafts within thunderstorms tend to bring air with less NO_X from the middle troposphere into the boundary layer. Lightning produces NO which is directly injected chiefly into the middle and upper troposphere. The total global production of NO by lightning remains uncertain, but is on the order of 10% of the total.

The first unequivocal observations of deep convective transport of boundary layer pollutants to the upper troposphere were documented by Dickerson et al. (1987). Instrumentation aboard three research aircraft measured CO, O_3, NO, NO_X, NO_Y, and HCs in the vicinity of an active mesoscale convective system near the border of Oklahoma and Arkansas during the 1985 PRE-STORM experiment. Anvil penetrations about two hours after cloud maturity found greatly enhanced mixing ratios inside the cloud of all of the aforementioned species compared with outside it. NO mixing ratios in the anvil averaged 3 to 4 ppb, with individual 3-min observations reaching 6 ppb; boundary layer NO_X was typically 1.5 ppb or less outside the cloud. Therefore, the anvil observations represent a mixture of boundary layer NO_X and NO_X contributed by lightning. Luke et al. (1992) summarized the air chemistry data from all 18 flights during PRE-STORM by categorizing each case according to synoptic flow patterns. Storms in the maritime tropical flow regime transported large amounts of CO, O_3, and NO_Y into the upper troposphere while the midtroposphere remained relatively clean. During frontal passages a combination of stratiform and convective clouds mixed pollutants more uniformly into the middle and upper levels.

Thunderstorm clouds are optically very thick and, therefore, have major effects on radiative fluxes and photolysis rates. Madronich (1987) provided modeling estimates of the effects of clouds of various optical depths on photolysis rates. In the upper portion of a thunderstorm anvil, photolysis is likely to be enhanced by a factor of 2 or more due to multiple reflections off the ice crystals. In the lower portion and beneath the cloud, photolysis is substantially decreased. With enhanced photolysis rates, the NO-to-NO_2 ratio in the upper troposphere is driven to larger values than under clear-sky conditions.

Thunderstorm updraft regions, which contain copious amounts of water, are regions where efficient scavenging of soluble species can occur (Balkanski et al., 1993). NO_2 itself is not very soluble; hence, wet scavenging is not a major removal process for it. However, a major NO_X reservoir species, HNO_3, is

highly soluble. Very few direct field measurements of the amounts of specific trace gases, including HNO_3, that are scavenged in storms are available. Pickering et al. (2001) used a combination of model estimates of soluble species that did not include wet scavenging and observations of these species from the upper tropospheric outflow region of a major line of convection observed near Fiji. Over 90% of the NO_X in the outflow air appeared to have been removed by the storm.

2.7. Sampling and Analysis Techniques

2.7.1. Methods for Relevant Gas-Phase N Species

Separate sections here on field-deployed measurement techniques focus on current methods and promising new technologies so no attempt is made to cover development of these methods or methods no longer in widespread use. Rather, the descriptions in this chapter concern chiefly the Federal Reference Methods and Federal Equivalent Methods (FRM and FEM, respectively). More detailed discussions of the FRM, FEM, and other, newer methods including issues about their field use are found in Clemitshaw (2004); Edgerton et al. (2006, 2007); McClenny (2000); Parrish and Fehsenfeld (2000); and U.S. EPA (1996a, 2008a, 2008b).

2.7.1.1. NO and NO_2

Chemiluminescence

NO can be measured reliably using the principle of gas-phase chemiluminescence (CL) induced by the reaction of NO with O_3 at low pressure. Modern commercial NO_X analyzers have sufficient sensitivity for adequate measurement in urban and many rural locations (U.S. EPA, 1993a, 2006b). Research grade CL instruments have been compared under realistic field conditions to spectroscopic instruments with results that indicate that both methods are reliable at concentrations relevant to smog studies to better than 15% when using a 95% confidence response time of 60 seconds (see Crosley, 1996). Near-source, urban, and rural and remote concentrations of NO are routinely measured using CL. However, Cardelino and Chameides (2000) reported that measured NO concentrations during the afternoon were frequently at or below the operational limit of detection (LOD), ~1 ppb, of the regulatory NO_X instruments even in large metropolitan regions such as Washington, DC, Houston, TX, and New York, NY.

The FRM for NO_2 also makes use of this NO detection technique using a prerequisite step to reduce NO_2 to NO on the surface of a molybdenum oxide (MoO_X) substrate heated to ~340 °C. Because the FRM monitor cannot detect NO_2 directly, the NO_2 level is computed as the difference between the sample passed over the heated MoO_X substrate (the NO_X total) and the sample not so reduced (the NO alone). Reduction of NO_2 to NO on the MoO_X substrate is not specific to NO_2, however; hence, the CL analyzers are subject to unknown and varying levels of interferences produced by the presence in the sample of other oxidized N compounds, the NO_Z species shown in the outer box of Figure 2-16. This interference is often termed a "positive artifact" in the NO_2 concentration estimate since the presence of NO_Z always results in an over-estimate in the reported measurement of the actual NO_2 concentration.

This interference by NO_Z compounds has long been known (see Crosley, 1996; Fehsenfeld et al., 1987; McClenny et al., 2002; Nunnermacker et al., 1998; Parrish and Fehsenfeld, 2000; Rodgers and Davis, 1989; Steinbacher et al., 2007; U.S. EPA, 2008a). These studies have relied on intercomparisons of measurements using the FRM and other techniques for measuring NO_2. The sensitivity of the FRM to potential interference by individual NO_Z compounds is variable and depends in part on characteristics of

individual monitors, such as design of the instrument inlet, the temperature and composition of the reducing substrate, and the interactions of atmospheric species with the reducing substrate.

Only recently have attempts been made to quantify systematically the magnitude and variability of the interference by NO_Z species in ambient measurements of NO_2. Dunlea et al. (2007) found an average of ~22% of ambient NO_2 (~9 to 50 ppb) measured in Mexico City was due to interference from NO_Z compounds; that is to say, the true ambient NO_2 concentration was ~22% lower than what was reported at monitors using the CL difference technique. Although comparable levels of NO_2 are found in many locations in the U.S., the same comparison for distinct places in the U.S. is difficult to make because significant uncertainty remains in determining the concentrations of the higher oxidation NO_Z products since they are not routinely measured. Dunlea et al. (2007) compared NO_2 measured using the conventional CL instrument with optical techniques. The main sources of interference were HNO_3 and various $RONO_2$ which can be converted to NO on the catalyst with varying rates of efficiency. In this study, the efficiency of conversion on the catalyst — that is, how much of the compound introduced to the catalyst was converted to NO — was estimated to be ~38% for HNO_3; ~95% for PAN, and ~95% for other $RONO_2$. Peak interference (over-estimation) in the reported estimate of NO_2 concentrations from the presence of NO_Z compounds of up to 50% was found during afternoon hours and was associated with O_3 and NO_Z compounds such as HNO_3, and with multifunctional alkyl nitrates.

In a study in rural Switzerland, Steinbacher et al. (2007) compared measurements of NO_2 continuously measured using a conventional CL-NO_X monitor and measurements in which NO_2 was photolyzed to NO. They found that the conventional CL technique overestimated the reported NO_2 concentration, on average, by 10% during winter and 50% during summer.

Another approach to estimating the NO_2 measurement interference uses model calculations in conjunction with known data on the reduction efficiencies of NO_Z species on the MoO_X converters. Lamsal et al. (2008) used the conversion efficiencies noted above along with output for NO_Y species from the GEOS-Chem CTM to derive seasonal correction factors for the ambient monitoring data across the U.S. These factors range from <10% in winter in the East to >80% in the West, with the highest values found during summer in relatively unpopulated areas. Lamsal et al. (2008) also used these corrected data to determine the feasibility of using satellite data to supplement the ground-based data. However, the current generation of satellite monitors are in low earth orbit and so the NO_2 values are restricted to time of satellite overpass in early afternoon local time.

Calculations using CMAQ for the mid-Atlantic region in a domain extending from Virginia to southern New Jersey (see http://www.mde.state.md.us /Programs/AirPrograms/air_planning/index.asp) were made at much higher spatial resolution than the GEOS-Chem simulations by Lamsal et al. (2008). The daily average interference for an episode during the summer of 2002 estimated using model-derived concentration fields for NO_Z species and using the conversion efficiencies for NO_Z species given above, ranged from ~20% in Baltimore to ~80% in Madison, VA. Highest values were found during the afternoon, when photochemical activity is highest and production and accumulation of the higher oxidized NO_Z compounds is greatest; lowest values occurred during the middle of the night when photochemistry stops. The model calculations showed episode averages of the NO_Z-to-NO_2 ratio ranging from 0.26 to 3.6 in rural Virginia, with the highest ratios in rural areas and lowest in urban centers closer to sources of fresh NO_X emissions. (The capabilities of three-dimensional CTMs such as GEOS-Chem and CMAQ and issues associated with their use are presented in Section 2.8 below.)

In summary, the current CL method of determining ambient NO_X and then reporting NO_2 concentrations by subtraction of NO is subject to positive interference by NO_2 oxidation products, chiefly HNO_3 and PAN as well as other oxidized N-containing compounds, though the magnitude of this positive bias is largely unknown and can be rapidly changing. Measurements of these higher-order oxidation products in urban areas are sparse. Concentrations of these oxidation products are expected to peak in the afternoon because of the continued oxidation of NO_2 from NO emitted during the morning rush hours and during conditions conducive to photochemistry in areas well downwind of sources, particularly during summer.

Within the urban core of metropolitan areas, where many of the ambient monitors are sited close to strong NO_X sources such as motor vehicles on busy streets and highways, these positive artifacts due to NO_2 oxidation products are much smaller than outside the urban core farther downwind, and are typically <10%. Conversely, the positive artifacts are larger in locations more distant from NO_X sources where NO_2 concentrations are lowest and can exceed 50% as noted above. Therefore, variable, positive artifacts associated with measuring NO_2 using the FRM severely hamper its ability to serve as an accurate and precise indicator of NO_2 concentrations at the typical ambient levels generally encountered in remote areas outside of urban cores where they would be most relevant for the environmental exposures of concern to a secondary NAAQS.

Other Methods

NO has also been successfully measured in ambient air with direct spectroscopic methods; these include two-photon laser-induced fluorescence (TPLIF), tunable diode laser absorption spectroscopy (TDLAS), and two-tone frequency-modulated spectroscopy (TTFMS). These were reviewed thoroughly in the 2008 NO_X ISA (U.S. EPA 2008a). The spectroscopic methods demonstrate excellent sensitivity and selectivity for NO with detection limits on the order of 10 ppt for integration times of 1 min and spectroscopic methods compare well with the CL method for NO in controlled laboratory air, ambient air, and heavily polluted air (see Gregory et al., 1990; Kireev et al., 1999; Walega et al., 1984). However, these spectroscopic methods remain research grade rather than field deployable due to their complexity, size, and cost, but are essential for demonstrating that CL methods are reliable.

There are approaches to measuring NO_2 not affected by the artifacts mentioned above. For example, NO_2 can be photolytically reduced to NO with an efficiency of ~70% as used in Steinbacher et al. (2007). Ryerson et al. (2000) developed a gas-phase CL method using a photolytic converter based on a Hg lamp with increased radiant intensity in the region of peak NO_2 photolysis, 350 to 400 nm, and producing conversion efficiencies of 70% or more in less than 1 second. Metal halide lamps with conversion efficiency of ~50% and accuracy on the order of 20% have been used (Nakamura et al., 2003). Because the converter produces little radiation at wavelengths less than 350 nm, interferences from HNO_3 and PAN are minimal. This method requires additional development to ensure its cost effectiveness and reliability for extensive field deployment.

Optical methods such as those using differential optical absorption spectroscopy (DOAS) or laser-induced fluorescence (LIF) are also available. However, these particular methods are more expensive than either the FRM monitors or photolytic reduction technique and require specialized expertise to operate. Moreover, the DOAS obtains an area-integrated measurement rather than a point measurement. Cavity attenuated phase shift (CAPS) monitors are an alternative optical approach potentially less costly than DOAS or LIF (Kebabian et al., 2007). However, this technique is not highly specific to NO_2 and is subject to interference by other species absorbing at 440 nm, such as the 1,2–dicarbonyl compounds. The extent of this interference and the potential of the CAPS technique for extensive field deployment have not been evaluated.

A DOAS system manufactured by OPSIS is designated as an FEM for measuring NO_2. DOAS systems can also be configured to measure NO, HNO_2, and NO_3. Typical detection limits are 0.2 to 0.3 ppb for NO, 0.05 to 0.1 ppb for NO_2, 0.05 to 0.1 ppb for HNO_2, and 0.001 to 0.002 ppb for NO_3, at path lengths of 0.2, 5, 5, and 10 km, respectively. The obvious advantage compared to fixed-point measurements is that concentrations relevant to a much larger area are obtained, especially if multiple targets are used. At the same time, any microenvironmental artifacts are minimized over the long path integration. However, comparisons to other measurements made at point locations are difficult to interpret. A major limitation in this technique had involved inadequate knowledge of absorption cross sections. Harder et al. (1997) conducted an experiment in rural Colorado involving simultaneous measurements of NO_2 by DOAS and by photolysis followed by CL. They found differences of as much as 110% in clean air from the west; but for NO_2 mixing ratios in excess of 300 ppt, the two methods agreed to better than 10%. Stutz et al. (2000) cites two intercomparisons of note. NO was measured by DOAS,

by photolysis of NO_2 followed by CL, and by LIF during July 1999 as part of the SOS in Nashville, TN. On average, the three methods agreed to within 2%, with some larger differences likely caused by spatial variability over the DOAS path. In another study in Europe, a multi-reflection set-up over a 15 km path negated the problem of spatial averaging. Here agreement with the CL detector following photolytic conversion was excellent (slope = 1.006 ± 0.005; intercept = 0.036 ± 0.019; $r^2 = 0.99$) over a concentration range from about 0.2 to 20 ppb.

Remote Sensing of NO_2

The paucity of specific in situ NO_2 measurements motivates the inference of ground-level NO_2 concentrations from satellite measurements of tropospheric NO_2 columns. This prospect would take advantage of the greater sensitivity of tropospheric NO_2 columns to NO_X in the lower troposphere than in the upper troposphere as in Section 2.2 above. Tropospheric NO_2 columns show a strong correlation with in situ NO_2 measurements in northern Italy (Ordonez et al., 2006). Quantitative calculation of surface NO_2 concentrations from a tropospheric NO_2 column requires information on the relative vertical profile. Comparison of vertical profiles of NO_2 in GEOS-Chem versus in situ measurements over and downwind of North America showed a high degree of consistency (Martin et al., 2004, 2006), suggesting that CTMs could be used to infer the relationship between surface NO_2 concentrations and satellite observations of the tropospheric NO_2 column.

Table 2-6 contains an overview of the three satellite instruments used to retrieve tropospheric NO_2 columns from measurements of solar backscatter. All three instruments are in polar sun-synchronous orbits with global measurements in the late morning and early afternoon local time. The spatial resolution of the measurement from SCIAMACHY is 7 times better than that from the GOME; and that from Ozone Monitoring Instrument (OMI) is 40 times better than that from GOME.

Table 2-6. Satellite instruments used to retrieve tropospheric NO_2 columns.

Instrument	Coverage	Typical U.S. Measurement Time	Typical Resolution (km)	Return Time (days)[1]	Instrument Overview
GOME	1995–2002	10:30–11:30 AM	320 × 40	3	Burrows et al. (1999)
SCIAMACHY	2002–	10:00–11:00 AM	30 × 60	6	Bovensmann et al. (1999)
OMI	2004–	12:45–1:45 PM	13 × 24	1	Levelt et al. (2006)

[1] Return time is reported here for cloud-free conditions. Note that due to precession of the satellite's orbit, return measurements are close to but not made over the same location. In practice, clouds decrease observation frequency by a factor of 2.

Figure 2-23 shows tropospheric NO_2 columns retrieved from SCIAMACHY. Pronounced enhancements are evident over major urban and industrial areas. The high degree of spatial heterogeneity over the southwestern U.S. provides empirical evidence that most of the tropospheric NO_2 column is concentrated in the lower troposphere. Tropospheric NO_2 columns are more sensitive to NO_X in the lower troposphere than in the upper troposphere (Martin et al., 2002). This sensitivity to NO_X in the lower troposphere is due to 25-fold decrease in the NO_2-to-NO ratio from the surface to the upper troposphere (Bradshaw et al., 1999), driven by the temperature dependence of the $NO + O_3$ reaction. Martin et al. (2004) integrated in situ airborne measurements of NO_2 and found that during summer the lower mixed layer contains 75% of the tropospheric NO_2 column over Houston and Nashville. However, it should be noted that these satellite measurements are also sensitive to surface albedo and aerosol loading which strongly vary locally.
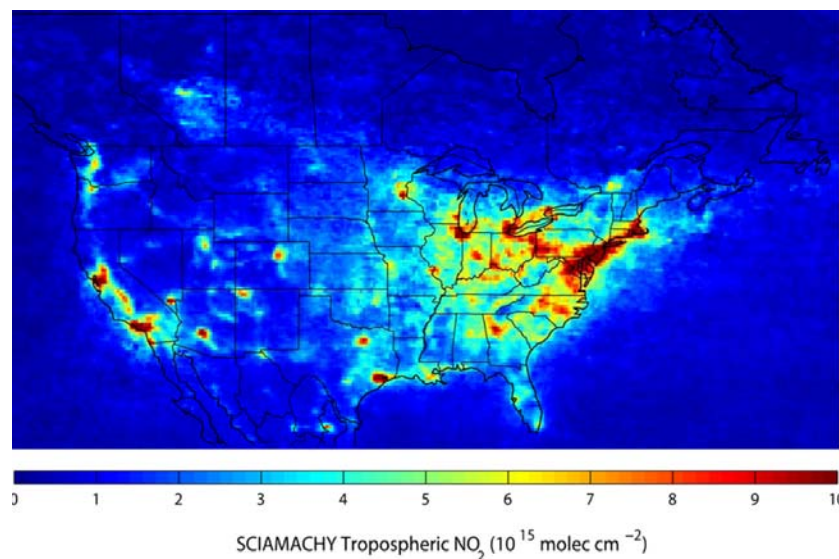
Figure 2-23. Tropospheric NO$_2$ column estimates (molecules NO$_2$/cm^2) retrieved from the SCIAMACHY satellite instrument for 2004–2005.

2.7.1.2. Total NO$_Y$

Gold-catalyzed CO or H$_2$ reduction, or conversion on heated MoO$_X$, have been used for many years to reduce total NO$_Y$ to NO before detection by CL (Crosley, 1996; Fehsenfeld et al., 1987). Both techniques offer generally reliable measurements, with response times on the order of 60 seconds and a linear dynamic range demonstrated in field intercomparisons from ~10 ppt to 10s of ppb. Under some conditions, hydrogen cyanide (HCN), NH$_3$, alkyl nitrates (RNO$_2$), and acetonitrile (CH$_3$CN) can be converted to NO; but at normal atmospheric concentrations and RH, and when convertor temperature is closely monitored, these are minor interferants. Thermal decomposition followed by LIF has also been used for NO$_Y$ detection. In field comparisons, instruments based on these two principles generally showed good agreement (Day et al., 2002) with experimental uncertainty estimated to be on the order of 15 to 30%.

Commercially available NO$_X$ monitors have been converted to NO$_Y$ monitors by moving the MoO$_X$ convertor to couple directly to the sample inlet. Because of losses on inlet surfaces and differences in the efficiency of reduction of NO$_Z$ compounds on the heated MoO$_X$ substrate, NO$_X$ measured by CL in standard mode cannot be considered a surrogate for NO$_Y$. However, in settings close to relatively high-concentration fresh emissions like those during urban rush hour, most of the NO$_Y$ is present as NO$_X$. Reliable measurements of NO$_Y$ and NO$_2$, especially at the low concentrations observed in many areas remote from sources remain crucial for evaluating the performance of CTMs; see Section 2-8 for additional details on CTM application and evaluation.

2.7.1.3. Nitric Acid

A major issue to be considered when measuring NO$_X$ and NO$_Y$ is the possibility that HNO$_3$, a major component of NO$_Y$, is sometimes lost in inlet tubes and not measured (Luke et al., 1998; Parrish and Fehsenfeld, 2000). This problem is especially important if measured NO$_Y$ is used to identify NO$_X$-limited versus NO$_X$-saturated conditions. The problem is substantially alleviated, although not necessarily completely solved, by using much shorter inlets on NO$_Y$ monitors than on standard NO$_X$ monitors and by

the use of surfaces less likely to take up HNO_3. The correlation between O_3 and NO_Y differs for NO_X-limited versus NO_X-saturated locations, but this difference is driven primarily by differences in the ratio of O_3 to HNO_3. If HNO_3 were omitted from the NO_Y measurements, then the measurements would represent a severely biased estimate.

Accurate measurement of HNO_3 has presented a long-standing analytical challenge. To understand why, it is useful to consider the major factors that control HNO_3 partitioning between the gas and deliquesced-particulate phases in ambient air as depicted in Reaction 45.

$$HNO_3(g) \xleftrightarrow{K_H} [HNO_3(aq)] \xleftrightarrow{K_a} [H^+] + [NO_3^-]$$
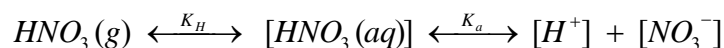
<div align="right">Reaction 45</div>

where K_H is the Henry's Law constant in M/atm and K_a is the acid dissociation constant in M. Thus, the primary controls on HNO_3 phase partitioning are its thermodynamic properties, aerosol liquid water content (LWC), solution pH, and reaction kinetics. Aerosol LWC and pH are controlled by the relative mix of acids and bases in the system, the hygroscopic properties of condensed compounds, and meteorological conditions, chiefly RH, temperature, and pressure.

In the presence of chemically distinct aerosols of varying acidities (e.g., supermicron, predominantly sea salt, and submicron, predominantly pSO_4), HNO_3 should partition preferentially to the less-acidic particles, and observations are consistent with this (see. e.g., Huebert et al., 1996; Keene et al., 1998). The kinetics of this phase partitioning are controlled by atmospheric concentrations of HNO_3 vapor and pNO_3, and the size distribution and τ of the particles against deposition. Submicron diameter aerosols typically equilibrate with the gas phase in seconds to minutes while supermicron aerosols require hours to a day or more; see, e.g., Erickson et al. (1999) and Meng and Seinfeld (1996). Consequently, smaller aerosol size fractions are typically close to thermodynamic equilibrium with respect to HNO_3, whereas larger size fractions, for which τ against deposition range from hours to a few days, are often undersaturated (Erickson et al., 1999; Keene et al., 1998).

Methods used widely for measuring HNO_3 include standard filter packs configured with nylon or alkaline-impregnated filters (see, e.g., Bardwell et al., 1990; Goldan et al., 1983), annular denuders like U.S. EPA method IP-9, and mist chambers (Talbot et al., 1990), all typically joined to ion chromatography detection. Intercomparisons of these measurement techniques by Hering et al. (1988), Tanner et al. (1989), and Talbot et al. (1990) reported differences on the order of a factor of 2 or more. In part, this variance is due to nonsystematic sampling error. When chemically distinct aerosols with different pH—for example, sea salt and pSO_4—mix together on a bulk filter, the acidity of the bulk mixture will be greater than that of the less-acidic aerosols with which most of the NO_3 is associated. This change in pH may cause the bulk mix to be supersaturated with respect to HNO_3 leading to volatilization and, thus, to a positive measurement bias in HNO_3 sampled downstream. Alternatively, when undersaturated supermicron size fractions like sea salt accumulate on a bulk filter and chemically interact over time with HNO_3 in the sample air stream, scavenging may lead to a negative bias in the HNO_3 sampled downstream. Because the magnitude of both effects will vary as functions of the overall composition and thermodynamic state of the multiphase systems, the combined influence can cause net positive or net negative measurement bias in data with unknown frequencies. Pressure drops across particle filters can also lead to artifact volatilization and associated positive bias in HNO_3 concentrations measured downstream.

Sensitive HNO_3 measurements based on the principle of chemical ionization mass spectroscopy (CIMS) have become more common; see Huey et al. (1998), Furutani and Akimoto (2002), Mauldin et al. (1998), and Neuman et al. (2002). The CIMS relies on selective formation of ions such as silicon pentafluoride–nitric acid ($SiF_5^- \cdot HNO_3$) or ($HSO_4^- \cdot HNO_3$) followed by detection via mass spectroscopy. Two CIMS techniques and a filter pack technique were intercompared in Boulder, CO (Fehsenfeld et al., 1998) where results indicated agreement to within 15% between the two CIMS instruments and between the CIMS and filterpack methods under relatively clean conditions of 50-400 ppt HNO_3. In more polluted

air, the filterpack technique generally yielded higher values than the CIMS, suggesting that interactions between chemically distinct particles on bulk filters is a more important source of bias in polluted continental air. Differences were also greater at lower temperature when pNO_3 accounted for a relatively greater fraction of total NO_3^-.

Three semi-continuous methods for detecting HNO_3 were tested against the annular denuder filterpack (ADS) integrated collection technique at the Tampa Bay Regional Atmospheric Chemistry Experiment (BRACE) Sydney research station ~20 km downwind of the Tampa, FL, urban core (Arnold and Luke, 2007). The semi-continuous instruments included: two slightly differing implementations of the NO_Y-NO_Y* (total oxides of nitrogen minus that total denuded of HNO_3) denuder difference technique, one from the NOAA Air Resources Lab (ARL), and one from Atmospheric Research and Analysis, Inc. (ARA); the parallel plate wet diffusion scrubber online ion chromatography technique from Texas Tech University (TTU); and the CIMS from the Georgia Institute of Technology (GIT). Integrated twelve hour ADS samples were collected by the University of South Florida (USF). Results for 10 min samples computed from the various higher sampling frequencies of each semi-continuous instrument showed good agreement ($R^2 > 0.7$) for afternoon periods of the highest production and accumulation of HNO_3. Further, agreement was within ± 30% for these instruments even at HNO_3 concentrations <0.30 ppb. The USF ADS results were biased low, however, by 44%, on average, compared to the corporate 12-h aggregated means from the semi-continuous methods, and by >600% for the nighttime samples; ADS results were below the corporate mean maximum HNO_3 concentration by >30% as well. The four instruments using semi-continuous methods, by contrast, were all within 10% of each other's 12-h mean mixing ratios. While only ARA employed a formal minimum detection limit at 0.050 ppb, error analysis with the other techniques established that at the same level of precision, TTU's effective limit was approximately the same as ARA's, and that ARL's limit was 0.030 ppb; analysis for GIT showed no apparent effective limit at the levels of HNO_3 encountered in this field study. The importance of sample inlet height for HNO_3 measurements was indirectly shown through comparison to previous fieldwork at this site when sample inlet heights ranged from 1.5–10 m and produced systematic discrepancies in HNO_3 concentrations correlated with height of more than a factor of 2.

2.7.1.4. Other Nitrates

Methods for sampling and analysis of $RONO_2$ in the atmosphere have been reviewed by Parrish and Fehsenfeld (2000). PAN, PPN, and MPAN were typically measured using a gas chromatograph followed by electron capture detectors (GC-ECD); see, e.g., Gaffney et al. (1998), although other techniques such as Fourrier Transform InfraRed (FTIR) analysis can also be used. Field measurements made using GC-ECD have reported a total uncertainty of ± 5 ppt + 15% (Gaffney et al., 1998; Roberts et al., 1998). Additional descriptions of specific techniques for $RONO_2$ and some of the issues involved with using data taken with them appear below in Section 2.10, accompanying descriptions of the methods used routinely to monitor ambient air concentrations and deposition amounts of $RONO_2$, and in the 2008 NO_X ISA (U.S. EPA, 2008a).

2.7.1.5. Ammonia

Because NH_3 plays a key role in the atmospheric chemistry of particle formation, several methods have been developed for ambient and higher-level concentrations; see Allegrini et al. (1992); Appel et al. (1988); Asman et al. (1998); Fehsenfeld et al. (1996); Genfa and Dasgupta (1989); Mennen et al. (1996); Pryor et al. (2001); Schwab et al. (2007); Williams et al. (1992); and Wyers et al. (1993). Measurement of NH_3 is made difficult by its chemistry, whereby it forms strong H bonds with itself and water, and can be lost either with hysteresis or irreversibly to many instrument surfaces. Moreover, the range of atmospheric

NH_3 concentrations extends over 4 or 5 orders of magnitude. Because of these challenges, many NH_3 techniques remain research-grade with steep requirements of time, care, and technical experience.

U.S. EPA has proposed to include ambient NH_3 measurements in its National Core (NCore) monitoring network (U.S. EPA, 2005b) and this has motivated additional development and testing of NH_3 monitors. The U.S. EPA Environmental Technology Verification (ETV) Program's Advanced Monitoring Systems (AMS) Center, has verified the performance of seven ambient NH_3 monitors for use at confined animal feeding operations (CAFOs). In collaboration with the U.S. Department of Agriculture (USDA), the AMS Center verified the seven ambient NH_3 monitors (see Table 2-7) in two phases of testing, each at separate CAFOs: Phase I was conducted at a swine finishing farm and Phase II at a cattle feedlot. These sites were selected to provide realistic testing conditions and a wide range of NH_3 concentrations. Table 2-8 summarizes some of the performance data for the individual technologies. (The full verification reports can be found at http://www.epa.gov/nrmrl/std/etv/vt-ams.html under the ambient NH_3 sensors category.)

Ambient NH_3 monitors utilize a wide range of analytical methods, including direct detection by spectroscopic techniques; indirect detection of NH_3 using selective membrane permeation with conductivity detection, catalytic conversion with CL detection; treatment with a chemical dopant followed by ion mobility detection; and other techniques. Ambient NH_3 monitors also can provide specialized features valuable in specific uses, such as long-term monitoring or determining NH_3 fluxes and emission rates.

For example, monitors that collect NH_3 concentration data with a frequency greater than 1 Hz can be used with simultaneous three-dimensional windspeed and direction data to determine NH_3 flux. Alternatively, open-path monitors can be used to calculate emission rates from CAFOs, since these monitors measure the average NH_3 concentration over a 1 to 100 m path. Some monitors also are suitable for long-term monitoring, since they can be operated without user intervention for weeks at a time.

Table 2-7.   Verified ambient NH_3 monitors.

Technology Name	Description
Aerodyne Research, Inc. QC-TILDAS	An infrared laser spectrometer, based on pulsed quantum cascade laser technology; continuous measurement
Bruker Daltonics OPAG 22 Open-Path Gas Analyzer	A broadband, open-path, Fourier transform infrared spectrometer for remote sensing continuous measurement
Molecular Analytics IonPro-IMSNH$_3$ Analyzer	An ion mobility spectrometer; continuous measurement
Omnisens SA TGA310 NH$_3$ Analyzer	A trace gas analyzer that uses photoacoustic spectrometry; continuous measurement
Pranalytica, Inc. Nitrolux^{TM} 1000 Ambient NH$_3$ Analyzer	A resonant photoacoustic spectrometer with a line-tunable CO_2 laser; continuous measurement
Mechatronics Instruments BV AiRRmonia NH$_3$ Analyzer	A single-point monitor composed of a membrane diffusion sampler, a detector block with a diffusion membrane, and two conductivity cells; continuous measurement
Thermo Electron Corp. Model 17C NH$_3$ Analyzer	A CL analyzer that uses NO and ozone (O_3) reactions; time-averaged measurement

Table 2-8.   Performance characteristics of the 7 U.S. EPA ETV tested NH₃ methods.

Vendor[a]	Testing	Average Relative Accuracy[b]	Relative Precision[b]	Response Time (95%)	Linearity			Comparability[c]		
					Slope	Intercept	r²	Slope	Intercept	r²
A	Phase I & Phase II	3.7 to 10.5%	0.3%	3 to 76 min	0.90 to 1.03	-24 to -0.6	1.000	0.86 to 1.20	-0.5 to 16	0.984 to 0.990
B	Phase I & Phase II	2.4 to 34%	0.7 to 2.1%	8 to 20 min	1.02 to 1.28	-2.4 to 136	0.9957 to 0.9999	0.41 to 1.18	-1.4 to 58	0.538 to 0.9755
C	Phase I & Phase II	10 to 44%	0.2 to 1.3%	1 to 32 min	0.716 to 1.25	-58.5 to 167	0.9854 to 0.9997	0.646 to 1.83	-6.7 to 21.6	0.9794 to 0.9842
D	Phase II	2.2%	0.9%	2 to 2.6 min	0.966	15.9	1.000	1.15	-4.1	0.994
E	Phase II	18.3%	1.0%	2.5 to 17 min	0.815	1.08	1.000	1.565	-16.5	0.994
F	Phase II	26%	1.8%	4 to 14 s	0.583	24.9	0.9144	NR	NR	NR
G	Phase I & Phase II	4.7 to 10%	1.9 to 2.5%	0.8 to 66 s	0.840 to 0.962	-8.8 to 35	0.9989 to 0.9998	0.984 to 1.09	-9.5 to 14.4	0.9943 to 0.9982

[a] Because the ETV Program does not compare technologies, the performance results shown in this table do not identify the vendor associated with each result and are not in the same order as the list of technologies in Table 2-7. [b] A result of 0% indicates perfect accuracy or precision. [c] The comparability of the verified technology with a standard reference method was established by comparing the average NH₃ sensors readings with time-integrated NH₃ samples collected using citric-acid-coated denuders. The reference samples were collected based on procedures described in the U.S. EPA Compendium Method IO-4.2, Determination of Reactive Acidic and Basic Gases and Acidity of Fine Particles (<2.5 μm). Comparability between the NH₃ sensors results and the reference method results with respect to ambient air was assessed by linear regression using the reference method NH₃ concentrations as the independent variable and results from the NH₃ sensor as the dependent variable.

In addition to the evaluation by U.S. EPA, ETV, a laboratory-based intercomparison of real-time ambient NH₃ instruments was conducted and reported by Schwab et al. (2007) with seven instruments using six methods. The tunable diode laser (TDL) absorption spectrometer, the wet scrubbing long-path absorption photometer (LOPAP), the wet effusive diffusion denuder (WEDD), the ion mobility spectrometer (IMS), the Nitrolux laser acousto-optical absorption analyzer, and a modified CL analyzer. Schwab et al. (2007) reported that all instruments performed well and agreed to within ~25% of the expected calibration value, with the exception of the CL analyzer which suffered from problems related to its MoO_X conversion of NO_Z to NO. (Work with a modification of this technique has been continuing with the Aerosol Research Inhalation Epidemiology Study (ARIES); see, e.g., Blanchard and Hidy, 2003.)

Instrument response time is known to be a crucial feature for ambient NH₃ measurements, and Schwab et al. (2007) showed response time to be sensitive to measurement history as well as the sample handling materials. Shortest response was for the TDL; the Nitrolux and IMS and WEDD instruments had unacceptably long time responses under some environmental conditions which rendered correlations across instruments meaningless. The TDL and LOPAP reported values closest to delivered concentration values; the IMS exhibited bias of ~ +25%; the Nitrolux bias was ~ −25%. Schwab et al. (2007) concluded that sub-ppb ambient NH₃ measurements can be taken reliably with some of these instruments, but that special care must still be exercised to ensure high-quality data.

These and other recent intercomparisons of ambient NH₃ instruments have confirmed that no single active sampling technique has yet been identified for automated, fast-response, low-concentration, high-quality continuous data.

Passive samplers for ambient NH₃ measurements, however, have been tested for multiple periods of 14-day exposures over several years in the small network of sites in the U.S. Upper Midwest listed in Table 2-9 and have performed well.

Table 2-9. Site codes and locations of passive NH$_3$ samplers in the U.S. EPA and Lake Michigan Air Directors and Illinois State Water Survey Consortium Project.

Site Code	Location
IL11	Bondville, IL
IN99	Indianapolis, IN
MI96	Allen Park, MI
MN18	Fernberg, MN
MN29	Blue Mounds S.P., MN
MN42	Great River Bluffs S.P., MN
OH02	Athens, OH
OH27	Cincinnati, OH
WI07	Mayville, WI

In this test, the Radiello® samplers demonstrated excellent reproducibility across the three samples taken at each site for each 14-day exposure period. Ambient NH$_3$ concentration from each sampler and the average value and standard deviation and percent relative standard deviation for each of the 14-day exposure periods was reported at every site in 2007 and 2008 (data not shown).
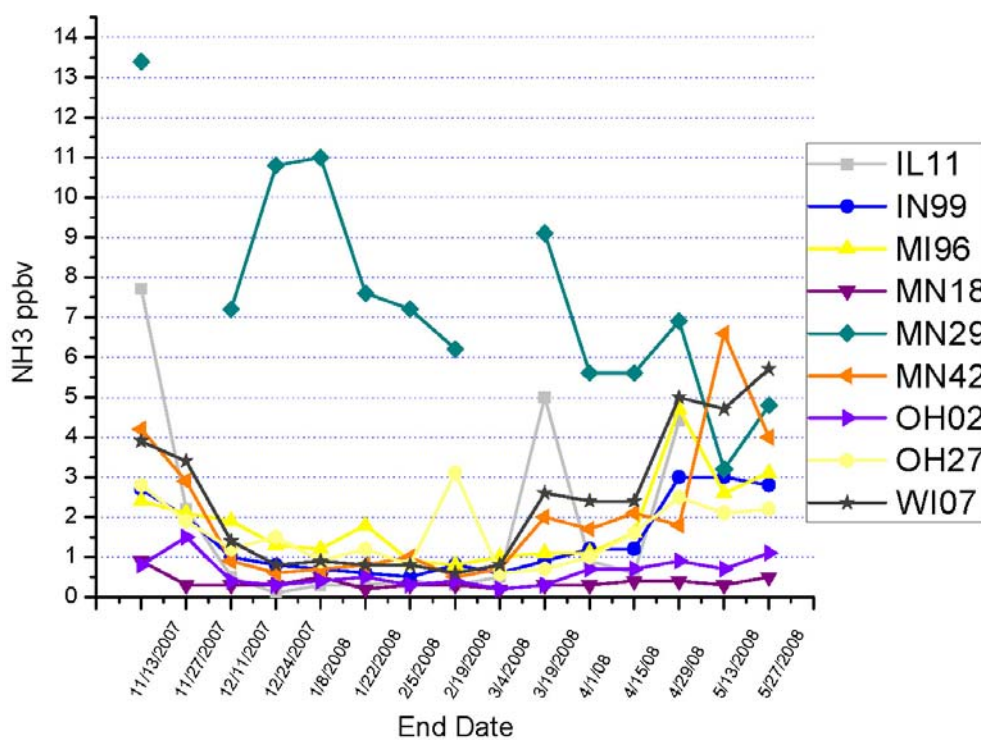
Figure 2-24. Average ambient NH$_3$ concentrations from the NH$_3$ passive samplers trial network, 2007-2008.

Figure 2-24 shows the average ambient NH_3 concentrations from each 14-day exposure period at each site from the Radiello® samplers. The irregularly high concentrations at Blue Mounds State Park, MN remains unexplained, but may be due to wintertime shifts in the location of a large bison herd nearer to the sample site.

2.7.2. Methods for Relevant Gas-Phase Sulfur Species

Currently, ambient SO_2 is measured using instruments based on pulsed fluorescence. The UV fluorescence monitoring method for atmospheric SO_2 was developed to improve upon the flame photometric detection (FPD) method for SO_2, which in turn had displaced the pararosaniline wet chemical method. The pararosaniline method is still the FRM for atmospheric SO_2, but is rarely used because of its complexity and slow response, even in its automated forms. Both the UV fluorescence and FPD methods are designated as FEMs by the U.S. EPA, but UV fluorescence has largely supplanted the FPD approach because of the UV method's inherent linearity, sensitivity, and the absence of consumables, such as the H_2 gas needed for FPD.

The LOD for a non-trace-level SO_2 analyzer is 10 ppb (CFR, 2006) However, most commercial analyzers report operational detection limits of ~3 ppb. This concentration is very near the current ambient annual average concentration of SO_2 of ~4 ppb.

SO_2 molecules absorb UV light at one wavelength and emit UV light at longer wavelengths. This fluorescence involves excitation of the SO_2 molecule to a higher energy (singlet) electronic state. Once excited, the molecule decays non-radiatively to a lower energy electronic state from which it then decays to the original, or ground, electronic state by emitting a photon of light at a longer wavelength (i.e., lower energy) than the original, incident photon. The process can be summarized by the following equations

$$SO_2 \; + \; h\nu_1 \; \longrightarrow \; SO_2^{\;*}$$

Reaction 46

$$SO_2^{\;*} \; \longrightarrow \; SO_2 \; + \; h\nu_2$$
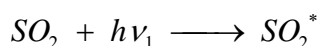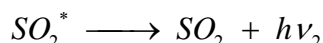
Reaction 47

where SO_2* represents the excited state of SO_2, $h\nu_1$, and $h\nu_2$ represent the energy of the excitation and fluorescence photons, respectively, and $h\nu_2 < h\nu_1$. The intensity of the emitted light is proportional to the number of SO_2 molecules in the sample gas. Additional information is found in the 2008 SO_X ISA (U.S. EPA 2008b).

2.7.2.1. Positive Interference

Luke (1997) reported the positive artifacts of a modified pulsed fluorescence detector generated by the co-existence of NO, CS_2, and a number of highly fluorescent aromatic HCs such as benzene, toluene, o-xylene, m-xylene, p-xylene, m-ethyltoluene, ethylbenzene, and 1,2,4–trimethylbenzene. The positive artifacts could be reduced by using a HC kicker membrane. At a flow rate of 300 standard cc/min and a pressure drop of 645 torr across the kicker, the interference from ppm levels of many aromatic HCs was eliminated entirely. More details appear in the 2008 SO_X ISA (U.S. EPA, 2008b).

2.7.2.2. Negative Interference

Nonradiative deactivation (quenching) of excited SO_2 molecules can occur from collisions with common molecules in air, including N, O_2, and H_2O. During collisional quenching, the excited SO_2 molecule transfers energy, kinetically allowing the SO_2 molecule to return to the original lower energy state without emitting a photon. Collisional quenching results in a decrease in the SO_2 fluorescence and results in the underestimation of SO_2 concentration in the air sample. The concentrations of N_2 and O_2 are constant in the ambient air, so quenching from those species at a surface site is also constant, but the water vapor content of air can vary. Luke (1997) reported that the response of the detector could be reduced by about 7% and 15% at water vapor mixing ratios of 1 and 1.5 mole percent (RH = 35 to 50%) at 20-25 °C and 1 atm for a modified pulsed fluorescence detector. At very high SO_2 concentrations, reactions between electronically excited SO_2 and ground state SO_2 to form SO_3 and SO are theoretically possible (Calvert et al., 1978), but this possibility has not been examined.

2.7.2.3. Other Methods

A more sensitive SO_2 measurement method than the UV-fluorescence method was reported by Thornton et al. (2002b) using an atmospheric pressure ionization mass spectrometer. The high measurement precision and instrument sensitivity were achieved by adding isotopically labeled SO_2 ($^{34}S^{16}O_2$) continuously to the manifold as an internal standard. Field studies showed that the method precision was better than 10%.

SO_2 can also be measured by LIF at ~220 nm (Matsumi et al., 2005). Because the laser wavelength is alternately tuned to an SO_2 absorption peak at 220.6 and a trough at 220.2 nm and the difference signal at the two wavelengths is used to extract the SO_2 concentration, the technique eliminates interference from either absorption or fluorescence by other species and has high sensitivity: 5 ppt in 60 s.

SO_2 can also be measured by the same DOAS instrument that can measure NO_2; see the discussion of DOAS in Section 2.7.1.1 above.

Photo-acoustic techniques have been employed for SO_2 detection, but generally have detection limits sutable only for source monitoring (Gondal, 1997; Gondal and Mastromarino, 2001).

CIMS techniques for SO_2 have been shown to have high sensitivity, 10 ppt or better, with uncertainty of ~15% when a charcoal scrubber is used for zeroing and the sensitivity is measured with isotopically labeled $^{34}SO_2$ (Hanke et al., 2003; Hennigan et al., 2006; Huey et al., 2004).

2.7.3. Methods for Relevant Aerosol-Phase Nitrogen and Sulfur Species

SO_4^{2-} is commonly present in $PM_{2.5}$. Most $PM_{2.5}$ samplers have a size-separation device to separate particles so that only those particles approximately 2.5 μm or less are collected on the sample filter. Air is drawn through the sample filter at a controlled flow rate by a pump located downstream of the sample filter. The systems have two critical flow rate components for the capture of fine particulates: both the flow of air through the sampler must be at a flow rate that ensures the size cut at 2.5 μm; and the flow rate must be optimized to capture the desired amount of particulate loading with respect to the analytical method detection limits.

Using the system described above to collect pSO4 sampling artifacts can introduce: positive sampling artifacts for pSO4, pNO3, and pNH4 due to chemical reactions, and negative sampling artifacts for NO_3^- and NH_4^+ due to decomposition and evaporation.

Several traditional and new methods could be used to quantify elemental S collected on filters: energy dispersive X-ray fluorescence, synchrotron induced X-ray fluorescence, proton induced X-ray

emission (PIXE), total reflection X-ray fluorescence (XRF), and scanning electron microscopy. Energy dispersive X-ray fluorescence (EDXRF) (Method IO-3.3, U.S. EPA, 1997; see U.S. EPA (2004) for details) and PIXE are the most commonly used methods. Since sample filters often contain very small amounts of particle deposits, preference is given to methods that can accommodate small sample sizes and which require little or no sample preparation or operator time after the samples are placed into the analyzer. XRF meets these needs and leaves the sample intact after analysis so it can be submitted for additional examinations by other methods as needed. To obtain the greatest efficiency and sensitivity, XRF typically places the filters in a vacuum which may cause volatile compounds to evaporate. As a result, species that can volatilize such as NH_4NO_3 and certain organic compounds can be lost during the analysis. The effects of this volatilization are important if the PTFE filter is to be subjected to subsequent analyses of volatile species.

Polyatomic ions such as SO_4^{2-}, NO_3^-, and NH_4^+ are quantified by methods such as IC or automated colorimetry for NH_4^+. All ion analysis methods require a fraction of the filter to be extracted in deionized distilled water for SO_4^{2-} and $Na_2CO_3/NaHCO_3$ solution for NO_3 and then filtered to remove insoluble residues before analysis. The extraction volume should be as small as possible to avoid over-diluting the solution and inhibiting the detection of the desired constituents at levels typical of those found in ambient $PM_{2.5}$ samples.

Continuous methods for the quantification of S compounds first remove gas-phase S from the sample stream by a diffusion tube denuder followed by analysis of pSO_4 (Cobourn et al., 1978; Durham et al., 1978; Huntzicker et al., 1978; Mueller and Collins, 1980; Tanner et al., 1980). Another approach is to measure total S and gas-phase S separately by alternately removing particles from the sample stream. pSO_4 is obtained as the difference between the total and gas-phase S (Kittelson et al., 1978). The total S content is measured by a FPD by introducing the sampling stream into a fuel-rich, H_2-air flame (e.g., Farwell and Rasmussen, 1976; Stevens et al., 1969) which reduces S compounds and measures the intensity of the CL from electronically excited sulfur molecules (S_2*). Sensitivities for pSO_4 as low as 0.1 $\mu g/m^3$ with time resolution ranging from 1 to 30 min have been reported. Continuous measurements of pSO_4 content have also been obtained by on-line XRF analysis with resolution of 30 min or less (Jaklevic et al., 1981). During a field-intercomparison study of five different S instruments, Camp et al. (1982) found four out of five FPD systems agreed to ± 5% during a 1-week sampling period.

There are two major PM speciation ambient air-monitoring networks in the U.S.: the Chemical Speciation Network (CSN), which now includes the former Speciation Trends Network (STN), and the Interagency Monitoring of Protected Visual Environments (IMPROVE) network. The current CSN samplers sample on a 1-in-3 days cycle using three filters: Teflon for equilibrated mass and elemental analysis including elemental S; a HNO_3 denuded nylon filter for ion analysis including NO_3 and SO_4^{2-}; a quartz-fiber filter for elemental and organic carbon (EC and OC, respectively). The IMPROVE sampler, which collects two 24-h samples per week, simultaneously collects one sample of PM_{10} on a Teflon filter, and three samples of $PM_{2.5}$ on Teflon, nylon, and quartz filters. $PM_{2.5}$ mass concentrations are determined gravimetrically from the $PM_{2.5}$ Teflon filter sample, which is also used to determine concentrations of selected elements. The $PM_{2.5}$ nylon filter sample, which is preceded by a denuder to remove acidic gases, is analyzed to determine pNO_3 and pSO_4 concentrations. Finally, the $PM_{2.5}$ quartz filter sample is analyzed for OC and EC using the thermal-optical reflectance (TOR) method for IMPROVE and thermal-optical transmittance (TOT) for CSN, though this network is in transition to TOR.

In a side-by-side comparison of two of the chief aerosol monitoring techniques, $PM_{2.5}$ mass and the major contributing species were moderately well correlated among the different methods with r >0.8 (Hains et al., 2007). Agreement was good for total mass, SO_4^{2-}, OC, total carbon (TC), and NH_4^+, while NO_3^- and black carbon (BC) showed less-good fits. Based on reported uncertainties, however, even daily concentrations of $PM_{2.5}$ mass and major contributing species were often significantly different at the 95% confidence level. The older STN/CSN methods reported generally higher values of $PM_{2.5}$ total mass and of individual species than did the IMPROVE-like ones. Since these differences can only be partially accounted for by known random errors, the authors concluded that the current uncertainty estimates used for data analyzed with the older STN protocol may underestimate the actual uncertainty.

2.7.3.1. Artifacts

The reaction of SO_2 and other acid gases with basic sites on glass fiber filters or with basic coarse particles on the filter leads to the formation of nonvolatile pSO_4, pNO_3, and Cl salts. These positive artifacts lead to overestimates of concentrations of PM total mass and SO_4^{2-} and likely NO_3^- as well. These problems were largely overcome by changing to quartz fiber or Teflon filters and by the separate collection of the $PM_{2.5}$ fraction. However, the possible reaction of acidic gases with basic coarse particles remains a possibility, especially with PM_{10} and $PM_{10-2.5}$ measurements. These positive artifacts could be effectively eliminated by removing acid gases in the sampling line with denuders coated with NaCl or Na_2CO_3.

Positive sampling artifacts also occur during measurement of pNH_4. The reaction of NH_3 with acid particles

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$
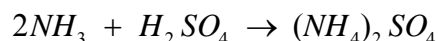
Reaction 48

either during sampling or during transportation, storage, and equilibration could lead to an overestimation of pNH_4 concentrations. Techniques have been developed to overcome this problem, including using a denuder coated with hydrofluoric, citric, or phosphoric acid to remove NH_3 during sampling and to protect the collected PM from NH_3 (Brauer et al., 1991; Keck and Wittmaack, 2006; Koutrakis et al., 1988a, 1988b; Possanzini et al., 1999; Suh et al., 1992, 1994; Winberry et al., 1999). Positive artifacts for pNH_4 can also develop during sample handling due to contamination with NH_3 emitted directly from human sweat, breath, and tobacco smoking to form $(NH_4)_2SO_4$ or NH_4HSO_4 if the filter is improperly handled (Sutton et al., 2000).

Although pSO_4 is relatively stable on a Teflon filter, it is now well known that volatilization losses of pNO_3 occur during sampling. For pNO_3, the effect on the accuracy of atmospheric measurements from these volatilization losses is more significant for $PM_{2.5}$ than for PM_{10}, partly because NO_3^- contributes a smaller fraction to PM_{10} and partly because NO_3^- is most often present in a non-volatile form such as $NaNO_3$, in the coarse mode.

Sampling artifacts resulting from the loss of pNO_3 species represents a significant problem in areas such as southern California that experience high total NO_3 loadings. Hering and Cass (1999) discussed errors in $PM_{2.5}$ mass measurements owing to the volatilization of pNO_3 using data from two field measurement campaigns conducted in southern California: the Southern California Air Quality Study (SCAQS) (Lawson, 1990); and the 1986 California Institute of Technology (CalTech) study (Solomon et al., 1992). In both studies, side-by-side sampling of $PM_{2.5}$ was conducted with one sampler collecting particles directly onto a Teflon filter and a second using an MgO-coated denuder (Appel et al., 1981) to remove gaseous HNO_3, followed by a nylon filter to absorb the evaporating HNO_3. In both studies, the $PM_{2.5}$ mass lost from NH_4NO_3 volatilization represented a significant fraction of the total $PM_{2.5}$ mass, and these losses were greater during summer than fall: 17% (summer) versus 9% (fall) during SCAQS, and 21% (summer) versus 13% (fall) during CalTech. With regard to percentage loss of pNO_3, as contrasted to percentage loss of mass discussed above, Hering and Cass (1999) found that the amount of pNO_3 remaining on the Teflon filter samples was, on average, 28% less than that on the HNO_3 denuded nylon filters.

Hering and Cass (1999) also analyzed these data by extending the evaporative model developed by Zhang and McMurry (1987). The extended model used by Hering and Cass (1999) takes into account the dissociation of collected NH_4NO_3 on Teflon filters into HNO_3 and NH_3 via three mechanisms: scrubbing of HNO_3 and NH_3 in the sampler inlet. John et al. (1988) showed that clean PM_{10} inlet surfaces serve as an effective denuder for HNO_3; heating of the filter substrate above ambient temperature by sampling; and pressure drop across the Teflon filter. For the sampling systems modeled, the flow-induced pressure drop was measured to be less than 0.02 atm, and the corresponding change in vapor pressure was 2%, so

losses driven by pressure drop were not considered to be significant in this work. Losses from Teflon filters were found to be higher during the summer than during the winter, higher during the day compared to night, and were reasonably consistent with modeled predictions.

Finally, during SCAQS (Lawson, 1990), particulate samples also were collected using a Berner impactor and greased Tedlar substrates in size ranges from 0.05 to 10 μm in aerodynamic diameter. The Berner impactor $PM_{2.5}$ NO_3^- values were much closer to those from the denuded nylon filter than those from the Teflon filter; the impactor NO_3^- values were ~2% lower than the nylon filter NO_3 for the fall measurements and ~7% lower for the summer measurements. When the impactor collection was compared to the Teflon filter collection for nonvolatile species, pSO_4, the results were in agreement. Chang et al. (2000) discussed reasons for reduced loss of NO_3^- from impactors.

Brook and Dann (1999) observed much higher NO_3^- losses during a study in which they measured NO_3^- in Windsor and Hamilton, Ontario, Canada, by three techniques: a single Teflon filter in a dichotomous sampler; the Teflon filter in an ADS; and total NO_3^- including both the Teflon filter and the nylon back-up filter from the ADS. The Teflon filter from the dichotomous sampler averaged only 13% of the total NO_3, whereas the Teflon filter from the ADS averaged 46% of total NO_3^-. Considerable NO_3 was lost from the dichotomous sampler filters during handling, which included weighing and XRF measurement in a vacuum.

Kim et al. (1999) also examined pNO_3 sampling artifacts by comparing denuded and non-denuded quartz and nylon filters during the PM_{10} Technical Enhancement Program (PTEP) in the California South Coast Air Basin. They observed NO_3^- losses for most measurements; however, for a significant number of measurements, they observed positive NO_3^- artifacts. Kim et al. (1999) pointed out that random measurement errors make it difficult to measure true amounts of NO_3^- loss.

Diffusion denuder samplers, developed primarily to measure particle strong acidity (Koutrakis et al., 1988a, 1992) also can be used to study NO_3^- volatilization. Measurements were made with two versions of the Harvard-U.S. EPA ADS (HEADS) for which HNO_3 vapor was removed by a Na_2CO_3 coated denuder and the remaining pNO_3 was reported either as the sum of nonvolatile NO_3^- collected on a Teflon filter, and volatized NO_3^- collected on a Na_2CO_3 coated filter downstream of the Teflon filter (full HEADS) or on a Nylon filter downstream of the Teflon filter (Nylon HEADS). The full HEADS consistently underestimated the total NO_3^- by ~20% compared to the Nylon HEADS.

This comparison technique was then used to measure loss of NO_3^- from Teflon filters in seven U.S. cities by Babich et al. (2000) who found significant pNO_3 losses in Riverside, CA, Philadelphia, PA, and Boston, MA, but not in Bakersfield, CA, Chicago, IL, Dallas, TX, or Phoenix, AZ, where measurements were made only during winter.

Negative sampling artifacts due to decomposition and volatilization are also significant for pNH_4, more often when it appears as NH_4NO_3 since $(NH_4)_2SO_4$ is much more stable. The presence and deposition of NH_4NO_3 is highly sensitive to environmental factors such as temperature, RH, acidity of aerosols, as well as to filter type (Keck and Wittmaack, 2005; Spurny, 1999). Any change in these parameters during the sampling period influences the position of the equilibrium between the particle and gas phases. Keck and Wittmaack (2005) observed that at temperatures <0 ºC, acetate–NO_3, quartz fiber, and Teflon filters could properly collect pNH_4, NH_3, and Cl^-; but at temperatures >0 ºC, the salts were lost from quartz fiber and Teflon filters, more so at higher temperatures and with no significant difference between quartz fiber and Teflon filters. The salts were lost completely from denuded quartz fiber filters at temperatures above ~20 ºC, and from non-undenuded quartz fiber and Teflon filters at temperatures above ~25 ºC. It is anticipated that current sampling techniques underestimate pNH_4 levels due to volatilization, but fine particle mass contains many acidic compounds, and, as a consequence, a fraction of volatilized NH_4^+ in the form of NH_3 can be retained on the Teflon filter by reactions with them. Owing to these positive and negative interference effects, the magnitude of pNH_4 remains largely unknown. However, techniques have been applied to pNH_4 sampling to correct its concentrations due to evaporation using a backup filter coated with hydrofluoric acids, citric acid, or phosphorous acids to absorb the evaporated NH_4 as NH_3. Total NH_4 concentration then is the sum of the pNH_4 collected on the Teflon filter and the concentration of the NH_3 collected on the backup filter.

Volatile compounds can also leave the filter after sampling and before filter weighing or chemical analysis. Losses of NO_3^-, NH_4^+, and Cl^- from glass and quartz-fiber filters that were stored in unsealed containers at ambient air temperatures for 2 to 4 weeks before analysis exceeded 50% (Witz et al., 1990).

2.7.3.2. Other Methods

An integrated collection and vaporization cell was developed by Stolzenburg and Hering (2000) that provides automated, 10–min resolution monitoring of fine pNO_3. In this system, particles are collected by a humidified impaction process and analyzed in place by flash vaporization and CL detection of the evolved NO_X. In field tests in which the system was co-located with two FRM samplers, the automated pNO_3 sampler results followed the results from the FRM, but were offset lower. The system also was co-located with a HEADS and a SASS speciation sampler (MetOne Instruments). In all these tests, the automated sampler was well correlated to other samplers with slopes ranging from 0.95 for the FRM to 1.06 for the HEADS, and correlation coefficients ranging from 0.94 to 0.996. During the Northern Front Range Air Quality Study in Colorado (Watson et al., 1998), the automated NO_3^- monitor captured the 12–min variability in pNO_3 concentrations with a precision of approximately $\pm$ 0.5 $\mu g/m^3$ (Chow et al., 1998). A comparison with denuded filter measurements followed by IC analysis (Chow and Watson, 1999) showed agreement within $\pm$ 0.6 $\mu g/m^3$ for most of the measurements, but exhibited a discrepancy of a factor of 2 for the periods of high pNO_3 concentrations. More recent intercomparisons took place during the 1997 Southern California Ozone Study (SCOS97) in Riverside, CA. Comparisons with 14 days of 24-h denuder-filter sampling gave a correlation coefficient of 0.87 and showed no significant bias. As currently configured, the system has a detection limit of 0.7 $\mu g/m^3$ and a precision of 0.2 $\mu g/m^3$.

The extent to which sampling artifacts for pNH_4 have been adequately addressed in the current networks is not clear. Recently, new denuder-filter sampling systems have been developed to measure pSO_4, pNO_3, and pNH_4 with an adequate correction of NH_4^+ sampling artifacts. The denuder-filter system, Chembcomb Model 3500 speciation sampling cartridge developed by Rupprecht & Patashnick Co, Inc. could be used to collect NO_3, SO_4^{2-}, and NH_4^+ simultaneously. The sampling system contains a single-nozzle size-selective inlet, two honeycomb denuders, the aerosol filter and two backup filters (Keck and Wittmaack, 2005). The first denuder in the system is coated with 0.5% sodium carbonate and 1% glycerol and collects acid gases such as HCl, SO_2, HNO_2, and HNO_3. The second denuder is coated with 0.5% phosphoric acid in methanol for collecting NH_3. Backup filters collect the gases behind denuded filters. The backup filters are coated with the same solutions as the denuders. A similar system based on the same principle was applied by Possanzini et al. (1999). The system contains two NaCl coated annular denuders followed by two denuders coated with $Na_2CO_3^+$ glycerol and citric acid, respectively. This configuration was adopted to remove HNO_3 quantitatively on the first NaCl denuder. The third and forth denuder remove SO_2 and NH_3, respectively. A polyethylene cyclone and a two-stage filter holder containing three filters are placed downstream of the denuders. Aerosol fine particles are collected on a Teflon membrane. A backup nylon filter and a subsequent citric acid impregnated filter paper collect dissociation products, NH_4NO_3, HNO_3 and NH_3, evaporated from the filtered particulate matter.

2.8. Methods to Compute NO$_X$ and SO$_X$ Concentrations, Chemical Interactions, and Deposition

2.8.1. Chemical Transport Models

CTMs are the prime tools used to compute the interactions among NO$_X$, SO$_X$, other pollutants and their precursors, the transport and transformation of air toxics, the production of secondary aerosols, the evolution of the particle size distribution, and deposition of pollutants. CTMs are driven by emissions inventories for primary species such as NO$_X$, SO$_X$, NH$_3$, and primary PM, and by meteorological fields produced by other numerical prediction models. Meteorological quantities such as winds and temperatures are taken from operational analyses, reanalyses, or weather circulation models. In most cases, these are off-line meteorological analyses, meaning that they are not modified by radiatively active species generated by the air quality model (AQM).

Emissions of precursor compounds can be divided into anthropogenic and biogenic source categories, and biogenic sources can be further divided into biotic (vegetation, microbes, animals) and abiotic (geogenic biomass burning, lightning) categories as presented in Section 2.2 above. However, the distinction between biogenic sources and anthropogenic sources is often difficult to make, as human activities affect directly or indirectly emissions from what would have been considered biogenic sources during the preindustrial era. Thus, emissions from plants and animals used in agriculture have been referred to as anthropogenic or biogenic in different applications. Wildfire emissions may be considered to be biogenic, except that forest management practices may have led to the buildup of fuels on the forest floor, thereby altering the frequency and severity of forest fires.

The initial conditions, or starting concentration fields of all species computed by a model, and the boundary conditions, or concentrations of species along the horizontal and upper boundaries of the model domain throughout the simulation, must be specified at the beginning of the simulation. Both initial and boundary conditions can be estimated from models or data or, more generally, model + data hybrids. Because data for vertical profiles of most species of interest are sparse, results of model simulations over larger, usually global, domains are often used. As might be expected, the influence of boundary conditions depends on the τ of the species under consideration and the time scales for transport from the boundaries to the interior of the model.

Each of the model components described above has associated uncertainties and the relative importance of these uncertainties varies with the modeling application. The largest errors in photochemical modeling are still thought to arise from the meteorological and emissions inputs to the model (Russell and Dennis, 2000). Within the model itself, horizontal advection algorithms are still thought to be significant sources of uncertainty (see, e.g., Chock and Winkler, 1994), though more recently, those errors are thought to have been reduced (see, e.g., Odman and Ingram, 1996). There are also indications that problems with mass conservation continue to be present in photochemical and meteorological models (see, e.g., Odman and Russell, 1999) and can result in significant simulation errors. The effects of errors in initial conditions can be minimized by including several days spin-up time in a simulation to allow the model to be driven by emitted species before the simulation of the period of interest begins.

While the effects of poorly specified boundary conditions propagate through the model's domain, the effects of these errors remain undetermined. Because many meteorological processes occur on spatial scales smaller than the model grid spacing (either horizontally or vertically) and thus are not calculated explicitly, parameterizations of these processes must be used and these introduce additional uncertainty.

Specific uncertainty also arises in modeling the chemistry of NO$_X$ transformations because they are strongly nonlinear. Thus, the volume of the grid cell into which emissions are injected is important because, for example, O$_3$ production or loss depends in a complicated way on the concentrations of NO$_X$

and OH as explained in Section 2.6.2.1 above. Use of ever-finer grid spacing allows more valid separation of regions of high NO_X concentrations from low NO_X regions and from regions where NO_X concentrations are optimal for $P(O_3)$.

The use of grid spacing fine enough to resolve the chemistry in individual power-plant plumes is too demanding of computer resources for this to be attempted in most regional air quality simulations. Instead, parameterizations of the effects of sub-grid-scale processes such as these must be developed, else serious errors can result if emissions are allowed to mix through an excessively large grid volume before the chemistry step in a model calculation is performed. In light of the significant differences between atmospheric chemistry taking place within and outside of a power plant plume identified by Ryerson et al. (1998), inclusion of a separate module for treating large, tight plumes can be useful. Because the photochemistry of NO_X transformation is nonlinear, emissions correctly modeled in a tight plume may be incorrectly modeled in a more dilute plume. Fortunately, it appears that the chemical mechanism used to follow a plume's development need not be as detailed as that used to simulate the rest of the domain, as the inorganic reactions are most important in the plume; see e.g., Kumar and Russell (1996).

Because the chemical production and loss terms in the continuity equations for individual species are coupled, the chemical calculations must be performed iteratively until calculated concentrations converge to within some preset criterion. The number of iterations and the convergence criteria chosen also can introduce error.

CTMs have been developed for application over a wide range of spatial scales ranging up from neighborhood to global. Regional scale CTMs are used to: obtain better understanding of the processes controlling the formation, transport, and destruction of gas- and particle-phase criteria and hazardous air pollutants; understand the relations between concentrations of secondary pollutant products and concentrations of their precursors such as NO_X and VOCs and the factors leading to acid deposition and possible damage to biota and ecosystems; understand relations among the concentration patterns of various pollutants that may exert adverse effects; and evaluate how changes in emissions propagate through the atmospheric system to secondary products and deposition.

CTMs in current use mostly have one of two forms. The first, grid-based or Eulerian air quality models subdivide the region to be modeled or the modeling domain, into a three-dimensional array of grid cells. Spatial derivatives in the species continuity equations are cast in finite-difference form over this grid and a system of equations for the concentrations of all the chemical species in the model are solved numerically at each grid point. Finite element Eulerian models also exist and have been exercised, but less frequently. Time-dependent continuity or mass conservation equations are solved for each species including terms for transport, chemical production and destruction, and emissions and deposition (if relevant), in each cell. Chemical processes are simulated with ordinary differential equations, and transport processes are simulated with partial differential equations. Because of a number of factors such as the different time scales inherent in different processes, the coupled, nonlinear nature of the chemical process terms, and computer storage limitations, not all of the terms in the equations are solved simultaneously in three dimensions. Instead, operator splitting, in which terms in the continuity equation involving individual processes are solved sequentially, is used.

In the second common CTM formulation, trajectory or Lagrangian models, a number of hypothetical air parcels are specified as though following wind trajectories. In these models, the original system of partial differential equations is transformed into a system of ordinary differential equations.

A less common approach is to use a hybrid Lagrangian-Eulerian model, in which certain aspects of atmospheric chemistry and transport are treated with a Lagrangian approach and others are treaded in an Eulerian manner; see e.g., Stein et al., 2000.

Each approach has advantages and disadvantages. The Eulerian approach is more general in that it includes processes that mix air parcels and allows integrations to be carried out for long periods during which individual air parcels lose their identity. There are, however, techniques for including the effects of mixing in Lagrangian models such as FLEXPART (Zanis et al., 2003), ATTILA (Reithmeier and Sausen, 2002), and CLaMS (McKenna et al., 2002).

2.8.1.1. Global Scale

Global-scale CTMs are used to address issues associated with climate change and stratospheric O_3 depletion, and to provide boundary conditions for the regional-scale models. The CTMs include simplified mathematical descriptions of atmospheric transport, the transfer of solar radiation through the atmosphere, chemical reactions, and removal to the surface by turbulent motions and precipitation for pollutants emitted into the model domain. The upper boundaries of the CTMs extend anywhere from the top of the mixed layer to the mesopause at ~80 km to obtain more realistic boundary conditions for problems involving stratospheric dynamics.

The importance of global transport of O_3 and O_3 precursors and their contribution to regional O_3 levels in the U.S. is now apparent. There are at present on the order of 20 three-dimensional global models developed by various groups to address problems in tropospheric chemistry. These models resolve synoptic meteorology, O_3-NO_X-CO-HC photochemistry, have parameterizations for wet and dry deposition, and parameterize sub-grid scale vertical mixing processes such as convection. Global models have proven useful for testing and advancing scientific understanding beyond what is possible with observations alone. For example, they can calculate quantities of interest that cannot be measured directly, such as export of pollution from one continent to the global atmosphere, or the response of the atmosphere to future perturbations in anthropogenic emissions.

Global simulations are typically conducted at a horizontal resolution of 200 km^2 or more. Simulations of the effects of transport from long-range transport link multiple horizontal resolutions from the global to the local scale. Finer resolution will only improve scientific understanding to the extent that the governing processes are more accurately described at that scale. Consequently, there is a critical need for observations at the appropriate scales to evaluate the scientific understanding represented by the models.

During the recent IPCC-AR4 tropospheric chemistry study coordinated by the European Union Atmospheric Composition Change: the European Network of excellence (ACCENT), 26 atmospheric CTMs were used to estimate the impacts of three emissions scenarios on global atmospheric composition, climate, and air quality in 2030 (Dentener et al., 2006a, b). All models were required to use anthropogenic emissions developed at IIASA (Dentener et al., 2005) and GFED version 1 biomass burning emissions (Van der Werf et al., 2003) as described in Stevenson et al. (2006). The base simulations from these models were evaluated against a suite of present-day observations. Most relevant to this assessment report are the evaluations with NO_2 and N deposition (Dentener et al., 2006b; Stevenson et al., 2006), which are summarized briefly below.

A subset of 17 of the 26 models used in the Stevenson et al. (2006) study was used to compare with three retrievals of NO_2 columns from the GOME instrument (van Noije et al., 2006) for the year 2000. The higher resolution models reproduced the observed patterns better, and the correlation among simulated and retrieved columns improved for all models when simulated values were smoothed to a 5° × 5° grid, implying that the models did not accurately reproduce the small-scale features of NO_2 (van Noije et al., 2006). Van Noije et al. (2006) also suggested that variability in simulated NO_2 columns may reflect model differences in OH distributions and the resulting NO_X lifetimes, as well as differences in vertical mixing which strongly affected partitioning between NO and NO_2. Overall, the models tended to underestimate concentrations in the retrievals in industrial regions including the eastern U.S. and to overestimate them in biomass burning regions (van Noije et al., 2006).

Over the eastern U.S. and in industrial regions more generally, the spread in absolute column abundances is generally larger among the retrievals than among the models, with the discrepancy among the retrievals particularly pronounced in winter (van Noije et al., 2006), suggesting that the models were biased low, or that the European retrievals may be biased high as the Dalhousie SAO retrieval is closer to the model estimates. The lack of seasonal variability in fossil fuel combustion emissions may have contributed to a wintertime model underestimate (van Noije et al., 2006) manifested most strongly over Asia. In biomass burning regions, the models generally reproduce the timing of the seasonal cycle of the retrievals, but tend to overestimate the seasonal cycle amplitude, partly due to lower values in the wet

season, which may reflect an underestimate in wet season soil NO emissions (Jaeglé et al., 2004; van Noije et al., 2006).

2.8.1.2. Regional Scale

Most major modeling efforts within the U.S. EPA use the Community Multiscale Air Quality modeling system (CMAQ) (Byun and Schere, 2006; Byun and Ching, 1999). A number of other modeling platforms using Lagrangian and Eulerian frameworks were reviewed in the 2006 O_3 AQCD (U.S. EPA, 2006b) and in Russell and Dennis (2000). Evaluations of the performance of CMAQ are given in Appel et al. (2005), Arnold et al. (2003), Eder and Yu (2006), and Fuentes and Raftery (2005). CMAQ's domain can extend from several hundred kilometers to the entire hemisphere. CMAQ is most often driven by the MM5 mesoscale meteorological model (Seaman, 2000), though it may be driven by other meteorological models, including the Regional Atmosphere Modeling System (RAMS); see http://atmet.com. Simulations of pollution episodes over regional domains have been performed with a horizontal resolution as low as 1 km, and smaller calculations over limited domains have been performed at even finer scales. However, simulations at such high resolutions require better parameterizations of meteorological processes such as boundary layer fluxes, deep convection, and clouds (Seaman, 2000), as well as finer-scale emissions data than are generally available. Finer spatial resolution is necessary to resolve features such as urban heat island circulation; sea, bay, and land breezes; mountain and valley breezes; and the nocturnal low-level jet; all of which can affect pollutant concentrations.

The most common approach to setting up the horizontal domain is to nest a finer grid within a larger domain of coarser resolution. However, there are other strategies such as the stretched grid (see e.g., Fox-Rabinovitz et al., 2002) and the adaptive grid. In a stretched grid, the grid's resolution continuously varies throughout the domain, thereby eliminating any potential problems with the sudden change from one resolution to another at the boundary. Caution should be exercised in using such a formulation because certain parameterizations like those for convection valid on a relatively coarse grid scale may not be valid on finer scales. Adaptive grids are not fixed at the start of the simulation, but instead adapt to the needs of the simulation as it evolves (see e.g., Hansen et al., 1994). They have the advantage that they can resolve processes at relevant spatial scales. However, they can be very slow if the situation to be modeled is complex. Additionally, if adaptive grids are used for separate meteorological, emissions, and photochemical models, there is no reason a priori why the resolution of each grid should match, and the gains realized from increased resolution in one model will be wasted in the transition to another model. The use of finer horizontal resolution in CTMs will necessitate finer-scale inventories of land use and better knowledge of the exact paths of roads, locations of factories, and, in general, better methods for locating sources and estimating their emissions.

The vertical resolution of these CTMs is variable, and usually configured to have more layers in the PBL, and fewer higher up. Because the height of the boundary layer is of critical importance in simulations of air quality, improved resolution of the boundary layer height would likely improve air quality simulations. Additionally, current CTMs do not adequately resolve fine scale features such as the nocturnal low-level jet in part because little is known about the nighttime boundary layer.

CTMs require time-dependent, three-dimensional wind fields for the period of simulation. The winds may be generated either by a model using initial fields alone or with four-dimensional data assimilation to improve the model's performance; i.e., model equations can be updated periodically or nudged to bring results into agreement with observations. Modeling series durations can range from simulations of several days' duration to several months or multiple seasons of the year.

Chemical kinetics mechanisms (sets of chemical reactions) representing the important reactions occurring in the atmosphere are used in CTMs to estimate the rates of chemical formation and destruction of each pollutant simulated as a function of time. Because of different approaches to the lumping of organic compounds into surrogate groups for computational efficiency, chemical mechanisms can produce somewhat different results under similar conditions. The CB-IV chemical mechanism (Gery

et al., 1989), the RADM II mechanism (Stockwell et al., 1990), the SAPRC (e.g., Carter, 1990; Wang et al., 2000a, b), and the RACM mechanisms can be used in CMAQ. Jimenez et al. (2003) provided brief descriptions of the features of the main mechanisms in use and compared concentrations of several key species predicted by seven chemical mechanisms in a box model simulation over 24 h. The average deviation from the average of all mechanism predictions for O_3 and NO over the daylight period was <20%, and was 10% for NO_2 for all mechanisms. However, much larger deviations were found for HNO_3, PAN, HO_2, H_2O_2, ethylene, and isoprene. The large deviations shown for most species imply differences between the τ of atmospheric species and the assignment of model simulations to either NO_X-limited or radical-limited regimes between mechanisms. Gross and Stockwell (2003) found small differences between mechanisms for clean conditions, with differences becoming more significant for polluted conditions, especially for NO_2 and RO_2 radicals.

CMAQ and other state-of-the-science CTMs incorporate processes and interactions of aerosol-phase chemistry (Mebust et al., 2003). There have also been several attempts to study the feedbacks of chemistry on atmospheric dynamics using meteorological models like MM5 (Grell et al., 2000; Liu et al., 2001; Lu et al., 1997; Park et al., 2001). This coupling is necessary to simulate accurately feedbacks such as may be caused by the heavy aerosol loading found in forest fire plumes (Lu et al., 1997; Park et al., 2001), or in heavily polluted areas. Photolysis rates in CMAQ can now be calculated interactively with model-produced O_3, NO_2, and aerosol fields (Binkowski et al., 2007).

Spatial and temporal characterizations of anthropogenic and biogenic precursor emissions must be specified as inputs to a CTM. Emissions inventories have been compiled on grids of varying resolution for many HCs, aldehydes, ketones, CO, NH_3, and NO_X. Emissions inventories for many species require the application of algorithms for calculating the dependence of emissions on physical variables such as temperature and to convert the inventories into formatted emission files that can be used by a CTM. For example, emissions data preprocessing for CMAQ is done by the Spare-Matrix Operator Kernel Emissions (SMOKE) system; see http://smoke-model.org. For many species, information concerning the temporal variability of emissions is lacking, so annual or O_3 season averages are used in short-term, episodic simulations. Annual emissions estimates are often modified by the emissions model to produce emissions more characteristic of the time of day and season. Significant errors in emissions can occur if inappropriate time dependence or a default profile is used.

2.8.1.3. Sub-Regional Scale

The grid spacing in regional CTMs of between 1 and 12 km^2 is usually too coarse to resolve spatial variations on the neighborhood scale. The interface between regional scale models and models of smaller exposure scales described is provided by smaller scale dispersion models. AERMOD (http://www.epa.gov /scram001/dispersion_prefrec.htm) is one example of a steady-state plume model formulated as a replacement to the ISC3 dispersion model. In the stable boundary layer (SBL), it assumes the concentration distribution to be Gaussian in both the vertical and horizontal dimensions. In the convective boundary layer, the horizontal distribution is also assumed to be Gaussian, but the vertical distribution is described with a bi-Gaussian probability density function. AERMOD has provisions to be applied to flat and complex terrain, and multiple source types (including, point, area and volume sources) in both urban and rural areas. It incorporates air dispersion based on PBL turbulence structure and scaling concepts, and is meant to treat both surface and elevated sources and simple and complex terrain in rural and urban areas. The dispersion of emissions from line sources like highways is treated as the sum of emissions from a number of point sources placed side by side. However, emissions are usually not in steady state and there are different functional relationships between buoyant plume rise in point and line sources. It should be remembered that NO_2 is largely secondary in nature. However, AERMOD does not have provision for including secondary sources. The more appropriate use of AERMOD would be to simulate the total of NO and NO_2, or NO_X.

There are non-steady state models that incorporate plume rise explicitly from different types of sources. For example, CALPUFF (http://www.src.com/calpuff/calpuff1.htm) is a non-steady-state puff dispersion model that simulates the effects of time- and space-varying meteorological conditions on pollution transport, transformation, and removal and has provisions for calculating dispersion from surface sources. However, it should be noted that neither model was designed to treat the dispersion of emissions from roads or to include secondary sources.

2.8.1.4. Modeling Effects of Convection for Chemical Transport

The effects of deep convection can be simulated using cloud-resolving models or in regional or global models in which the convection is parameterized. The Goddard Cumulus Ensemble (GCE) model (Tao and Simpson, 1993) has been used by Pickering et al. (1991, 1992a, b, 1993, 1996), Scala et al. (1990) and Stenchikov et al. (1996) in the analysis of convective transport of trace gases. The cloud model is nonhydrostatic and contains a detailed representation of cloud microphysical processes. Two- and three-dimensional versions of the model have been applied in transport analyses. The initial conditions for the model are usually from a sounding of temperature, water vapor, and winds representative of the region of storm development. Model-generated wind fields can be used to perform air parcel trajectory analyses and tracer advection calculations.

Such methods were used by Pickering et al. (1992a) to examine transport of urban plumes by deep convection. Transport of an Oklahoma City, OK, plume by the 10–11 June 1985 PRE-STORM squall line was simulated with the 2–D GCE model. This major squall line passed over the Oklahoma City metropolitan area, as well as more rural areas to the north. Chemical observations ahead of the squall line were conducted by the PRE-STORM aircraft. In this event, forward trajectories from the boundary layer at the leading edge of the storm showed that almost 75% of the low-level inflow was transported to altitudes exceeding 8 km. Over 35% of the air parcels reached altitudes over 12 km. Tracer transport calculations were performed for CO, NO_X, O_3, and HCs. Rural boundary layer NO_X was only 0.9 ppb, whereas the urban plume contained about 3 ppb. In the rural case, mixing ratios of 0.6 ppb were transported up to 11 km. Cleaner air descended at the rear of the storm lowering NO_X at the surface from 0.9 to 0.5 ppb. In the urban plume, mixing ratios in the updraft core reached 1 ppb between 14 and 15 km. At the surface, the main downdraft lowered the NO_X mixing ratios from 3 to 0.7 ppb.

Regional CTMs have been used for applications such as simulations of photochemical O_3 production, acid deposition, and fine PM. Walcek et al. (1990) included a parameterization of cloud-scale aqueous chemistry, scavenging, and vertical mixing in the chemistry model of Change et al. (1987). The vertical distribution of cloud microphysical properties and the amount of sub-cloud layer air lifted to each cloud layer are determined using a simple entrainment hypothesis (Walcek and Taylor, 1986). Vertically integrated O_3 formation rates over the northeast U. S. were enhanced by ~50% when the in-cloud vertical motions were included in the model.

Global models with parameterized convection and lightning have been run to examine the roles of these processes over North America. Lightning contributed 23% of upper tropospheric NO_Y over the SONEX region according to the UMD-CTM modeling analysis of Allen et al. (2000). During the summer of 2004 the NASA Intercontinental Chemical Transport Experiment – North America (INTEX-NA) was conducted primarily over the eastern two-thirds of the U.S., as a part of the International Consortium for Atmospheric Research on Transport and Transformation. Deep convection was prevalent over this region during the experimental period. Cooper et al. (2006) used a particle dispersion model simulation for NO_X to show that 69–84% of the upper tropospheric O_3 enhancement over the region in summer 2004 was due to lightning NO_X. The remainder of the enhancement was due to convective transport of O_3 from the boundary layer or other sources of NO_X. Hudman et al. (2007) used a GEOS-Chem model simulation to show that lightning was the dominant source of upper tropospheric NO_X over this region during this period. Approximately 15% of North American boundary layer NO_X emissions were shown to have been vented to the free troposphere over this region based on both the observations and the model.

2.8.2. Computed Deposition

Wet and dry deposition are important removal processes for pollutants on urban, regional, and global scales and so are included in CTMs. The general approach used to estimate deposition velocity (V_d) in most models is the resistance-in-series method described above and represented in Equation 5. This approach works for a range of substances, although it is inappropriate for species with substantial re-emissions from the surface or for species where deposition to the surface depends on concentrations at the surface itself. The approach is also modified somewhat for aerosols in that the terms R_b and R_c are replaced with a surface V_d to account for gravitational settling.

$$V_d = 1/(R_a + R_b + R_c)$$

Equation 5
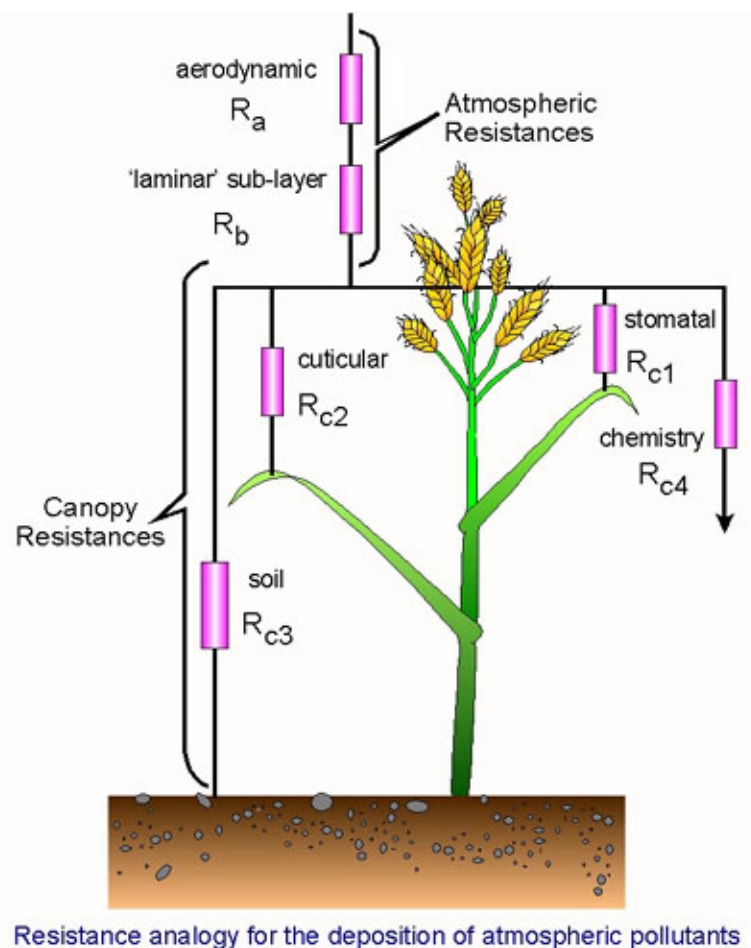
Resistance analogy for the deposition of atmospheric pollutants

Figure 2-25.   Schematic of the resistance-in-series analogy for atmospheric deposition. Function of wind speed, solar radiation, plant characteristics, precipitation/moisture, and soil/air temperature.

where *Ra*, *Rb*, and *Rc* represent the resistance due to atmospheric turbulence, transport in the fluid sublayer very near the elements of surface such as leaves or soil, and the resistance to uptake of the surface itself, respectively, as shown in Figure 2-25.

Wesley and Hicks (2000) listed several shortcomings of the then-current knowledge of dry deposition. Among those shortcomings were difficulties in representing dry deposition over varying terrain where horizontal advection plays a significant role in determining the magnitude of R_a and difficulties in adequately determining V_d for extremely stable conditions such as those occurring at night; see the discussion by Mahrt (1998), for example. Under optimal conditions, when a model is exercised over a relatively small area where dry deposition measurements have been made, models still generally showed uncertainties on the order of $\pm 30\%$ (see, e.g., Brook et al., 1996; Massman et al., 1994; Padro, 1996; Wesely and Hicks, 2000). Wesely and Hicks (2000) concluded that an important result of those comparisons was that the level of sophistication of most dry deposition models was relatively low, and that deposition estimates, therefore, must rely heavily on empirical data. Still larger uncertainties exist when the surface features in the built environment are not well known or when the surface comprises a patchwork of different surface types, as is common in the eastern U.S.

2.8.2.1. Deposition Forms

Wet Deposition

Wet deposition results from the incorporation of atmospheric particles and gases into cloud droplets and their subsequent precipitation as rain or snow, or from the scavenging of particles and gases by raindrops or snowflakes as they fall (Lovett, 1994). Wet deposition depends on precipitation amount and ambient pollutant concentrations. Receptor (i.e., vegetation) surface properties have little effect on wet deposition, although leaves can retain liquid and solubilized PM. In terrain containing extensive vegetative canopies, any material deposited via precipitation to the upper stratum of foliage is likely to be intercepted by several foliar surfaces before reaching the soil. This allows such processes as foliar uptake, chemical transformation, and re-suspension into the atmosphere to occur.

Landscape characteristics can affect wet deposition via orographic effects and by the closer aerodynamic coupling to the atmosphere of tall forest canopies as compared to the shorter shrub and herbaceous canopies. Following wet deposition, humidity and temperature conditions further affect the extent of drying versus concentrating of solutions on foliar surfaces, which influence the rate of metabolic uptake of surface solutes (Swietlik and Faust, 1984). The net consequence of these factors on direct physical effects of wet deposited PM on leaves is not known (U.S. EPA, 2004).

Rainfall introduces new wet deposition and also redistributes throughout the canopy previously dry-deposited particles (Peters and Eiden, 1992). The concentrations of suspended and dissolved materials are typically highest at the onset of precipitation and decline with duration of individual precipitation events (Hansen et al., 1994). Sustained rainfall removes much of the accumulation of dry-deposited particles from foliar surfaces, reducing direct foliar effects and combining the associated chemical burden with the wet-deposited material (Lovett, 1994) for transfer to the soil. Intense rainfall may contribute substantial total particulate inputs to the soil, but it also removes bioavailable or injurious pollutants from foliar surfaces. This washing effect, combined with differential foliar uptake and foliar leaching of different chemical constituents from particles, alters the composition of the rainwater that reaches the soil and the pollutant burden that is taken-up by plants. Once in the soil, these particle constituents may affect biogeochemical cycles of major, minor, and trace elements. Low intensity precipitation events, in contrast, may deposit significantly more particulate pollutants to foliar-surfaces than high intensity precipitation events. Additionally, low-intensity events may enhance foliar uptake through the hydrating of some previously dry-deposited particles (U.S. EPA, 2004).

Dry Deposition

Dry particulate deposition, especially of heavy metals, base cations, and organic contaminants, is a complex and poorly characterized process. It appears to be controlled primarily by such variables as atmospheric stability, macro- and micro-surface roughness, particle diameter, and surface characteristics

(Hosker and Lindberg, 1982). The range of particle sizes, the diversity of canopy surfaces, and the variety of chemical constituents in airborne particulates have made it difficult to predict and to estimate dry particulate deposition (U.S. EPA, 2004).

Dry deposition of atmospheric particles to plant and soil surfaces affects all exposed surfaces. Larger particles >5 μm diameter are dry deposited mainly by gravitational sedimentation and inertial impaction. Smaller particles, especially those with diameters between 0.2 and 2 μm, are not readily dry-deposited and may travel long distances in the atmosphere until their eventual deposition, most often via precipitation. Plant parts of all types, along with exposed soil and water surfaces, receive steady deposits of dry dusts, EC, and heterogeneous secondary particles formed from gaseous precursors (U.S. EPA, 1982b).

Estimates of regional particulate dry deposition infer fluxes from the product of variable and uncertain measured or modeled particulate concentrations in the atmosphere and even more variable and uncertain estimates of V_d parameterized for a variety of specific surfaces (see e.g., Brook et al., 1996). Even for specific sites and well-defined particles, uncertainties are large. Modeling the dry deposition of particles to vegetation is at a relatively early stage of development, and it is not currently possible to identify a best or most generally applicable modeling approach (U.S. EPA, 2004).

Occult Deposition

The occurrence of occult deposition tends to be geographically restricted to coastal and high mountain areas. Several factors make occult deposition particularly effective for the delivery of dissolved and suspended particulates to vegetation. Concentrations of particulate-derived materials are often many-fold higher in cloud or fog water than in precipitation or ambient air due to orographic effects and gas-liquid partitioning. In addition, fog and cloud water deliver particulate chemical species in a bioavailable-hydrated form to foliar surfaces. This enhances deposition by sedimentation and impaction of submicron aerosol particles that exhibit low V_d before fog droplet formation (Fowler et al., 1989). Deposition to vegetation in fog droplets is proportional to wind speed, droplet size, concentration, and fog density. In some areas, typically along foggy coastlines or at high elevations, occult deposition represents a substantial fraction of total deposition to foliar surfaces (Fowler et al., 1991).

2.8.2.2. Methods for Estimating Dry Deposition

Methods for estimating dry deposition of particles are more restricted than for gaseous species and fall into two major categories: surface analysis methods, which include all types of estimates of contaminant accumulation on surfaces of interest; and atmospheric deposition rate methods, which use measurements of contaminant concentrations in the atmosphere and descriptions of surrounding surface elements to estimate deposition rates (Davidson and Wu, 1990). Surface extraction or washing methods characterize the accumulation of particles on natural receptor surfaces of interest or on experimental surrogate surfaces. These techniques rely on methods designed specifically to remove only surface-deposited material. Total surface rinsate may be equated to accumulated deposition or to the difference in concentrations in rinsate between exposed and control (sheltered) surfaces and may be used to refine estimates of deposition. Foliar extraction techniques may underestimate deposition to leaves because of uptake and translocation processes that remove pollutants from the leaf surface (Garten and Hanson, 1990; Taylor et al., 1988). Foliar extraction methods also cannot distinguish gas from particle-phase sources (Bytnerowicz et al., 1987a, 1987b; Dasch, 1987; Lindberg and Lovett, 1985; Van Aalst, 1982).

The National Dry Deposition Network was established in 1986 to document the magnitude, spatial variability, and trends in dry deposition across the U.S.. Currently, the network operates as a component of the CASTNet (Clarke et al., 1997). A significant limitation on current capacity to estimate regional effects of NO_X and SO_X deposition is inadequate knowledge of the mechanisms and factors governing particle dry deposition to diverse surfaces (U.S. EPA, 2004).

Dry deposition cannot be directly measured. Deposition rates and totals are often calculated as the product of measured ambient concentration and a modeled V_d. This method is widely used because atmospheric concentrations are easier to measure than are dry deposition rates, and models have been developed to estimate V_d. Ambient pollutant concentrations and meteorological conditions required for application of inferential models are routinely collected at CASTNet dry deposition sites. Monitored chemical species are limited to O_3, SO_4^{2-}, NO_3^-, NH_4^+, SO_2, and HNO_3. The temporal resolution for the ambient concentration measurements and dry deposition flux calculations is hourly for O_3 and weekly for the other species (Clarke et al., 1997).

Collection and analysis of stem flow and throughfall can also provide useful estimates of particulate deposition when compared to directly sampled precipitation. The method is most precise for particle deposition when gaseous deposition is a small component of the total dry deposition and when leaching or uptake of compounds of interest out of or into the foliage is not a significant fraction of the deposition because these lead to positive and negative artifacts in the calculated totals.

Foliar washing, whether using precipitation or experimental lavage, is one of the best available methods to determine dry deposition to vegetated ecosystems. Major limitations include the site specificity of the measurements and the restriction to elements that are largely conserved within the vegetative system. Surrogate surfaces have not been found that can adequately replicate essential features of natural surfaces; and therefore do not produce reliable estimates of particle deposition to the landscape.

Micrometeorological methods employ eddy covariance, eddy accumulation, or flux gradient protocols for quantifying dry deposition. These techniques require measurements of particulate concentrations and of atmospheric transport processes. They are currently well developed for ideal conditions of flat, homogeneous, and extensive landscapes and for chemical species for which accurate and rapid sensors are available. Additional studies are needed to extend these techniques to more complex terrain and more chemical species.

2.8.2.3. Factors Affecting Dry Deposition Rates and Totals

In the size range of ~0.1 to 1.0 μm where V_d is relatively independent of particle diameter as shown in Figure 2-26, particulate deposition is controlled by roughness of the surface and by the stability and turbulence of the atmospheric surface layer. Impaction and interception dominate over diffusion as dry deposition processes, and the V_d is considerably lower than for particles that are either smaller or larger than this size range (Shinn, 1978).

Deposition of particles between 1 and 10 μm diameter is strongly dependent on particle size (Shinn, 1978). Larger particles within this size range are collected more efficiently at typical wind speeds than are smaller particles (Clough, 1975), suggesting the importance of impaction. Impaction is related to wind speed, the square of particle diameter, and the inverse of receptor diameter as a depositing particle fails to follow the streamlines of the air in which it is suspended around the receptor. When particle trajectory favors a collision, increasing either wind speed or the ratio of particle size to receptor cross-section increases the probability of collision.
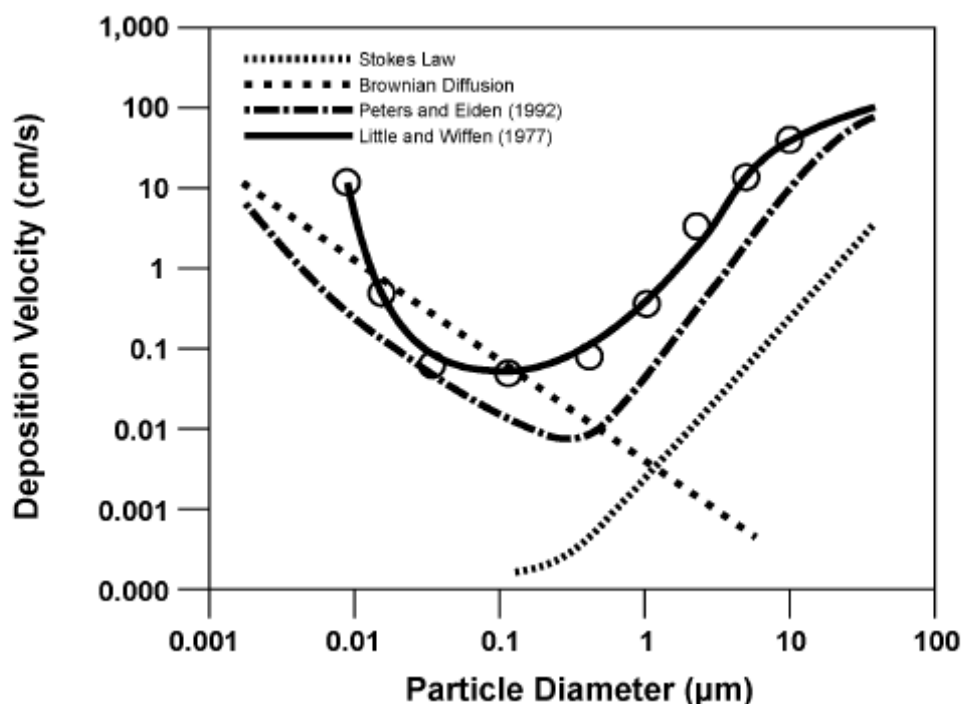
Figure 2-26. The relationship between particle diameter and deposition velocity for particles. Values measured in wind tunnels by Little and Wiffen (1977) over short grass with wind speed of 2.5 m/s closely approximate the theoretical distribution determined by Peters and Eiden (1992) for a tall spruce forest. These distributions reflect the interaction of Brownian diffusivity (descending dashed line), which decreases with particle size and sedimentation velocity (ascending dotted line from Stokes Law), which increases with particle size. Intermediate-sized particles (.0.1 to 1.0 μm) are influenced strongly by both particle size and sedimentation velocity, and deposition is independent of size. Source: U.S. EPA (2004).

Empirical estimates of V_d for fine particles under wind tunnel and field conditions are often several-fold greater than predicted by theory (Unsworth and Wilshaw, 1989). A large number of transport phenomena, including streamlining of foliar obstacles, turbulence structure near surfaces, and various phoretic transport mechanisms are not well characterized (U.S. EPA, 2004). The discrepancy between estimated and predicted values of V_d may reflect model limitations or experimental limitations in the specification of the effective size and number of receptor obstacles. Available reviews (e.g., U.S. EPA, 1996a, 2004) suggest the following generalizations: particles >10 μm exhibit variable V_d between 0.5 and 1.1 cm/s depending on friction velocities, whereas a minimum particle V_d of 0.03 cm/s exists for particles in the size range 0.1 to 1.0 μm; the V_d of particles is approximately a linear function of friction velocity; and deposition of particles from the atmosphere to a forest canopy is from 2 to 16 times greater than deposition in adjacent open terrain like grasslands or other low vegetation.

Leaf Surface Effects on V_d

The chemical composition of a particle is not usually considered to be a primary determinant of its V_d. Rather, the plant leaf surface has an important influence on the V_d of particles, and therefore on the flux of dry deposition to the terrestrial environment. Relevant leaf surface properties include stickiness, microscale roughness, and cross-sectional area. These properties affect the probability of impaction and particle bounce. The efficiency of deposition to vegetation also varies with leaf shape. Particles impact

more frequently on the adaxial (upper surface) surface than on the abaxial (lower surface). Most particles accumulate in the midvein, central portion of leaves. The greatest particle loading on dicotyledonous leaves is frequently on the adaxial surface at the base of the blade, just above the petiole junction. Precipitation washing probably plays an important role in this distribution pattern (U.S. EPA, 2004).

Lead particles have been shown to accumulate to a greater extent on older as compared with younger needles and twigs of white pine, suggesting that wind and rain may be insufficient to fully wash the foliage. Fungal mycelia (derived from windborne spores) were frequently observed in intimate contact with other particles on leaves, which may reflect minimal re-entrainment of the spore due to shelter by the particles, mycelia development near sources of soluble nutrients provided by the particles, or simply co-deposition (Smith and Staskawicz, 1977).

Leaves with complex shapes tend to collect more particles than do those with shapes that are more regular. Conifer needles are more efficient than broad leaves in collecting particles by impaction, reflecting the small cross-section of the needles relative to the larger leaf laminae of broadleaves and the greater penetration of wind into conifer canopies than broadleaf ones (U.S. EPA, 2004).

Canopy Surface Effects on V_d

Surface roughness increases particulate deposition, and V_d is usually greater for a forest than for a nonforested area and greater for a field than for a water surface. Different size particles have different transport properties and V_d. The upwind leading edges of forests, hedgerows, and individual plants are primary sites of coarse particle deposition. Impaction at high wind speed and the sedimentation that follows the reduction in wind speed and carrying capacity of the air in these areas lead to preferential deposition of larger particles (U.S. EPA, 2004).

Air movement is slowed in proximity to vegetated surfaces. Canopies of uneven age or with a diversity of species are typically aerodynamically rougher and receive larger inputs of dry-deposited pollutants than do smooth, low, or monoculture vegetation (Garner et al., 1989; U.S. EPA, 2004). Canopies on slopes facing the prevailing winds receive larger inputs of pollutants than more sheltered, interior canopy regions.

All foliar surfaces within a forest canopy are not equally exposed to particle deposition. Upper canopy foliage tends to receive maximum exposure to coarse and fine particles, but foliage within the canopy tends to receive primarily fine particles.

2.8.2.4. Nitrogen Deposition and Flux with Biota

Several N_r are species are deposited to vegetation, among them, HNO_3, NO_2, and PAN and other $RONO_2$.

Field observations based on concentration gradients of HNO_3 and using eddy covariance techniques demonstrate rapid deposition that approaches the aerodynamic limit (as constrained by atmospheric turbulence) in the Weseley and Lesht (1989) formulation based on analogy to resistance; see Figure 2-25 and Equation 5. Surface resistance to HNO_3 uptake by vegetation is negligible and its deposition rates are independent of leaf area or stomatal conductance, implying that deposition occurs to branches, soil, and the leaf cuticle as well as leaf surfaces. The HNO_3 V_d typically exceeds 1 cm/s and exhibits a diel pattern controlled by turbulence characteristics of midday maxima and lower values at night in the more stable boundary layer.

Compared with HNO_3, NO_2 interaction with vegetation is more difficult to understand in part because very fast measurements of NO_2 flux are confounded by the rapid interconversion of NO and NO_2 with O_3 (Gao et al., 1991). Application of ^{15}N-labeled NO_2 has demonstrated that NO_2 is absorbed and metabolized by foliage (Mocker et al., 1998; Segschneider et al., 1995; Siegwolf et al., 2001; Weber et al., 1995). Exposure to NO_2 induces activation of NO_3^- reductase (Weber et al., 1995, 1998), a necessary enzyme for assimilating oxidized N. Current understanding of NO_2 interactions with foliage is largely based on leaf cuvette and growth chamber studies, which expose foliage or whole plants to controlled

NO$_2$ concentrations, and measure the fraction of NO$_2$ removed from the chamber air. A key finding is that the fit of NO$_2$ flux to NO$_2$ concentratin has a non-zero intercept, implying a compensation point or internal concentration. In studies at very low NO$_2$ concentrations, emission from foliage is observed (Teklemariam and Sparks, 2006). Evidence for a compensation point is not solely based on the fitted intercept. The NO$_2$ uptake rate to foliage is clearly related to stomatal conductance. Internal resistance is variable, and may be associated with concentrations of reactive species such as ascorbate in the plant tissue that react with NO$_2$ (Teklemariam and Sparks, 2006). Foliar NO$_2$ emissions show some dependence on N content (Teklemariam and Sparks, 2006). Internal NO$_2$ appears to derive from plant N metabolism.

Two approaches to modeling NO$_2$ uptake by vegetation are the resistance-in-series analogy which considers flux (F) as the product of concentration (C) and V$_d$, related to the sum of aerodynamic, boundary layer, and internal resistances (R_a, R_b, and R_c, respectively, from Equation 5 and Figure 2-25); by convention, positive fluxes are in the direction from atmosphere to foliage. Note that this approach is the method most often used to predict deposition in AQMs, that of Wesely and Lesht (1989), as described above. Typically, the NO$_2$ V$_d$ is less than that for O$_3$ due to the surface's generally higher resistance to NO$_2$ uptake, consistent with NO$_2$'s lower reactivity.

Alternatively, NO$_2$ exchange with foliage can be modeled from a physiological standpoint where the flux from the leaf (J) is related to the stomatal conductance (g_s) and a concentration gradient between the ambient air NO$_2$ concentration (C$_a$) and interstitial air NO$_2$ concentration (C$_i$) in the leaf ($C_a - C_i$) as depicted in Equation 6.

$$J = g_s (C_a - C_i)$$

Equation 6

This approach best describes results for exchange with individual foliage elements, and is expressed per unit leaf or needle area. While this approach provides linkage to leaf physiology, it is not straightforward to scale up from the leaf to the ecosystem. This model implicitly associates the compensation point with a finite internal concentration. Typically observed compensation points are ~1 ppb; values of internal NO$_2$ concentrations are consistent with metabolic pathways that include NO$_X$. In this formulation, the uptake will be linear with NO$_2$, which is typically measured in foliar chamber studies.

Several studies have shown the UV dependence of NO$_2$ emissions, which implies some photo-induced surface reactions to release NO$_2$. Rather than model this as a UV-dependent internal concentration, it would be more realistic to add an additional term to account for emission that is dependent on light levels and other surface characteristics

$$J = g_s (C_a - C_i) = J_s (UV)$$

Equation 7

PAN is phytotoxic and absorbed at the leaf. Observations based on inference from concentration gradients and rates of loss at night (Schrimpf et al., 1996; Shepson et al., 1992) and from leaf chamber studies (Teklemariam and Sparks, 2004) have indicated that uptake of PAN is slower than that of O$_3$. However, recent work in coniferous canopies with direct eddy covariance PAN flux measurements indicated a V$_d$ more similar to that of O$_3$. Uptake of PAN is under stomatal control, has non-zero deposition at night, and is influenced by leaf wetness (Turnipseed et al., 2006). On the other hand, flux measurements determined by gradient methods over a grass surface showed a V$_d$ closer to 0.1 cm/s, with uncertainty on the order of a factor of 10 (Doskey et al., 2004). Whether the discrepancies are methodological or indicate intrinsic differences between different vegetation is unknown. Uptake of PAN is a smaller loss process than its thermal decomposition in all cases.

The biosphere also interacts with NO$_X$ through HC emissions and their subsequent reactions to form multi-functional RONO$_2$. Formation of the hydroxyalkyl nitrates occurs after OH attack on VOCs. In one sense, this mechanism is simply an alternate pathway for OH to react with NO$_X$ to form a rapidly

depositing species. If VOC were not present, OH would be available to react with NO_2 when it is present to form HNO_3.

Isoprene nitrates are an important class of $RONO_2$. Isoprene reacts with OH to form a radical that adds NO_2 to form the hydroxyalkyl nitrate. The combination of hydroxyl and NO_3 functional group makes these compounds especially soluble with low vapor pressures, so they likely deposit rapidly (Shepson et al., 1996; Treves et al., 2000). Many other unsaturated HCs react by analogous routes. Observations at Harvard Forest show a substantial fraction of the total of all gas-phase forms of oxidized N is not accounted for by NO, NO_2 and PAN, and the remainder is attributed to the missing fraction of $RONO_2$ (Horii et al., 2006; Munger et al., 1998). Furthermore, the total NO_Y flux exceeds the sum of HNO_3, NO_X, and PAN, which implies that the $RONO_2$ are a substantial fraction of the total N deposition. Other observations showing evidence of hydoxyalkyl nitrates include those of Grossenbacher et al. (2001) and Day et al. (2003).

HNO_2 formation on vegetative surfaces at night has long been observed based on measurements of positive gradients (Harrison and Kitto, 1994). Surface reactions of NO_2 enhanced by moisture were proposed to explain these results. Production was evident at sites with high ambient NO_2; at low concentration, uptake of HNO_2 exceeded the source. Daytime observations of HNO_2 when rapid photolysis is expected to deplete ambient concentrations to very low levels implies a substantial source of photo-induced HNO_2 formation at a variety of forested sites where measurements have been made. Estimated source strengths are 200 to 1800 ppt/h in the surface layer (Zhou et al., 2002a, 2003b), which is ~20 times faster than all nighttime sources.

HNO_2 sources could be important to HO_X budgets as HNO_2 is rapidly photolyzed by sunlight to OH and NO. Additional evidence of light-dependent reactions to produce HNO_2 comes from discovery of a HNO_2 artifact in Pyrex sample inlet lines exposed to ambient light. Either covering the inlet or washing it eliminated the HNO_2 formation (Zhou et al., 2002b). Similar reactions might serve to explain observations of UV-dependent production of NO_X in empty foliar cuvettes that had been exposed to ambient air (Hari et al., 2003; Raivonen et al., 2003).

Production of HNO_2 in the dark is currently believed to occur via a heterogeneous reaction involving NO_2 on wet surfaces (He et al., 2006; Jenkin et al., 1988; Pitts et al., 1984; Sakamaki et al., 1983). It has been proposed that the mechanism has first-order dependence in both NO_2 and H_2O (Kleffmann et al., 1998; Svensson et al., 1987) despite the stoichiometry. However, the molecular pathway of the mechanism is still under debate. Jenkin et al. (1988) postulated a $H_2O \cdot NO_2$ water complex reacting with gas phase NO_2 to produce HNO_2, which is inconsistent with the formation of an N_2O_4 intermediate leading to HNO_2 as proposed by Finlayson-Pitts et al. (2003). Another uncertainty is whether the reaction forming HNO_2 is dependent on water vapor (Stutz et al., 2004; Svensson et al., 1987) or water adsorbed on surfaces (Kleffmann et al., 1998). Furthermore, the composition of the surface and the available amount of surface or surface-to-volume ratio can significantly influence the HNO_2 production rates (Kaiser and Wu, 1977; Kleffmann et al., 1998; Svensson et al., 1987), which may explain the difference in the rates observed between laboratory and atmospheric measurements.

There is no consensus on a chemical mechanism for photo-induced HNO_2 production. Photolysis of HNO_3 or NO_3^- absorbed on ice or in surface water films has been proposed (Honrath et al., 2002; Ramazan et al., 2004; Zhou et al., 2001, 2003b). Alternative pathways include NO_2 interaction with organic surfaces such as humic substances (George et al., 2005; Stemmler et al., 2006). Note that either NO_3^- photolysis or heterogeneous reaction of NO_2 are routes for recycling deposited NO_X back to the atmosphere in an active form. NO_3^- photolysis would return N that heretofore was considered irreversibly deposited, while surface reactions between NO_2 and water films or organic molecules would decrease the effectiveness of observed NO_2 deposition if the HNO_2 were re-emitted.

2.8.3. Air Quality Model Evaluation

Urban and regional air quality is determined by a complex system of coupled chemical and physical processes including emissions of pollutants and pollutant precursors, complex chemical reactions, physical transport and diffusion, and wet and dry deposition. NO_X in these systems has long been known to act nonlinearly in $P(O_3)$ and other secondary pollutants (Dodge, 1977); to extend over multiple spatial and temporal scales; and to involve complicated cross-media environmental issues such as acidic or nutrient deposition to sensitive biota and degradation of visibility.

NO_Y species emitted and transformed from emissions control the production and fate of O_3 and aerosols by sustaining or suppressing OH cycling. Correctly characterizing the interrelated NO_Y and OH dynamics for O_3 formation and fate in the polluted troposphere depends on new techniques using combinations of several NO_Y species for diagnostically probing the complex atmospheric dynamics in typical urban and regional airsheds.

Arnold et al. (1998) described a model evaluation methodology that distinguished several types of AQM testing. Two components of that methodology were: operational testing to judge the performance and overall behavior of a model over specific attributes; and diagnostic testing to help reveal potential compensating error in model inputs or processing. Diagnostic testing is in situ testing of model components using data that emphasize atmospheric processes, often with mass balance techniques, special species ratios, and process rate and reaction rate information not typically stored by the model for output. Some of these probes have been developed through process-oriented studies using theoretical assumptions, model-derived explanations, and results from instrumented models ranging from one-dimensional box models to the full 4-dimensional photochemical modeling system (Tonnesen and Dennis, 2000). Additional information on instrumenting AQMs for diagnostic analysis with model process and reaction rate information is found in Dennis et al. (2002); information pertaining to the specific implementation of these techniques in CMAQ is found in (Gipson and Young, 1999); and results from application of diagnostic probes to modeling experiments are found in Arnold and Dennis (2003, 2006).

Evaluation results from a recent U.S. EPA exercise of CMAQ in the Tampa Bay, FL, airshed are presented here as an example of the present level of skill of state-of-the-science AQMs for predicting atmospheric concentrations of the relevant NO_X, SO_X, and NH_X species for this NAAQS assessment. This modeling series exercised CMAQ version 4.4 and with the University of California at Davis (UCD) sectional aerosol module in place of the standard CMAQ modal module and was driven by meteorology from MM5 v3.6 and with NEI emissions as augmented by continuous emissions monitoring data where available. (The UCD size-segregated module was preferred for this application because of the importance of sea salt particles in the bay airshed. Testing of this new engineering extension revealed that its performance was very similar to CMAQ's standard modal; hence, model behavior and performance reported here can stand as a general indication of CMAQ's skill.)

The CTM was run with 21 vertical layers for the month of May 2002. For this evaluation, CMAQ-UCD was run in a one-way nested series of three domains with 32 km, 8 km, and 2 km horizontal grid spacings from the CONUS (32 km) to central Florida and the eastern Gulf of Mexico (2 km).

Depictions of the 8 km and 2 km domains used here zoomed over the central Tampa area are shown in Figure 2-27 and Figure 2-28.
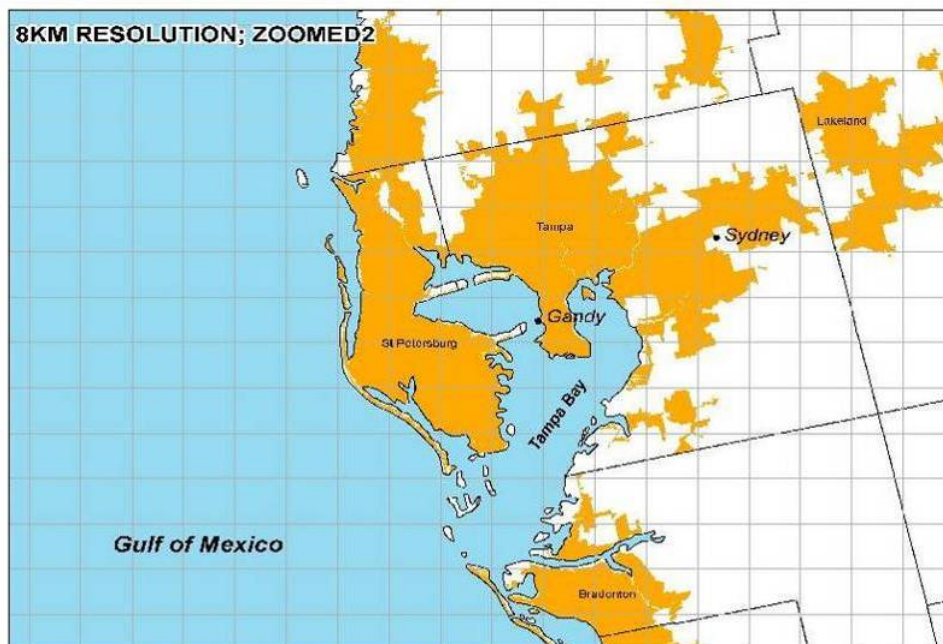
Figure 2-27.   8 km southeast U.S. CMAQ domain zoomed over Tampa Bay, FL.
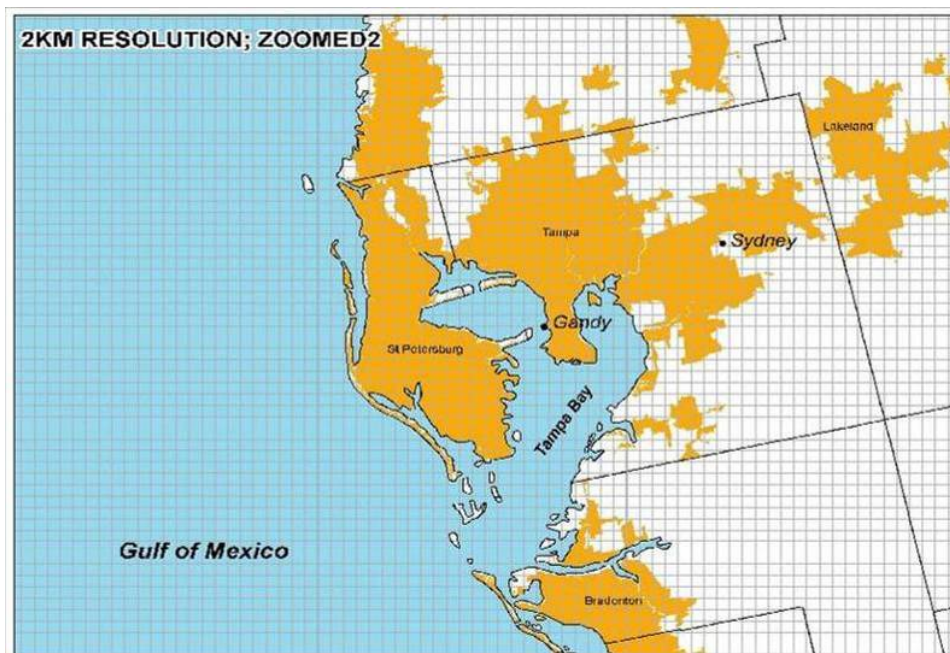
Figure 2-28.   2 km southeast U.S. CMAQ domain zoomed over Tampa Bay, FL.

2.8.3.1. Ground-based Comparisons of Photochemical Dynamics

Errors in the NO_X concentrations in the model most likely from on-road emissions (Figure 2-29) affected NO_X predictions, but CMAQ-UCD's general responses were reasonable. The model also replicated well anthropogenic and biogenic VOC emissions; see Figure 2-30 and Figure 2-31,

respectively. After initial errors leading to underprediction in the first 21 days, CMAQ's predictions of hourly PM$_{2.5}$ concentrations and trends over the whole month also replicated the observed concentrations well; see Figure 2-32.
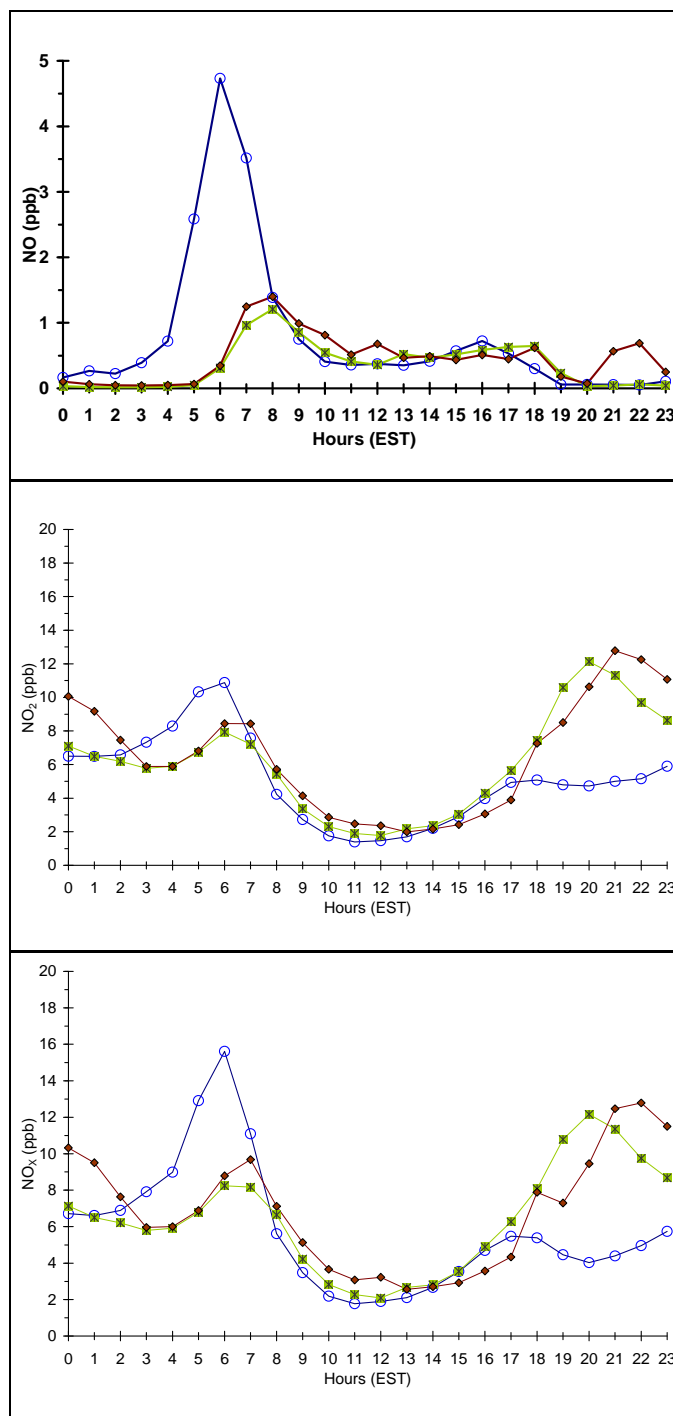
Figure 2-29. Hourly averages for May 1-31, 2002. CMAQ 8 km and 2 km results and measured concentrations of NO (top), NO$_2$ (middle), and total NO$_X$ (bottom). Legend: blue circles = Observations (OBS); green squares = 8 km; red diamonds = 2 km CMAQ solutions.
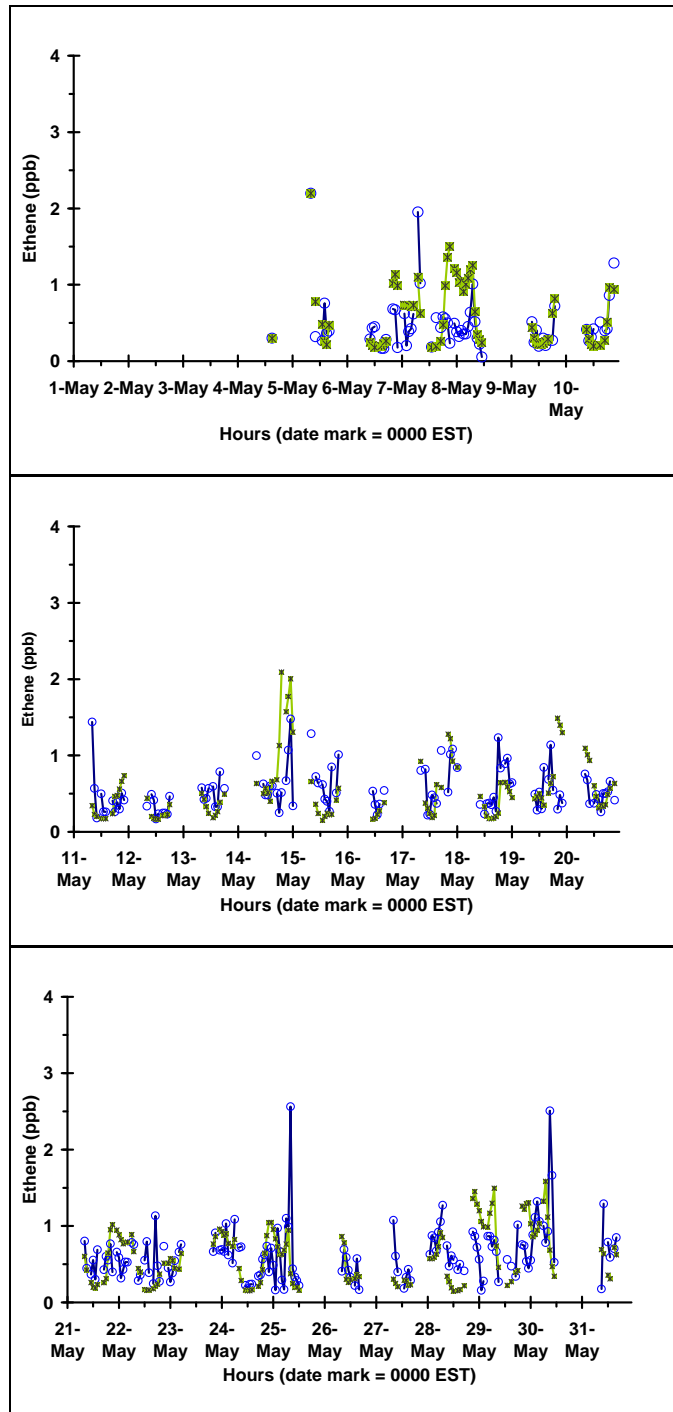
Figure 2-30. May 2002 daily concentrations and 8 km CMAQ predictions for ethene at Sydney, FL. Legend: blue circles = OBS; green squares = 8 km CMAQ solutions.
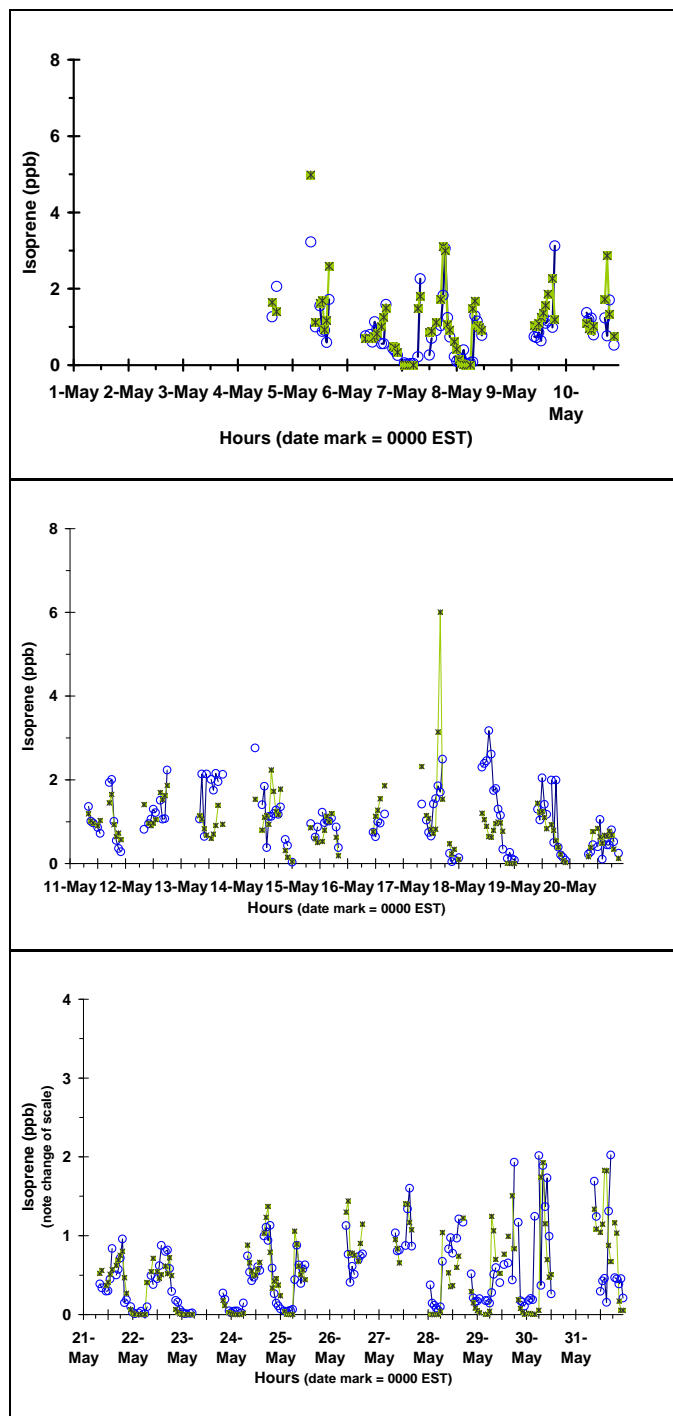
Figure 2-31. **May 2002 daily concentrations and 8 km CMAQ predictions for isoprene at Sydney, FL. Legend: blue circles = OBS; green squares = 8 km CMAQ solutions.**
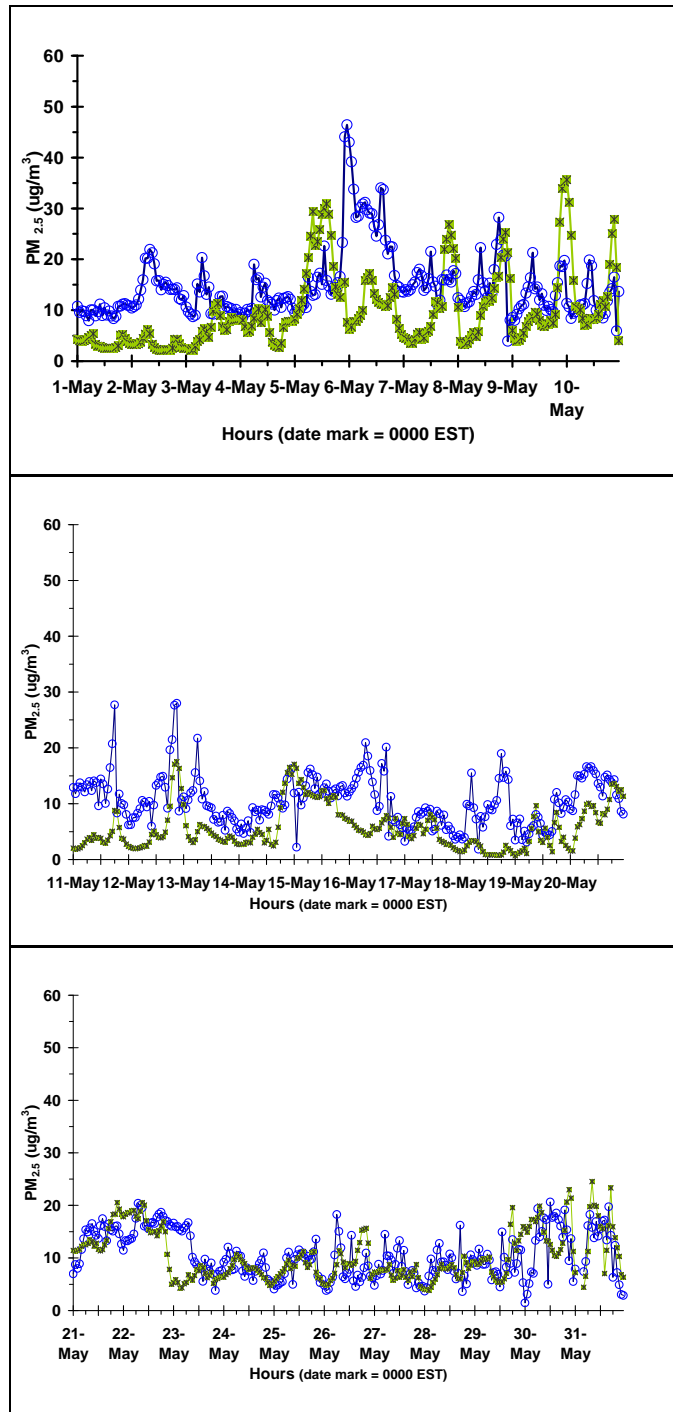
Figure 2-32. Observed hourly PM$_{2.5}$ concentrations at St. Petersburg, FL and results from CMAQ 8 km. Legend: blue circles = OBS; green squares = 8 km CMAQ solutions.
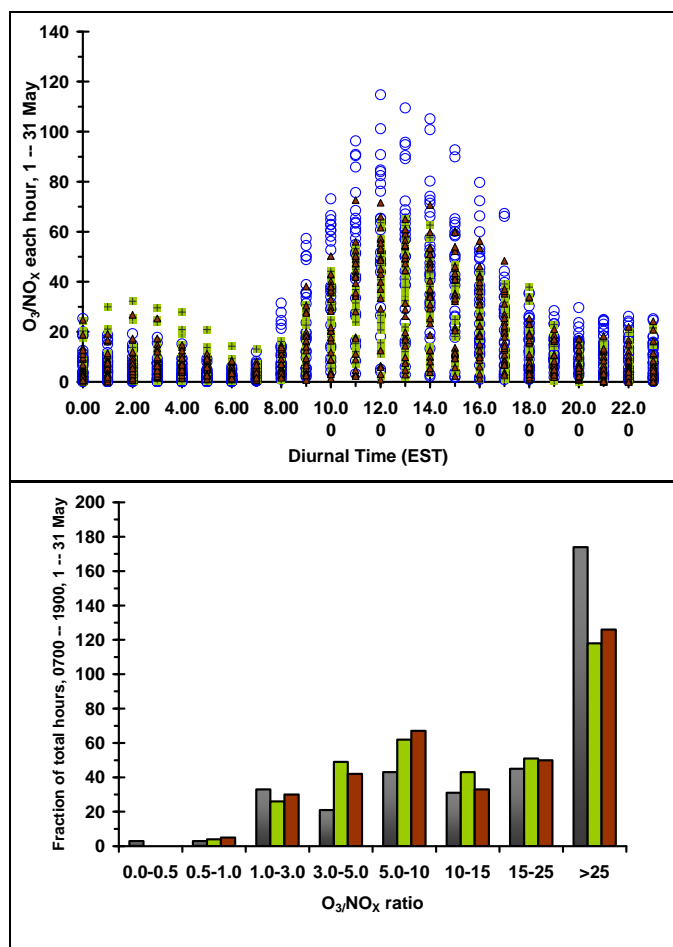
Figure 2-33. Observed and modeled ratios of O_3 to NO_X. Diel curves from hourly averages over May 1-31, 2002 (top), and distribution of O_3 to NO_X ratio values binned to show fractions of total daylight hours, May 1–31, 2002 (bottom panel). Legend: blue circles or bars = OBS; green squares or bars = 8 km; red triangles or bars = 2 km.

The $P(O_3)$ efficiency curves in the model agreed well with those observed at Sydney, FL; see Figure 2-33. However, tests of CH_2O (Figure 2-34) and H_2O_2 (Figure 2-35) seemed to indicate an error in the model's OH chemistry related to these radical reservoir species since both were substantially and systematically different from the observations at the ground-based Sydney site. These species have historically been very difficult to model well, however, and the overall excellent agreement of CMAQ-UCD to production curves in relation to NO_X processing mean that this error was likely restricted to these species and of limited influence in the overall model solutions and for this evaluation.
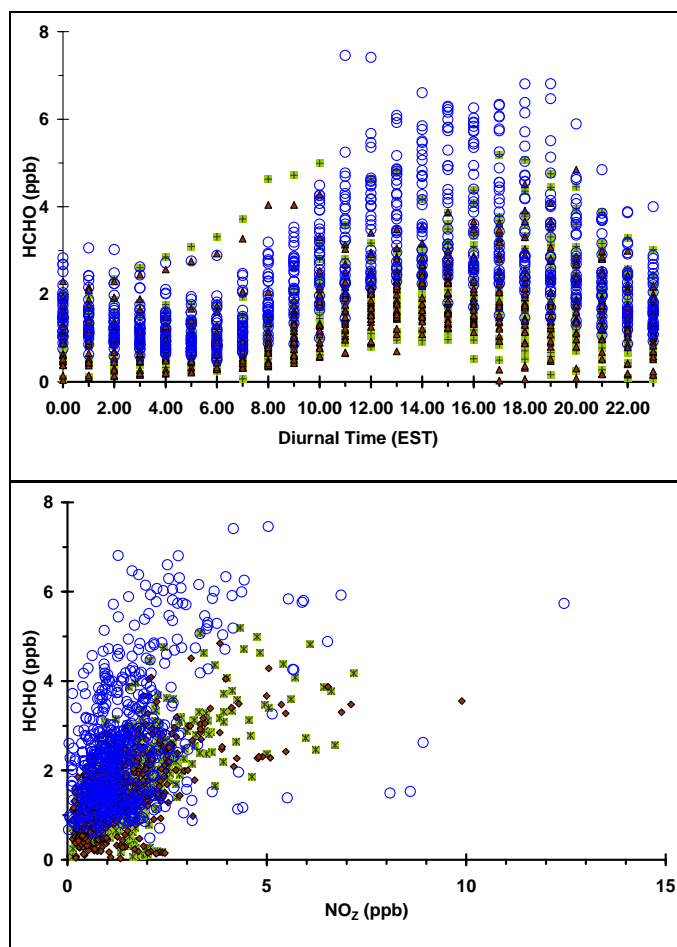
Figure 2-34. Observed and CMAQ 8 km and 2 km predicted formaldehyde concentrations. Hourly averages from each day, May 1-31, 2002 (top), and formaldehyde concentrations as a function of NO_Z concentrations (bottom). Legend: blue circles = OBS; green squares = 8 km; red triangles or diamonds = 2 km.
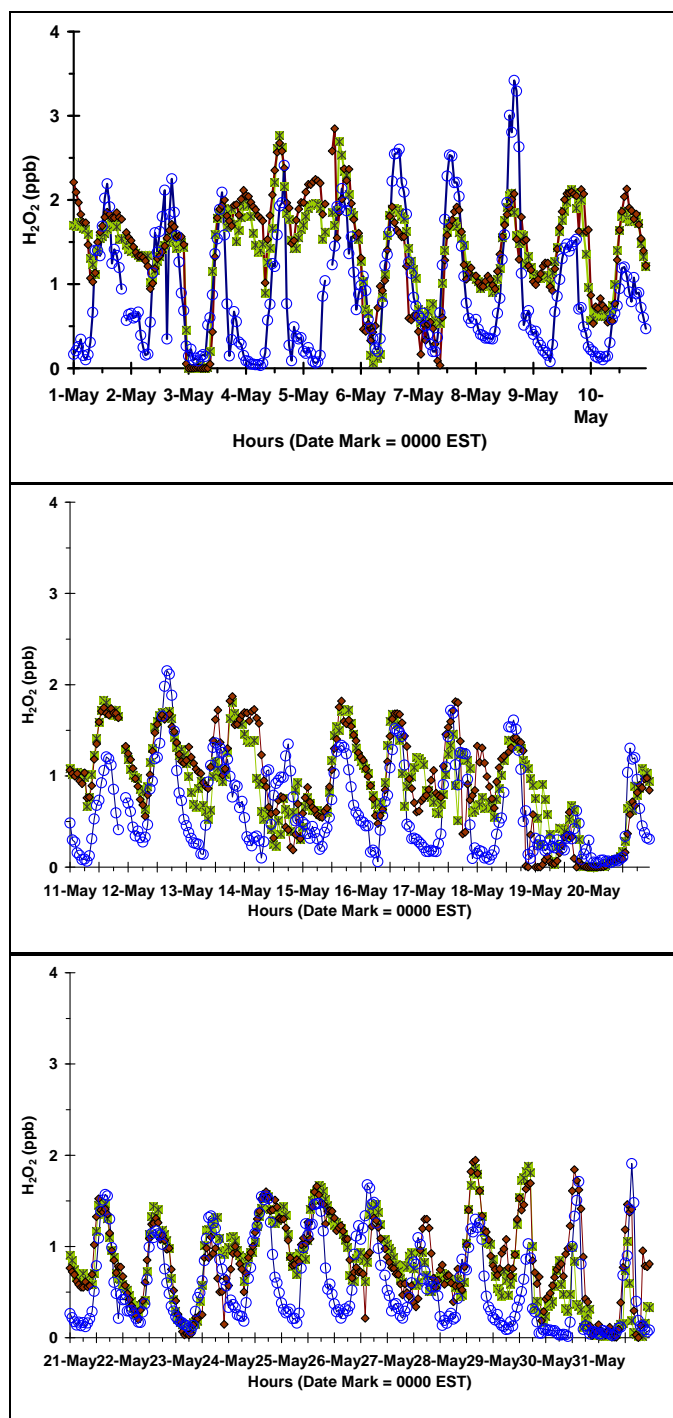
Figure 2-35. Hourly concentrations of hydrogen peroxide, observed and predicted by CMAQ 8 km and 2 km, May 1-31, 2002 at Sydney, FL. Legend: blue circles = OBS; green squares = 8 km; red diamonds = 2 km.

2.8.3.2. Predicted Chemistry for Nitrates and Related Compounds

pNO$_3$ plays a crucial and complex role in the health of aquatic and estuarine ecosystems. Gas-phase NO$_3^-$ replacement of Cl$^-$ on sea salt particles is often favored thermodynamically and the V$_d$ of the coarse NO$_3$ formed through this replacement is more than an order of magnitude greater than for fine NO$_3$. Over open bodies of salt water such as the Gulf of Mexico and Tampa Bay, FL, NO$_3^-$ from this reaction dominates dry deposition and is estimated to be of the same order as NO$_3^-$ wet deposition.

However, NO$_3^-$ concentrations are driven, buffered, and altered by a wide range of photochemical gas-phase reactions, heterogeneous reactions, and aerosol dynamics, making them especially difficult to model well. Because pNO$_3$ is derived mostly from gas-phase HNO$_3$ and will interact with Na$^+$, NH$_4^+$, Cl$^-$, and SO$_4^{2-}$, all these species and the physical parameters governing their creation, transport, transformation, and fate must be accurately replicated to predict pNO$_3$ with high fidelity. This has historically been a difficult problem for numerical process models, owing not least to the pervasive dearth of reliable ambient measurements of NO$_3^-$ in its various forms. Normalized mean error (NME) for the large-scale Eulerian CTM-predicted pNO$_3$ has typically been on the order of a factor of 3 greater than the NME for pSO$_4$ (Odman et al., 2002; Pun et al., 2003).

SO$_4^{2-}$, NH$_4^+$, Na$^+$, and Cl$^-$ were all predicted to within a factor of 2 and with no significant bias during the photochemical day in the 8 km CMAQ-UCD solution, although a significant bias in Na$^+$ and Cl$^-$ was evident in the 2 km solution for two near water sites. This grid-size dependent bias is still being explored. Size segregation maxima were correct to within two size bins every day for which there were observations for both SO$_4^{2-}$ and NH$_4^+$ (0.2 to 1.0 μm), and Na$^+$ and Cl$^-$ (2.0 to 10.0 μm). Cl$^-$ concentrations were greatly overpredicted during dark hours, but were nearer to observed values during the photochemical day. CMAQ performance for HNO$_3$ and NH$_3$ are shown in Figure 2-37 and Figure 2-40, respectively.

Figure 2-36 shows that CMAQ-UCD systematically underpredicted the hourly time series of measured pNO$_3$ concentrations at the Sydney supersite, the only location with discrete pNO$_3$ data. These time series data establish that CMAQ-UCD's largest errors were on four days in the first 2 weeks of the month, but that the total peak pNO$_3$ concentrations were nearly all underpredicted.

Since pNO$_3$ is derived in large part from gas-phase HNO$_3$, its underprediction may be due to an underprediction of HNO$_3$ concentrations or an underrepresentation of the gas- to aerosol-phase change. At Sydney, FL, in fact, both these conditions held. Figure 2-37 depicts the model's bias for HNO$_3$ underprediction in both the 8 km and 2 km solutions, excepting four days of very large peak overpredictions. This trend was especially true overnight; on eight other days the model overpredicted the one hour peak concentration as well, though not so substantially, but the chief effect was still one of an artificial and inappropriate N limitation in the model.

A time series molar equivalent ratio of HNO$_3$ to total NO$_3$ depicts which phase stores the NO$_3^-$ and how that storage ratio changes over time. Figure 2-38 shows that at Sydney, FL, CMAQ-UCD stored too much NO$_3^-$ in the gas phase as HNO$_3$ (and recall that the daytime HNO$_3$ concentrations were sometimes overpredicted by the model) and too little in the gas phase overnight, when the model was regularly low against the measurements; compare Figures 2-37 and 2-38. Note again here the self-similarity of the 8 km and 2 km solutions in this comparison.

Interestingly, the 23 hour integrated data did not reveal this important difference in nitrate form between the model and measurements as Figure 2-39 shows in the stacked bar percentage plots of fine and coarse pNO$_3$ together with gas-phase HNO$_3$. Both the 8 km (Figure 2-39 (middle panel) and the 2 km (Figure 2-39 (bottom panel) solutions predicted distributions between the two general ranges of aerosol size, and between gas and aerosol phases, with good fidelity to the daily observations (Figure 2-39 (top panel)) at Sydney, FL. This result illustrates that while discrete time series data are crucial for diagnosing model behavior, on the integrated total daily and longer basis used for computing total annual N loads, CMAQ-UCD predicted approximately the correct distributions for pNO$_3$, even though the total NO$_3^-$ concentration prediction was biased low.
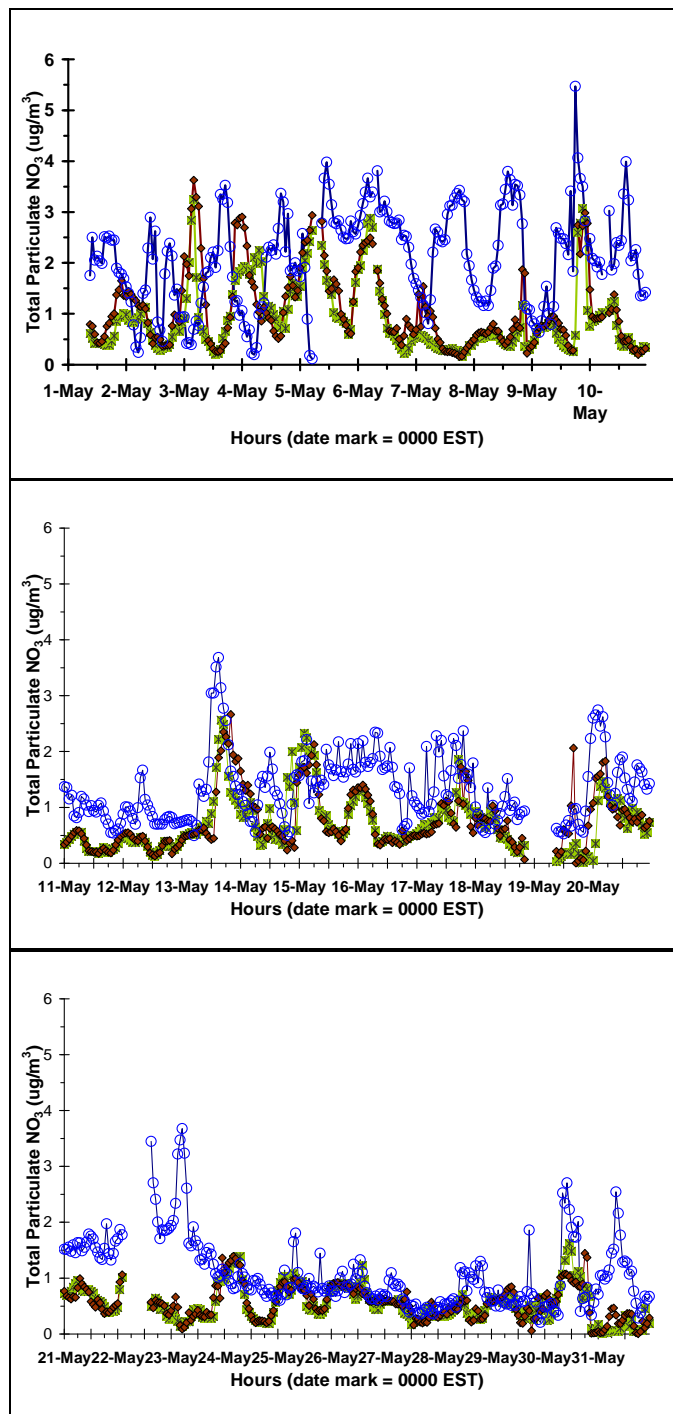
Figure 2-36. Hourly and CMAQ-UCD-predicted total pNO₃ concentrations at Tampa Bay, FL, and observations at Sydney, FL May 1-31, 2002. Legend: blue circles = OBS; green x's = 8 km; red diamonds = 2 km.
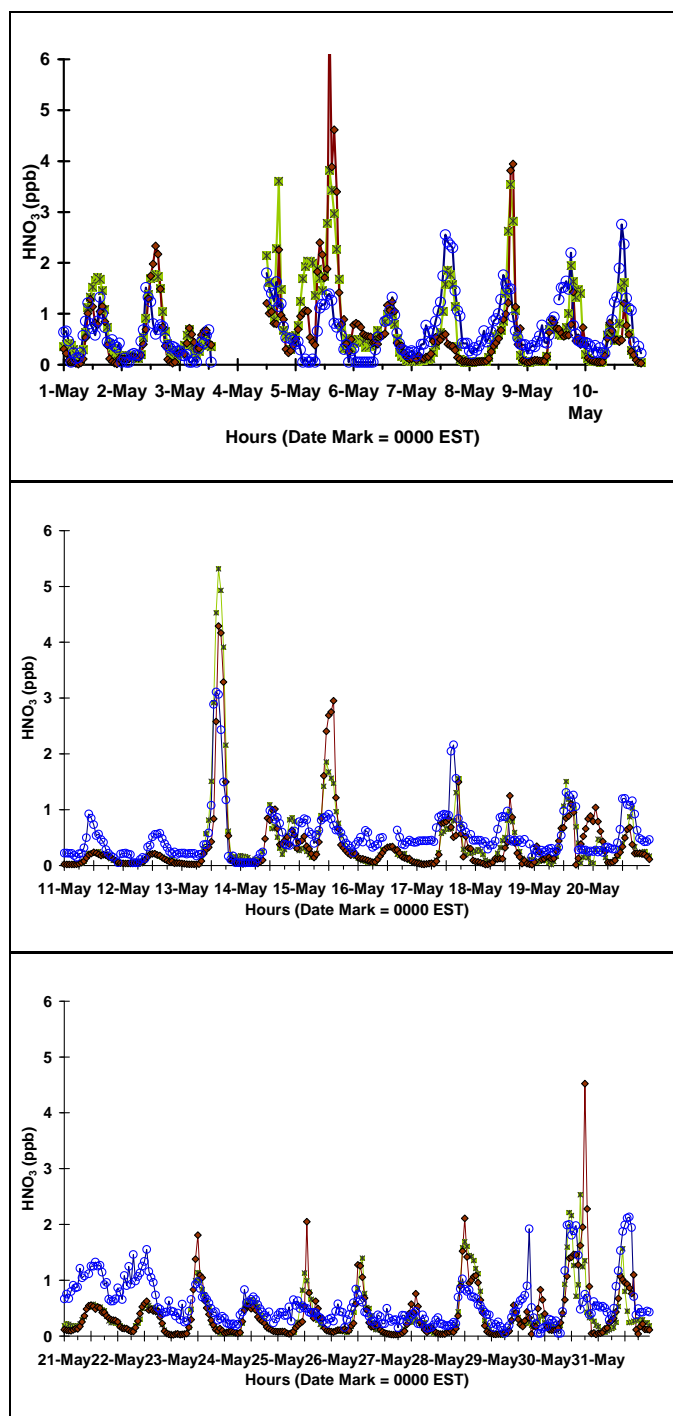
Figure 2-37. Hourly and CMAQ-predicted HNO$_3$ concentrations at Sydney, FL, May 1-31, 2002. Legend: blue circles = OBS; green squares = 8 km; red diamonds = 2 km.
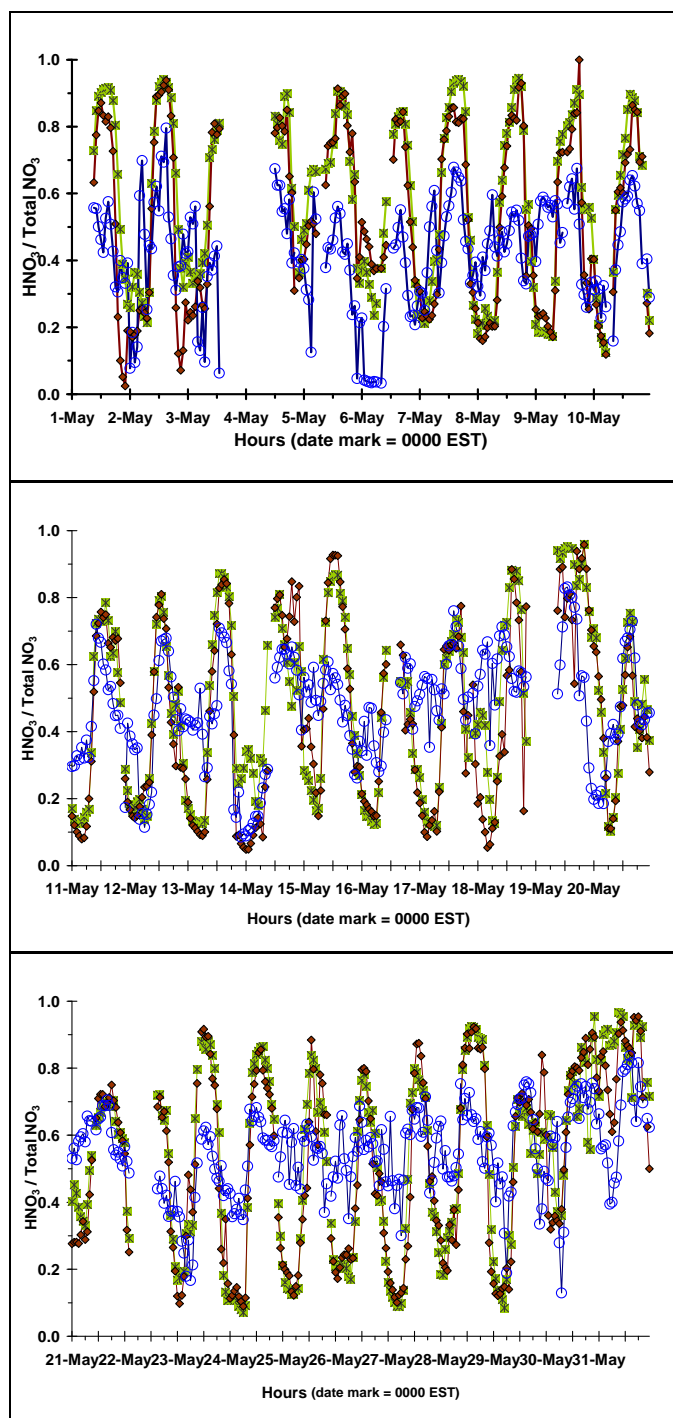
Figure 2-38. Hourly and CMAQ-UCD-predicted ratio of HNO$_3$ to total NO$_3$ at Tampa Bay, FL and observations at Sydney, FL, May 1-31, 2002. Legend: blue circles = OBS; green x's = 8 km; red diamonds = 2 km.
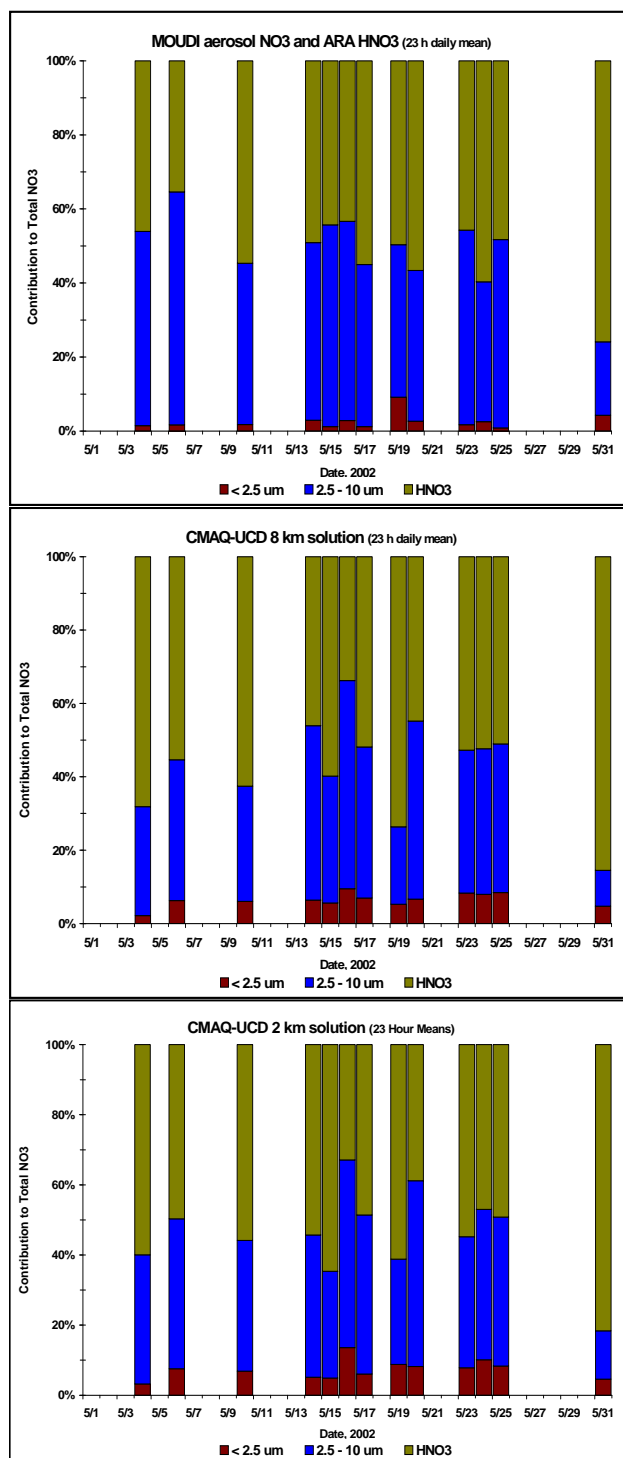
Figure 2-39. CMAQ-UCD predicted fractions and totals of total NO_3 for days in May 2002 with measurements in Tampa Bay, FL. Legend: red bars = <2.5 μm; blue bars = 2.5–10 μm; green bars = HNO_3. Measured concentrations (top panel), CMAQ-UCD 8 km solution (middle panel) and CMAQ-UCD 2 km solution (bottom panel).
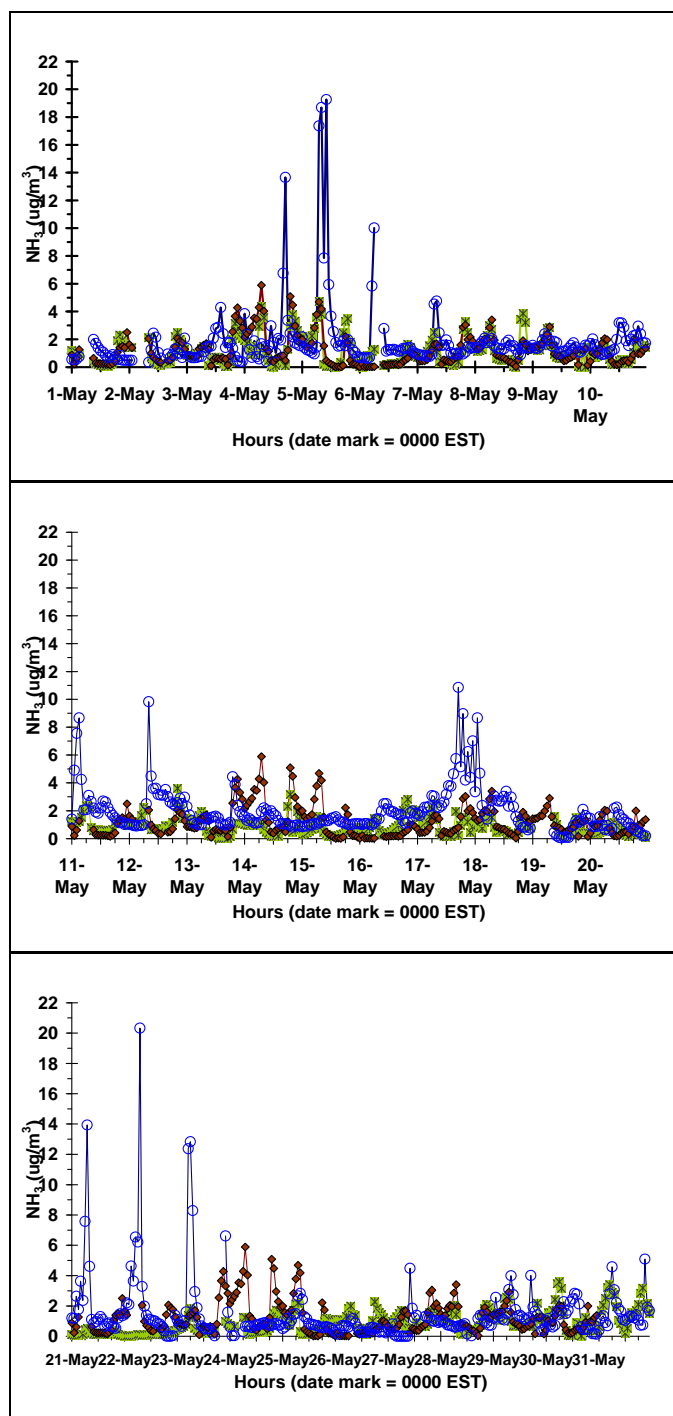
Figure 2-40. Hourly and CMAQ-predicted NH$_3$ concentrations at Sydney, FL, May 1-31, 2002. Legend: blue circles = OBS; green squares = 8 km; red diamonds = 2 km.

While the coarse fraction inorganic aerosol anion totals were dominated by NO$_3^-$, and SO$_4^{2-}$ dominated the fine fraction aerosol inorganic anions, there was sufficient NH$_X$ (NH$_X$ = NH$_3$ + NH$_4^+$) at Sydney, FL, to form fine aerosol NH$_4$NO$_3$ in some circumstances. Figure 2-40 depicts the hourly mass concentration of NH$_3$ at Sydney, FL, showing again the strong self-similarity of the 8 km and 2 km

solutions. Each solution, however, underpredicted the measured NH_3 concentrations consistently, and especially for the nine very large excursions of 10–20 µg/m^3 during the month.

Overall, CMAQ-UCD was found to be operationally sound in this evaluation of its 8 km and 2 km solutions for the Tampa Bay airshed using the ground-based and aloft data (not shown here) from the May 2002 field intensive. Moreover, results from diagnostic tests of the model's photochemical dynamics were generally in excellent agreement with results from the ambient atmosphere. However, CMAQ-UCD was biased low in this application for total NO_3 and for NO_3 present as gas-phase HNO_3. In addition, the model was biased low for the HO_X radical reservoir species CH_2O and H_2O_2, though this bias appeared to have been limited to these species. Performance of the new UCD aerosol module was judged to be entirely adequate, allocating aerosols by chemical makeup to the appropriate size fractions. Model performance for fine-mode aerosols was also judged to be fully adequate.

2.8.3.3. Evaluating Deposition with CTMs

Global CTM Performance

Both wet and dry deposition are of necessity highly parameterized in all CTMs. While all current models implement resistance schemes for dry deposition, the V_d generated from different models can vary highly across terrain types (Stevenson et al., 2006). The accuracy of wet deposition in global CTMs is tied to spatial and temporal distribution of model precipitation and the treatment of chemical scavenging. Dentener et al. (2006b) compared wet deposition across 23 models with available measurements around the globe. Figure 2-41 and Figure 2-42 extract results of a comparison of the 23-model mean versus observations over the eastern U.S. for pNO_3 and pSO_4 deposition, respectively. The mean model results were strongly correlated with the observations (r >0.8), and usually captured the magnitude of wet deposition to within a factor of 2 over the eastern U.S. Dentener et al. (2006b) concluded that 60 to 70% of the participating models captured the measurements to within 50% in regions with quality controlled observations.
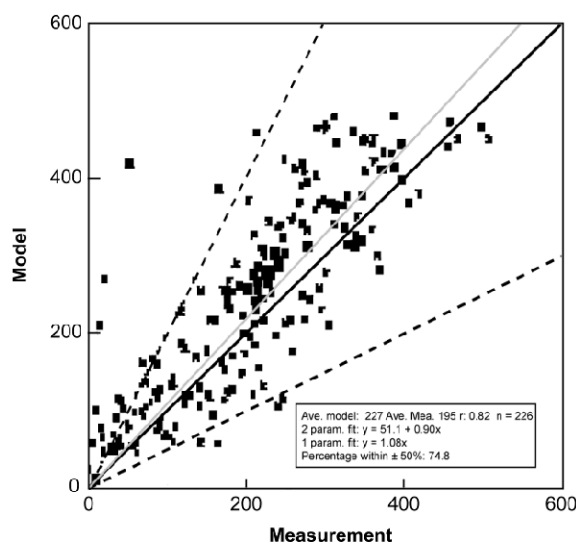
Figure 2-41. Scatter plot of total nitrate (HNO$_3$ plus pNO$_3$) wet deposition (mg N/m^2/yr) of the model mean versus measurements for the North American Deposition Program (NADP) network. Dashed lines indicate factor of 2. The gray line is the result of a linear regression fitting through zero.
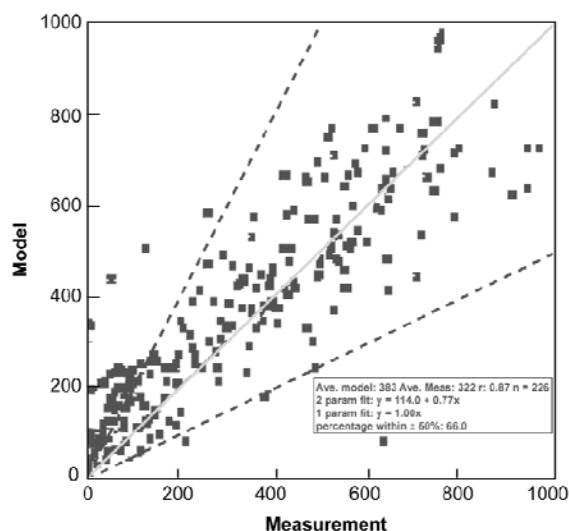
Figure 2-42. **Scatter plot of total SO$_4^{2-}$ wet deposition (mg S/m^2/yr) of the model mean versus measurements for the National Atmospheric Deposition Program (NADP) network. Dashed lines indicate factor of 2. The gray line is the result of a linear regression fitting through zero.**

2.8.3.4. Regional CTM Performance

Regional CTM performance for concentration and deposition of relevant NO$_X$ and SO$_X$ species is illustrated here with examples from CMAQ version 4.6.1 as configured and run for exposure and risk assessments reported in the *Draft Risk and Exposure Assessment for the Review of the Secondary National Ambient Air Quality Standards for Oxides of Nitrogen and Oxides of Sulfur* (U.S. EPA 2008c); additional details on the model configuration and application are found there. A map of the 36 km parent domain and two 12 km (east and west) progeny domains appears in Figure 2-43.
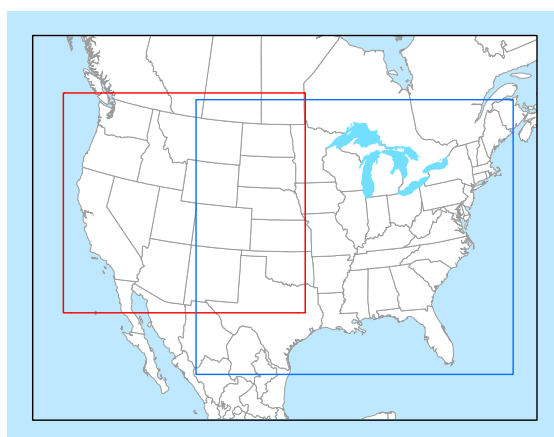
Figure 2-43. **CMAQ modeling domains for the OAQPS risk and exposure assessments: 36 km outer parent domain in black; 12 km western U.S. (WUS) domain in red; 12 km eastern U.S. (EUS) domain in blue.**

Comparisons from the 2002 annual run of CMAQ for the exposure assessment are shown here against measured concentrations and deposition totals from nodes in three networks: IMPROVE, CSN (labeled STN in the plots) and CASTNet; see the full description of these networks in Section 2.9 below. Comparisons were made as model-observation pairs at all sites having sufficient data for the seasonal or the 2002 annual time period in the two 12 km east and west domains and were evaluated with these descriptive statistics: correlation, root mean square error, normalized mean bias, and normalized mean error.

Summertime pSO_4 concentrations are well predicted by CMAQ, to within a factor of 2 at nearly every point, and with R^2 >0.8 across all three networks; see Figure 2-44. This result tracks the generally well-predicted pSO_4 concentrations found in earlier CMAQ evaluations: see Eder and Yu, 2006; Mebust et al., 2003; and Tesche et al., 2006. Since pSO_4 concentrations are strongly a function of precipitation, care must be taken to ensure that the meteorological solution driving individual CMAQ chemical applications produces precipitation fields with low bias as discussed by Appel et al., (2008).
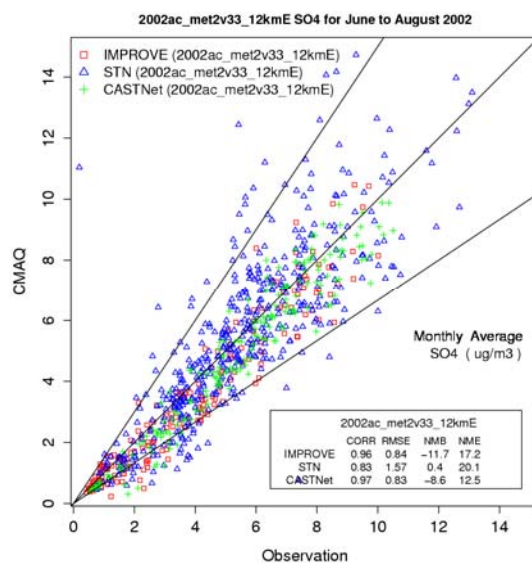
Figure 2-44.   **12-km EUS Summer sulfate PM, each data point represents a paired monthly averaged (June/July/August) observation and CMAQ prediction at a particular IMPROVE, STN, and CASTNet site. Solid lines indicate the factor of 2 around the 1:1 line shown between them.**

Wintertime pNO_3 (Figure 2-45) and total NO_3 (HNO_3+pNO_3) (Figure 2-46) concentrations are predicted less well by CMAQ; but NO_3^- is a pervasively difficult species to measure and model for the reasons described in detail in Sections 2.6 and 2.7 above. Still, at the CASTNet nodes where the total NO_3 concentrations are higher than they are at all but a few of the remote IMPROVE sites, CMAQ predicts concentrations for nearly every node to within a factor of 2 and with an R^2 >0.8.
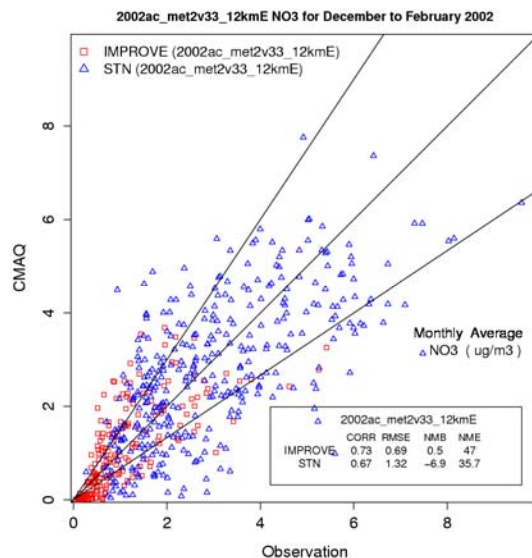
Figure 2-45. 12-km EUS Winter nitrate PM, each data point represents a paired monthly averaged (December/January/February) observation and CMAQ prediction at a particular IMPROVE and STN site. Solid lines indicate the factor of 2 around the 1:1 line shown between them.
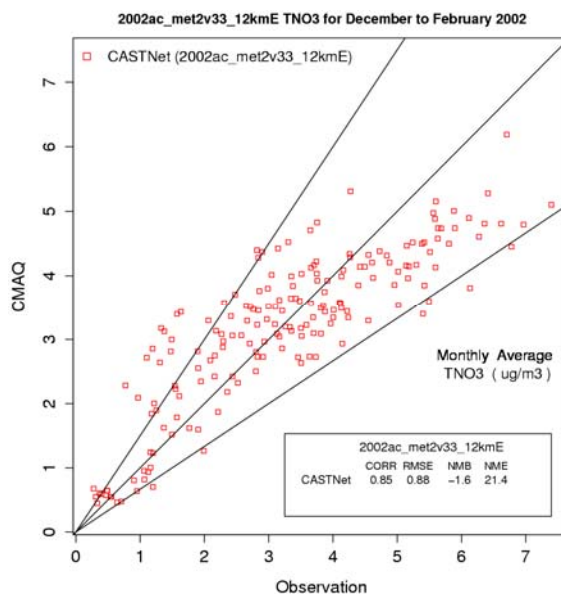
Figure 2-46. 12-km EUS Winter total nitrate (HNO_3 + total pNO_3), each data point represents a paired monthly averaged (December/January/February) observation and CMAQ prediction at a particular CASTNet site. Solid lines indicate the factor of 2 around the 1:1 line shown between them.

These CMAQ-predicted concentrations, coupled with modeled cloud and precipitation fields produce wet deposition fields for SO_4^{2-} and NO_3^- in the east domain as shown in Figures 2-47 and 2-48, respectively.
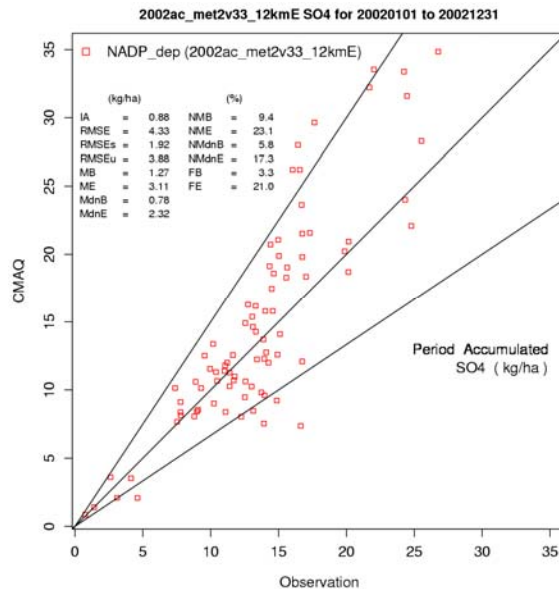
Figure 2-47. 12-km EUS annual sulfate wet deposition, each data point represents an annual average paired observation and CMAQ prediction at a particular NADP site. Solid lines indicate the factor of 2 around the 1:1 line shown between them.
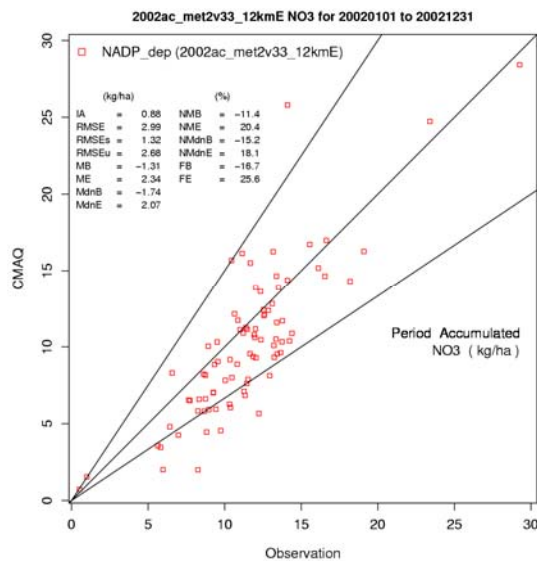
Figure 2-48. 12-km EUS annual nitrate wet deposition, each data point represents an annual average paired observation and CMAQ prediction at a particular NADP site. Solid lines indicate the factor of 2 around the 1:1 line shown between them.

2.8.4. Computing Atmospheric Deposition to Specific Locations

Inputs of new N, i.e., non-recycled, exogenous N mostly anthropogenic in origin, are often key factors controlling primary productivity in N-sensitive estuarine and coastal waters (Paerl et al., 2000). Increasing trends in urbanization, agricultural intensity, and industrial expansion have led to increases in N deposited from the atmosphere on the order of a factor of 10 in the previous 100 years (Swackhamer et al., 2004). Direct loadings of atmospheric N to ocean and gulf waters along the northeast and southeast U.S. are now roughly equal to or exceed the load of new N from riverine inputs (Duce et al., 1991) at 11, 5.6, and 5.6 kg N/ha for the northeast Atlantic coast of the U.S., the southeast Atlantic coast of the U.S., and the U.S. eastern Gulf of Mexico, respectively (Paerl, 2002).

This N deposition takes different forms physically and chemically. Physically, deposition can be direct, with the loads resulting from air pollutants depositing directly to the surface of a body of water, usually a large body of water like an estuary or lake. In addition, there is indirect deposition component derived from deposition to the rest of the watershed, both land and water, of which some fraction is transported through runoff, rivers, streams, and groundwater to the waterbody of concern.
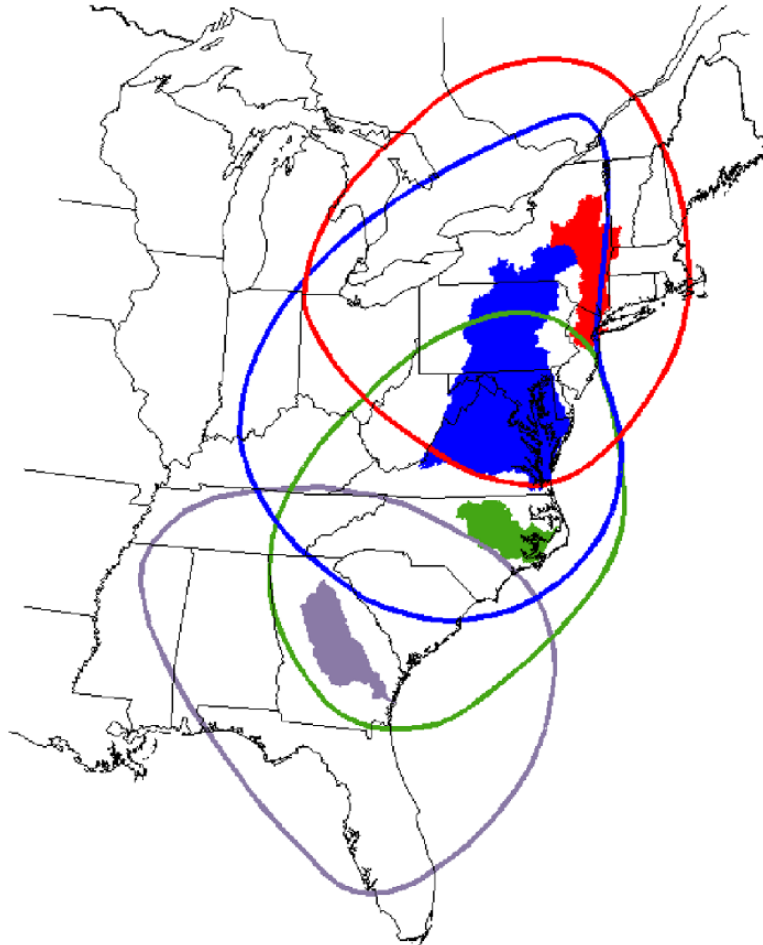
Airshed extents developed and used courtesy of R. Dennis, U.S. EPA/ORD/NERL/Atmospheric Modeling Division.

Figure 2-49.   Principal airsheds and watersheds NO$_X$ for these estuaries: Hudson/Raritan Bay; Chesapeake Bay; Pamlico Sound; and Altamaha Sound.

Direct and indirect depositions to watersheds depend on air pollutant concentrations in the airshed above the watershed. The shape and extent of the airshed is quite different from that of the watershed. In a watershed, everything that falls in its area, by definition, flows into a single body of water. An airshed, by contrast, is a theoretical concept that defines the area containing the emissions contributing a given level, often 75%, to the deposition in a particular watershed or to a given waterbody. Hence, airsheds are modeled domains containing the sources estimated to contribute a given level of deposition from each pollutant of concern. Four U.S. East Coast watersheds and their corresponding NO_X airsheds are shown in Figure 2-49.

Table 2-10. Atmospheric N loads relative to total N loads in selected great waters.*

Waterbody	Total N Load (million kg/yr)	Atmospheric N Load (million kg/yr)	Percent Load from the Atmosphere
Albemarle-Pamlico Sounds	23	9	38
Chesapeake Bay	170	36	21
Delaware Bay	54	8	15
Long Island Sound	60	12	20
Narragansett Bay	5	0.6	12
New York Bight	164	62	38
BASED ON ADN LOADS FROM THE WATERSHED ONLY (EXCLUDING DIRECT N DEPOSITION TO THE BAY SURFACE):			
Waquoit Bay, MA	0.022	0.0065	29
BASED ON ADN DIRECTLY TO THE WATERBODY (EXCLUDING ADN LOADS FROM THE WATERSHED):			
Delaware Inland Bays	1.3	0.28	21
Flanders Bay, NY	0.36	0.027	7
Guadalupe Estuary, TX	4.2–15.9	0.31	2–8
Massachusetts Bays	22–30	1.6–6	5–27
Narragansett Bay	9	0.4	4
Newport River Coastal Waters, NC	0.27–0.85	0.095–0.68	>35
Potomac River, MD	35.5	1.9	5
Sarasota Bay, FL	0.6	0.16	26
Tampa Bay, FL	3.8	1.1	28

ADN = atmospheric deposition of N
Source: U.S. EPA, 2000d

N inputs have been studied in several East and Gulf Coast estuaries owing to eutrophication concerns there. N from atmospheric deposition in these locations is estimated to be 10 to 40% of the total input of N to many of these estuaries, and could be higher for some. Estimates of total N loadings to estuaries or to other large-scale elements in the landscape are then computed using measurements of wet and dry N deposition where these are available and interpolated with or without a set of air quality model predictions such as the Extended Regional Acid Deposition Model (Ext-RADM) (Dennis et al., 2001;

Mathur and Dennis, 2003). Ext-RADM has been shown to capture spatial and seasonal variations in N deposition; to predict the constituent deposition species correctly; and to simulate the chemistry and physics relating reduced and oxidized forms of N with high validity.

Extensive evaluation by Mathur and Dennis of the performance of Ext-RADM showed that model-predicted ambient levels, gas-to-particle partitioning ratios, and deposition totals were in good agreement with available measurements, having R^2 for both annual and seasonal totals in the range of 0.4 to 0.7 for most species. Ext-RADM correctly predicted that most particles in the eastern U.S. are fully neutralized, further demonstrating that most modeled chemistry is correct as judged against measurements. Experiments with Ext-RADM to characterize atmospheric conditions over the eastern U.S. in the period at the end of the 1980s and early 1990s showed that the model predicted that reduced N species were contributed $47 \pm 8\%$ of total N wet deposition, in excellent agreement with the number inferred from measurements, $43 \pm 9\%$.

Table 2-10 lists several waterbodies for which atmospheric N inputs have been computed and ratioed to total N loads. The contribution from the atmosphere ranges from a low of 2–8% for the Guadalupe Estuary in South Texas to highs of ~38% in the New York Bight and the Albemarle-Pamlico Sound in North Carolina.

The North Carolina case is a particularly rich example of computing defined airsheds and characterizing the contributions from oxidized and reduced forms of N to underlying water bodies; see the summary reported by Dennis and Mathur (2001). The Albemarle-Pamlico principal N airsheds were computed to be 665,600 km^2 for oxidized N, and 406,400 km^2 for reduced N; these are factors of 25 and 15, respectively, larger than the watershed drainage area. NO emissions from within the oxidized N principal airshed was estimated to explain 63% of all oxidized N deposition to the Albemarle-Pamlico system, very similar to the total of 60% of all reduced N deposition accounted for by NH_3 emissions in the reduced N principal airshed. The regional component to these computed N deposition totals varied with the form of N such that local NH_3 emissions inside North Carolina were estimated to account for 45% (hence, 55% left from the regional component) of the total reduced N deposition, while local NO and NO_2 emissions accounted for only 20% of the oxidized N deposition total (hence, leaving a regional component of 80%).

Chemically, N deposited from the atmosphere directly or indirectly can be present as an oxide or in reduced form as NH_3 and NH_4^+ or as dissolved or particulate organic N; see the listing in Table 2-11 for a division of these and an approximate ranking of source strengths. NO and NO_2, chiefly from fossil fuel combustion, dominate total N pollution in the U.S. at ~50 to 75% of the total; see the descriptions of this chemistry in Section 2.6.2 and of sources in Section 2.2. above.

CAFOs and other intensified agricultural production methods have resulted in greatly increased volumes of animal wastes, of which 30 to 70% may be emitted as NH_3 (Whitall and Paerl, 2001). The increase in reduced N deposition in the U.S. measured as increased NH_4^+ deposition correlates well with the local and regional increases in this agricultural intensity (Whitall and Paerl, 2001). Moreover, the increases in NH_4^+ deposition in the U.S. track the effects in Europe where animal operations have dominated agricultural production for much of the previous 100 years and where NH_4^+ is the dominant form of N deposited from the atmosphere (Holland et al., 1999). Tables 2-12 and 2-13 list several important watersheds and their respective oxidized (Table 2-12) and reduced (Table 2-13) airsheds. Airsheds for oxidized N tend to be larger than those for reduced N owing to differences in the transport and deposition of NO_X and NH_X described above in Section 2.6.

Table 2-11.   Natural and anthropogenic sources of atmospheric N compounds.

Chemical Form	Sources (in approximate order of importance)
Reduced N NH_3NH_4	Agricultural
	Livestock waste (volatilized NH_3)
	Chemical fertilizers (volatilized NH_3)
	Biomass burning
	Dust from deforestation and land clearing
	Urban and Rural (non-agricultural)
	Wastewater treatment (volatilized NH_3)
	Fossil fuel combustion (from automobile catalytic converters)
	Natural
	Biomass burning (forest and grass fire)
	Decomposition of organic matter
	Dust and aerosols
	Volcanism
Oxidized Nitrogen NO, NO_2, NO_3^-	Urban and Rural (non-agricultural)
	Fossil fuel combustion
	Mobile and stationary engines
	Powerplants and industrial
	Natural
	Biomass burning
	Lightning
	Photolysis of N_2O (air, land, water)
	Dust and aerosols generated by storms
	Microbially mediated volatilization
Organic Nitrogen (Dissolved and Particulate)	Agricultural
	Dust and volatilization of wastes*
	Urban and Rural (non-agricultural)
	Dust or aerosols*
	Natural
	Atmospheric photochemical and lighting
	Biological production in oceans*

* = possible, but little known about sources (the major chemical forms of atmospheric N compounds are the reduced, oxidized, and organic forms)
Source: Swackhamer et al. (2004). Reprinted with permission.

Considerable uncertainty attaches to estimates of the third form of atmospherically derived N, organic N, in part because convenient methods for measurement and analysis are not widely available; see Table 2-11. Intensive studies at individual sites have shown, however, that for the North Carolina coast, for example, 30% of rain water N and deposition consisted of organic N, 20–30% of which was then available to primary producers on time scales of hours to days (Peierls and Paerl, 1997).

Table 2-12.   Characteristics of oxidized-nitrogen airsheds.

Watershed	Size (km²)	Size Factor over Watershed Area	% Oxidized-N Deposition Explained	Airshed NOₓ Emissions as % of Eastern North America	Efficiency of Deposition: % Deposition / % Emission
Casco Bay	624,000	244	47	10	4.7
Great Bay	547,000	214	60	13	4.6
Narragansett Bay	595,200	138	73	18	4.1
Long Island Sound	905,600	22	70	23	3.0
Hudson/Raritan Bay	912,000	22	62	25	2.5
Barnegat Bay	505,600	361	67	16	4.2
Delaware Bay	729,600	22	75	26	2.9
Delaware Inland Bays	326,400	584	52	12	4.3
Chesapeake Bay	1,081,600	6.5	76	34	2.2
Pamlico Sound	665,600	25	63	18	3.5
Winyah Bay	886,400	19	69	24	2.9
Charleston Harbor	806,400	20	56	18	3.1
St. Helena Sound	588,800	48	59	11	5.4
Altamaha	678,400	18	68	13	5.2
Tampa Bay	256,000	45	76	5	15.2
Apalachee Bay	441,600	31	50	9	5.6
Apalachicola Bay	812,800	16	69	17	4.1
Mobile Bay	992,000	8.7	68	17	4.0
Lake Pontchartrain	659,200	17	63	11	5.7
Barataria-Terrebonne	409,600	55	63	8	7.9

Source: http://www.epa.gov/AMD/Multimedia/characteristicstable.html. Table generated by and used courtesy of R. Dennis, U.S. EPA/ORD/NERL/Atmospheric Modeling Division

Table 2-13.   Characteristics of principal airsheds for reduced-N (Red-N) deposition.

Watershed	Principal Red-N Airshed Area (km²)	Red-N Area as % of Ox-N Area	% Red-N Deposition Explained by Airshed Emissions	Airshed NH₃ Emission as % of Eastern North American Emissions
Chesapeake Bay	668,000	64%	55%	11%
Pamlico Sound	406,000	61%	60%	6.8%
Apalachee Bay	310,000	70%	45–50% est.	4.3%

Source: http://www.epa.gov/AMD/Multimedia/reducedTable.html. Table generated by and used courtesy of R. Dennis, U.S. EPA/ORD/NERL/Atmospheric Modeling Division

Although deposition of atmospheric N to most locations is dominated at present by oxidized N produced from fuel combustion, reduced N also contributes, perhaps becoming the dominate contributor in areas near source regions. However, not all of the reduced N in the form of NH_3 is deposited locally near to the source, as is often assumed.

AQMs like CMAQ can be instrumented to provide analytical output on modeled processes including emissions, chemical production, and horizontal and vertical transport; see Gipson, 1999. This process analysis output makes possible experiments with modeled emissions and transport to explore the fraction of species like total NH_X deposited locally and the size of the remaining fraction available for transport to locations remote from the high concentration sources of NH_3. An example of this work for areas on the east coast of the U.S. near areas of extremely high NH_3 emissions in North Carolina was performed by Dennis and Mathur in the U.S. EPA Atmospheric Modeling Division using CMAQ version 4.5 with 12 km grid spacings. This example is provided here to illustrate the importance of transport to calculated local and remote deposition totals.

CMAQ includes all chemical and physical processes now known to be relevant for building an analysis of the vertical and horizontal budget of NH_3 for either surface cells in the model's first layer, nominally 38 m deep, or the total column of air above the surface, generally extending through the mixed layer into the free troposphere. The diagram in Figure 2-50 illustrates these processes and the surface cell and total column as present in the model.
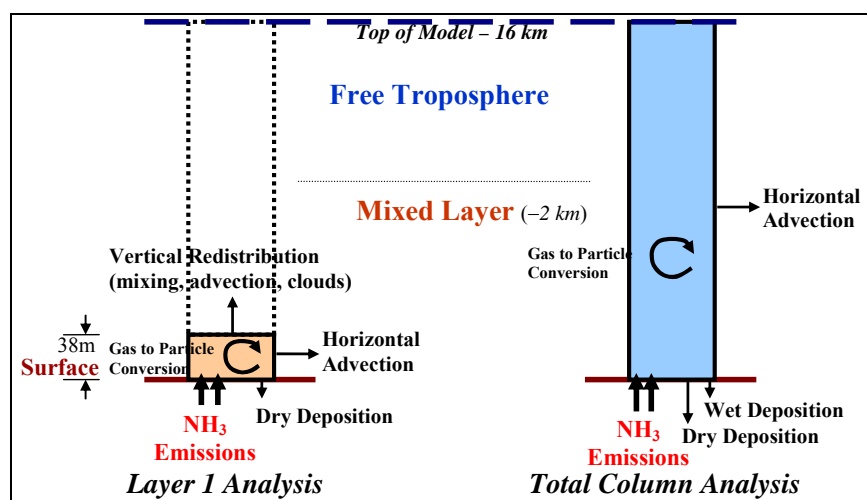
Figure 2-50.   Typical surface layer cell and total column structure and processes represented in CMAQ.

Importantly, CMAQ captures the chief spatial patterns and magnitudes of air concentrations and wet deposition relevant to computing these budgets, as shown in Figures 2-51 for concentrations and 2-52 for deposition.
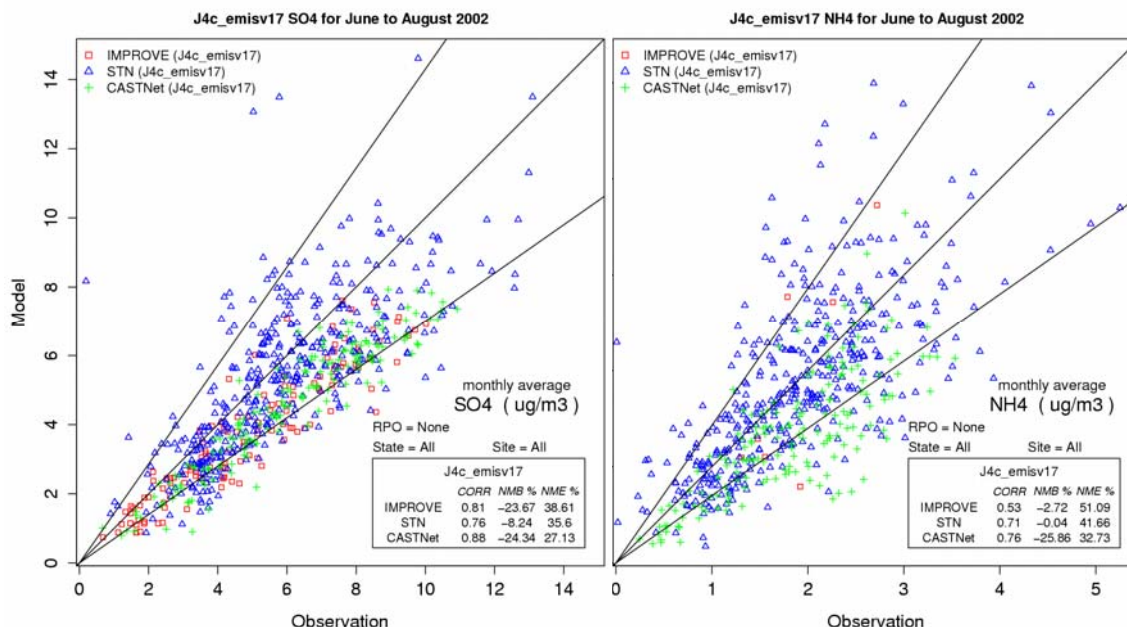
Figure 2-51. **CMAQ vs. measured air concentrations from east-coast sites in the IMPROVE, CSN (labeled STN), and CASTNet networks in the summer of 2002: (left) sulfate and (right) ammonium. Solid lines indicate the factor of 2 around the 1:1 line shown between them.**

More specifically, CMAQ's predictions of NH_3 and SO_4^{2-} for both high and low concentration sites are well-within the range of measurements there; see Figure 2-53.

Deposition velocities are difficult to estimate for reasons described in Sections 2.8.2 and 2.8.3 above Recent work in the U.S. EPA Atmospheric Modeling Division with CMAQ showed that the original V_d for NH_3 was very likely too high and should be nearer to the values for SO_2 deposition, or even lower over some land use surface types. A sensitivity study with the model was performed to test the effects of changing NH_3 V_d on the fraction of NH_3 available for transport away from cells with high emissions concentrations. Comparisons were made for the surface cells and total column NH_3 concentrations similar to the analysis represented in Figure 2-54.

In the highest emissions cells during June 2002, the surface NH_X budget was dominated by turbulent transport or vertical mixing moving a majority of the surface NH_3 emissions up and away from the surface into the mixed layer. Figure 2-54 depicts the NH_X budget under the base case (Base V_d) and the sensitivity case (SO_2 V_d) for which the NH_3 V_d was set equal to the SO_2 V_d. Lower NH_3 V_d decreased NH_X deposition to the surface from 15 to 8 %, leaving more NH_X for transport horizontally, 22% up from 20% in the base case, and vertically, 69% up from 64% in the base case.
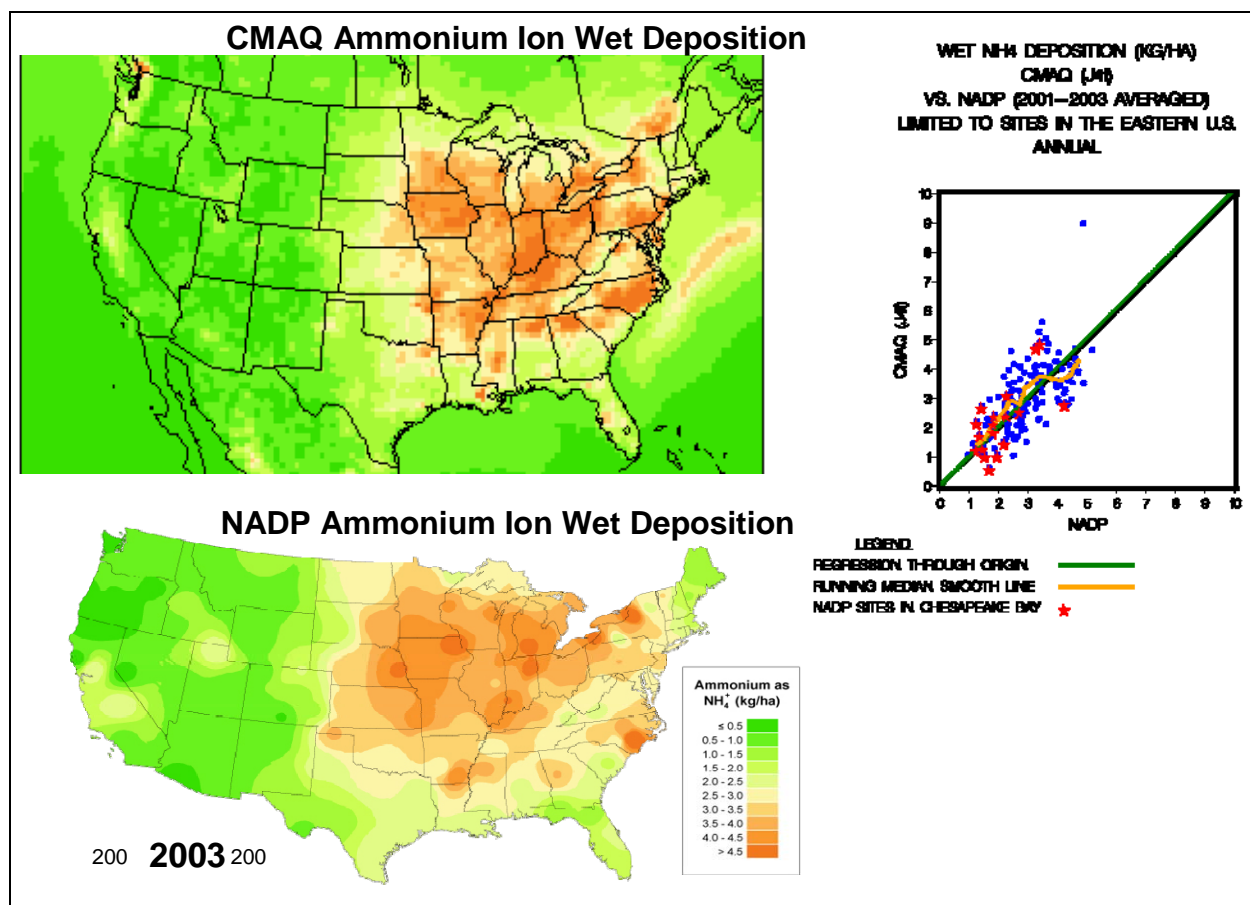
Figure 2-52. Comparison of CMAQ-predicted and NADP-measured NH$_4^+$ wet deposition. (top left) CMAQ prediction; (bottom left) NADP-measurements; (right) regression and smoothed median line through CMAQ predictions and NADP measurements with sites in the Chesapeake Bay watershed highlighted.

Typically, ~67% of surface emissions were moved aloft where most was advected away from the high emissions cell, with a small fraction converted to pNH$_4$ and an even smaller fraction wet-deposited to the surface. The total column analyses for NH$_3$ and NH$_X$ are shown in Figure 2-55.

Local total deposition (wet + dry) is a significant but not dominant loss pathway for surface NH$_3$ emissions. In these simulations, CMAQ deposited ~25% of the NH$_3$ emissions from the single high concentration cell in Sampson County, NC, back into that cell. By far, the largest contribution to the local deposition total was dry deposition: dry-to-wet deposition ratios for the Sampson County high emissions cell and surrounding surface cells ranged from 2 to 10.

Deposition to cells farther away from the high concentration, immediately surrounding cells was significantly affected by the change in NH$_3$ V$_d$ tested in this case. Figure 2-56 depicts the range of influence of the high concentration cell, where that range is defined to be the distance by which 50% of the emissions attributable to that cell have deposited. The range of influence of the high concentration Sampson County cell was extended in the V$_d$ sensitivity tested here from ~180 km in the base case to ~400 km in the case using the lower, more realistic V$_d$ for NH$_3$. The areal extent of this difference in range of influence is mapped in Figure 2-57.
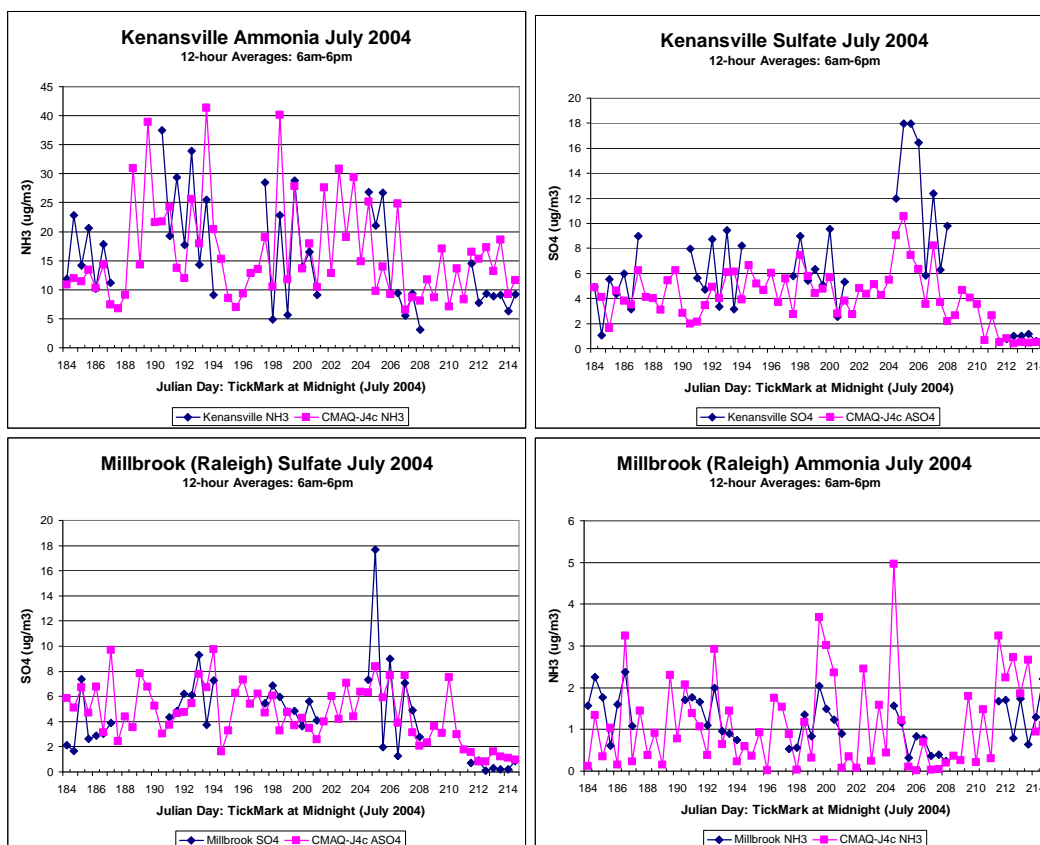
Figure 2-53. CMAQ-predicted (red symbols and lines) and 12-h measured (blue symbols and lines) NH₃ and SO₄²⁻ surface concentrations at high and low concentration cells in North Carolina in July 2004. (top left) High concentration NH₃ in Kenansville; (top right) high concentration SO₄²⁻ in Kenansville; (bottom left) low concentration NH₃ in Raleigh; (bottom right) low concentration SO₄²⁻ in Raleigh.
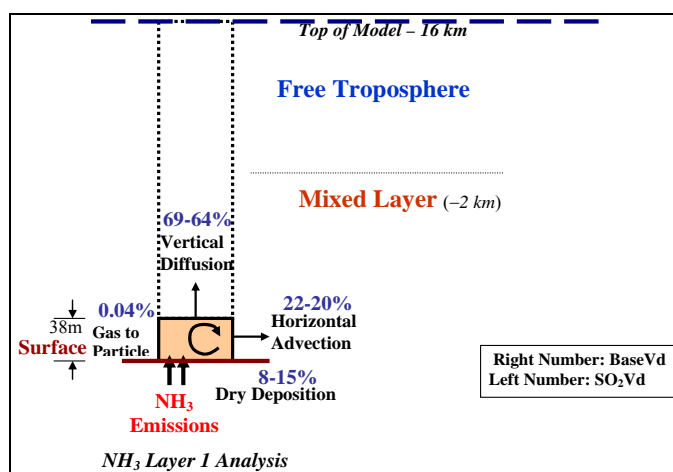
Figure 2-54. Surface cell (layer 1) analysis of the sensitivity of NH$_X$ deposition and transport to the change in NH₃ V$_d$ in CMAQ for June 2002.
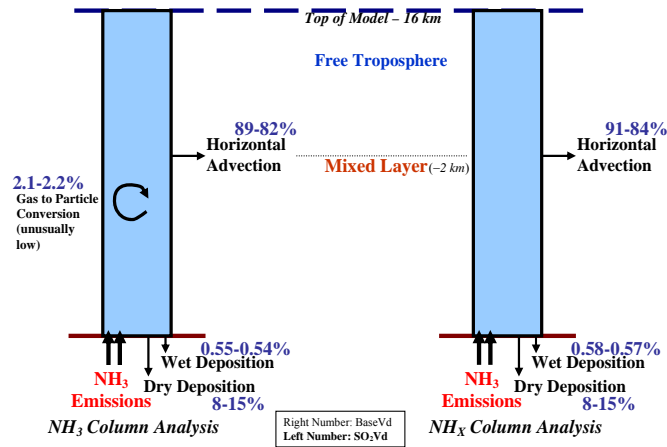
Figure 2-55. Total column analysis for NH₃ (left) and NH_X (right) showing modeled NH₃ emissions, transformation, and transport throughout the mixed layer and up to the free troposphere.
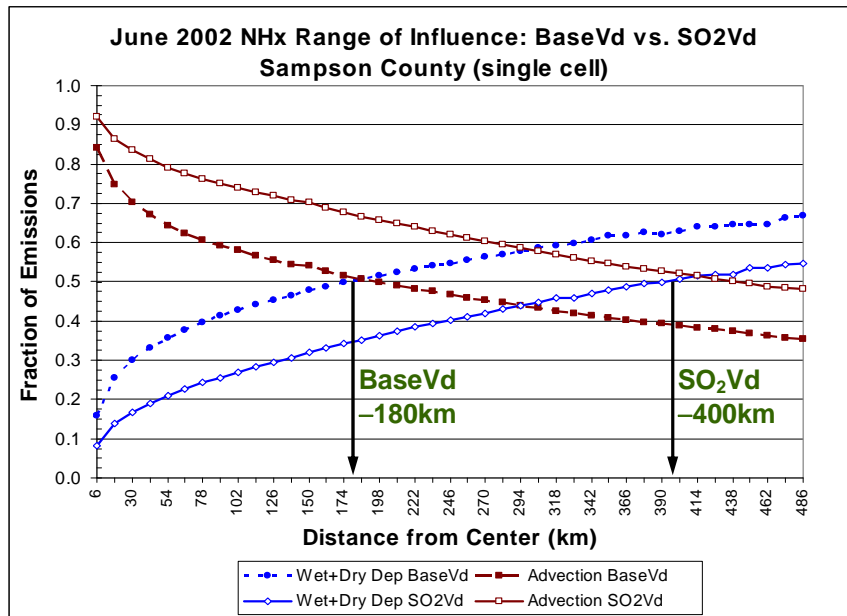
Figure 2-56. Range of influence (where 50% of emitted NH₃ deposits) from the high concentration Sampson County, NC, cell in the June 2002 CMAQ simulation of V_d sensitivities. Base case and sensitivity case total deposition (blue symbols and lines); base case and sensitivity case advection totals (red symbols and lines).
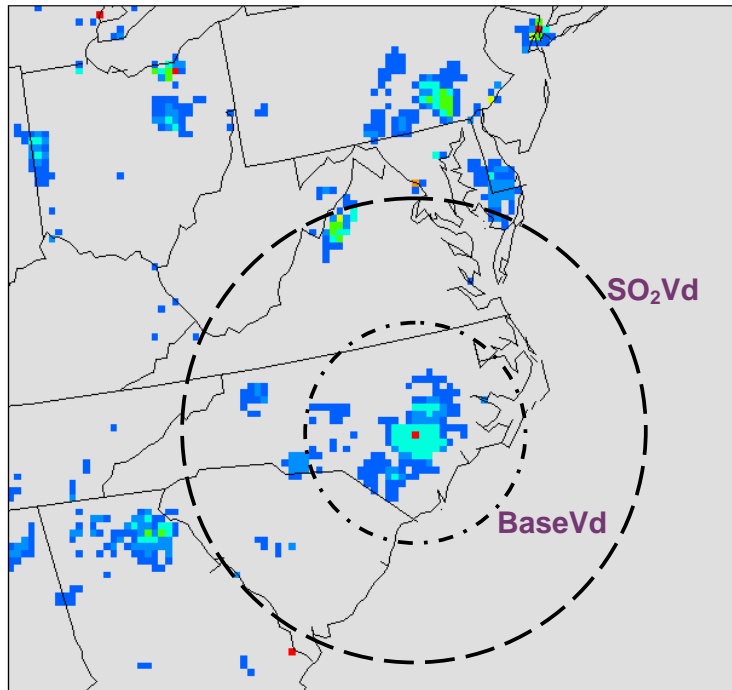
Figure 2-57. Areal extent of the change in NH_X range of influence as predicted by CMAQ for the Sampson County high concentration cell (center of range circles) in June 2002 using the base case and sensitivity case V_d.

2.8.5. Policy Relevant Background Concentrations of NO_X and SO_X

Background concentrations of NO_X and SO_X used for purposes of informing decisions about NAAQS are referred to as PRB concentrations. PRB concentrations are those concentrations that would occur in the U.S. in the absence of anthropogenic emissions in continental North America, defined here as the U.S., Canada, and Mexico. PRB concentrations include contributions from natural sources everywhere in the world and from anthropogenic sources outside those three countries. Biogenic emissions from agricultural activities are not considered in the formation of PRB concentrations.

Background levels so defined facilitate separation of pollution levels that can be controlled by U.S. regulations (or through international agreements with neighboring countries) from levels that are generally uncontrollable by the U.S. EPA assesses risks to human health and environmental effects from NO_2 and SO_2 levels in excess of these PRB concentrations.

The MOZART-2 global model of tropospheric chemistry (Horowitz et al., 2003) is used to diagnose the PRB contribution to NO_X and SO_X levels and to total (wet + dry) deposition. The model setup for the present-day simulation has been published in a series of papers from a recent model intercomparison (Dentener et al., 2006a, b; Shindell et al., 2006; Stevenson et al., 2006; van Noije et al., 2006).
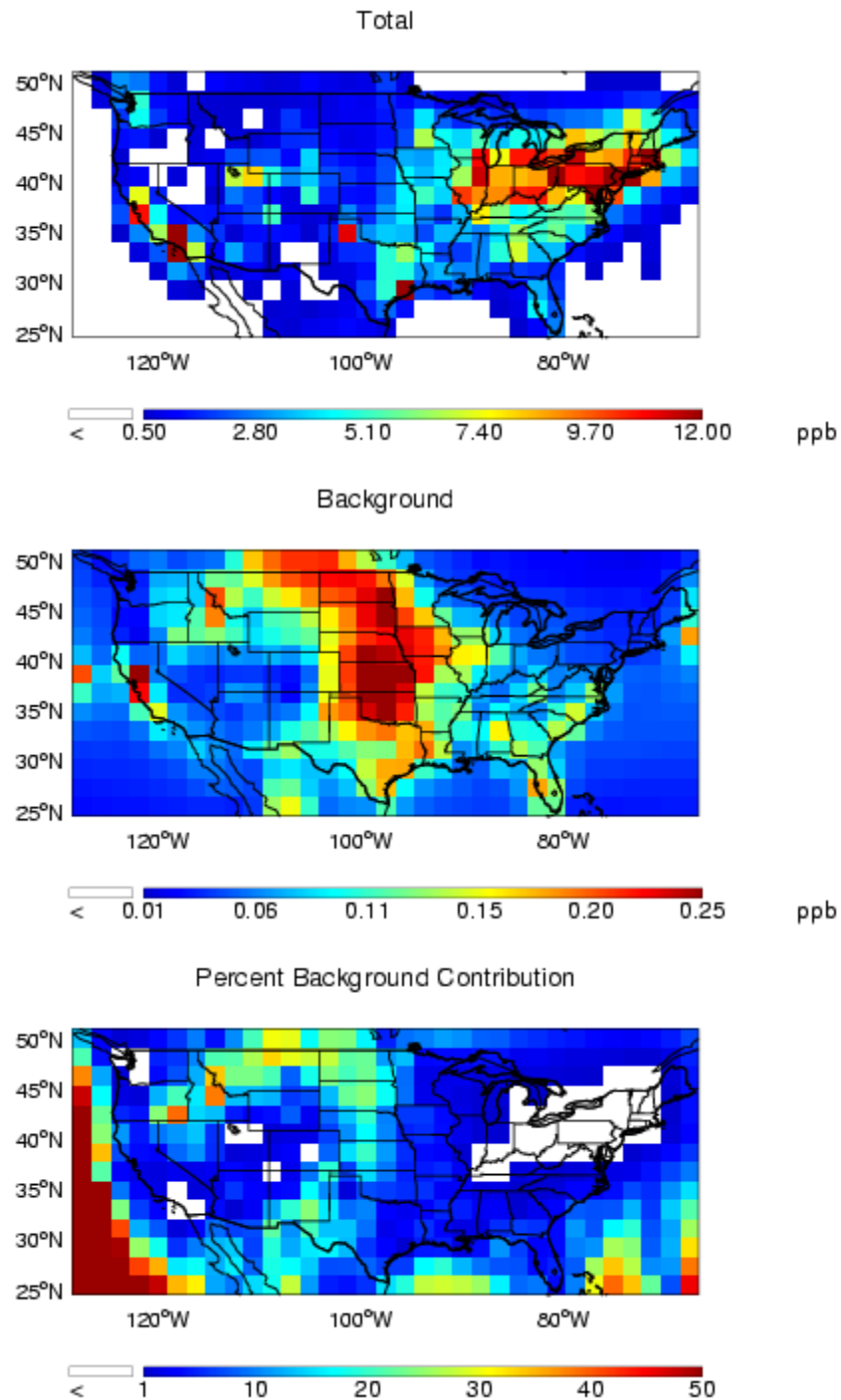
Figure 2-58. Annual mean concentrations of NO$_2$ (ppb) in surface air over the U.S. in the present-day (upper panel) and policy relevant background (middle panel) MOZART-2 simulations. The bottom panel shows the percentage contribution of the background to the present-day concentrations.
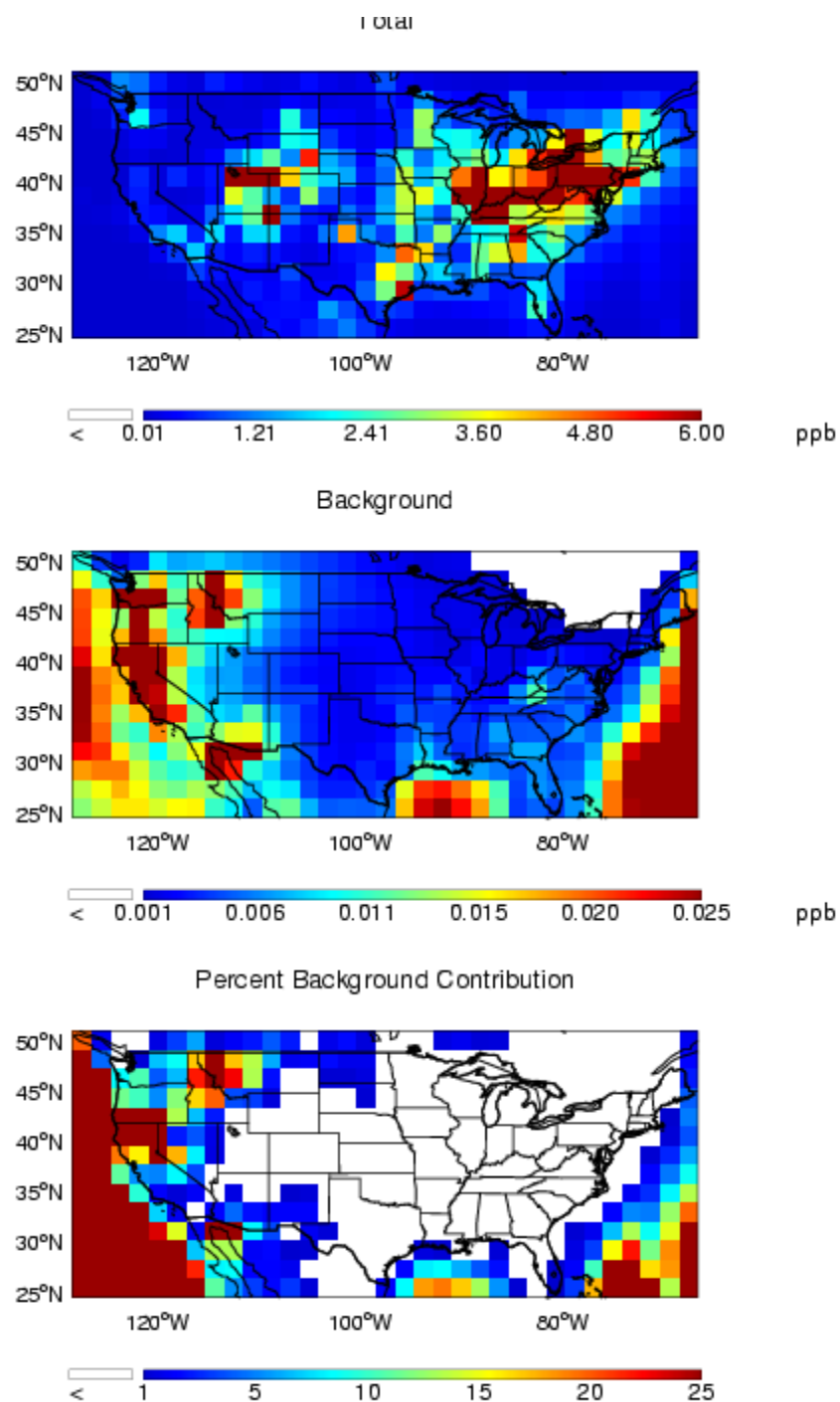
Figure 2-59. Annual mean concentrations of SO_2 (ppb) in surface air over the U.S. in the present-day (upper panel) and policy relevant background (middle panel) MOZART-2 simulations. The bottom panel shows the percentage contribution of the background to the present-day concentrations.

First, the role of PRB in contributing to NO_2 and SO_2 concentrations in surface air is considered. Figure 2-58 shows the annual mean predicted NO_2 concentration in surface air in the base case simulation (top) and from the PRB simulation (middle panel), along with the percentage contribution of the predicted background to the total base case NO_2 concentrations (bottom). Maximum concentrations in the base case simulation occurred along the Ohio River Valley and in the Los Angeles basin just as they do in reported measurements; see Section 2.2 above. While present-day concentrations are often >5 ppb, predicted PRB was <300 ppt over most of the CONUS and <100 ppt in the eastern U.S. The distribution of PRB largely reflects the distribution of soil NO_2 emissions, with some local enhancements due to biomass burning such as is seen in western Montana. In the northeastern U.S., where present-day NO_2 concentrations are highest, PRB was predicted to contribute <1% to the total concentrations.

Background SO_2 concentrations computed with MOZART-2 are orders of magnitude smaller than measured ambient concentrations, <10 ppt over much of the CONUS as shown in the middle panel of Figure 2-59. Maximum PRB SO_2 concentrations are 30 ppt. In the Northwest where there are geothermal sources of SO_2, the contribution of PRB to total SO_2 is 70 to 80%. However, excepting this, PRB contributes <1% to present-day SO_2 concentrations in surface air as shown in the bottom panel.

The spatial pattern of NO_Y (defined in the model as $HNO_3 + NH_4NO_3 + NO_X + HO_2NO_2 + RONO_2$) in wet and dry deposition is shown in Figure 2-60. The upper panel of this figure shows that highest values are found in the eastern U.S. in and downwind of the Ohio River Valley. The pattern of N deposition in the PRB simulation shown in the Figure 2-60 middle panel, however, shows maximum deposition centered over Texas and in the Gulf Coast region, reflecting a combination of N emissions from lightning in the Gulf region, biomass burning in the Southeast, and microbial activity in soils with maxima in central Texas and Oklahoma. The bottom panel of Figure 2-60 shows that the PRB contribution to N deposition is <20% over the eastern U.S., and typically <50% in the western U.S. where NO_Y deposition is already lower.

Present-day deposition of SO_X (SO_2 and pSO_4 is largest in the Ohio River Valley, due to coal-burning power plants in that region, while background deposition is typically at least an order of magnitude smaller; see Figure 2-61. Over the eastern U.S., the predicted background contribution to SO_X deposition was <10%, and even smaller, <1%, where present-day SO_X deposition was highest. The predicted contribution of PRB to S deposition was highest in the western U.S. at >20% because of the geothermal sources of SO_2 and oxidation of DMS at the water surface of the eastern Pacific.

Figure 2-62 shows results from MOZART-2 discussed above as compared with those from another tropospheric chemistry model, GEOS-Chem (Bey et al., 2001), which was previously used to diagnose PRB O_3 concentrations (Fiore et al., 2003). In both models, the predicted surface PRB NO_X concentrations tended to mirror the distribution of soil NO emissions, which were highest in the Midwest. The NO emissions in GEOS-Chem were greater than those in MOZART-2 by nearly a factor of 2. This is largely explained by the different assumptions regarding the contribution to soil NO emissions through fertilizer since GEOS-Chem total soil NO emissions were actually higher than MOZART-2 at 0.07 versus 0.11 Tg N over the U.S. in July. Even with the larger PRB soil NO emissions, however, surface NO_X concentrations in GEOS-Chem were typically <500 ppt.

It is also instructive to consider measurements of SO_2 at relatively remote monitoring sites, i.e., ones located in sparsely populated areas not subject to obvious local sources of pollution. Berresheim et al. (1993) used a type of atmospheric pressure ionization mass spectrometer (APIMS) at Cheeka Peak, WA (48°30'N, 124°62'W, 480 m asl), in April 1991 during a field study for DMS oxidation products: SO_2 concentrations there ranged from 20 to 40 ppt. Thornton et al. (2002a) have also used an APIMS with an isotopically labeled internal standard to determine background SO_2 levels and found 25 to 40 ppt in northwestern Nebraska in October 1999 at 150 m above ground using the NCAR C-130. These values are comparable to remote central south Pacific convective boundary layer SO_2 (Thornton, 1999).

In summary, the PRB contribution to NO_X and SO_X concentrations and deposition over the CONUS is very small, except for SO_2 in areas with volcanic activity.
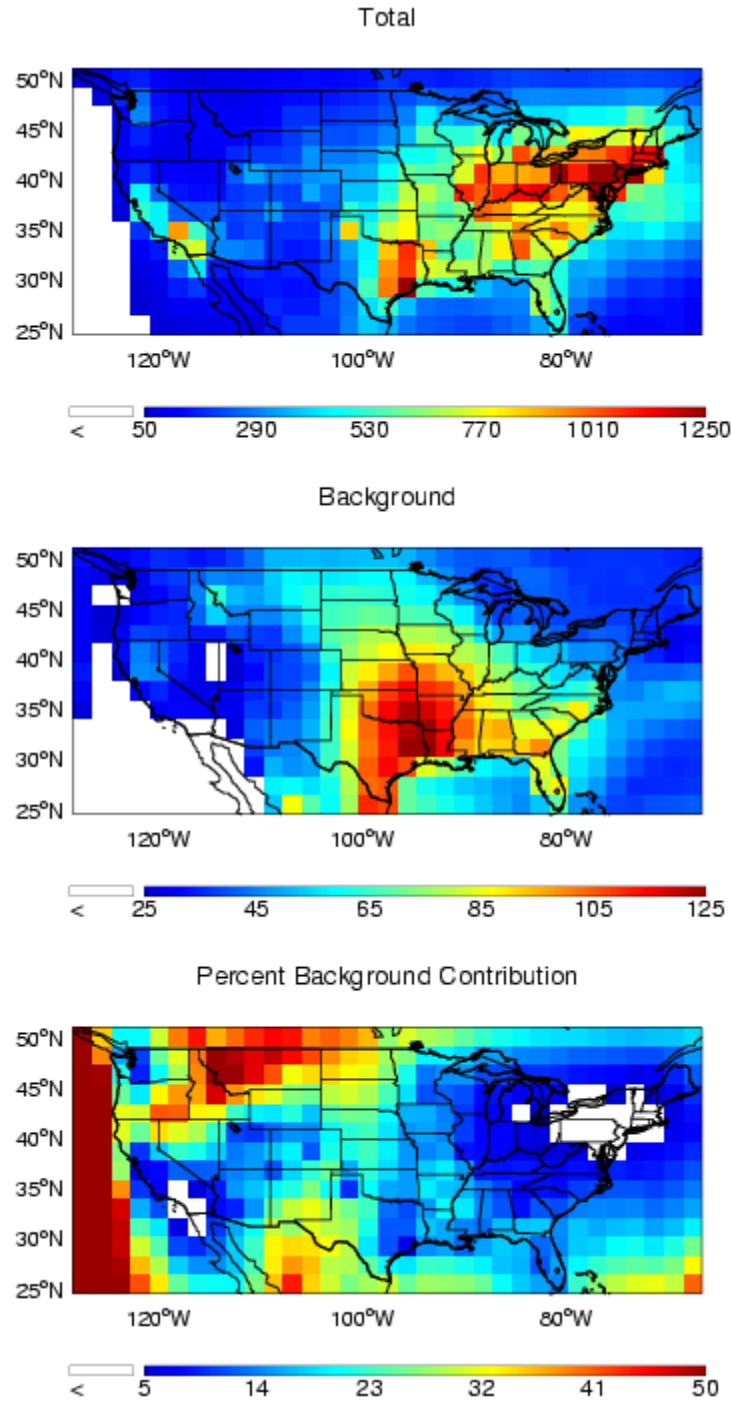
Figure 2-60. Annual mean concentrations of wet and dry deposition of $NHNO_3$, NH_4NO_3, NO_X, HO_2NO_2, and organic nitrates (mg N/m^2/yr) in surface air over the U.S. in the present-day (upper panel) and policy relevant background (middle panel) MOZART-2 simulations. The bottom panel shows the percentage contribution of the background to the present-day concentrations.
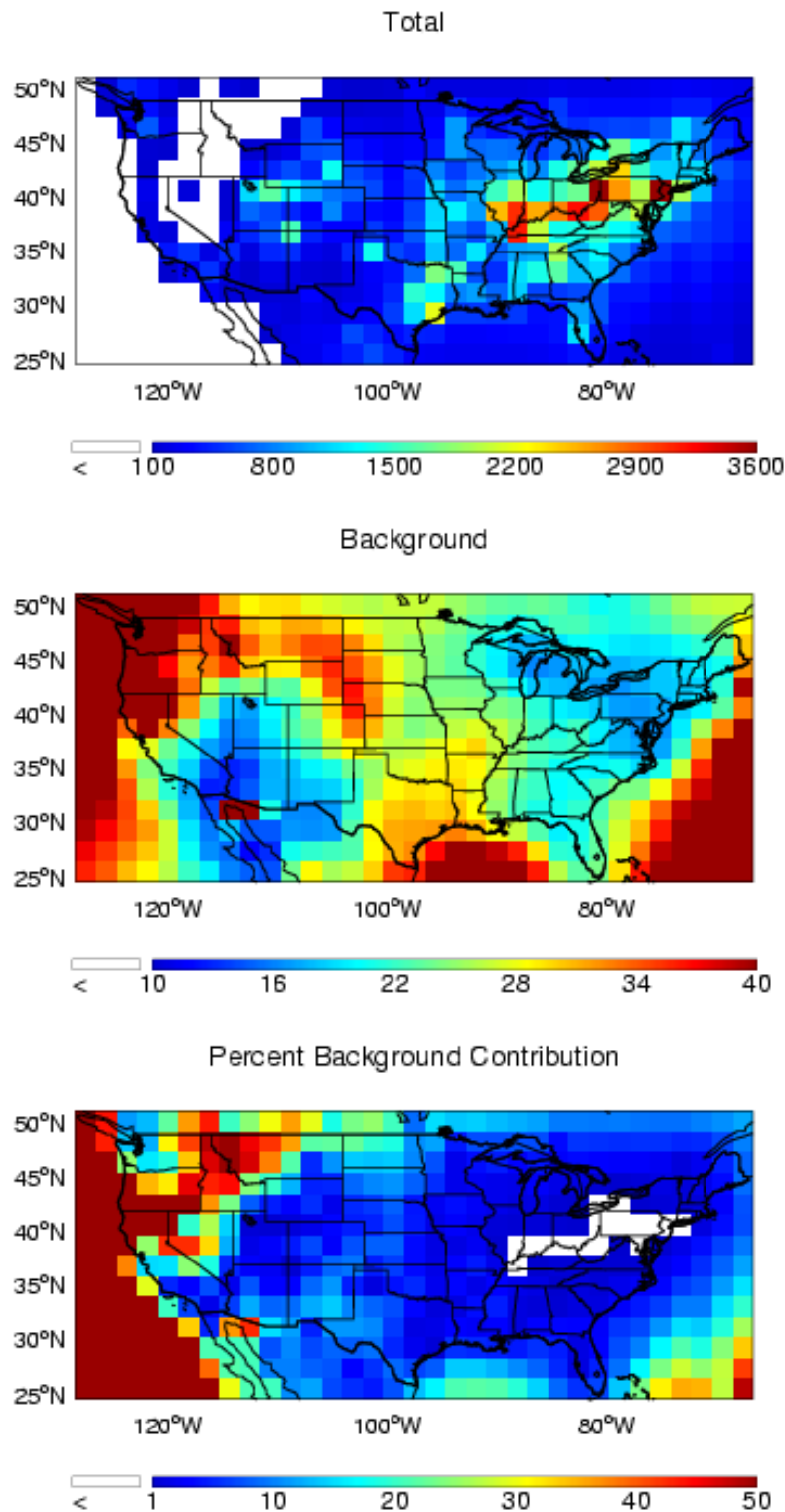
Figure 2-61. Annual mean concentrations of SO_X deposition (SO_2 + pSO_4) (mg S/m²/yr) in surface air over the U.S. in the present-day (upper panel) and policy relevant background (middle panel) MOZART-2 simulations. The bottom panel shows the percentage contribution of the background to the present-day concentrations.
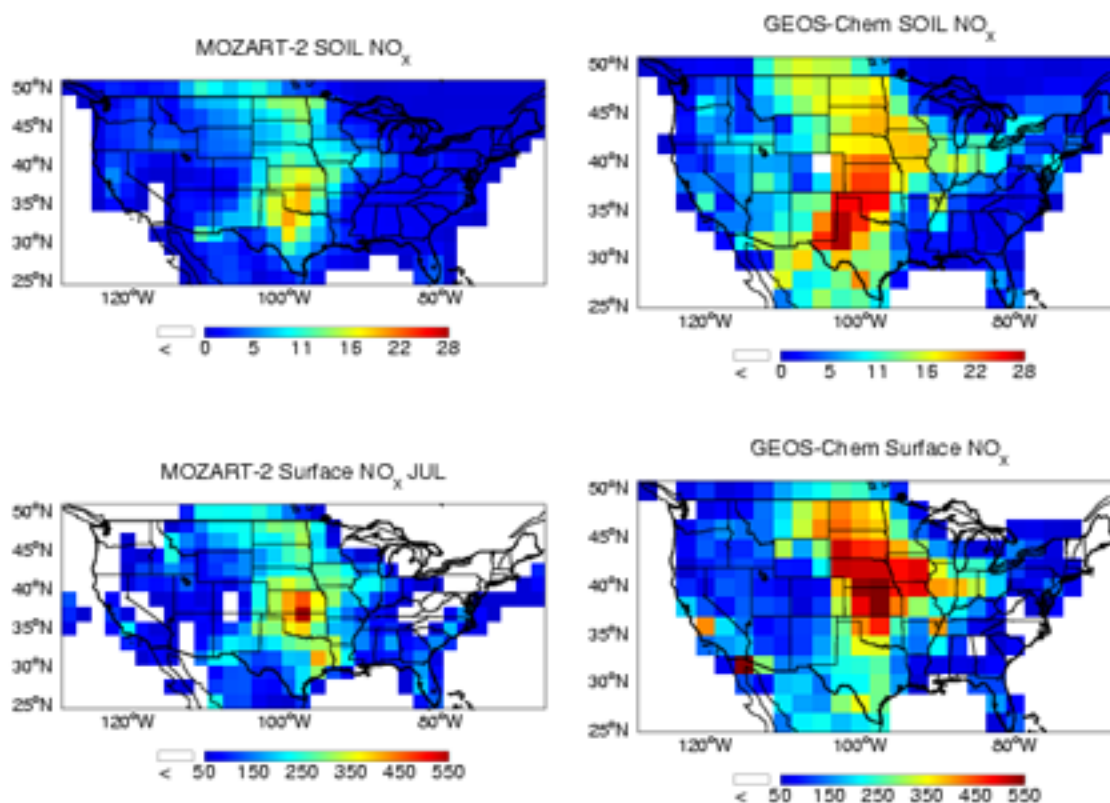
Figure 2-62. July mean soil NO emissions (upper panels; 1×10^9 molecules/cm^2/s) and surface PRB NO$_X$ concentrations (lower panels; ppt) over the U.S. from MOZART-2 (left) and GEOS-Chem (right) model simulations in which anthropogenic O$_3$ precursor emissions were set to zero in North America.

2.9. Ambient Monitoring and Reported Concentrations of Relevant Nitrogen and Sulfur Species

Observational systems supporting air quality and related assessments include routine regulatory networks, deposition networks, intensive field studies, remote sensing systems, sondes, aircraft campaigns, satellites, and focused fixed site special purpose networks. The focus in this section is on routinely operating North American air quality networks with limited coverage of European and international efforts relevant to North American assessments.

The scope of network coverage is broad and relatively shallow, reflecting intent to describe the observational foundation enabling integration of spatial scales, environmental media, and pollutant categories. In addition to fixed-site, surface-based air quality networks, systems providing total Earth column and vertical gradient information meteorological programs are included. Cursory descriptions of recent intensive field campaigns are included in this section to foster integration of multiple observation platforms and air quality modeling platforms.

2.9.1. Routine Air Monitoring Networks in North America

Routine ambient air concentration and deposition monitoring networks in North America provide more than 3000 fixed platforms measuring numerous species and chemical and physical properties. Many of these long-standing network systems were initialized after the 1970 CAA, subsequent CAAA, NAAQS reviews and National Academy of Sciences (NAS) recommendations resulting in periodic step enhancements to these routine networks. Examples include CASTNet and NADP addressing acidification; the Photochemical Assessment Monitoring Stations (PAMS) in response to persistent O_3 pollution and to monitor O_3 precursors including NO_X; and the $PM_{2.5}$ network. Table 2-14 lists the networks, sponsoring agencies, monitoring site densities, and their dates of operation, locations, and measurement parameters.

Table 2-14.   Major routine operating air monitoring networks.

Network	Lead Agency	# of Sites	Initiated	Measurement Parameters	Location of Information and/or Data
STATE / LOCAL / FEDERAL NETWORKS					
NCore—National Core Monitoring Network	U.S. EPA	75	2008	O_3, $NO/NO_2/NO_Y$, SO_2, CO, $PM_{2.5}$/ $PM_{10-2.5}$, $PM_{2.5}$ speciation, NH_3, HNO_3, surface meteorology	http://www.epa.gov/ttn/ amtic/monstratdoc.htm
SLAMS—State and Local Ambient Monitoring Stations	U.S. EPA	~3000	1978	O_3, NO_X/NO_2, SO_2, $PM_{2.5}/PM_{10}$, CO, Pb	http://www.epa.gov/ttn/airs/ airsaqs/aqsweb/aqswebhome.htm
STN—PM2.5 Speciation Trends Network	U.S. EPA	300	1999	$PM_{2.5}$, $PM_{2.5}$ speciation, major ions, metals	http://www.epa.gov/ttn/airs/ airsaqs/aqsweb/aqswebhome.html
PAMS—Photochemical Assessment Monitoring Network	U.S. EPA	75	1994	O_3, NO_X/NO_Y, CO, speciated VOCs, carbonyls, surface meteorology and upper air	http://www.epa.gov/ttn/airs/ airsaqs/aqsweb/aqswebhome.htm
IMPROVE—Interagency Monitoring of Protected Visual Environments	NPS	110 plus 67 proto-col sites	1988	$PM_{2.5}/PM_{10}$, major ions, metals, light extinction, scattering coefficient	http://vista.cira.colostate.edu/IMPROVE/
CASTNet—Clean Air Status and Trends Network	U.S. EPA	80+	1987	O_3, SO_2, major ions, calculated dry deposition, wet deposition, total deposition for S/N, surface meteorology	http://www.epa.gov/castnet/
GPMP—Gaseous Pollutant Monitoring Network	NPS	33	1987	O_3, $NO_X/NO/NO_2$, SO_2, CO, surface meteorology, (plus enhanced monitoring of CO, NO, NO_X, NO_Y, and SO_2 plus canister samples for VOC at three sites)	http://www2.nature.nps.gov/air/ Monitoring/network.cfm#data
POMS—Portable Ozone Monitoring Stations	NPS	14	2002	O_3, surface meteorology, with CASTNet-protocol filter pack (optional) SO_4^{2-}, NO_3, NH_4^+, HNO_3, SO_2	http://www2.nature.nps.gov/ air/studies/portO3.cfm
Passive Ozone Sampler Monitoring Program	NPS	43	1995	O_3 dose (weekly)	http://www2.nature.nps.gov/ air/Studies/Passives.cfm

Network	Lead Agency	# of Sites	Initiated	Measurement Parameters	Location of Information and/or Data
NADP/NTN—National Atmospheric Deposition Program / National Trends Network	USGS	200+	1978	Major ions from precipitation chemistry	http://nadp.sws.uiuc.edu/
NADP/MDN—National Atmospheric Deposition Program / Mercury Deposition Network	None	90+	1996	Mercury from precipitation chemistry	http://nadp.sws.uiuc.edu/mdn/
AIRMoN—National Atmospheric Deposition Program / Atmospheric Integrated Research Monitoring Network	NOAA	8	1984	Major ions from precipitation chemistry	http://nadp.sws.uiuc.edu/AIRMoN/
IADN—Integrated Atmospheric Deposition Network	U.S. EPA	20	1990	PAHs, PCBs, and organochlorine compounds are measured in air and precipitation samples	http://www.epa.gov/glnpo/monitoring/air
NAPS—National Air Pollution Surveillance Network	Canada	152+	1969	SO_2, CO, O_3, NO, NO_2, NO_X, VOCs, SVOCs, PM_{10}, $PM_{2.5}$, TSP, metals	http://www.etcentre.org/NAPS/
CAPMoN—Canadian Air and Precipitation Monitoring Network	Canada	29	2002	O_3, NO, NO_2, NO_Y mass, $PM_{2.5}$ speciation, major ions for particles and trace gases, precipitation chemistry for major ions	http://www.msc.ec.gc.ca/ cap mon/index_e.cfm
Mexican Metropolitan Air Quality Network	Mexico	93	???	O_3, NO_X, CO, SO_2, PM_{10}, TSP	See (Ceccotti and Messick, 1997) http://www.cec.org/pubs_docs/-publications/index.cfm?varlan=english

AIR TOXICS MONITORING NETWORKS

Network	Lead Agency	# of Sites	Initiated	Measurement Parameters	Location of Information and/or Data
NATTS—National Air Toxics Trends Station	U.S. EPA	23	2005	VOCs, Carbonyls, PM_{10} metals, Hg	http://www.epa.gov/ttn/airs/airsaqs/aqsweb/aqswebhome.htm
State/Local Air Toxics Monitoring	U.S. EPA	250+	1987	VOCs, Carbonyls, PM_{10} metals, Hg	http://www.epa.gov/ttn/airs/airsaqs/aqsweb/aqswebhome.htm
NDAMN—National Dioxin Air Monitoring Network	U.S. EPA	34	1998–2005	CDDs, CDFs, dioxin-like PCBs	http://cfpub2.epa.gov/ncea/cfm/recordisplay.cfm?deid=22423

TRIBAL MONITORING NETWORKS

Network	Lead Agency	# of Sites	Initiated	Measurement Parameters	Location of Information and/or Data
Tribal Monitoring	U.S. EPA	120+	1995	O_3, NO_X/NO_2, SO_2, $PM_{2.5}$/ PM_{10}, PAN, NH_3, $PM_{2.5}$, PM_{10} and coarse fraction CO, Pb	http://www.epa.gov/ttn/airs/airsaqs/aqsweb/aqswebhome.htm

INDUSTRY/RESEARCH NETWORKS

Network	Lead Agency	# of Sites	Initiated	Measurement Parameters	Location of Information and/or Data
New Source Permit Monitoring	None	variable	variable	O_3, NO_X/NO_2, SO_2, $PM_{2.5}$/PM_{10}, CO Pb	Contact specific industrial facilities
HRM Network—Houston Regional Monitoring Network	None	9	1980	O_3, NO_X, $PM_{2.5}$/PM_{10}, CO, SO_2, Pb, VOCs, surface meteorology	http://hrm.radian.com/ houston/how/index.htm

Network	Lead Agency	# of Sites	Initiated	Measurement Parameters	Location of Information and/or Data
ARIES / SEARCH—Aerosol Research Inhalation Epidemiology Study / Southeastern Aerosol Research and Characterization Study experiment	None	8	1992	O_3, $NO/NO_2/NO_Y$, SO_2, CO, $PM_{2.5}/PM_{10}$, $PM_{2.5}$ speciation, major ions, NH_3, HNO_3, scattering coefficient, surface meteorology	http://www.atmospheric-research.com/studies/ SEARCH/index.html
SOS - SERON—Southern Oxidant Study – Southeastern Regional Oxidant Networks	U.S. EPA	~40	1990	O_3, NO, NO_Y, VOCs, CO, surface meteorology	http://www.ncsu.edu/sos/pubs/ sos3/State_of_SOS_3.pdf

Two important ambient air networks focused on environmental welfare effects were established in the mid-1980s. IMPROVE with >100 sites in National Parks and other remote locations is used primarily to assess visibility impairment, but has provided a reliable long-term record of particulate mass and major speciation components and served as a model for the later deployment of STN; see Figure 2-63. STN (now part of CSN) has provided an urban complement to characterize aerosol composition; see Figure 2-64. Additional, minor networks identified in Figure 2-63 include those of the state and local air agencies deployed since the mid-1980s measuring a variety of aerosol- and gas-phase, hazardous air pollutants (HAPs) at ~200 locations, and a modest National Air Toxics Trends (NATTS) network of 23 sites; see the list and brief descriptions in Table 2-14 above.

Ambient Air Monitoring Stations in the United States
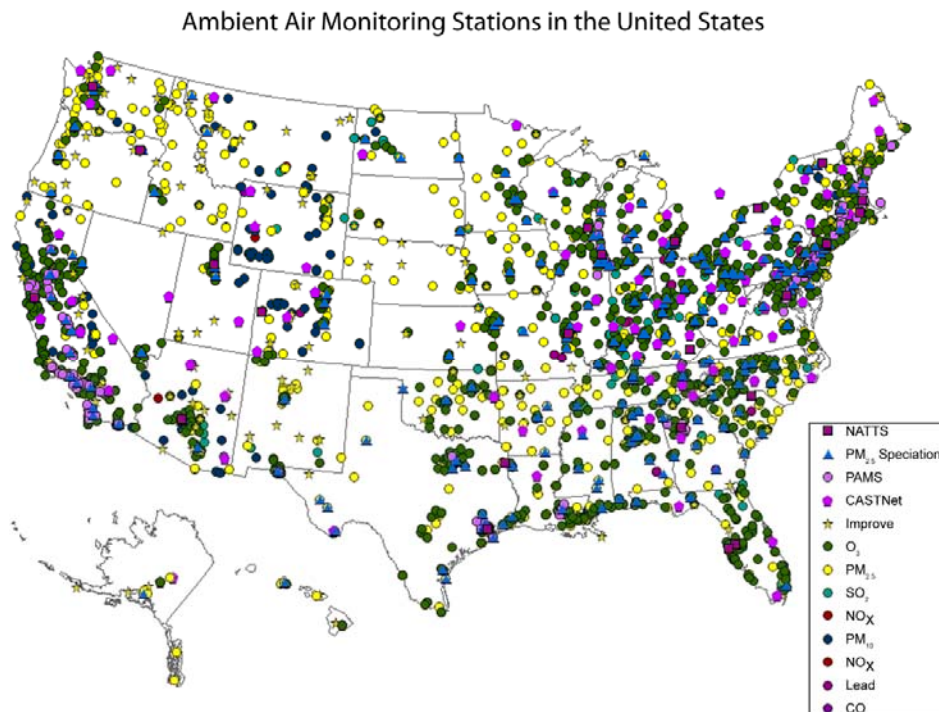
Figure 2-63.   Aggregate map of most routine U.S. monitoring stations.

CASTNet was established in the early 1990s to track changes in dry deposition of major inorganic ions and gaseous precursors associated with the CAA Title IV reductions in SO_2 and NO_X or S and N. Complementing ongoing precipitation measurements from NADP, CASTNet (see Figure 2-63) has provided a valuable source of model evaluation data for many of the large regional scale applications since the 1990s.
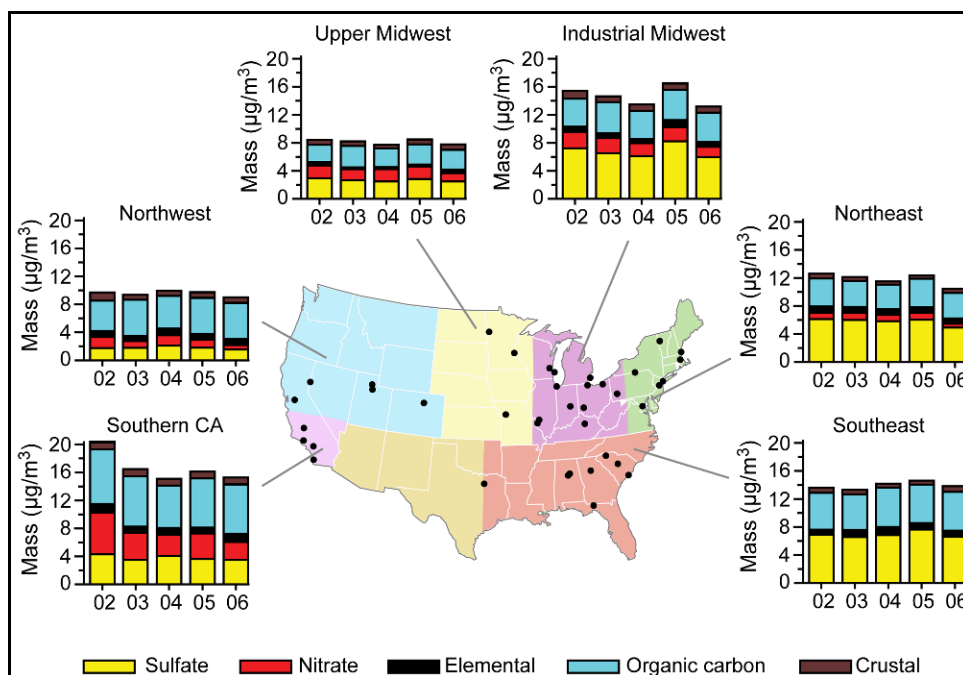
Figure 2-64. Trends in regional chemical composition of PM$_{2.5}$ aerosols based on urban speciation sites and averaged over the entire 2006 sampling period.
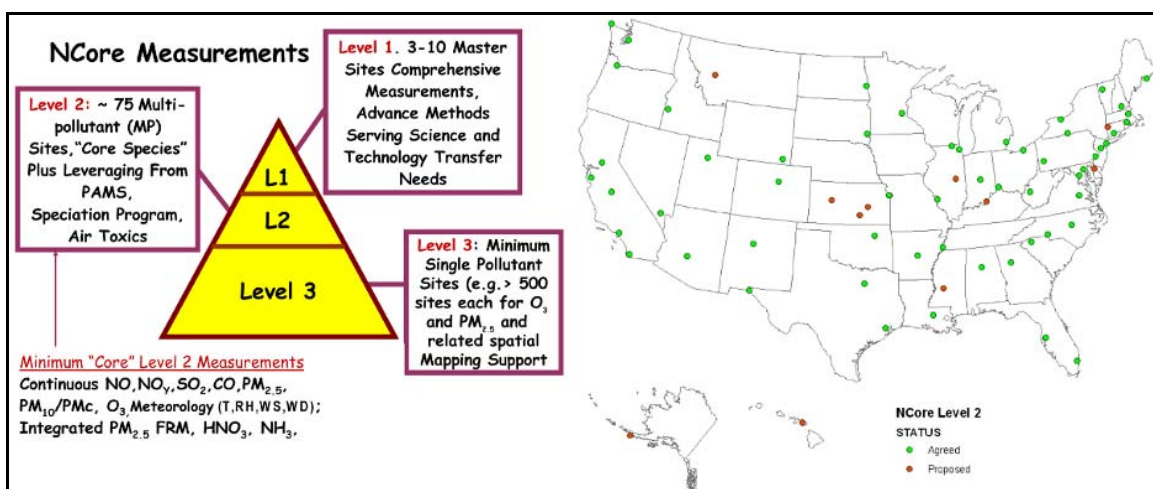
Figure 2-65. Original 3−tiered NCore design (left) and proposed site locations for Level 2 multiple pollutant sites.

Deployment of the PAMS and the $PM_{2.5}$ networks from the early 1990s through 2002 markedly enhanced the spatial, temporal, and compositional attributes of gases and aerosols.

A new multiple pollutant-monitoring network, NCore was begun in 2006. When implemented in 2009, NCore will provide a minimum of 75 Level-2 sites (Figure 2-65) in most major urban areas and important transport corridor and background locations. NCore will include a variety of trace gas and aerosol mass and speciation measurements which are intended to support multiple data user needs including air quality model evaluation and long-term epidemiological studies.

2.9.1.1. Pollutant Categories

Inorganic Gas-phase Species

Most U.S. sites measuring NO_X and SO_2 are incorporated within the State and Local Air Monitoring Systems (SLAMS) networks. Most of the SLAMS sites are located in populated urban locations with a variety of monitor siting requirements typically intended to site for high concentration locations resulting in an emphasis on center-city locations for NO_X and proximity to major power generating facilities for SO_2.

Measurements of NO_Y, HNO_3, and NH_3 are useful in a variety of ways important for assessing NO_X and SO_X environmental pollution effects; some of these ways include: evaluation of emissions inventories; inputs to and sources of evaluation for numerical and observation–based models; and establishing baseline N budgets for watershed and field accountability assessments. NO_Y, HNO_3, and NH_3, together with true NO_2 and pNH_4, are significant components of the total N budget but remain poorly characterized at the national scale. In largest part, a lack of reliable, cost effective continuous measurement methods has hindered deployment of instruments for HNO_3 and NH_3 as described in Section 2.7. In the U.S., the Southeastern Aerosol Research and Characterization Study (SEARCH) network of eight monitoring sites is the only source of routine, continuous ambient air measurements of NO_Y together with NH_3 and HNO_3; see discussions in Blanchard and Hidy (2003) and Zhang et al. (2006). CASTNet recently deployed a network of inexpensive passive NH_3 samplers which have promise for characterizing broad spatial patterns, with extended averaging times beyond 24 h.

Particulate Matter Mass

Nearly 1500 $PM_{2.5}$ gravimetric sites were established before 2000 to determine nonattainment status of counties throughout the U.S. following the 1997 promulgation of the $PM_{2.5}$ particulate matter standard. The network has evolved to add over 500 continuous $PM_{2.5}$ monitors and a reduction of 24-h gravimetric samplers below 1000 sites (see Figure 2-66) that support air quality forecasting and public notification of adverse air quality using the Air Quality Index (AQI), a generalized indicator of exposure concern linked to the NAAQS (http://www.epa.gov/airnow/). While this expansion of continuous $PM_{2.5}$ sites adds spatial coverage of highly temporally resolved information, the mix of instrument types compromises data harmonization across sites and geographic areas with different operational characteristics.
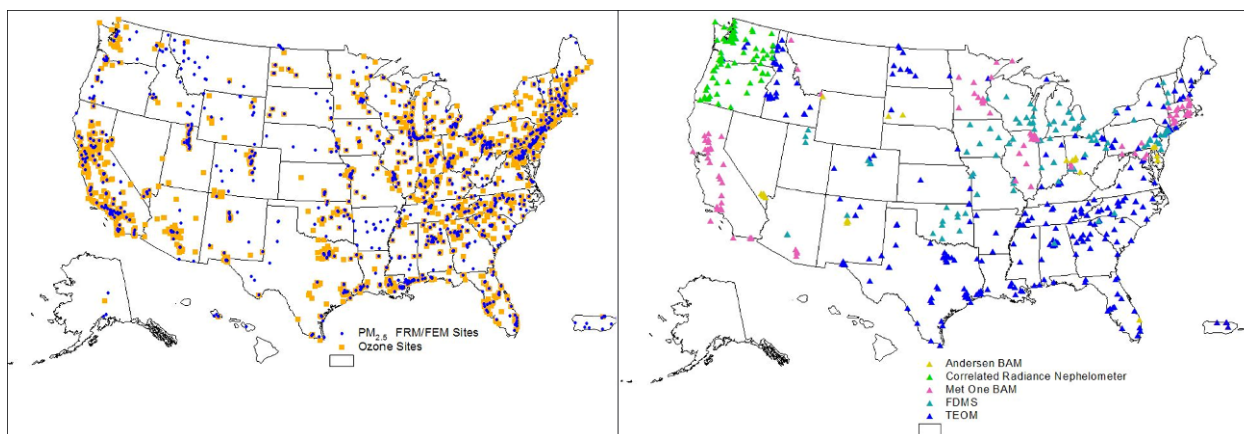
Figure 2-66. Maps illustrating coverage of PM$_{2.5}$ FRM and FEM and O$_3$ network (left); and PM$_{2.5}$ continuous samplers (right).

Particulate Matter Speciation

The speciation networks typically collect a 24-h sample once every 3 or 6 days. CASTNet provides weekly averaged measurements of major ions including SO$_4^{2-}$, NO$_3^-$, calcium (Ca^{2+}), Na$^+$, potassium (K$^+$), NH$_4^+$, and magnesium (Mg^{2+}) integrated over all aerosol sizes by means of open-face filter packs. Daily, 24-h speciated samples is limited to fewer than five sites in the U.S. and Canada. Similarly, a small and variable number of sites, fewer than 10 in most years, provide near-continuous speciation data, usually limited to some combination of pSO$_4$, pNO$_3$, and EC and OC. In addition, the 22 NATTS sites include aetholometers measuring semi-continuous light absorption, often used as a surrogate for EC.

The U.S. EPA PM Supersites Program (Wittig and Solomon, 2006) provided highly time-resolved aerosol measurements at eight cities in the U.S. for a mix of time periods between 1999 and 2004. Depending on location and time period, a number of different instrument configurations were deployed ranging from additional spatial coverage of standard speciation sites to systems capturing near-continuous size-distributed chemical composition profiles.

The SEARCH program, funded since 1998 by EPRI and Southern Company, has provided continuous, semi-continuous and integrated data on a wide variety of species from eight highly instrumented paired research sites in the southeastern U.S. in the states of AL, FL, GA, and MS; see descriptions in Hansen et al. (2003) for additional details. At present, the suite of measurements made at all sites includes: 24-h PM$_{2.5}$ filter samples, analyzed for mass, ions (SO$_4^{2-}$, NO$_3^-$, NH$_4^+$), OC, EC, BC, and elements as measured by XRF; 24-h PM coarse mass, ions, and XRF elements; 24-h gaseous NH$_3$; continuous (minute-to-hourly) PM$_{2.5}$ mass, OC, EC, NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$; light-scattering and light absorption; continuous gaseous O$_3$, NO$_2$, NO$_Y$, NO$_3^-$, CO, and SO$_2$; and continuous, 10-m meteorological parameters: wind speed, wind direction, temperature, RH, solar radiation, barometric pressure and precipitation.

Precipitation-based Networks

Precipitation chemistry is the primary measured link between atmospheric, terrestrial, and aquatic systems. NADP oversees a network of more than 250 sites (see Figure 2-67) where most of the major ions key to aquatic chemistry addressing acidification and eutrophication effects are measured. The NADP includes the Mercury Deposition Network (MDN) of ~90 sites and seven Atmospheric Integrated Research Monitoring Network (AIRMoN) sites providing greater temporal resolution.

2.9.2. Intensive Field Campaigns

Intensive field campaigns of relatively short duration supplement routine, longer-term monitoring networks by enhancing spatial, temporal, and compositional distribution of atmospheric species to better elucidate physical and chemical processes relevant to the fate, transport, and removal of secondarily formed gases and aerosols. Typically, these campaigns utilize some combination of aircraft studies, high time resolved instrumentation and advanced analytical methods (in-situ and laboratory) to complement routine ground-based measurements.
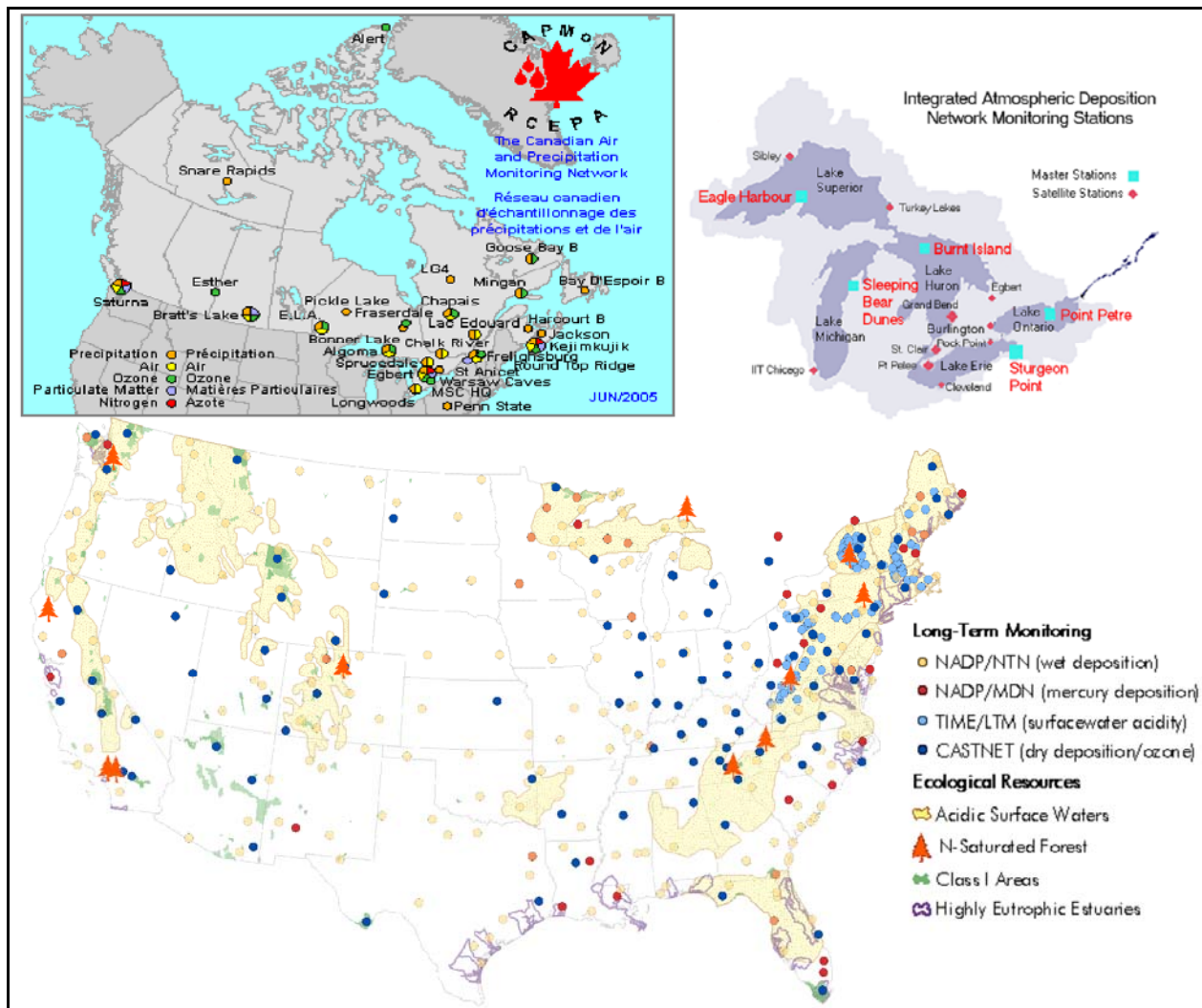
Figure 2-67. Routinely operating North American precipitation and surface water networks. Upper left, Canadian Air and Precipitation Monitoring Network (CAPMoN); Upper right, Integrated Atmospheric Monitoring Deposition Network (IADN); Bottom, National Atmospheric Deposition Program (NADP) with Time/LTM surface chemistry sites.

Table 2-15. Air monitoring networks/campaigns for non-routine special intensive studies conducted since the mid-1990s.

Lead Agency[1]	# of Sites	Initiated	Measurement Parameters	Location of Information and/or Data	Notes
Texas	17	2006	O_3, NO_X, NO_Y, SO_2, haze, visibility, CO, VOC, solar radiation, surface meteorology, upper air	http://www.utexas.edu/research/ceer/texaqsII/PDF/12-12-04_Projected_SurfaceSites_tbl.pdf	Researchers from universities, state and federal agencies, private industry, and local governments are joining forces to conduct a major field study to address air quality issues in the eastern half of Texas. The study, planned for a period extending from Apr 2005 through Oct 2006, will examine regional O_3 formation, transport of O_3 and O_3 precursors, meteorological and chemical modeling, issues related to O_3 formation by highly reactive emissions, and PM formation. It is anticipated that the information from the study will be the scientific basis used for developing State Implementation Plans (SIPs) for O_3 (with concentrations averaged over 8 h), regional haze, and, if necessary, for fine PM (PM < 2.5 μm in diameter, $PM_{2.5}$).
NOAA	1 ship, 2 aircraft	2006	O_3, NO, NO_2, NO_Y, VOCs, CO_2, CO, SO_2, HNO_3, NH_3, other reactive pollutants, aerosols, meteorological parameters and upper air	http://esrl.noaa.gov/csd/2006/	For TexAQS 2006, the NOAA air quality component will investigate, through airborne and sea-based measurements, the sources, and processes that are responsible for photochemical pollution and regional haze during the summertime in Texas. The focus of the study will be the transport of O_3 and O_3 precursors within the state and the impact of the long-range transport of O_3 or its precursors.
NOAA	3 aircraft	2006	O_3, NO, NO_2, NO_Y, VOCs, CO_2, CO, SO_2, HNO_3, NH_3, other reactive pollutants, aerosols, meteorological parameters, altitude — NOAA aircraft	http://cloud1.arc.nasa.gov/intex-b/	The export of air pollutants from urban to regional and global environments is a major concern because of wide-ranging potential consequences for human health, cultivated and natural ecosystems, visibility degradation, weather modification, changes in radiative forcing, and tropospheric oxidizing capacity. During the spring of 2006, a highly integrated atmospheric field experiment was performed over and around North America. The Megacity Initiative: Local and Global Research Observations (MILAGRO), http://www.eol.ucar.edu/projects/milagro/ , resulted through a highly coordinated collaboration between NSF (through MIRAGE-Mex), DOE (through MAX-Mex), NASA (through INTEX-B) and a variety of research institution in the U.S. and Mexico and involved ground and air borne activities centered on Mexico City, Mexico during March 2006. MILAGRO goals were greatly facilitated and enhanced by a number of concurrent and coordinated national and international field campaigns and global satellite observations.

[1]EPA— Environmental Protection Agency; NASA — National Aeronautics and Space Administration; NOAA — National Oceanic and Atmospheric Administration; NPS — National Park Service\NSF — National Science Foundation; UCSD — University of California San Diego (Scripts Institution of Oceanography)

[2]This study is part of the Central California Air Quality Studies (CCAQS) which comprise the California Regional Particulate Air Quality Study (CRPAQS) and the Central California Ozone Study (CCOS). CCAQS is a multi-year effort of meteorological and air quality monitoring, emission inventory development, data analysis, and air quality simulation modeling. Prior studies in California included: Southern California Ozone Study (SCOS97) — 1997; Integrated Monitoring Study (IMS95) — 1995; San Joaquin Valley Air Quality Study (SJVAQS) — 1990; SARMAP Ozone Study — 1990; Southern California Air Quality Study (SCAQS) — 1987.

[3]Historically, there have been many other field studies in the 1960s - 1990s that are not reflected in this table that involve both fixed monitoring sites and aircraft; well known examples include Regional Air Pollution Study (RAPS), Large Power Plant Effluent Study (LAPPES), Northeast Corridor Regional Modeling Program (NECRMP), Northeast Regional Oxidant Study (NEROS), Persistent Elevated Pollutant Episode (PEPE), and Lake Michigan Ozone Study (LMOS).

There has been a long history of intensive field campaigns starting with the RAPS in the 1970s, which formed the basis for evaluating the early photochemical gridded Eulerian airshed models used in acid deposition and O_3 assessments. Landmark campaigns in the U.S. through the 1980s and 1990s such as the SCAQS (Lawson, 1990), the SJAQS/Atmospheric Utility Signatures, Predictions, and Experiments (AUSPEX) (Roth et al. 1988) and the Southern Oxidant Study (SOS) (Cowling and Furiness, 2001). Over the last decade there have been a series of field campaigns focusing on characterization of surface level aerosols through the PM Supersites program (Solomon and Hopke, 2008). While the early campaigns focused on urban environments, the Eulerian Model Evaluation Field Study (EMEFS) and SOS during the early 1990s shifted focus toward regional spatial scales. In addition to addressing urban areas of concern such as Houston, TX, and Los Angeles, CA, more recent campaigns have extended spatial scales beyond regional studies to address oceanic transport and a variety of air pollution issues across the Northern Hemisphere, recognizing the importance of far-ranging source regions and continental-scale atmospheric processes. Some of these campaigns included local and regional studies for the northeast and southeast U.S., portions of Texas, and central and southern California. A variety of federal and state entities have served as lead agencies for these studies. Table 2-15 provides a listing of studies conducted since the mid-1990s.

A synthesis of key findings from major field campaigns conducted over the last two decades would elevate exposure of these programs to a wider audience potentially generating support to enhance and sustain atmospheric process and model evaluation studies, which are important complements to routine ground-based and satellite observation platforms. While the NARSTO database (http://eosweb.larc.nasa.gov/PRODOCS/narsto/table_narsto.html) provides access to raw data for various field campaigns, coverage of campaigns beyond North America must be acquired from other sources. The National Aeronautics and Space Agency (NASA)'s Atmospheric Data Science Center (http://eosweb.larc.nasa.gov/) also provides access to some of the more recent field campaigns.

2.9.3. Satellite-Based Air Quality Observing Systems

An extensive array of satellite-based systems (see Table 2-16 and Table 2-17) with the capability of measuring atmospheric column total species has been established by U.S. and European Satellite programs lead by NASA and the National Oceanic and Atmospheric Administration (NOAA) in the U.S. and the European Space Agency (ESA). A suite of satellites including Aqua, Aura, CALIPSO, OCO, Glory, as well as NOAA-17, NOAA-18 and NPOESS, have either been launched since about the year 2000 or have other near-term proposed launch dates. Collectively, the remote sensing platforms include techniques for measuring columns and/or profiles of aerosol optical depth (AOD), O_3, CO, CO_2, CH_4, SO_2, NO_2, chlorinated fluorocarbon compounds (CFCs), other pollutants, and atmospheric parameters such as temperature and H_2O content. Most of these satellites have a near-polar orbit allowing for two passes per day over a given location. When taken together, a group of six satellites (Aqua, Aura, CALIPSO, OCO, as well as CloudSat and PARASOL), coined the A-Train, is being configured to fly in a formation that crosses the equator a few minutes apart at around 1330 local time to give a comprehensive picture of earth weather, climate, and atmospheric conditions.

Satellite imagery offers the potential to cover broad spatial areas; however, an understanding of their spatial, temporal and measurement limitations is necessary to determine how these systems complement ground based networks and support air quality management assessments.

Table 2-16.   Satellite-based air quality observing systems.[1,4]

Instrument	Satellite Platform[3]	Lead Agency	Initiated	Measurement Parameters	Orbit & Hor. Resolution	Location of Information and/or Data
OLS (Operational Linescan System)	DMSP satellites	DOD	1962?	Identify fires and smoke plume	Polar Imagery only	http://www.af.mil/factsheets/-factsheet.asp?fsID=94
BUV (Backscatter Ultraviolet Spectrometer)	Nimbus 4	NASA	1970–1980	O_3, CO_2, SO_2	Sun synchronous	http://nssdc.gsfc.nasa.gov/database/MasterCatalog?sc=1970-025A
SBUV (Solar Backscatter Ultraviolet Spectrometer)	Nimbus 7	NASA	1978–1993	O_3, SO_2	Polar	http://jwocky.gsfc.nasa.gov/-n7toms/nimbus7tech.html
TOMS (Total Ozone Mapping Spectrometer)	Nimbus 7 Meteor 3 Earth-Probe	NASA	1978–1993 1991–1994 1996	O_3, SO_2, Aerosols	Polar ~100 km	http://toms.gsfc.nasa.gov/-fltmodel/spacecr.html
LIMS (Limb Infrared Monitor of the Stratosphere	Nimbus 7	NASA	1978–1979	O_3, HNO_3, NO_2,	Polar	http://lims.gats-inc.com/-about_lims.html
ATMOS (Atmospheric Trace Molecule Spectroscopy)	Spacelab 3 ATLAS — 1,2,3	NASA	1985, 1992, 1993, 1994	O_3, $CFCl_3$, CF_2Cl_2, $ClONO_2$, HCl, HF, CO, CH_4, HCN, HNO_3, NO, NO_2, N_2O_5, Aerosols		http://remus.jpl.nasa.gov/-atmos/sl3.html
CLAES (Cryogenic Limb Array Etalon Spectrometer)	UARS	NASA	1991–1993	O_3, $CFCl_3$, CF_2Cl_2 $ClONO_2$, CH_4, HNO_3, NO, NO_2, N_2O, N_2O_5, Aerosols		http://umpgal.gsfc.nasa.gov/
HALOE (Halogen Occultation Experiment)	UARS	NASA	1991–2005	O_3, HCl, HF, CH_4, NO, NO_2, Aerosols		http://umpgal.gsfc.nasa.gov/
ISAMS (Improved Stratospheric and Mesospheric Sounder)	UARS	NASA	1991–1992	O_3, CO, CH_4, NO_2, N_2O, N_2O_5 Aerosols		http://umpgal.gsfc.nasa.gov/
MLS (Microwave Limb Sounder)	UARS	NASA	1991–1999	O_3, ClO, CH_3CN, HNO_3, SO_2		http://umpgal.gsfc.nasa.gov/
GOES Imager (Geostationary Operational Environmental Satellites)	GOES-10 GOES-12	NOAA	1994	Fire products for WF_ABBA (imagery) and GASP (aerosol optical depth)	Geostationary	http://www.nesdis.noaa.gov/
GOES Sounder (Geostationary Operational Environmental Satellites)	GOES-10 GOES-12	NOAA	1994	Total column O_3	Geostationary	http://cimss.ssec.wisc.edu/-goes/goesmain.html#sndrinfo
AVHRR (Advanced Very High Resolution Radiometer)	NOAA-15 NOAA-16 NOAA-172	NOAA	1998	Aerosol optical depth, particle size information and vegetation/drought index products related to air quality through fires	Polar 4 km	http://noaasis.noaa.gov/-NOAASIS/ml/avhrr.html
SBUV/2 (Solar Backscattered Ultraviolet Radiometer Model 2)	NOAA-16 NOAA-172	NOAA	2000	Total and profile O_3 from surface to top of atmosphere in ~5 km thick Umkehr layers	Polar	http://www2.ncdc.noaa.gov/-docs/podug/html/c4/sec4–4.htm

Instrument	Satellite Platform[3]	Lead Agency	Initiated	Measurement Parameters	Orbit & Hor. Resolution	Location of Information and/or Data
MOPITT (Measurement of Pollution in the Tropo-sphere)	EOS Terra	NASA	1999	CO, CH_4	Polar 22 × 22 km^2	http://www.eos.ucar.edu/mopitt/
MISR (Multi-angle Imaging SpectroRadiomenter)	EOS Terra	NASA	1999	Aerosol properties and plume height information near the vicinity of fires	Polar ~1 km	http://www-misr.jpl.nasa.gov/-mission/-introduction/welcome.html
MODIS (Moderate Resolution Imaging Spectroradiometer)	EOS Terra EOS Aqua	NASA	1999 2002	O_3, aerosol optical depth, particle size information, fine particle fraction, and forest fires	Polar 1 km	http://modarch.gsfc.nasa.gov/index.php
AIRS (Atmospheric Infrared Sounder)	EOS Aqua	NASA	2002	Total column O_3, surface temperature, temperature and moisture vertical profiles, (plus under development are CO and CO_2 total column, O_3 vertical distribution, and CH_4 distribution)	Polar 50 km	http://www-airs.jpl.nasa.gov/
HIRDLS (High Resolution Dynamics Limb Sounder)	EOS Aura	NASA	2004	O_3, $CFCl_3$, CF_2Cl_2, $ClONO_2$, CH_4, HNO_3, NO_2, N_2O, N_2O_5,	Aerosols	Polar: http://aura.gsfc.nasa.gov/index.html
MLS (Microwave Limb Sounder)	EOS Aura	NASA	2004	O_3, BrO, ClO, $HOCl$, HCl, CO, HCN, CH_3CN, HNO_3, N_2O, OH, HO_2, SO_2	Polar	http://aura.gsfc.nasa.gov/index.html
OMI (Ozone Monitoring Instrument)	EOS Aura	NASA	2004	O_3, BrO, $OClO$, $HCHO$, NO_2, SO_2 and aerosol	Polar	12 × 24 km^2 http://aura.gsfc.nasa.gov/index.html
TES (Total Emission Spectrometer)	EOS Aura	NASA	2004	O_3, NO_Y, CO, SO_2, CH_4	Polar 26 × 42 km	http://aura.gsfc.nasa.gov/index.html
CALIPSO (Cloud-Aerosol Lidar & Infrared Pathfind-er Satellite Observations)	CALIPSO	NASA	2005	AOD, backscatter, extinction	Polar 0.3 × 0.3 km^2	http://www-calipso.larc.nasa.gov/about/
OMPS	Ozone Mapping and Profiling Suite NPOESS Preparatory Project	NOAA	2006	Total column and vertical profile O_3 data	Polar	http://www.ipo.noaa.gov/-Projects/npp.html
VIIRS (Visible Infrared Imaging Radiometer Suite)	NPOESS - Preparatory Project	NOAA	2006	AOD	Polar	http://www.ipo.noaa.gov/-Projects/npp.html
Orbiting Carbon Observatory	OCO	NASA	2008	CO_2	Polar	http://oco.jpl.nasa.gov/
APS & TIM (Aerosol Polarimetry Sensor & Total Irradiance Monitor)	Glory	NASA	2008	BC soot, other aerosols, total solar irradiance, cloud images Sun- synchronous, circular	Low Earth Orbit	http://glory.gsfc.nasa.gov/

[1]Non-U.S. satellite systems are not included in table at this time.
[2]As of 3/15/06 the operational satellite platforms may need to include NOAA-18.
[3]CALIPSO — Cloud-Aerosol Lidar & Infrared Pathfinder Satellite Observations
DMSP— Defense Meteorological Satellite Program. EOS — Earth Observing System. GOES — Geostationary Operational Environmental Satellites
NOAA — National Oceanic and Atmospheric Administration|. NPOESS — National Polar-orbiting Operational Environmental Satellite System. OCO — Orbiting Carbon Observatory
UARS — Upper Atmosphere Research Satellite. [4]See the following table for additional information on NASA satellites, instrument systems, pollutants measured, and data availability:

Table 2-17.   Key atmospheric chemistry and dynamics data sets at the NASA Goddard DAAC.

Missions	Nimbus 4		Nimbus 7		Nimbus 7 Meteor 3 ADEOS 1 Earth-Probe	Nimbus 7		Spacelab 3, ATLAS 1, 2, 3	UARS	ERS-2	Terra Aqua		Aqua			Aura
Instruments	BUV	SBUV	TOMS	LIMS	ATMOS	CLAES	HALOE	SAMS	MLS	GOME	MODIS	AIRS	OMI	HIRDLS	MLS	TES*
Data Period	Apr '70–May '77	Nov '78–May '93	Nov '78–Present	Oct '78–May '79	'85, '92, '93, '94	Oct '91–May '93	Oct '91–Present	Sep '91–Jul '92	Sep '91–Jul '99	April '95–Present	Mar '00–Present	Sep '02–Present	Jul '04–Present	Jul '04–Present	Jul '04–Present	Jul '04–Present
Spectral Region	255–380 nm	255–340 nm	309–360 312–380 nm	6.2–15 µm	2.98–15 µm	3.5–12.7 µm	2.43–10.25 µm	4.6–16.6 µm	63, 183, 205 GHz	240–790 nm	0.4–14 µm	0.4–1.1, 3.74–15.4 µm	270–500 nm	6.12–17.76 µm	118, 190, 240, 640 GHz, 2.5 THz	3.2–15.4 µm
Bands	13	13	6	6	16	9	8	8	3	3072	36	2382	1560	22	5	12
O_3	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
BrO										•			•		•	
$CFCl_3$					•	•								•		
CF_2Cl_2					•	•								•		
ClO									•						•	
OClO										•			•			
$ClONO_2$					•	•								•		
HOCl															•	
HCl					•		•								•	
HF					•		•									
HCHO										•			•			
CO					•			•				•			•	•
CH_4					•	•	•	•				•		•		•
CH_3CN									•							
HCN					•										•	
HNO_3				•	•	•			•					•	•	•
NO					•	•	•									
NO_2				•	•	•	•	•		•			•	•		•
N_2O					•	•		•						•	•	
N_2O_5					•	•		•						•		
OH															•	
H_2O/ Humidity				•	•	•	•	•	•	•	•	•		•	•	•
SO_2	•	•	•						•	•			•		•	
Aerosols		•			•		•	•				•	•	•		
Cloud	•	•	•								•	•	•	•		
Temperature				•		•	•	•	•			•	•	•	•	•
Geopotential Height				•					•			•		•	•	
Reflectance	•	•	•								•	•	•			

Please note that the table above does not contain parameters from all sensors and products. Also available from the GES DAAC are many more Atmospheric and Earth Sciences data products from AIRS, AMSU-A, HSB, MODIS, SeaWiFS, OCTS, CZCS, TRMM (PR, TMI, VIRS), TOVS Pathfinder, Data Assimilation Model (GEOS-1, GEOS-DAS, CPC/ACDB), UARS (HRDI, WINDII, SOLSTICE, SUSIM, PEM), SORCE, several Field Campaigns, and Interdisciplinary data sets consisting of 70 geophysical Earth Sciences parameters. TOMS & SBUV reprocessed data (version-8) are now available on DVD-ROM. The MLS and OMI-Aura products and Visualization tools are now available from GES DIC.
Source: Aura instrument 'TES' is archived at the NASA Langley Atmospheric Sciences Data Center (http://eosweb.larc.nasa.gov/) http://disc.gsfc.nasa.gov/.

2.9.3.1. Satellite Coverages

The near polar orbiting tracks of most satellites performing trace gas measurements provides wide spatial coverage of horizontal resolution on the order of 10 to 50 km, but delivers only twice-daily snapshots of a particular species. Consequently, temporal patterns of pollutants as well as a time-integrated measure of pollutant concentrations cannot be delineated explicitly through satellite measurements alone. The geostationary satellite platforms such as the GOES systems of NOAA do provide near-continuous coverage of physical parameters for weather tracking and forecasting purposes. Polar orbiting satellites typically provide horizontal spatial resolution between 10 and 100 km, depending on the angle of a particular swath segment. Spatial resolution less than 10 km is possible with geostationary platforms.

Characterization of elevated pollutants delivered by satellite systems complements of our ground based in-situ measurement networks – especially considering that a considerable fraction of pollutant mass resides well above Earth's surface. With few exceptions, satellite data typically represents a total atmospheric column estimate. For certain important trace gases (e.g., NO_2, SO_2, CH_2O) and aerosols, most mass resides in the boundary layer of the lower troposphere, enabling associations linking column data to surface concentrations or emissions fields. For example, reasonable correlations, especially in the eastern U.S., have been developed between concentrations from ground level $PM_{2.5}$ stations and AOD from NASA's Moderate Resolution Imaging Spectroradiometer (MODIS) aboard the Aqua and Terra satellites (Engel-Cox et al., 2004); see the example in Figure 2-68. The Infusing Satellite Data into Environmental Applications (IDEA; http://idea.ssec.wisc.edu/) site provides daily displays and interpretations of MODIS and surface air quality data. The Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) satellite (discussed below) provides some ability to resolve aerosol vertical gradients.

2.9.3.2. Measurement Issues

Most satellite air quality observations are based on spectroscopic techniques typically using reflected solar radiation as a broad source of UV-through-IR electromagnetic radiation (LIDAR aboard CALIPSO does utilize an active laser as the radiation source). While the science of satellite based measurements of trace gases and aerosols is relatively mature, interferences related to surface reflections, cloud attenuation and overlapping spectra of nearby species require adequate filtering and accounting for in processing remote signals. For example, aerosol events episodes associated with clouds often are screened out in developing in applications involving AOD characterizations through MODIS. Correlations between AOD and surface aerosols generally are better in the eastern U.S. relative to the West due to excessive surface light scattering from relatively barren land surfaces.

2.9.4. European Air Monitoring Networks

Extensive air monitoring networks have also been implemented in Europe. In addition to the programs discussed above, many European-based programs are served by centralized organization structures linked to international efforts such as Convention on Long Range Transport of Air Pollution (LRTAP) (http://www.unece.org/env/lrtap/) and the underlying technical assessment body, the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP). The Global Atmospheric Watch (GAW) program (http://www.wmo.int/pages/prog/-arep/gaw/gaw_home_en.html) under the World Meteorological Organization (WMO) provides quality assurance guidelines and data access to an important body of air quality measurements relevant to assessing intercontinental pollution transport and climate forcing phenomena. The Norwegian Institute for

Air Research (NILU) (http://www.nilu.no/index.cfm?ac=topics&folder_id=4572&lan_id=3), maintains a database for much of the European based networks.
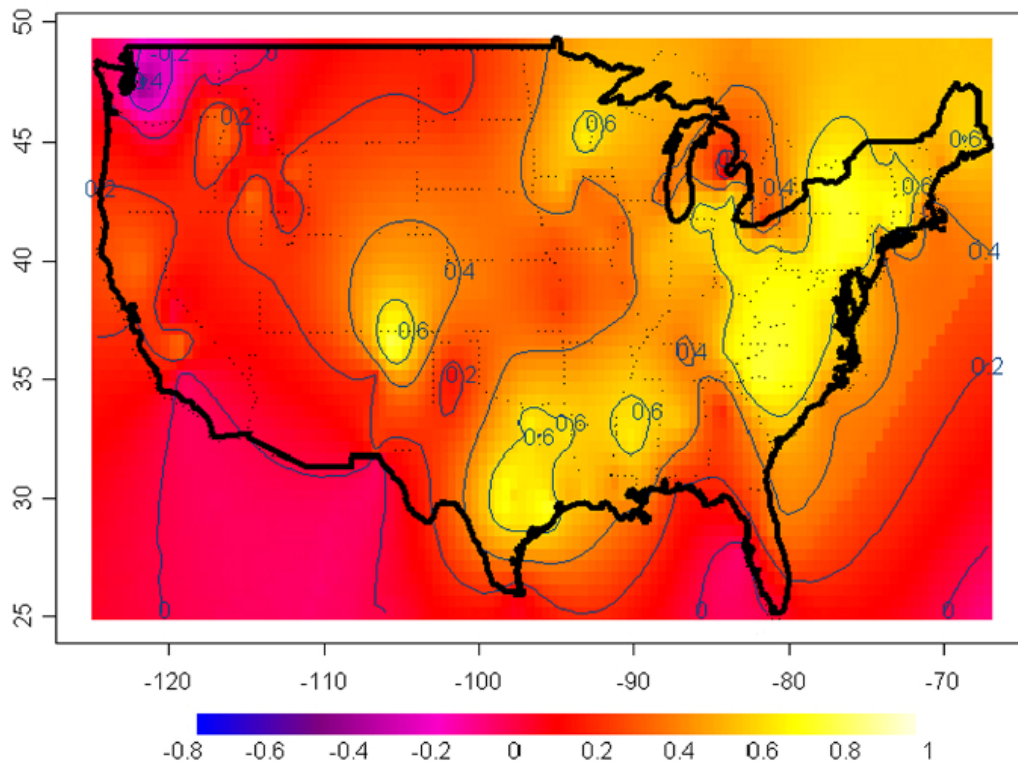
Figure 2-68.   Correlation surfaces between MODIS AOD and hourly PM$_{2.5}$ surface sites from April-September 2002.

Table 2-18 includes combined contributions from all countries ranging from a few sites to tens of sites per country. Measurements for a variety of air pollutants are addressed including O$_3$, heavy metals, persistent organic pollutants (POPs), PM, VOCs, and deposition from acidifying and eutrophying compounds.

Table 2-18.   International and European air monitoring programs.

Network	Lead Agency	Number of Sites	Initiated	Measurement Parameters	Location of Information / Data
EMEP – Co-operative Programmed for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (encompasses networks for ~37 European countries and organizations)	UNECE	270	1977	Acidifying / Eutrophying Compounds (precipitation): SO_4^{2-}, NO_3, NH_4, trace elements, pH, acidity (A): SO_2, NO_2, HNO_3, NH_3, PM_{10}, $PM_{2.5}$, major ions O_3 Heavy Metals precipitation, major ions, $PM_{2.5}$, PM_{10}, Hg, wet deposition POPs precipitation, air, deposition PM, $PM_{2.5}$, PM_{10}, EC, OC, TC, BC VOC HCs, Carbonyls	http://www.nilu.no/projects/ccc/emepdata.html
EUROTRAC—The European Experiment on the Transport and Transformation of Environmentally Relevant Trace Constituents over Europe	International Executive Committee (European Countries)	???	1986	EUROTRAC programs performed analyses utilizing data from existing or specially designed monitoring networks to: 1. elucidate the chemistry and transport of O_3 and other photo-oxidants in the troposphere, e.g., TOR—30 O_3 stations and ALPTRAC—15 snow-monitoring sites 2. identify processes leading to the formation of acidity in the atmosphere, particularly those involving aerosols and clouds. 3. understand uptake and release of atmospheric trace substances by the biosphere.	http://www.gsf.de/eurotrac/index_what_is.html
EUROTRAC-2 — The EUREKA project on the transport and chemical transformation of trace constituents in the troposphere over Europe; second phase. Subprojects: – AEROSOL – BIATEX-2 – CAPMAN – CMD – EXPORT-E2 – GENEMIS – GLOREAM – LOOP – MEPOP – PROCLOUD – SATURN – TOR-2 – TRAP45 – TROPOSAT	International Scientific Secretariat (European Countries and EU)	???	1996	EUROTRAC-2 programs performed analyses utilizing data from existing monitoring networks to: support the further development of abatement strategies within Europe by providing an improved scientific basis for the quantification of source-receptor relationships for photo-oxidants and acidifying substances.	http://www.gsf.de/eurotrac/index_what_is.html

2.9.5. Ambient Concentrations of Relevant N Compounds

2.9.5.1. NO and NO₂

Species concentrations described in this section were taken from two types of networks described in Section 2.9.1 above: the mostly urban networks designed and maintained for NAAQS attainment demonstrations; and the mostly rural and remote networks designed and operated to comply with a range of requirements for protection of landscapes and views.

Figure 2-69 shows the distribution of monitoring sites for ambient-level, continuous NO_2 across the U.S. Data for ambient NO_2 are missing or are collected at very few sites over large areas of the U.S. Few cities have more than two monitors and several large cities, including Seattle, WA, have none. Note that the number of NO_2 monitors has been decreasing in the U.S. as ambient average concentrations have fallen to far below the level of the NAAQS. There were, for example, 375 NO_2 monitors identified in mid-2006, but only 280 in November 2007.
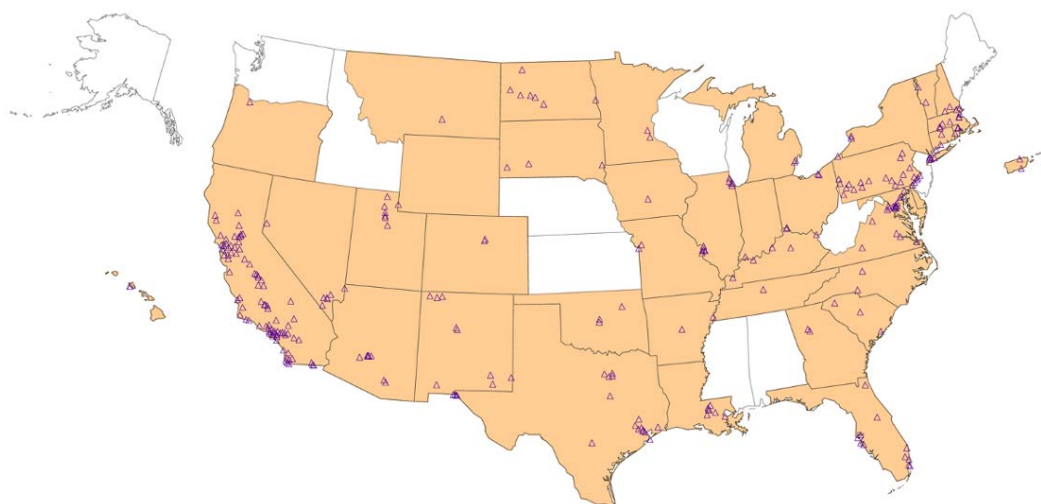
Figure 2-69. Location of ambient-level NO₂ monitors for NAAQS compliance in 2007. Shaded states have NO₂ monitors; unshaded states have none.

Criteria for siting ambient monitors for NAAQS pollutants are given in the SLAMS / NAMS / PAMS Network Review Guidance (U.S. EPA, 1998). As might be expected, criteria for siting monitors differ by pollutant. NO_2 monitors are meant to be representative of several scales: middle, or several city blocks, 300 to 500 m; neighborhood, or 0.5 to 4 km; and urban, or 4 to 50 km. Middle- and neighborhood-scale monitors are used to determine highest concentrations and source effects, while neighborhood- and urban-scale monitors are used for monitoring population exposures. As can be seen, there is considerable overlap between monitoring objectives and scales of representativeness. The distance of neighborhood- and urban-scale monitor inlets from roadways increases with traffic volume and can vary from 10 to 250 m away from roadways as traffic volume increases. Where the distance of an inlet to a road is shorter than the value in this range for the indicated traffic volume on that road, that monitor is classified as middle scale. Vertically, the inlets to NO_2 monitors can be set at a height from 2 to 15 m.

Figure 2-70 shows box plots of ambient concentrations of NO_2 measured at all monitoring sites located within MSAs or urbanized areas in the U.S. from 2003 through 2005. As can be seen, mean NO_2

concentrations are ~15 ppb for averaging periods ranging from a day to a year, with an interquartile range (IQR) of 10 to 25 ppb. However, the average of the daily 1-h maximum NO_2 concentration over this 3 year period is ~30 ppb. These values are about twice as high as the 24-h average. The highest maximum hourly concentration, ~200 ppb, found during the period of 2003 to 2005 was more than a factor of 10 greater than the overall mean 24-h concentrations. The ratio of the 99th percentile concentration to the mean ranges from 2.1 for the 1-year averages, to 3.5 for the 1-h averages.
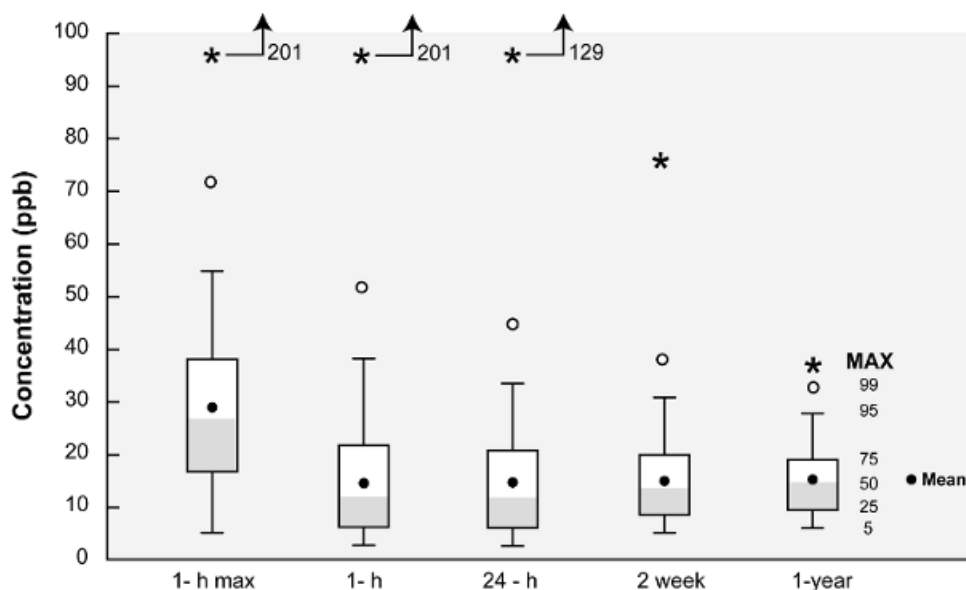
Figure 2-70. **Ambient concentrations of NO_2 measured at all monitoring sites located within Metropolitan Statistical Areas (MSAs) in the U.S. from 2003 through 2005. * max; • mean**

Because ambient NO_2 monitoring data are so sparse across the U.S., and are particularly so in rural areas, it would not be appropriate to use these data for constructing a complete coverage map of NO_2 concentrations. The short τ of NO_2 with respect to conversion to NO_Z species and the concentrated nature of NO_2 emissions result in steep gradients and low concentrations away from major sources that are not adequately captured by the existing monitoring networks. For this reason, model predictions might be more useful for showing large-scale features in the distribution of NO_2 and could be used in conjunction with the values shown in Figure 2-71 to provide a more complete picture of the variability of NO_2 across the U.S. Monthly average NO_2 concentrations for January and July 2002 calculated using U.S. EPA's CMAQ model are shown in Figure 2-72. (A description of the capabilities of CMAQ and other three-dimensional CTMs is given in Section 2.8) The high variation in NO_2 concentrations of at least a factor of 10 is apparent in these model estimates. As expected, the highest NO_2 concentrations are seen in large urban regions, such as the northeast corridor, and lowest values are found in sparsely populated regions located mainly in the West. NO_2 concentrations tend to be higher in January than in July.
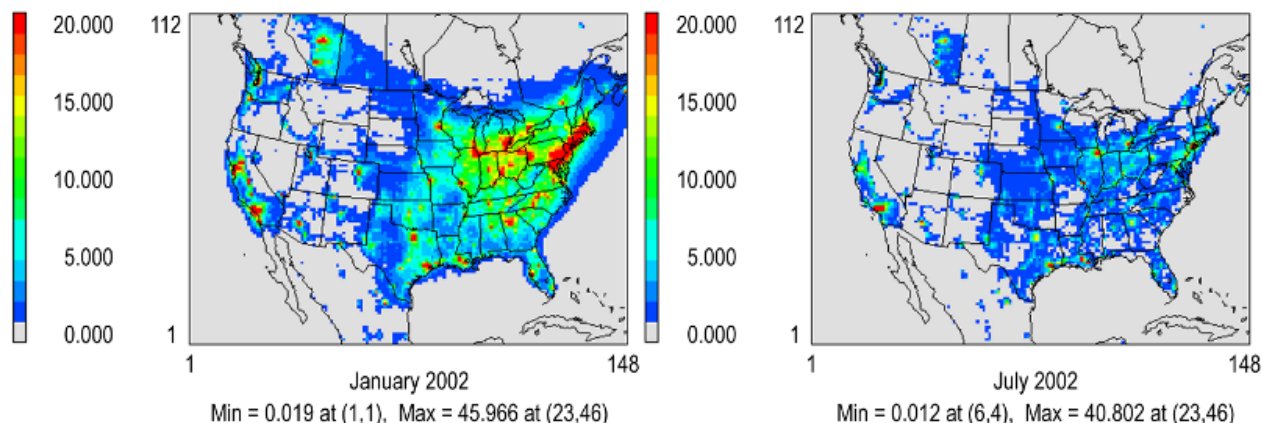
Figure 2-71. Monthly average NO₂ concentrations (ppb) for January 2002 (left panel) and July 2002 (right panel) calculated by CMAQ (36 X 36 km horizontal resolution).

Trends in NO₂ concentrations across the U.S. from 1990 to 2006 are shown in Figure 2-72. The white line shows the mean values and the upper and lower borders of the shaded areas represent the 10th and 90th percentile values. Information on trends at individual local air monitoring sites can be found at www.epa.gov/airtrends/nitrogen.html.

Figure 2-72. Nationwide trend in NO₂ concentrations. The white line shows the mean values, and the upper and lower borders of the green (shaded) areas represent the 10th and 90th percentile values. The current NAAQS of 0.53 ppm is shown with the dotted line.

Concentrations were substantially higher during earlier years in selected locations and contributed in those years to the brown clouds observed in many cities. Residents in Chattanooga, TN, for example, were exposed more than 30 years ago to high levels of NO₂ from a munitions plant (Shy and Love, 1980). Annual mean NO₂ concentrations there declined from ~102 ppb in 1968 to ~51 ppb in 1972. There was a strike at the munitions plant in 1973 and levels declined to ~32 ppb. With the implementation of control

strategies, values dropped further. In 1988, the annual mean NO_2 concentration varied from ~20 ppb in Dallas, TX and Minneapolis, MN to 61 ppb in Los Angeles, CA. However, New York City, with the second-highest annual mean concentration in the U.S. in 1988, the mean NO_2 concentration was 41 ppb.

The month-to-month variability in 24-h average NO_2 concentrations at two sites in Atlanta, GA, is shown in Figure 2-73. (Similar plots of variability at other individual sites in selected urban areas are shown in Figure 2-74 through Figure 2-81; these cities were chosen to represent regions with large populations and, hence, large emissions from on-road vehicles and combustion for energy production, the two largest sources of NO and NO_2.
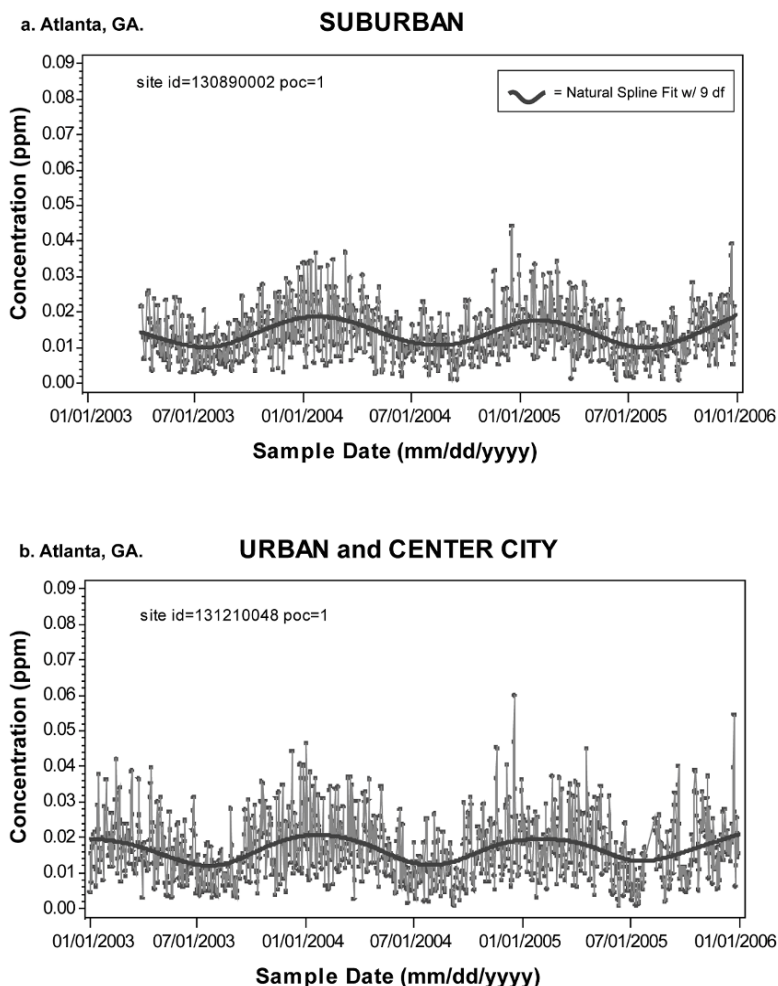
Figure 2-73. Time series of 24-h average NO_2 concentrations at individual monitoring sites in Atlanta, GA from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).
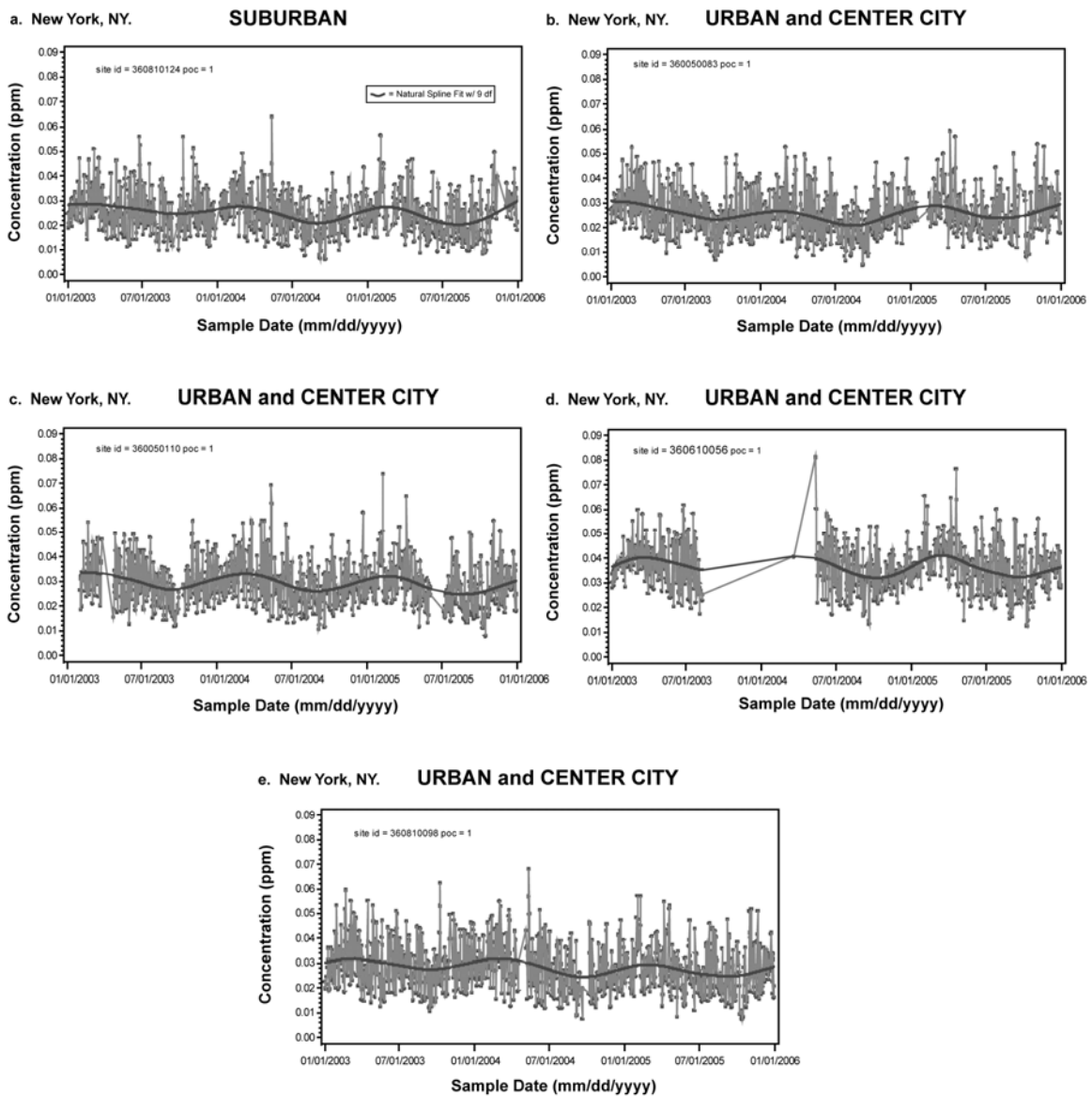
Figure 2-74. Time series of 24-h average NO_2 concentrations at individual monitoring sites in New York City from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).
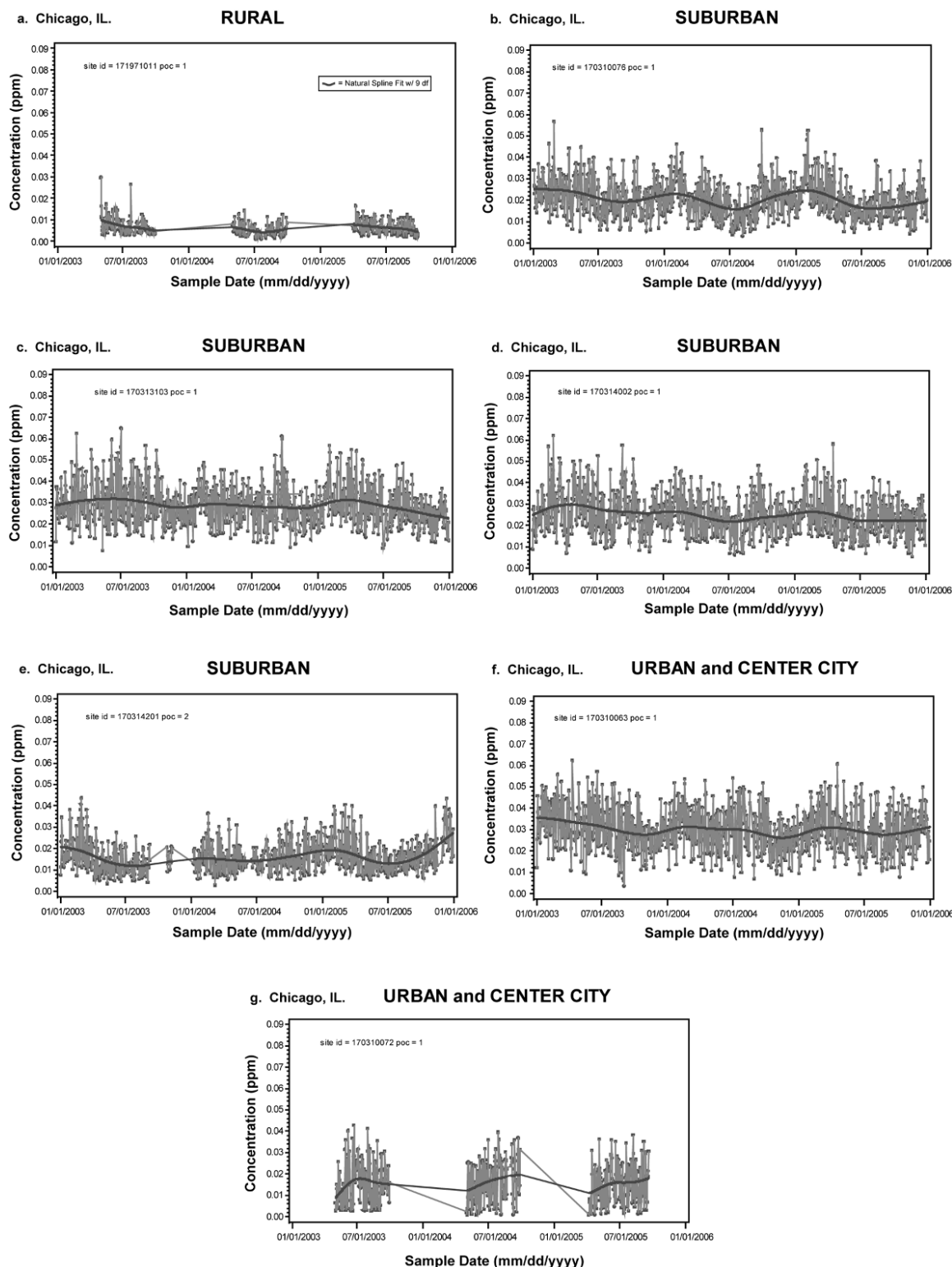
Figure 2-75.   Time series of 24-h average NO_2 concentrations at individual monitoring sites in Chicago, IL from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).
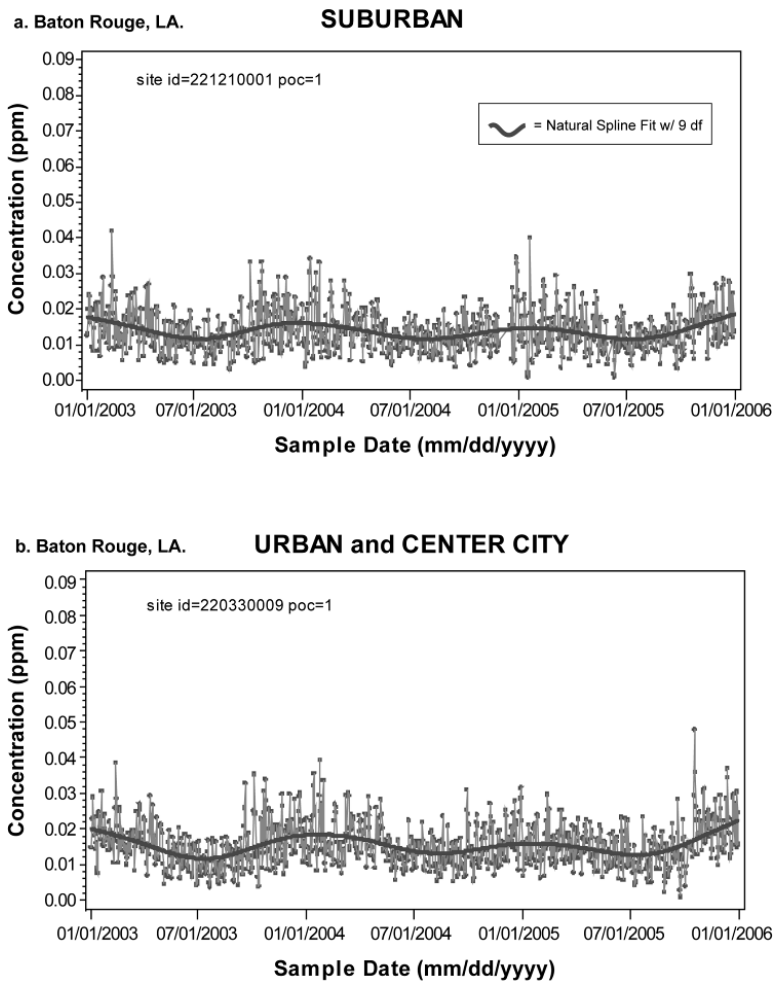
Figure 2-76.   Time series of 24-h average NO$_2$ concentrations at individual monitoring sites in Baton Rouge, LA from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).
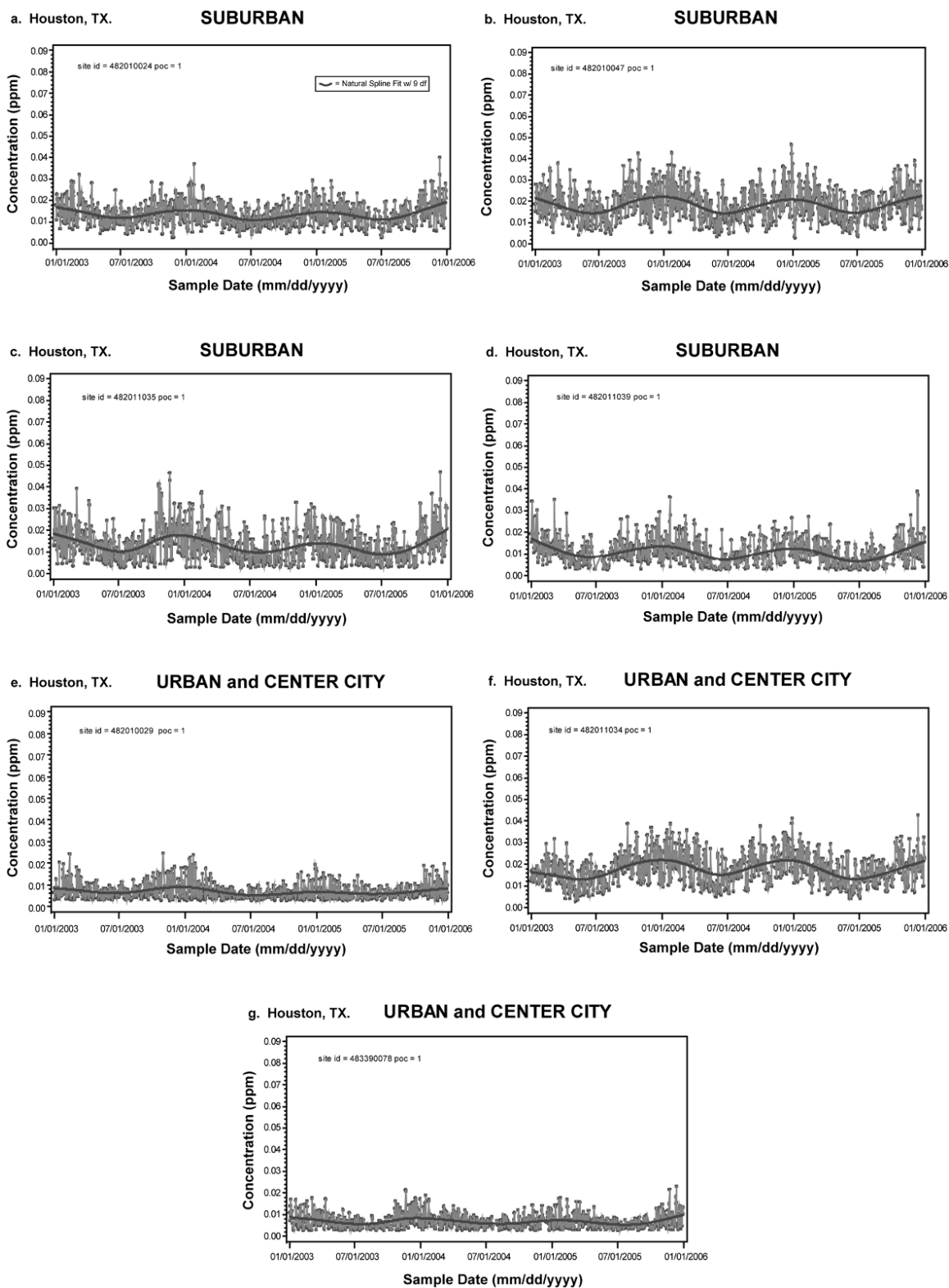
Figure 2-77.   Time series of 24-h average NO₂ concentrations at individual monitoring sites in Houston, TX from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).
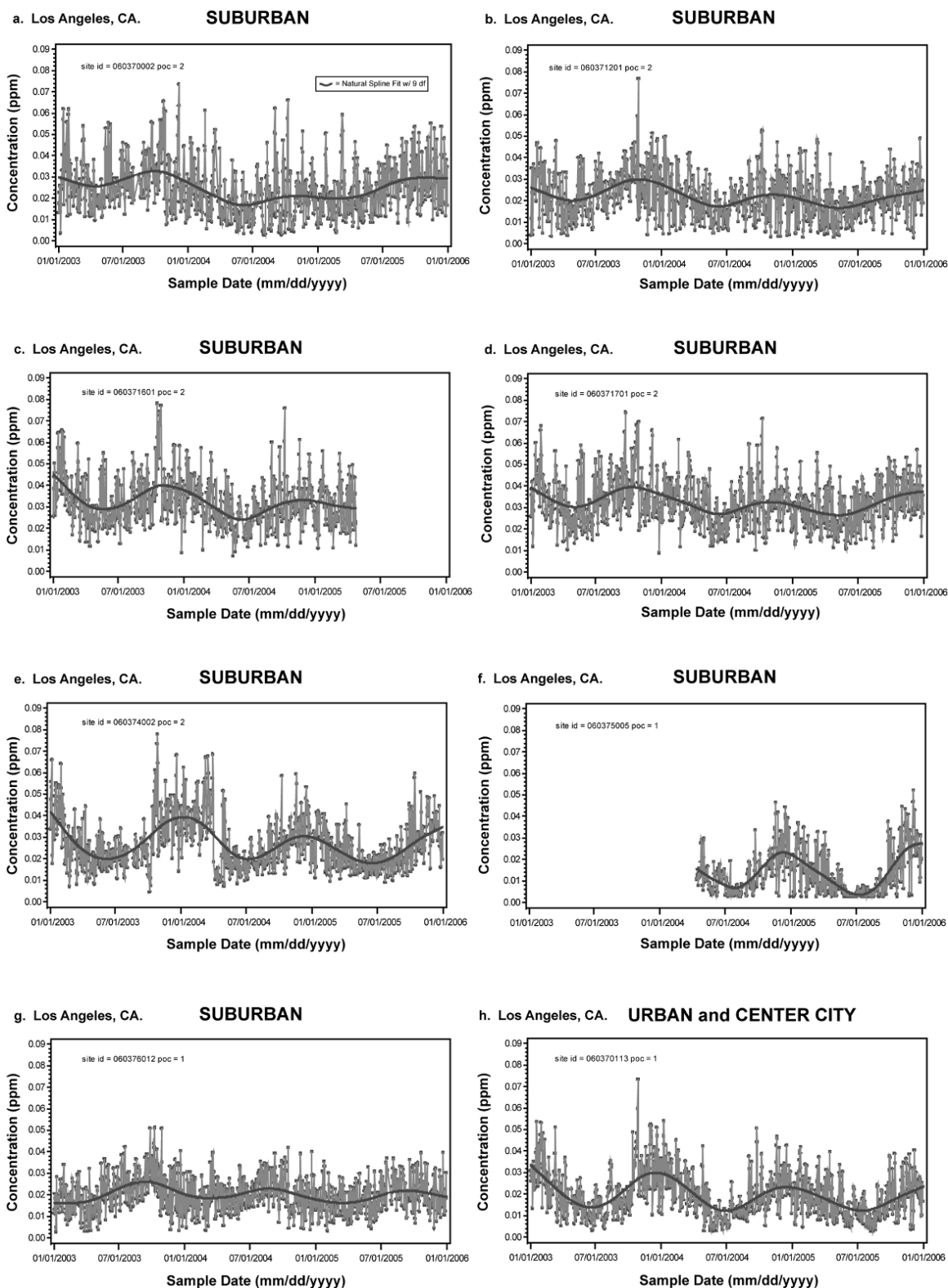
Figure 2-78. Time series of 24-h average NO₂ concentrations at individual monitoring sites in Los Angeles, CA from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).
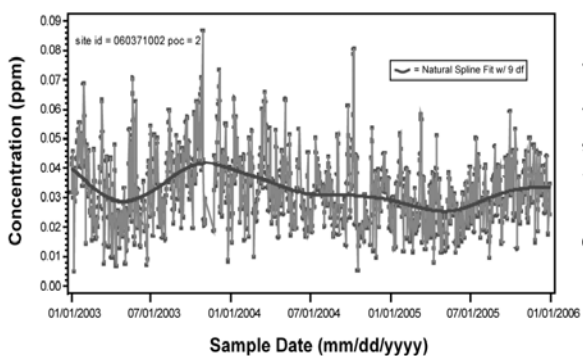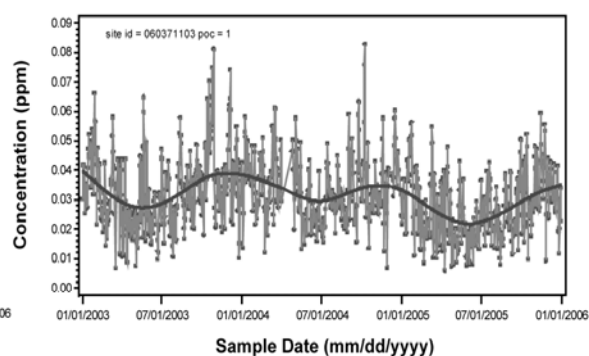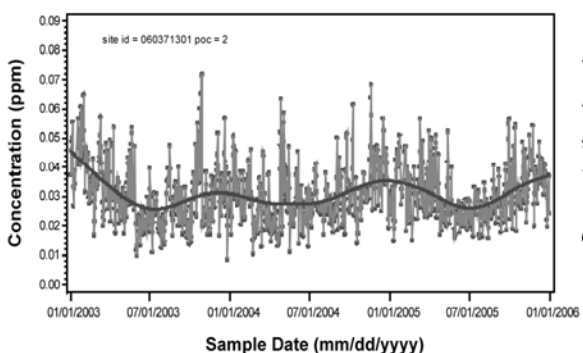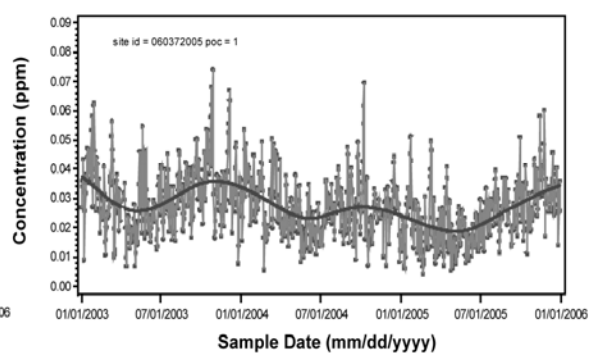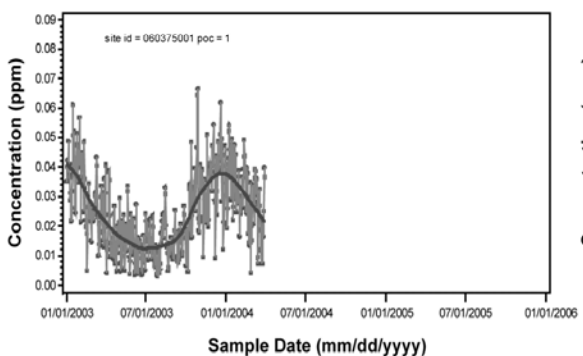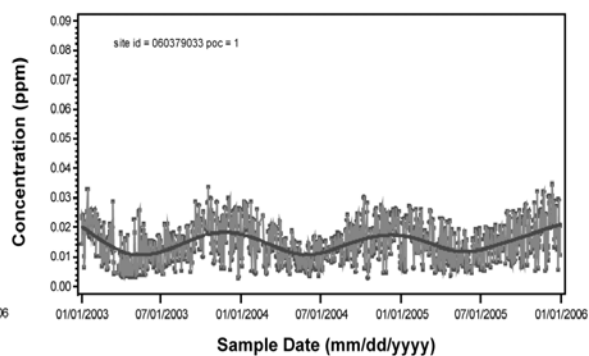
Figure 2-79.   Time series of 24-h average NO_2 concentrations at individual monitoring sites in Los Angeles, CA from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).
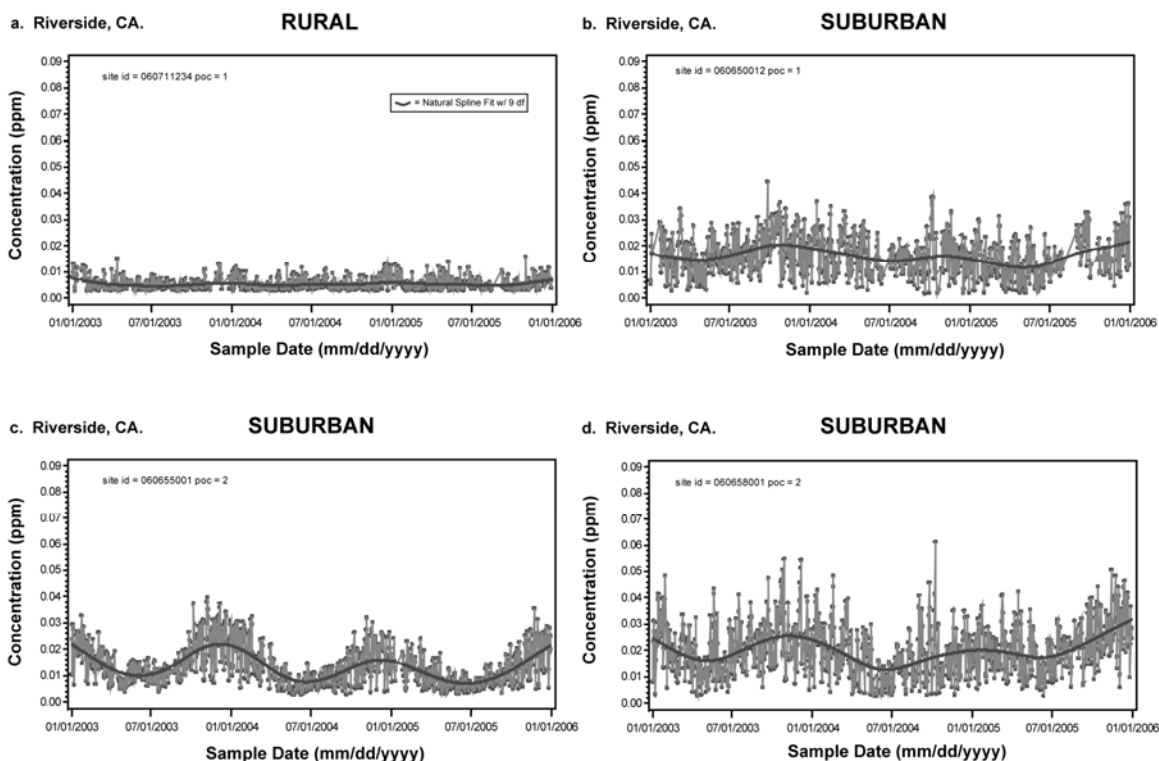
Figure 2-80.   Time series of 24-h average NO$_2$ concentrations at individual monitoring sites in Riverside, CA from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).

Strong seasonal variability exists in NO$_2$ concentrations in the data shown above. Higher concentrations are found during winter, consistent with the generally lower PBL depths in winter. Lower concentrations are found during summer, consistent with deeper PBLs and increased rates of photochemical oxidation of NO$_2$ to NO$_Z$. Note also the day-to-day variability in NO$_2$ concentration, which also tends to be larger during the winter. There appears to be a somewhat regular pattern for the other southern cities examined with their winter maxima and summer minima.

Monthly maxima tend to be found from late winter to early spring in Chicago, IL, and New York, NY, with minima occurring from summer through fall. However, in Los Angeles and Riverside, CA, monthly maxima tend to occur from fall through early winter, with minima occurring from spring through early summer. Mean and peak NO$_2$ concentrations during winter can be up to a factor of 2 greater than those during the summer at sites in Los Angeles.

The diel variability in NO$_2$ concentrations at the same two sites in the Atlanta metropolitan area shown in Figure 2-73 is illustrated in Figure 2-82. As can be seen from these figures, NO$_2$ typically exhibits daily maxima during the morning rush hours, although they can occur at other times of day. In addition, there are differences between weekdays and weekends. At both Atlanta sites, NO$_2$ concentrations are generally lower and the diel cycles more compressed on weekends than on weekdays. The diel variability of NO$_2$ at these sites is typical of that observed at other urban sites. Monitor siting plays a role in determining diel variability in the sense that monitors located farther from traffic will sometimes measure lower concentrations and show a flatter overall distribution of data compared to monitors located closer to traffic.
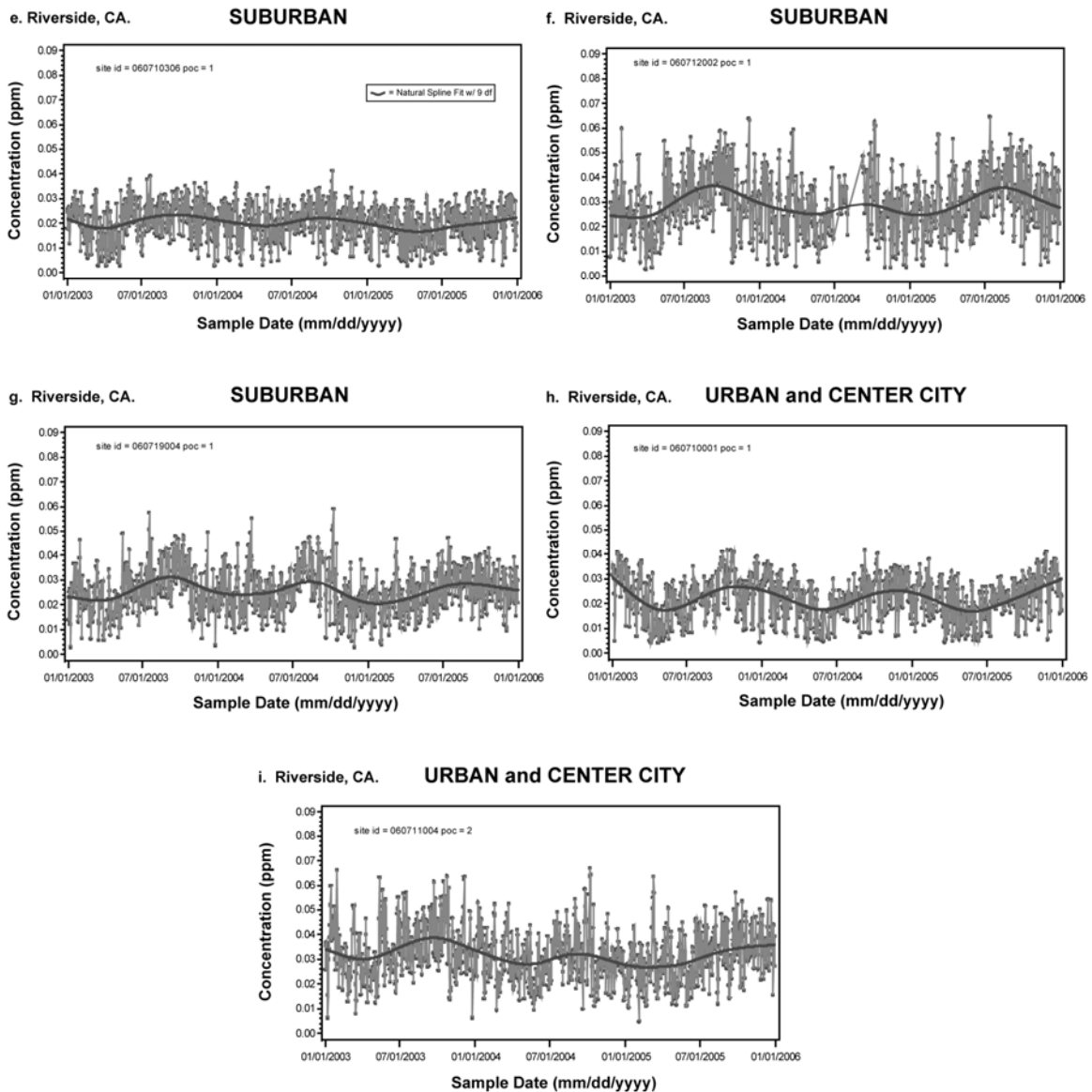
Source: U.S. EPA (2006a)

Figure 2-81. Time series of 24-h average NO$_2$ concentrations at individual monitoring sites in Riverside, CA from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).
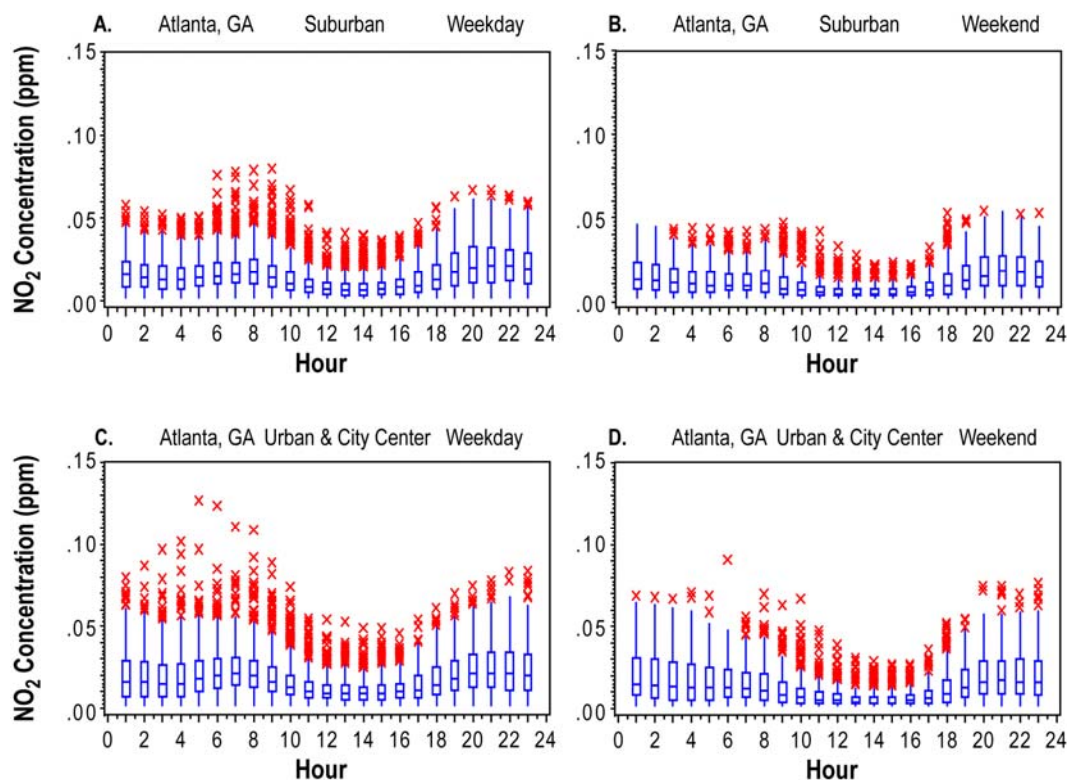
Figure 2-82.   Mean hourly NO$_2$ concentrations on weekdays and weekends measured at two sites in Atlanta, GA. (A) and (B) refer to a suburban site, and (C) and (D) refer to a site classified as urban and city center.

2.9.5.2. NO$_Y$ and NO$_Z$

Data for individual NO$_Y$ species are much less abundant than for NO$_X$ or for total NO$_Y$. Data for several individual NO$_Y$ species are collected typically only as part of research field studies, like SOS, Texas Air Quality Study, and others. As a result, this information is not available for a large number of areas in the U.S.

PANs

At warm temperatures, the concentration of PAN forms a photochemical steady state with its radical precursors on a timescale of roughly 30 min. This steady-state value increases with the ambient concentration of O$_3$ (Sillman et al., 1990). O$_3$ and PAN may show different seasonal cycles because they are affected differently by temperature. Ambient O$_3$ increases with temperature, driven in part by the photochemistry of PAN. The atmospheric τ of PAN decreases rapidly with increasing temperature due to thermal decomposition. Based on the above, the ratio of O$_3$ to PAN is expected to show seasonal changes, with highest ratios in summer, although there is no evidence from measurements. Measured ambient concentrations show a strong nonlinear association between PAN and O$_3$ (Pippin et al., 2001; Roberts et al., 1998) (Figure 2-83). Moreover, uncertainty in the relationship between O$_3$ and PAN grows as the level of PAN increases.
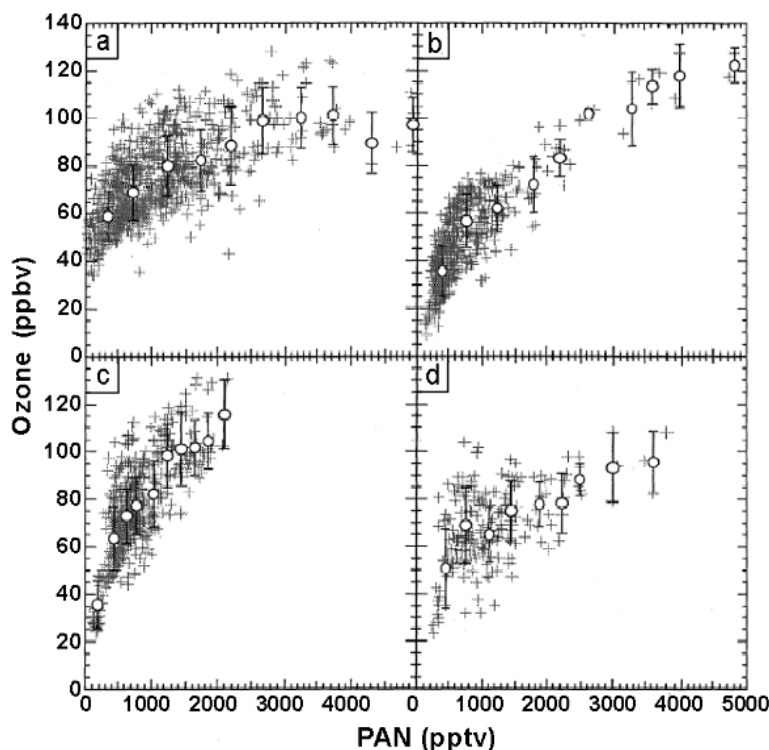
Figure 2-83.   Measured O$_3$ (ppb by volume) versus PAN (ppt by volume) in Tennessee, including (a) aircraft measurements, and (b, c, and d) suburban sites near Nashville.

Measurements and models show that PANs in the U.S. includes major contributions from both anthropogenic and biogenic VOC precursors (Horowitz et al., 1998; Roberts et al., 1998). Measurements in Nashville during the 1999 summertime SOS showed PPN and MPAN amounting to 14% and 25% of PANs, respectively (Roberts et al., 2002). Measurements during the TexAQS 2000 study in Houston indicated PAN concentrations of up to 6.5 ppb (Roberts et al., 2003). PAN measurements in southern California during the SCOS97–NARSTO study indicated peak concentrations of 5–10 ppb, which can be contrasted to values of 60–70 ppb measured in 1960 (Grosjean, 2003). Vertical profiles measured from aircraft over the U.S. and off the Pacific coasts typically show PAN concentrations above the boundary layer of only a few hundred ppt, although there have been significant enhancements associated with long-range transport of pollution plumes from Asia (Kotchenruther et al., 2001; Roberts et al., 2004).

Observed ratios of PAN to NO$_2$ as a function of NO$_X$ at a site at Silwood Park, Ascot, Berkshire, UK are shown in Figure 2-84 (U.K AQEG, 2004). As can be seen there is a very strong inverse relation between the ratio and the NO$_X$ concentration, indicating photochemical oxidation of NO$_X$ has occurred in aged air masses and that PAN can make a significant contribution to measurements of NO$_2$ especially at low levels of NO$_2$. It should be noted that these ratios will likely differ from those found in the U.S. because of differences in the composition of precursor emissions, the higher solar zenith angles found in the UK compared to the U.S., and different climactic conditions. Nevertheless, these results indicate the potential importance of interference from these compounds in measurements of NO$_2$.
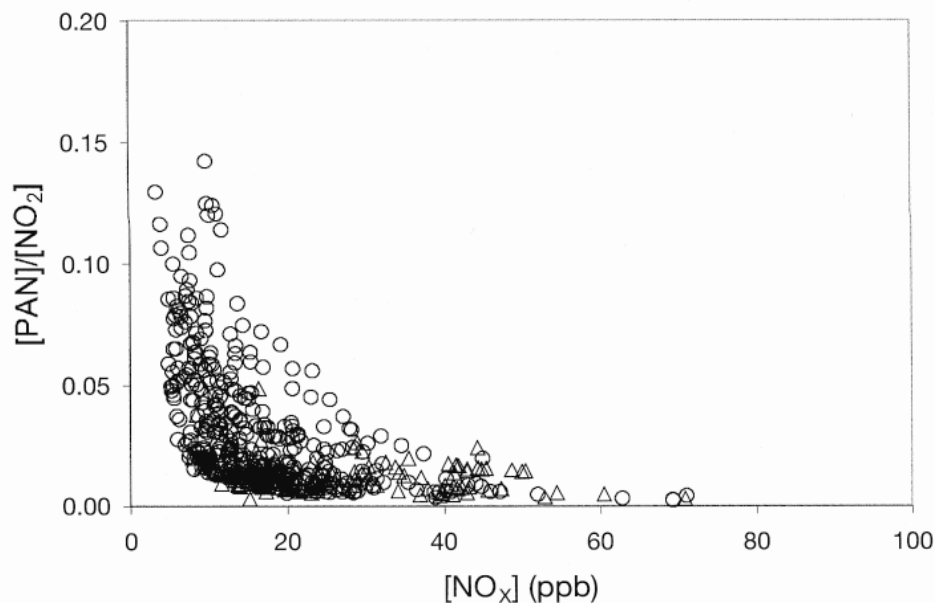
Figure 2-84. Ratios of PAN to NO_2 observed at Silwood Park, Ascot, Berkshire, U.K. from July 24 to August 12, 1999. Each data point represents a measurement averaged over 30 min.

HNO_2

Measurements of HNO_2 in urban areas are extremely limited; however, data from Stutz et al. (2004) and Wang and Lu (2006) indicate that levels of HNO_2 are <1 ppb even under heavily polluted conditions, with the highest levels found during the night and just after dawn and the lowest values found in the afternoon. However, data collected in the U.K. (Lammel and Cape, 1996; U.K. AQEG, 2004) and in the U.S. (Kirchstetter and Harley, 1996) indicate that HNO_2-to-NO_X ratios could be of the order of ~5% in motor vehicle emissions. These results indicate that HNO_2 levels in traffic could be comparable to those of NO_2. Several field studies conducted at ground level (Hayden et al., 2003, near Boulder, CO) and aircraft flights (Singh et al., 2007, over eastern North America), have found much higher NO_Z concentrations than NO_X concentrations in relatively unpolluted rural air, some of which could be attributed to PAN.

The ratio of HNO_2 to NO_2 as a function of NO_X measured at a curbside site in a street canyon in London, UK is shown in Figure 2-85, where HNO_2 is labeled HONO. The ratio is highly variable, ranging from about 0.01 to 0.1, with a mean ~0.05. As NO_2 constitutes several percent of motor vehicle emissions of NO_X, the above implies that emissions of HNO_2 represent a few tenths of a percent of mobile NO_X emissions. A similar range of ratios has been observed at other urban sites in the United Kingdom (Lammel and Cape, 1996).
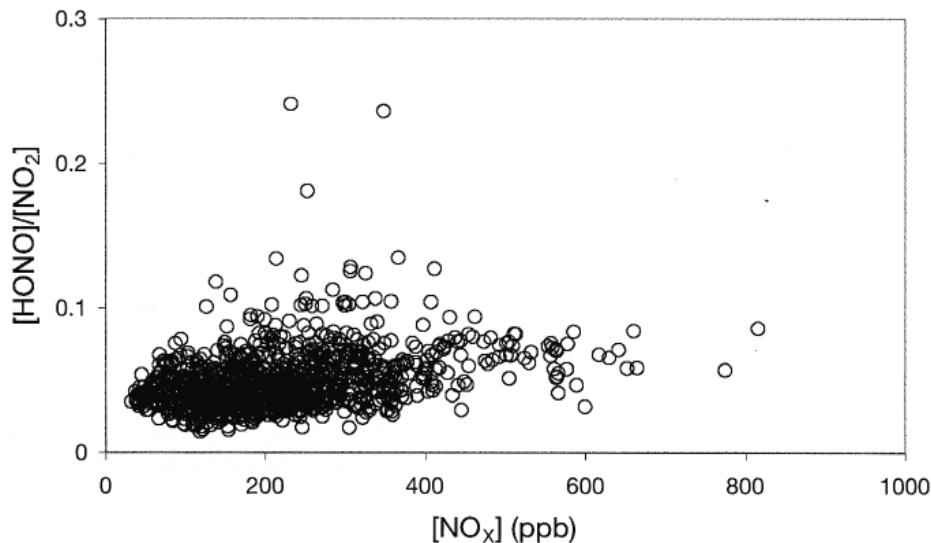
Figure 2-85.   Ratios of HNO$_2$ to NO$_2$ observed in a street canyon (Marylebone Road) in London, U.K. from 11 a.m. to midnight during October 1999. Data points reflect 15–min average concentrations of HONO and NO$_2$.

HNO$_3$ and NO$_3^-$

Data for concentrations of HNO$_3$ and NO$_3^-$ in urban areas in the U.S. are sparse. The most geospatially intensive set of data for any HNO$_3$ were taken as part of the Children's Health Study for which gas-phase HNO$_3$ was measured at 12 sites in southern California from 1994 through 2001 (Alcorn and Lurmann, 2004). Two week average concentrations ranged from <1 ppb to >10 ppb, with the highest HNO$_3$ concentrations and highest ratio of HNO$_3$ to NO$_2$, ~0.2, was found downwind from central Los Angeles in the San Bernardino area during summer, as one would expect for this more oxidized N product.

HNO$_3$ data have also been reported from the SEARCH network of four pairs (eight total sites) of urban and rural sites in the southeastern U.S using increasingly sophisticated methods since 1998; see Zhang et al. (2006). Concentrations of HNO$_3$ in this area have ranged from <1 ppb to >10 ppb.

Maps of ambient concentrations from CASTNet data for rural and remote areas are available below. The CASTNet ambient concentration maps were produced with ArcInfo using an inverse distance weighting (IDW) interpolation technique. Using IDW, the surface is most influenced by the nearest point values and less so by more distant points. CASTNet sites within 400 km of each grid point were used in this calculation. As noted above, thin data coverage complicates interpretation of these maps and renders them most useful as heuristic guides to large areas of possible differences. Strict quantitative values should not be imputed to areas away from the measurement sites.

Ranges of years in the chart represent 3 year averages. For example, 2004–2006 is the average concentration of 2004, 2005 and 2006, as calculated from gridded output for each of the years. The three annual grids from the 3 year period were averaged to derive the mean concentration of the 3 year period. Only sites meeting completeness criteria for at least two of the three years of the averaging period were included.

Figure 2-86 shows annual average concentrations for gas-phase HNO$_3$ from CASTNet for the years 2004 through 2006. Because HNO$_3$ is produced mostly as a secondary product from emitted NO, the regions of higher concentrations HNO$_3$ are geographically similar to those of high concentration NO and NO$_2$: the northeast corridor and southern California.
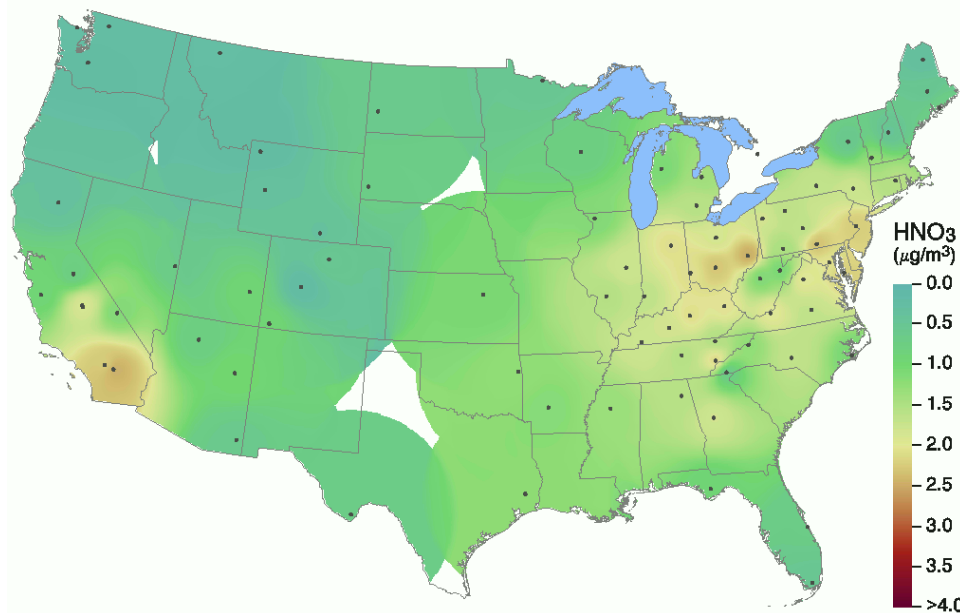
Figure 2-86.   Annual average gas-phase HNO_3 concentrations, 2004–2006. White areas on the map are areas where monitoring sites are absent and no information is available.

Because they have the same precursor reactants in NO and NO_2, elevated O_3 concentrations are often associated with elevated HNO_3 concentrations. However, HNO_3 can be produced in significant quantities in winter, even when O_3 concentrations are low. The ratio between O_3 and HNO_3 also shows great variation in air pollution events, with NO_X-saturated environments having much lower ratios of O_3 to HNO_3 (Ryerson et al., 2001). pNO_3 is formed primarily by combining NO_3 supplied by HNO_3 and NH_3 and may be limited by the availability of either reactant. pNO_3 is expected to correlate loosely with O_3, whereas NH_3 is not expected to correlate with O_3.

Thus, annual average pNO_3 can account for several ppb of NO_Y, with higher values in the West. There is strong seasonal variation, which is especially pronounced in western areas where there is extensive wood burning in the winter resulting in a larger fractional contribution of local sources. Areas in the East where there are topographic barriers might be expected to show higher fractional contributions from local sources than other eastern areas that are influenced by regionally dispersed sources. Figure 2-87 shows a map of annual average NO_3^- concentrations in the years 2004 to 2006 produced from CASTNet measurements of ambient concentrations. This maps indicates at least qualitatively that maximum NO_3^- concentrations are found in areas of maximum NO and NO_2 emissions.
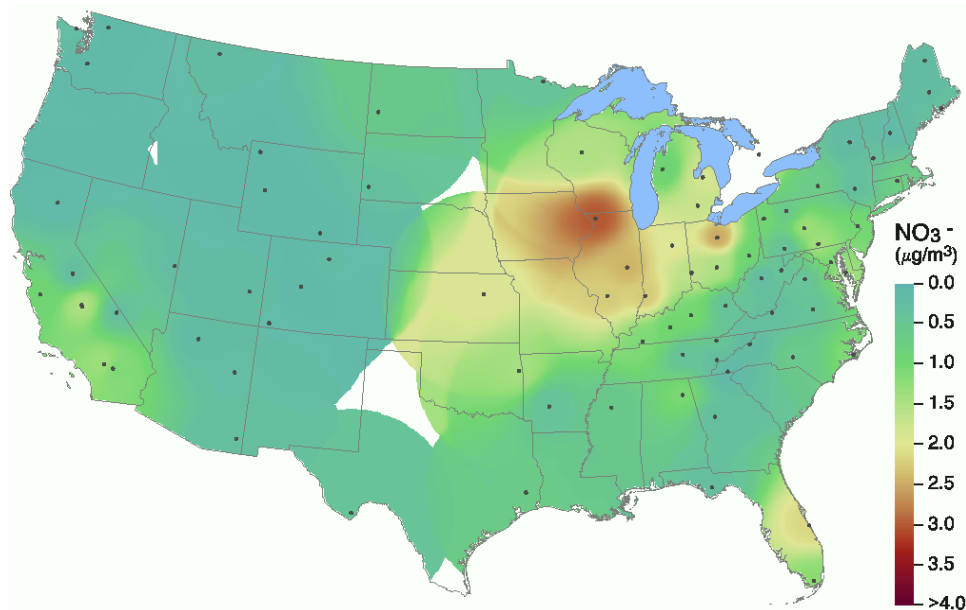
Figure 2-87. Annual average gas-phase NO₃ concentrations, 2004–2006. White areas on the map are areas where monitoring sites are absent and no information is available.

2.9.5.3. Nitro-PAHs

Nitro-PAHs are widespread and found even in high altitude, relatively unpolluted environments (Schauer et al., 2004). However, there are differences in composition and concentration profiles both within and between monitoring sites (rural vs. urban) as well as between and within urban areas (Albinet et al., 2006; Naumova et al., 2003; Söderström et al., 2005), with some differences in relative abundances of nitro- and oxo-PAHs also reported. Source attribution has remained largely qualitative with respect to concentrations or mutagenicity (Eide et al., 2002). The spatial and temporal concentration pattern for the nitro-PAHs may differ from that of the parent compounds because concentrations of the latter are dominated by direct emission from local combustion sources. These emissions results in higher concentrations during atmospheric conditions more typical of wintertime when mixing heights tend to be low. The concentrations of secondary nitro-PAHs are elevated under conditions that favor hydroxyl and NO_3 radical formation, i.e., during conditions more typical of summertime, and are enhanced downwind of areas of high emission density of parent PAHs and show diurnal variation (Fraser et al., 1998; Kameda et al., 2004; Reisen and Arey, 2005). Nitro-napthalene concentrations in Los Angeles, CA varied between about 0.15 to almost 0.30 ng/m^3 compared to 760 to 1500 ng/m^3 for napthalene. Corresponding values for Riverside, CA were 0.012 to more than 0.30 ng/m^3 for nitro-napthalene and 100 to 500 ng/m^3 for napthalene. Nitro-pyrene concentrations in LA varied between approximately 0.020 to 0.060 ng/m^3 compared to 3.3 to 6.9 ng/m^3 pyrene, whereas corresponding values for Riverside were 0.012 to 0.025 ng/m^3 and 0.9 to 2.7 ng/m^3.

2.9.5.4. Ammonia

Section 2.7.1.5 above established that a successful real-time continuous monitoring technique for ambient NH_3 has not been identified; and, of equal importance, Section 2.4 above described the severely limiting unknowns related to NH_3 emissions on national and local scales. With these important

information gaps, estimates of NH_3 concentrations at any scale for the U.S. must be constructed and interpreted with caution. It is possible, for example, to rank NH_3 concentrations by land use types from the few special field campaigns where it was measured as Walker et al. (2004) did for agricultural, non-agricultural, and urban types; see Table 2-19. This table shows the enormous range in NH_3 concentrations by season and land use type, from a low of 0.02 µg/m^3 in summer over alpine tundra on Niwot Ridge, CO, (Rattray and Sievering, 2001) to 11.0 µg/m^3 over fertilized lands in Wekerom in the central Netherlands (Buijsman et al., 1998).

Table 2-19.   Ambient NH$_3$ concentrations summarized by study.

Concentration (µgm³)	Land Use	Comment
3.0	Agricultural	Low NH$_3$ emissions
11.0	Agricultural	Moderate NH$_3$ emissions [a]
10.48	Agricultural	Fall [b]
0.65-1.2	Agricultural	Spring [c]
0.26	Agricultural	Winter [c]
0.34	Non-agricultural	High elevation, summer and fall [d]
0.02	Non-agricultural	High elevation, summer [e]
0.62-1.47	Non-agricultural	High elevation, summer [f]
0.29	Non-agricultural	High elevation, summer [g]
0.22	Non-agricultural	Coastal, summer [g]
0.21	Non-agricultural	Forest, summer [g]
0.16	Non-agricultural	Forest [h]
0.21	Non-agricultural	Wetland, summer [g]
0.23	Non-agricultural	Wetland, summer [g]
0.63	Non-agricultural	Desert, summer [g]
4.75	Non-agricultural	Grassland, summer [g]
0.38-1.49	Urban	Pittsburgh, PA; summer [i]
0.63-0.72	Urban	Research Triangle Park, NC; fall [j]
1.18	Urban	Vinton, VA; summer [k]

[a] Buijsman et al. (1998).
[b] McCulloch et al. (1998).
[c] Pryor et al. (2001).
[d] Tarnay et al. (2001).
[e] Rattray and Sievering (2001)
[f] Aneja et al. (2000).
[g] Langford et al. (1992).
[h] Lefer et al. (1999)
[i] McCurdy et al. (1999).
[j] Sickles et al. (1990).
[k] Leaderer et al. (1999)

A preliminary draft U.S. national-scale, county-level NH_3 map was created by the U.S. EPA using emissions data from the widely-used Carnegie Mellon University (CMU) NH_3 emissions model, version 3. See Pinder et al., (2007) for a description of the model and application information. The map included an empirical relationship between emissions and ambient concentration derived from field measurements over five different land use types in North Carolina, covering the range of expected NH_3

emissions densities. In the CMU emissions model used for this analysis, fertilized soils were included but NH_3 emissions from natural (non-fertilized soils) were not because of overwhelmingly large uncertainties in their emissions factors. Emissions from mobile sources are included in this analysis, although uncertainties in those values are also large; see Section 2.4. above. Emissions from a small number of counties having very low emissions rates were set to missing because their extremely low values invalidated determination of densities in those counties.

The CMU-derived county-level NH_3 emissions map is shown in Figure 2-88. Differences in the techniques for estimating NH_3 emissions and the very large uncertainties in NH_3 emissions factors and totals complicate direct, fine-scale comparisons to other NH_3 emissions maps. However, both the magnitude and areal extent of Walker's emissions map compare very favorably to the U.S. EPA NEI database NH_3 emissions map shown in Section 2.4 above.

Ammonia Emission Density
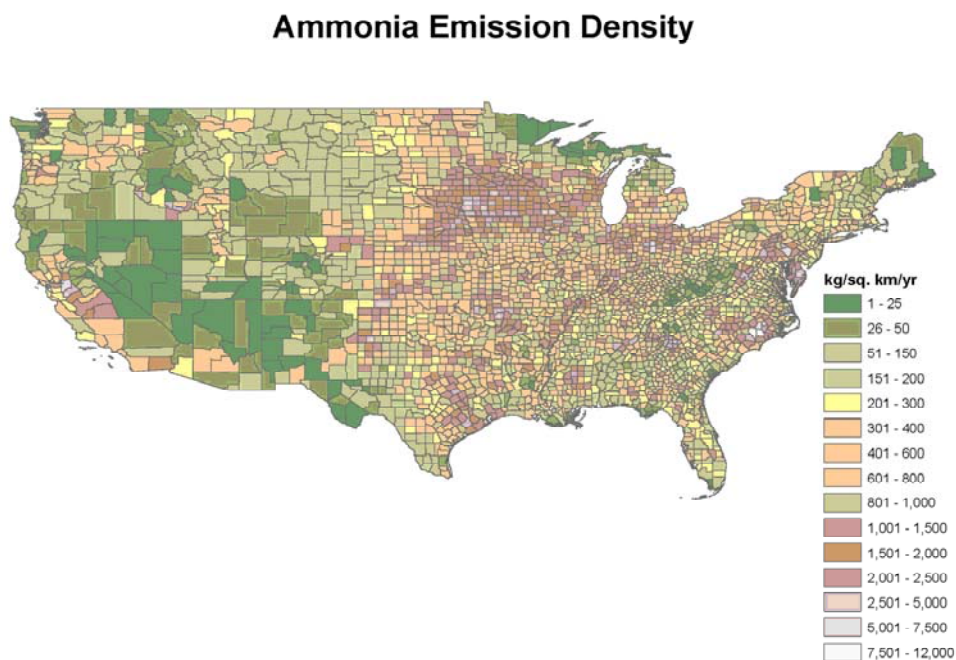
Source: J. Walker, USEPA/ORD/NRMRL

Figure 2-88   County-scale NH_3 emissions densities from the CMU inventory model.

The empirical relationship between NH_3 emissions and ambient NH_3 concentration is shown in Figure 2-89.

$$y = 0.63 + 5.562e\text{-}4x$$
$$R^2 = 0.99$$
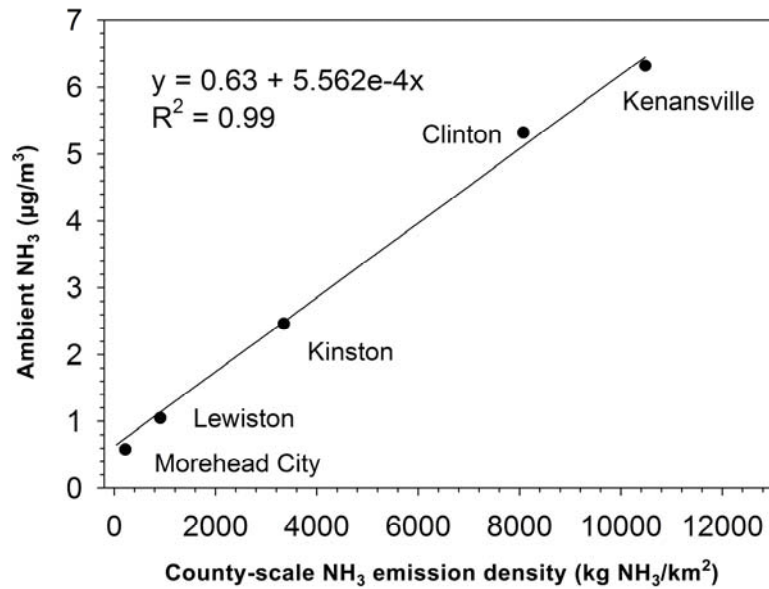
Source : J Walker, U.S. EPA/ORD/NRMRL

Figure 2-89. Ambient NH_3 concentration as a function of county scale NH_3 emissions.

The map of estimated ambient NH_3 concentration from the CMU emissions model and empirical relationship illustrated above is shown in Figure 2-90.

Ambient Ammonia Concentration
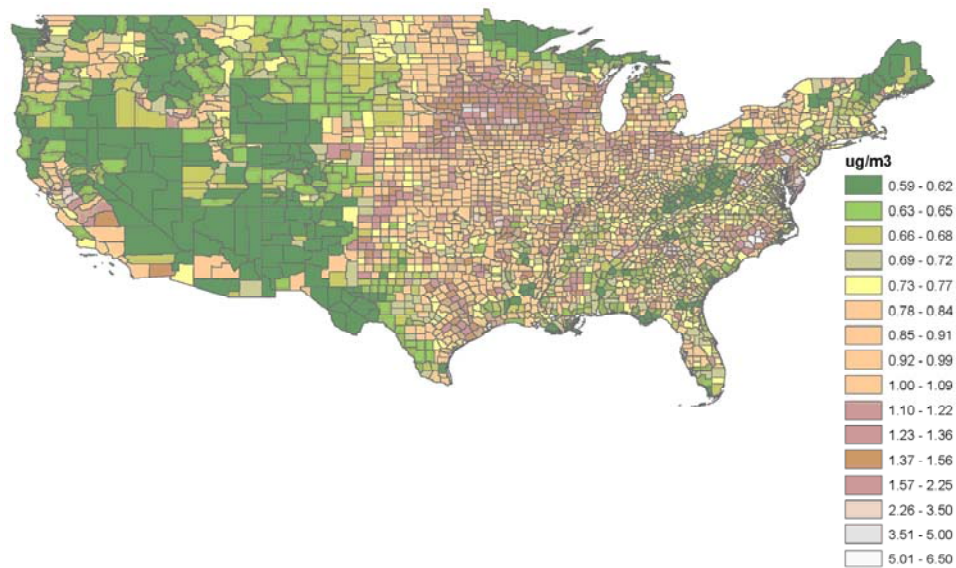
Source: J. Walker, USEPA/ORD/NRMRL

Figure 2-90. Estimated county-scale ambient NH_3 concentrations.

2.9.5.5. NH_4NO_3

The IMPROVE network is the premier source of data about the spatial and temporal patterns of rural and remote pNO_3 in the U.S. Data about urban pNO_3 and other particles comes primarily from the CSN, which includes STN and others (Jayanty, 2003). Although IMPROVE began and still functions primarily to characterize visibility impairments in protected areas, the network has been expanded several times since its inception to include coverage of remote areas in central and western states of the U.S. to better understand regional components of particulate pollution. Except where noted, information in this section was derived from the IMPROVE IV Report (DeBell, 2006) with data displays created with data and tools available at http://vista.cira.colostate.edu/views/. Much of these data and conclusions are also to appear in Pitchford et al. (2008).

IMPROVE monitors the major fine particle components pSO_4, pNO_3, crustal EC and OC, and coarse mass concentration computed as the concentration difference PM_{10} minus $PM_{2.5}$. An implicit assumption is that most of the pNO_3 is present as NH_4NO_3 in the $PM_{2.5}$ size range. One component of the Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study, conducted at Big Bend National Park, TX, in the summer and fall of 1999, entailed use of detailed measurements of aerosol chemical composition, size distribution, water growth, and optical properties to characterize the aerosol and assess the relationships among aerosol physical, chemical, and optical properties (Schichtel, et al., 2004). Fine pNO_3 accounted for <5% of the mass concentration in these samples and was present mostly as $NaNO_3$. Approximately 67% of the pNO_3, again inferred to be $NaNO_3$, was found in the coarse mode where it comprised ~8% of the mass concentration.

However, depending on the acidity of the particles, which in turn depends strongly on their SO_4^{2-} and NH_4^+ contents, higher pNO_3 concentrations could be found in coarse mode particles ($PM_{10-2.5}$) than in $PM_{2.5}$ samples. The average pNO_3 content of $PM_{2.5}$ and PM_{10} is typically ~1% in the eastern U.S. and 15.7% and 4.5%, respectively, in the western U.S. (U.S. EPA, 1996a). These values suggest that most of the pNO_3 was in the $PM_{2.5}$ size fraction in the studies conducted in the western U.S., but pNO_3 in the studies in the eastern U.S. was mainly in the $PM_{10-2.5}$ size fraction.

A year-long special study of PM_{10} speciation was conducted at nine IMPROVE remote area monitoring sites during 2003 and 2004 to provide additional information about the geographic and seasonal variations in coarse particle composition; see Malm et al. (2007). The same sampling and analytical procedures were used for the PM_{10} samples as are routinely used on the IMPROVE $PM_{2.5}$ samples. IMPROVE PM_{10} speciation study did not include NH_4^+ analysis, so pNO_3 was assumed again to be NH_4NO_3. As expected, crustal minerals were the largest contributors to PM_{10} mass overall at ~60%, and organic particles contributed ~25%. On average, NO_3^- was the third largest contributor to PM_{10} mass at ~8% on average for the nine monitoring sites. The sites with the highest coarse pNO_3 concentrations were the two in California, San Gorgonio, 0.74 μg/m^3 and Sequoia, 0.69 μg/m^3, where $PM_{2.5}$ pNO_3 were also high on average, 2.66 μg/m^3 and 2.14 μg/m^3 respectively. Brigantine, a coastal site in New Jersey had the highest fraction of total PM_{10} pNO_3 at 36%. The authors speculated that Brigantine's pNO_3 was likely $NaNO_3$, the result of HNO_3 reactions with sea-salt NaCl. The nine-site average fraction of total coarse pNO_3 was 26%.

Figure 2-91 shows maps of remote NH_4NO_3 for two years selected to demonstrate the additional information available after expansion of IMPROVE into the central U.S. The locations of monitoring sites supplying the data shown as color contours are shown as dot on the maps. As above, concentration contour maps carry the caution that their isolines are provided merely to guide visual similarities among sites reporting similar values, and should not be read to suggest any quantitative spatial interpolation where sites do not exist. These plots, showing the so-called Midwest pNO_3 bulge illustrate why that caution is always warranted.
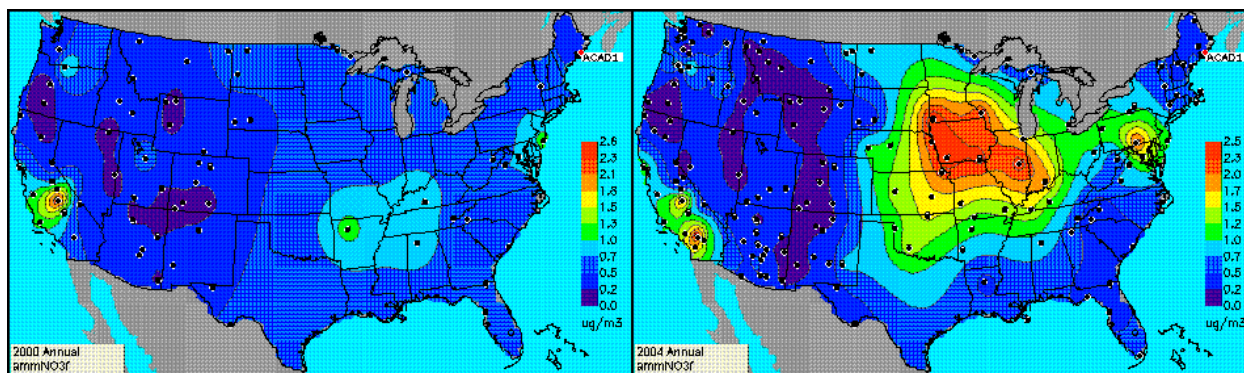
Figure 2-91.   IMPROVE network measured annual averaged NH$_4$NO$_3$ concentration for 2000 (left) and for 2004 (right).

Before 2001, no IMPROVE or any other regular remote-area aerosol speciation monitoring sites existed in the central states between northern Minnesota and Michigan to the north, and Arkansas and Kentucky to the south. The lack of monitoring over such a large region in the center of the country hid the largest regional distribution of particulate matter dominated by NH$_4$NO$_3$, previously thought to be a phenomenon isolated to California. However, with fewer than 6 years of complete data for this region, insufficient information exists to test for long-term trends.

Combining IMPROVE and CSN data makes possible comparison of urban pNO$_3$ to surrounding remote-area regional values. These are shown as paired color contour maps for IMPROVE and IMPROVE plus CSN in Figure 2-92. U.S. EPA (2004) used the pairing of IMPROVE and CSN monitoring sites at 13 selected areas to separate local and regional contributions to the major contributors of PM$_{2.5}$, as shown for pNO$_3$ in Figure 2-93.
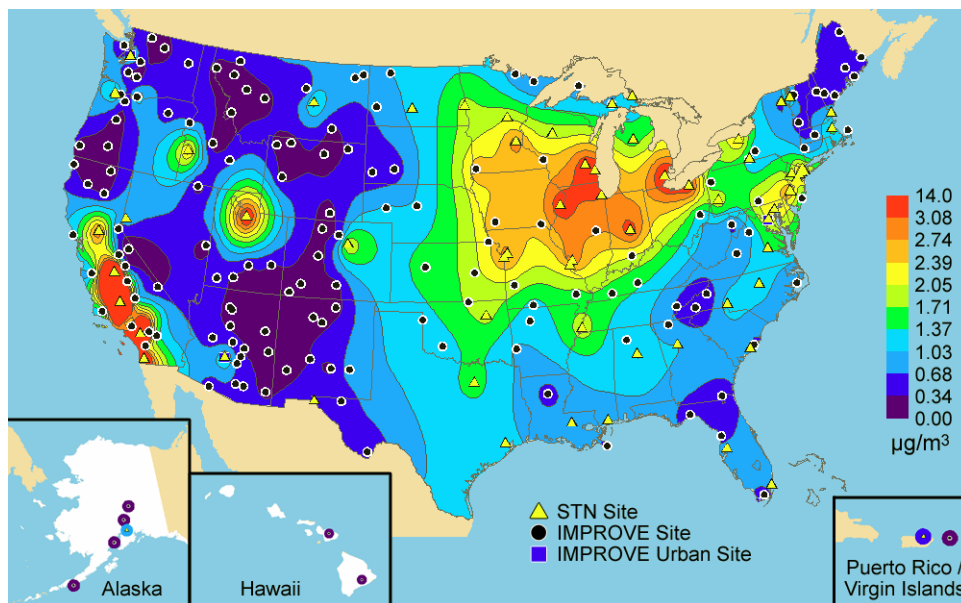
Figure 2-92.   IMPROVE and CSN (labeled STN) monitored mean NH$_4$NO$_3$ concentrations for 2000 through 2004.

Nitrates
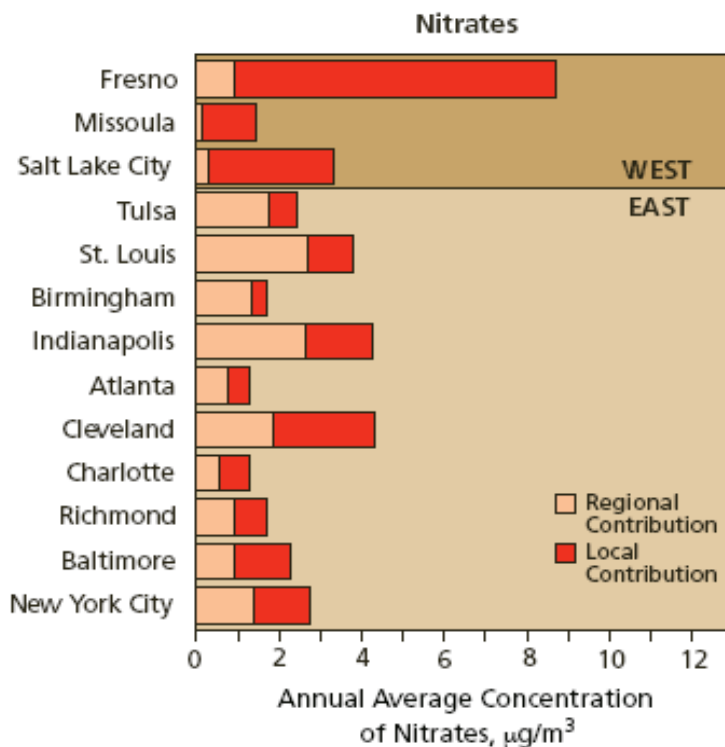
Source: U.S. EPA (2004).

Figure 2-93. Regional and local contributions to annual average PM$_{2.5}$ by pNO$_3$ for select urban areas based on paired IMPROVE and CSN monitoring sites.

Urban pNO$_3$ concentrations in western states are, in general, more than a factor of 2 greater than the remote-area regional concentrations. For the Central Valley of California and Los Angeles areas, the urban excess NH$_4$NO$_3$ exceed regional concentrations by amounts ranging from 2 μg/m^3 to 12 μg/m^3. In the region of the recently identified Midwest pNO$_3$ bulge (see Figures 2-91 and 2-92), the urban concentrations were less than twice the background concentrations for an annual urban excess of about 1 μg/m^3. Northeast and southeast of the Midwest NO$_3$ bulge, annual urban pNO$_3$ were ~1 μg/m^3 or less above the remote-area regional concentrations, with warmer southern locations tending to have smaller concentrations of both regional and urban excess pNO$_3$.

Holland et al. (1999) developed NO$_X$ emissions trends from 1989 to 1995 and compared them to corresponding trends in total NO$_3$ (pNO$_3$ + gas-phase HNO$_3$) for the states in the U.S. between Louisiana and Minnesota and east of that line based on data from 34 rural CASTNet dry deposition monitoring sites. They reported a decrease in total NO$_3$ median values of ~8% associated with a decrease of 5.4% in non-biogenic NO$_X$ emissions. Because of the form of total NO$_3$ assumed in this analysis, it is not possible to determine whether this change is larger for HNO$_3$ or pNO$_3$. For situations with limited gas-phase NH$_3$ or with elevated temperatures, it may be assumed that the trend in total NO$_3$ is principally in HNO$_3$ with no net change in pNO$_3$. Where NH$_3$ concentrations are substantially in excess of those required to neutralize pSO$_4$ and where temperatures are lower, this trend may be assumed to be reversed.

Potential causes of the Midwest pNO$_3$ bulge can be examined through comparison of the pNO$_3$ areal extent to that of NO$_X$ and NH$_3$ emissions. Figure 2-94 shows a map of the annual average pNO$_3$ concentrations (top) with a map of NH$_3$ emissions (bottom). The spatial extent of NH$_3$ emissions in the

Midwest is strikingly similar to that of pNO_3 concentrations, each having regional maxima centered on Iowa. NO and NO_2 emissions are high over a broad region of the country associated with the larger population densities and greater numbers of fossil fueled EGUs to the east of the Midwest pNO_3 bulge. While both NH_3 and HNO_3 are needed to form NH_4NO_3, the maps suggest the Midwest NO_3 bulge is due primarily to the abundance of free NH_3, defined as the amount beyond that required to neutralize the acidic pSO_4. By contrast, the region east of the Midwest NO_3 bulge might be expected to have excess HNO_3 given greater emissions of NO and NO_2, but apparently has a deficiency of free NH_3. The few eastern monitoring sites with locally high pNO_3 (near southern Pennsylvania) are located within a small region of high density animal agricultural sites identified as a high NH_3 emissions region in Figure 2-94. Note that California's South Coast and Central Valley have both high NH_3 and NO and NO_2 emissions, explaining its own high pNO_3 concentrations.
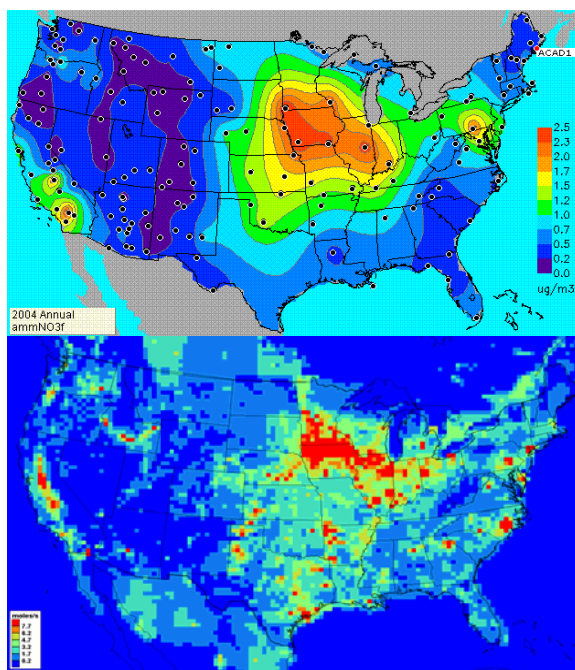
Figure 2-94.   Maps of spatial patterns for average annual pNO$_3$ measurements (top), and for NH$_3$ emissions for April 2002 from the WRAP emissions inventory (bottom).

Importantly, although the Midwest pNO_3 bulge was not apparent before measurements were made in its region, air quality modeling using national-scale emissions data predicted it in 1996 in CMAQ applications for the U.S. EPA Western Regional Air Partnership (http://www.wrapair.org). Figure 2-95 shows the CMAQ-predicted average pNO_3 concentration for the month of January 1996 (left panel) and the model-predicted sensitivities of pNO_3 to a 50% decrease in NH_3 emissions (right panel). Decreases of ~3 $\mu g/m^3$ in the heart of the Midwest NO_3 bulge and in its areal extent were predicted as a result of the NH_3 emissions decrease.
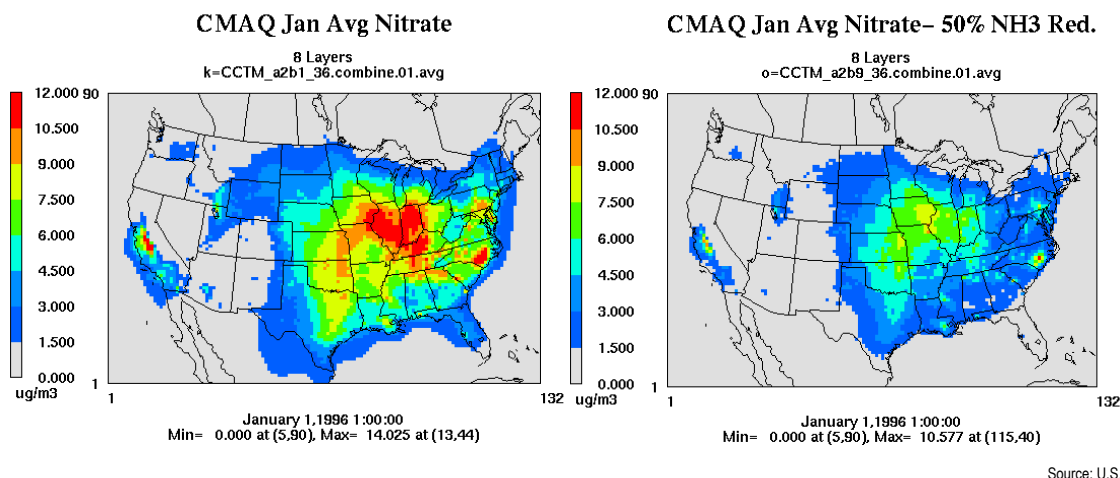
Figure 2-95. CMAQ simulation of January monthly averaged pNO_3 concentration using 1996 emissions (left), and for a 50% decrease in NH_3 emissions (right).
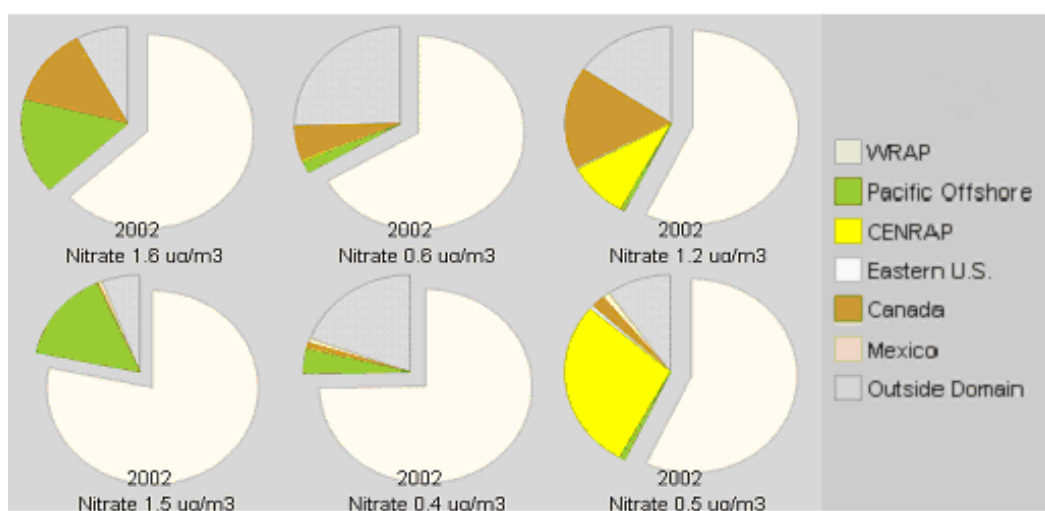
Figure 2-96. Particulate NO_3 source attribution by region using CAMx modeling for six western remote area monitoring sites Top left to right Olympic NP, WA; Yellowstone NP, WY; Badlands NP, SD; bottom left to right San Gorgonio (W), CA; Grand Canyon NP, AZ; and Salt Creek (W), NM. WRAP includes North Dakota, South Dakota, Wyoming, Colorado, New Mexico and all states further west. CENRAP includes all states east of WRAP and west of the Mississippi River including Minnesota. Eastern U.S. includes all states east of CENRAP. The Pacific Offshore extends 300km to the west of California, Oregon, and Washington. Outside Domain refers to the modeling domain, which extend hundreds of kilometers into the Pacific and Atlantic Oceans and from Hudson Bay Canada to just north of Mexico City.

Several example monitoring locations distributed across the northern and southern portions of the eastern U.S. have been selected to illustrate the attribution results from air quality simulation modeling by source region and source type for pNO_3. The modeling for this work was done with the Comprehensive Air Model with extensions (CAMx); see http://camx.com for model code and descriptions. They include Olympic National Park (NP), WA; Yellowstone NP, WY; and Badlands NP, SD across the north, and San

Gorgonio Wilderness (W), CA; Grand Canyon NP, AZ and Salt Creek W, NM across the south. Pie diagrams of pNO_3 attribution results by source region for each of these sites are shown in Figure 2-96. Based on these sites, 25% or less of the pNO_3 in remote areas of the Pacific coastal states is from outside of the U.S. (Pacific Offshore and Outside of the Domain). The Outside of the Domain values are derived by simulating the fate of the boundary condition concentrations, which for the WRAP air quality modeling were obtained using output from the GEOS-CHEM global air quality model (Fiore et al., 2003).

By comparison, pNO_3 at these western sites is much more from domestic regional emission sources, with ~60 to ~80% being from emissions within the WRAP region. For the west coast sites, ~25% of pNO_3 is from a combination of Pacific Offshore emissions (i.e. marine shipping) and Outside Domain regions. Canadian emissions are responsible for ~10 to 30% of pNO_3, but Mexican emissions do not contribute appreciably to pNO_3 for the three southern sites. Motor vehicles are the largest contributing $NO + NO_2$ source category responsible for pNO_3 for these six WRAP sites, with a combination of point, area, and wildfire source categories also contributing from ~10 to 50% of the WRAP regional emissions.

2.9.6. Ambient Concentrations of Relevant Sulfur Compounds

2.9.6.1. SO$_2$ and SO$_4$ Near Urban Areas

SO_2 data collected from the SLAMS and NAMS networks show that the decline in SO_2 emissions from EGUs has improved air quality. There has not been a single monitored exceedance of the SO_2 annual ambient air quality standard in the U.S. since 2000 (U.S. EPA, 2006a). EPA's trends data (www.epa.gov/airtrends) reveal that the national composite average SO_2 annual mean ambient concentration decreased by 48% from 1990 to 2005, with the largest single-year reduction coming in 1994–1995 (U.S. EPA, 2006a).

In 2007, there were ~500 SO_2 monitors reporting values to the U.S. EPA Air Quality System database (AQS). Trace level SO_2 monitoring is currently required at the approximately 75 proposed NCore sites, as noted in CFR 40 Part 58 Appendices C and D. Continued operation of existing SLAMS for SO_2 using FRM or FEM is required until discontinuation is approved by the U.S. EPA Regional Administrator. Where SLAMS SO_2 monitoring is required, at least one of the sites must be a maximum concentration site for that area.

Figures 2-97 through 2-102 illustrate geospatial locations of monitors for SO_2, NO_2, CO, PM_{10}, $PM_{2.5}$, and O_3 in 2005. These locations, sited in several cities in six states, were selected as relevant for SO_2 environmental effects to complement measurements from rural and remote CASTNet sites and to be near large sources of SO_2. For each state, map A of each figure shows locations of each monitor for all six pollutants; map B of each figure shows only the SO_2 monitor locations. Totals for each monitor type are included. These figures demonstrate the important point that not all SO_2 monitors in any Consolidated Metropolitan Statistical Area (CMSA) are co-located with monitors for other pollutants. Two examples are given below.

Table 2-20 lists the totals for all criteria air pollutant monitors (except Pb) in California, as well as the subset of these monitors in San Diego County. At each of the four sites where SO_2 was measured, NO_2, CO, PM_{10}, $PM_{2.5}$, and O_3 were also measured, with the exception of $PM_{2.5}$ at one site (AQS ID 060732007) in Otay Mesa, CA. Table 2-21 lists the totals for all criteria air pollutant monitors (except Pb) in Ohio, as well as the subset of in Cuyahoga County.

In Cuyahoga County, OH, PM_{10} and $PM_{2.5}$ were measured at all four sites where SO_2 was also measured in 2005, but O_3 and CO were not measured at any of those four sites; NO_2 was only measured at one site (AQS ID 39050060) near Cleveland's city center and ~0.5 km from the intersection of Interstate Highways 77 and 90.

Table 2-20.   Number of monitors in California and San Diego County, 2005.

	SO$_2$	NO$_2$	O$_3$	CO	PM$_{10}$	PM$_{2.5}$
California (all)	35	105	176	86	177	97
San Diego County	4	9	10	6	7	7

Table 2-21.   Number of monitors in Ohio and Cuyahoga County, 2005.

	SO$_2$	NO$_2$	O$_3$	CO	PM$_{10}$	PM$_{2.5}$
Ohio (all)	31	4	49	15	49	49
Cuyahoga County	4	2	3	4	6	7

The regional distribution of SO$_2$ and SO$_4^{2-}$ concentrations through the CONUS is shown in Table 2-22. As for the country on the whole, in and around most individual CMSAs, the trends are also toward lower SO$_2$ levels. Table 2-23 shows that many annual and even 1-h mean concentrations for the years 2003 through 2005 were consistently at or below the operating LOD of ~3 ppb for the standard sensitivity UV fluorescence SO$_2$ monitors deployed in the regulatory networks. The aggregate mean value over all 3 years and all monitoring sites in and around the CMSAs was just above the LOD at ~4 ppb, and was identical to the 1-h and 24-h means.

The maximum 1-h concentration observed at some sites in and around some CMSAs exceeded the mean by a large margin, with maximum 1-h values of >600 ppb. However, the 50th percentile maximum value outside CMSAs, 5 ppb, was only slightly greater than the 1-h, 24-h, and annual mean value, 4 ppb. The 50th percentile maximum value inside CMSAs, 7 ppb, was 75% greater than these longer-term averages, reflecting heterogeneity in source strength and location. In addition, even with 1-h max values of >600 ppb, the maximum annualized mean value for all CMSAs was still <16 ppb, which is below the current annual primary SO$_2$ NAAQS.

The strong west-to-east increasing gradient in SO$_2$ emissions described above is well replicated in the observed concentrations in individual CMSAs. For example, Table 2-24 shows the mean annual concentrations from 2003–2005 for the 12 CMSAs with four or more SO$_2$ regulatory monitors. Values ranged from a reported low of ~1 ppb in Riverside, CA, and San Francisco, CA, to a high of ~12 ppb in Pittsburgh, PA, and Steubenville, OH, in the highest SO$_2$ source region.
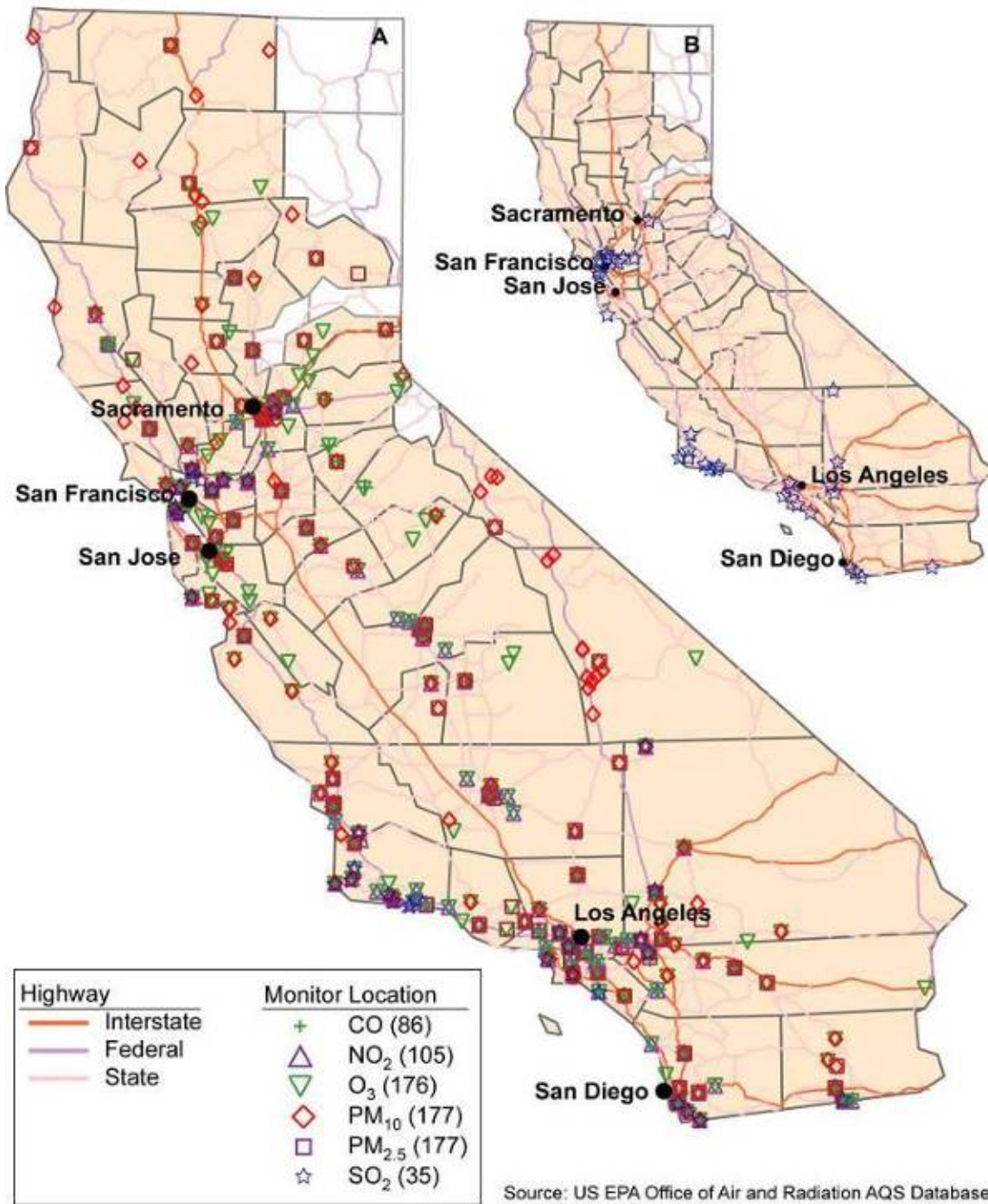
Figure 2-97. Criteria pollutant monitor locations (A) and SO₂ monitor locations (B), California, 2005. Shaded counties have at least one monitor. Map A shows locations of each monitor for all six criteria pollutants. Map B shows only the SO₂ monitor locations.
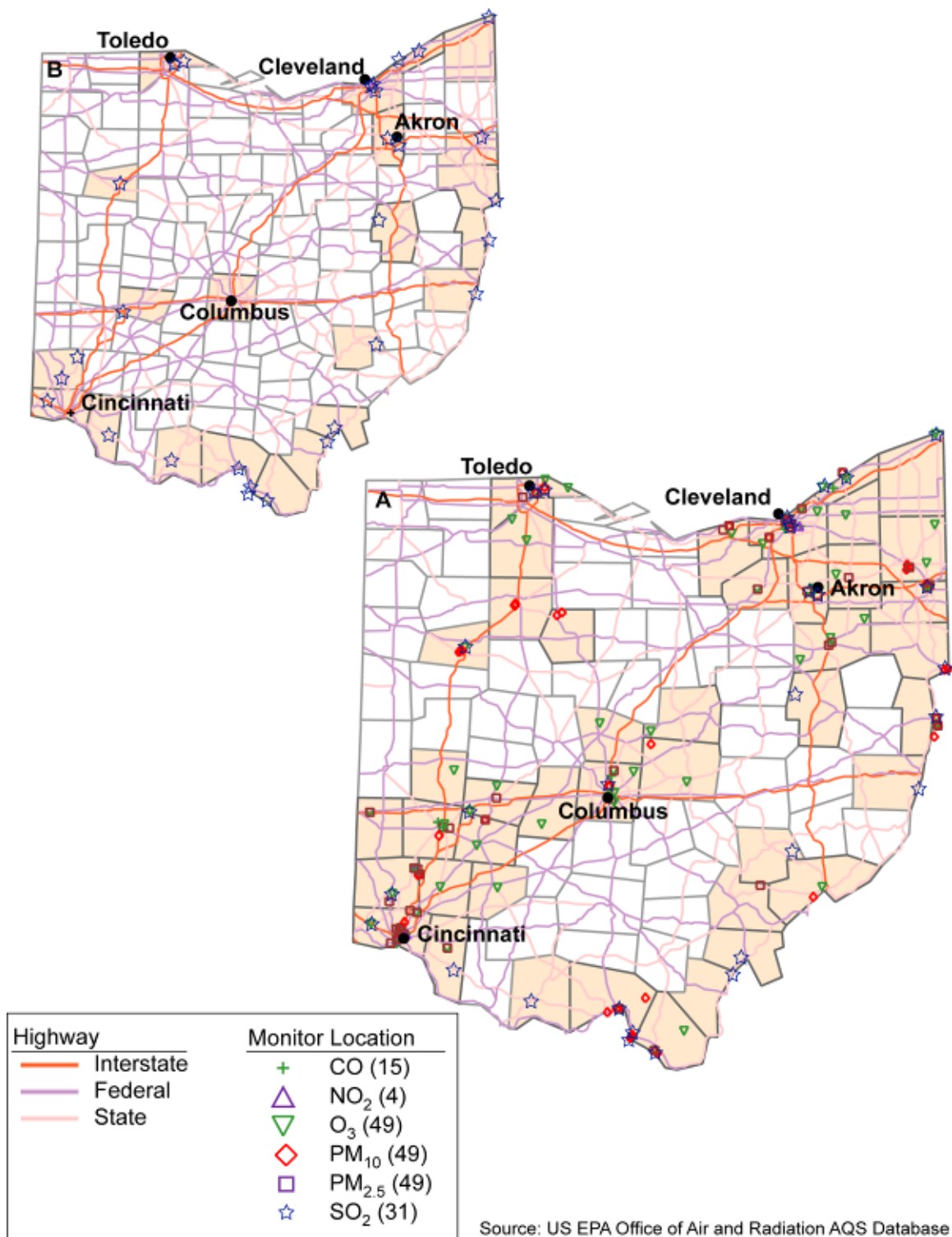
Figure 2-98. Criteria pollutant monitor locations (A) and SO₂ monitor locations (B), Ohio, 2005. Shaded counties have at least one monitor. Map A shows locations of each monitor for all six criteria pollutants. Map B shows only the SO₂ monitor locations.

Legend:

Highway
- Interstate
- Federal
- State

Monitor Location
- + CO (15)
- △ NO₂ (4)
- ▽ O₃ (49)
- ◇ PM₁₀ (49)
- □ PM₂.₅ (49)
- ☆ SO₂ (31)

Source: US EPA Office of Air and Radiation AQS Database
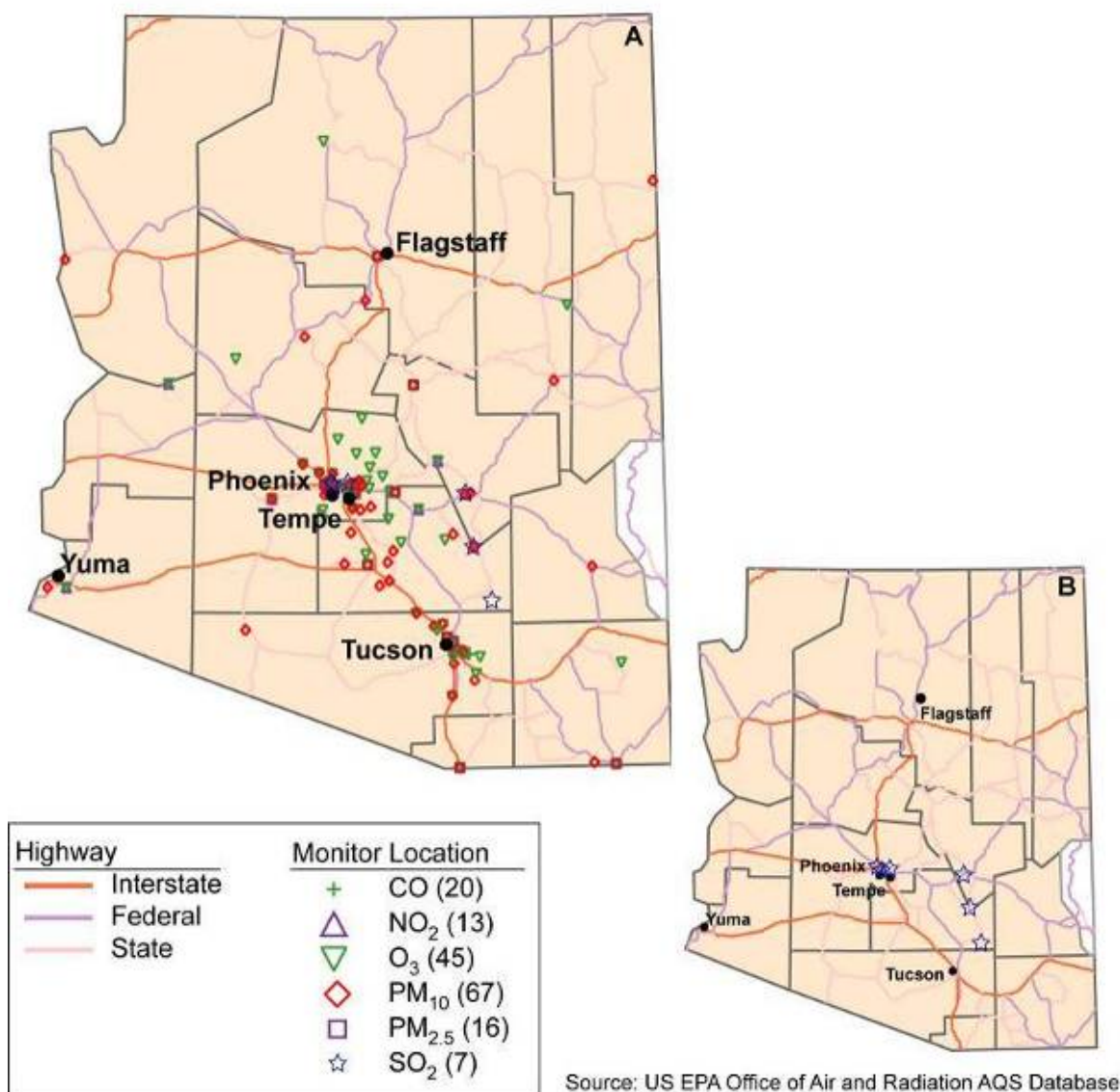
Figure 2-99. Criteria pollutant monitor locations (A) and SO$_2$ monitor locations (B), Arizona, 2005. Shaded counties have at least one monitor. Map A shows locations of each monitor for all six criteria pollutants. Map B shows only the SO$_2$ monitor locations.

Highway
— Interstate
— Federal
— State

Monitor Location
+ CO (25)
△ NO$_2$ (29)
▽ O$_3$ (47)
◇ PM$_{10}$ (46)
□ PM$_{2.5}$ (49)
☆ SO$_2$ (42)

Source: US EPA Office of Air and Radiation AQS Database
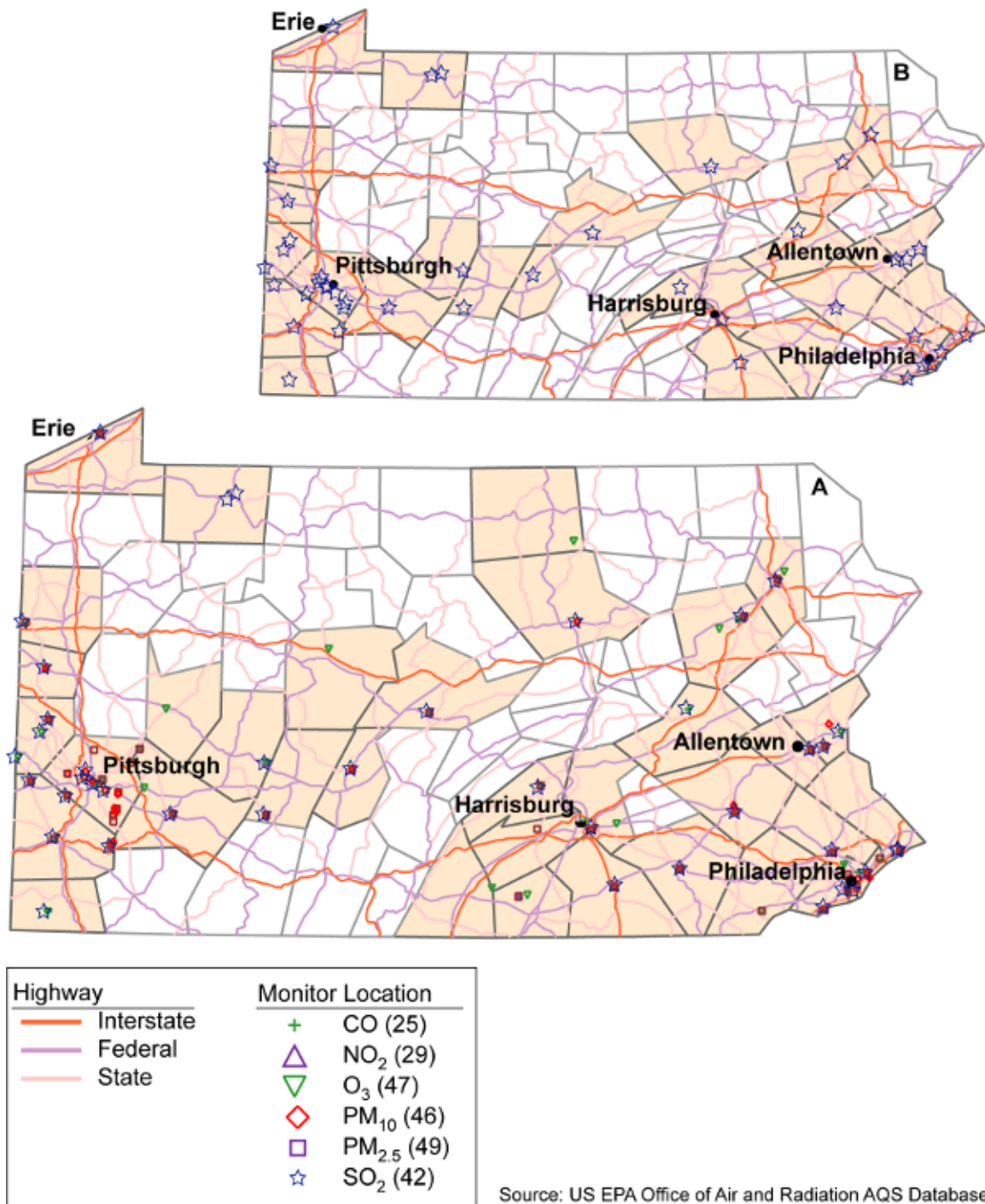
Figure 2-100. Criteria pollutant monitor locations (A) and SO$_2$ monitor locations (B), Pennsylvania, 2005. Shaded counties have at least one monitor. Map A shows locations of each monitor for all six criteria pollutants. Map B shows only the SO$_2$ monitor locations.
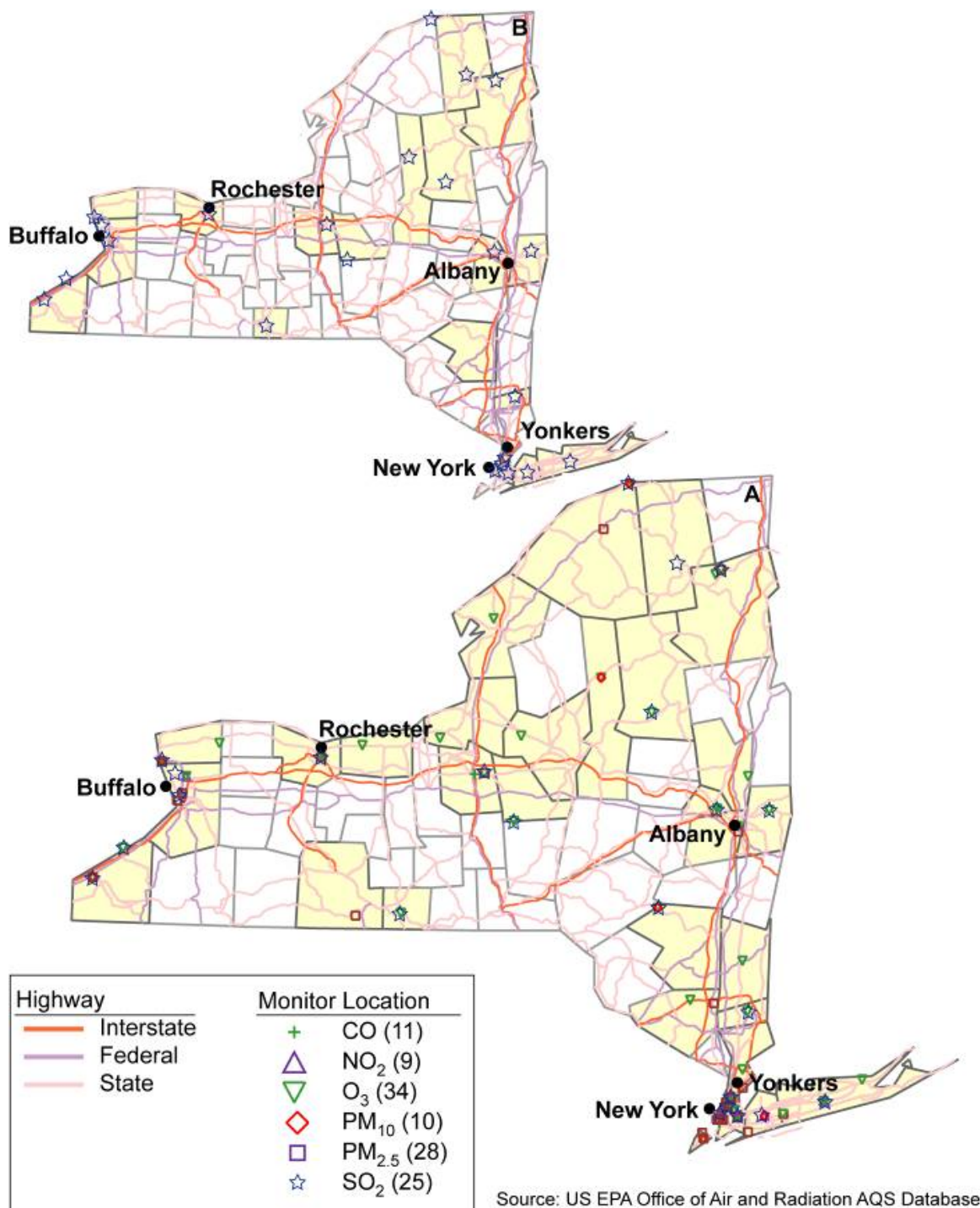
Figure 2-101. Criteria pollutant monitor locations (A) and SO₂ monitor locations (B), New York, 2005. Shaded counties have at least one monitor. Map A shows locations of each monitor for all six criteria pollutants. Map B shows only the SO₂ monitor locations.

Figure 2-102. Criteria pollutant monitor locations (A) and SO₂ monitor locations (B), Massachusetts, 2005. Shaded counties have at least one monitor. Map A shows locations of each monitor for all six criteria pollutants. Map B shows only the SO₂ monitor locations.

Table 2-22. Regional distribution of SO_2 and SO_4^{2-} ambient concentrations, averaged for 2003−2005.

Region	Concentration	
	SO_2 (ppb)	SO_4^{2-} (µg/m³)
Mid-Atlantic	3.3	4.5
Midwest	2.3	3.8
Northeast	1.2	2.5
Southeast	1.3	4.1

Table 2-23. Distributions of temporal averaging of SO_2 concentrations inside and outside CMSAs.

Averaging Time Monitor Locations	n	Mean	Percentiles											Max
			1	5	10	25	30	50	70	75	90	95	99	
1-h MAX CONCENTRATION														
Inside CMSAs	332405	13	1	1	1	3	4	7	13	16	30	45	92	714
Outside CMSAs	53417	13	1	1	1	1	2	5	10	13	31	51	116	636
1-h AVG CONCENTRATION														
Inside CMSAs	7408145	4	1	1	1	1	1	2	4	5	10	15	34	714
Outside CMSAs	1197179	4	1	1	1	1	1	2	3	3	7	13	36	636
24-h AVG CONCENTRATION														
Inside CMSAs	327918	4	1	1	1	1	2	3	5	6	10	13	23	148
Outside CMSAs	52871	4	1	1	1	1	1	2	3	4	8	12	25	123
ANNUAL AVG CONCENTRATION														
Inside CMSAs	898	4	1	1	1	1	2	4	5	6	8	10	12	15
Outside CMSAs	143	4	1	1	1	1	2	3	4	5	8	9	13	14
AGGREGATE 3-YR AVG CONCENTRATION, 2003−2005														
Inside CMSAs	283	4	1	1	1	2	3	3	5	5	8	10	12	14
Outside CMSAs	42	4	1	1	1	2	2	3	4	5	8	9	13	13

* Values are ppb. ** CMSA = Consolidate.d Metropolitan Statistical Area

The Pearson correlation coefficients (r) for multiple monitors in these CMSAs were generally very low for all cities, especially at the lower end of the observed concentration ranges, and even negative at the very lowest levels on the West Coast; see Table 2-24. This reflects strong heterogeneity in SO_2

ambient concentrations even within any one CMSA. At higher concentrations, the r-values were also higher. In some CMSAs, this heterogeneity may result from meteorological effects, whereby a generally well-mixed subsiding air mass containing one or more SO_2 plumes with relatively high concentration would be more uniformly spread than faster-moving plumes with lower concentrations. However, instrument error may also play a role, because the highest r-values, i.e., those >0.7, correspond to the highest SO_2 concentrations, i.e., >6 and >10 ppb. Since the lowest SO_2 concentrations are at or below the operating LOD, and demonstrate the lowest /correlation across monitors that share at least some air mass characteristics most of the year, the unbiased instrument error in this range may be confounding interpretation of any possible correlation. This could be because the same actual ambient value would be reported by different monitors (with different error profiles) in the CMSA as different values in this lowest concentration range.

   To better characterize the extent and spatiotemporal variance of SO_2 concentrations within each of the CMSAs having four or more SO_2 monitors, the means, minima, and maxima were computed from daily mean data across all available monitors for each month for the years 2003 through 2005. Because many of these CMSAs with SO_2 monitors also reported SO_4^{2-}, it is possible to compute the degree of correlation between SO_2, the emitted species, and SO_4^{2-}, the most prominent oxidized product from SO_2. SO_4^{2-} values, however, while averaged over all available data at each site are generally available at their monitoring sites on a schedule of only 1 in 3 days or 1 in 6 days. Furthermore, SO_2 and SO_4^{2-} monitors are not all collocated throughout the CMSAs. For each of the five example CMSAs in Figures 2-103 through 2-107, monthly aggregated values are depicted from daily means of: (a) the monthly mean, minimum, and maximum SO_2 concentrations; (b) the monthly mean, minimum and maximum SO_4^{2-} concentrations; and (c) a scatterplot of SO_2 versus SO_4^{2-} concentrations.

Table 2-24.   Range of mean annual SO_2 concentrations and Pearson correlation coefficients in urban areas having at least four regulatory monitors, 2003–2005.

CMSA (# Monitors)	Mean SO_2 Concentration (ppb)	Pearson Correlation Coefficient
Philadelphia, PA (10)	3.6 – 5.9	0.37 – 0.84
Washington, DC (5)	3.2 – 6.5	0.30 – 0.68
Jacksonville, FL (5)	1.7 – 3.4	−0.03 – 0.51
Tampa, FL (8)	2.0 – 4.6	−0.02 – 0.18
Pittsburgh, PA (10)	6.8 – 12	0.07 – 0.77
Steubenville, OH (13)	8.6 – 14	0.11 – 0.88
Chicago, IL (9)	2.4 – 6.7	0.04 – 0.45
Salt Lake City, UT (5)	2.2 – 4.1	0.01 – 0.25
Phoenix, AZ (4)	1.6 – 2.8	−0.01 – 0.48
San Francisco, CA (7)	1.4 – 2.8	−0.03 – 0.60
Riverside, CA (4)	1.3 – 3.2	−0.06 – 0.15
Los Angeles, CA (5)	1.4 – 4.9	−0.16 – 0.31

Moving across the CONUS from highest to lowest SO_2 concentrations, first consider Steubenville, OH (Figure 2-103), where the area of highest SO_2 concentrations of all 12 CMSAs with more than four monitors, all monthly mean SO_2 concentrations (a) were substantially <30 ppb, though max daily means in some months were often >60 ppb, or even >90 ppb. SO_4^{2-} data (b) at Steubenville were insufficient to make meaningful comparisons, though the 12 months of available SO_4^{2-} data suggest no correlation with SO_2 (c).

Next, consider Philadelphia, PA (Figure 2-104). SO_2 in Philadelphia, PA (a) is present at roughly one-half the monthly mean concentrations in Steubenville, OH, and demonstrates a strong seasonality with SO_2 concentrations peaking in winter. By contrast, SO_4^{2-} concentrations in Philadelphia peak in the three summer seasons, with pronounced wintertime minima. This seasonal anticorrelation still contains considerable monthly scatter, however.

Los Angeles, CA (Figure 2-105) presents a special case, since its size and power requirements place a larger number of SO_2 emitters near it than would otherwise be expected on the West Coast. Concentrations of SO_2 demonstrate weak seasonality in these 3 years, with summertime means of ~3 to 4 ppb, and maxima generally higher than wintertime ones, though the highest means and maxima occur during the winter of 2004–2005. SO_4^{2-} at Los Angeles shows stronger seasonality, most likely because the longer summer days of sunny weather allow for additional oxidation of SO_2 to SO_4^{2-} than would be available in winter. Weak seasonal effects in SO_2 likely explain the complete lack of correlation between SO_2 and SO_4^{2-} here.
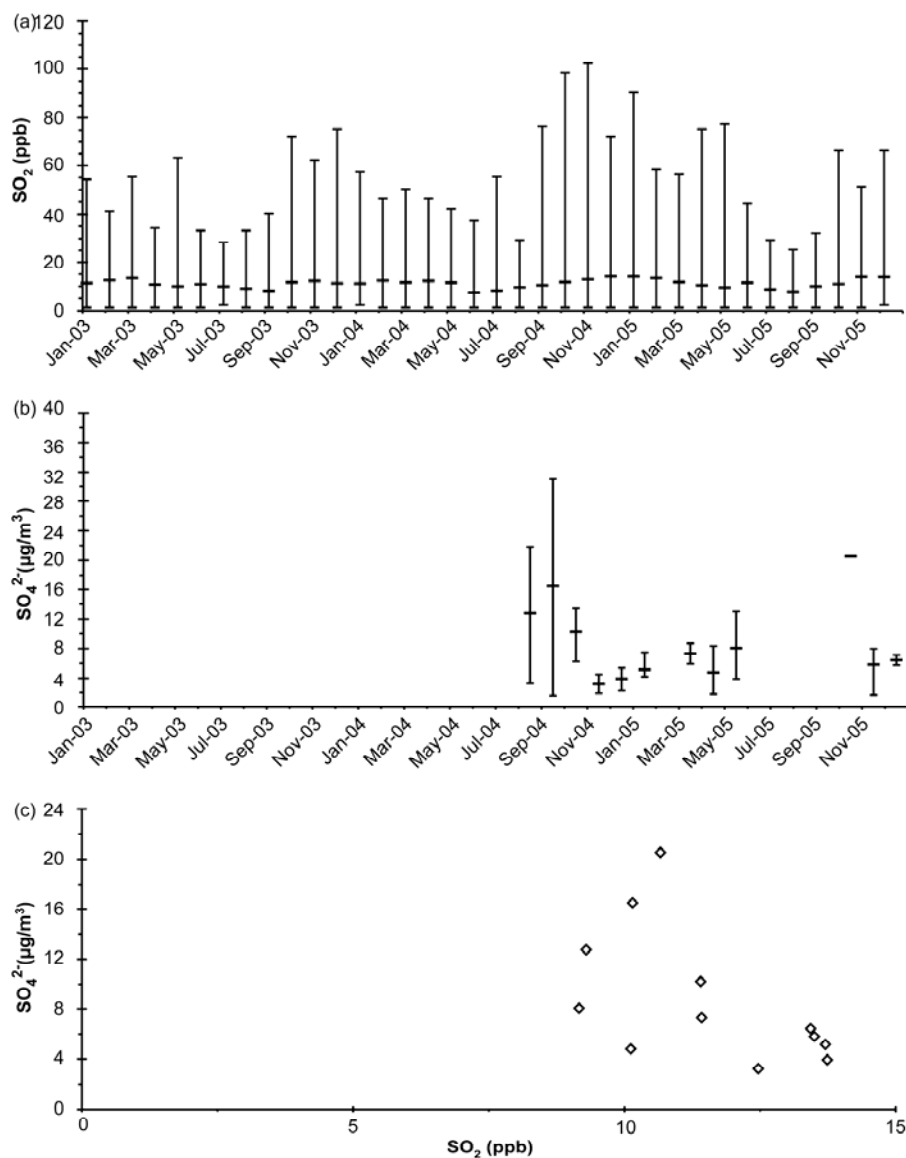
Figure 2-103. Steubenville, OH, 2003–2005. (a) Monthly mean, minimum, and maximum SO$_2$ concentrations. (b) Monthly mean, minimum, and maximum SO$_4^{2-}$ concentrations. (c) Monthly mean SO$_4^{2-}$ concentrations as a function of SO$_2$ concentrations.
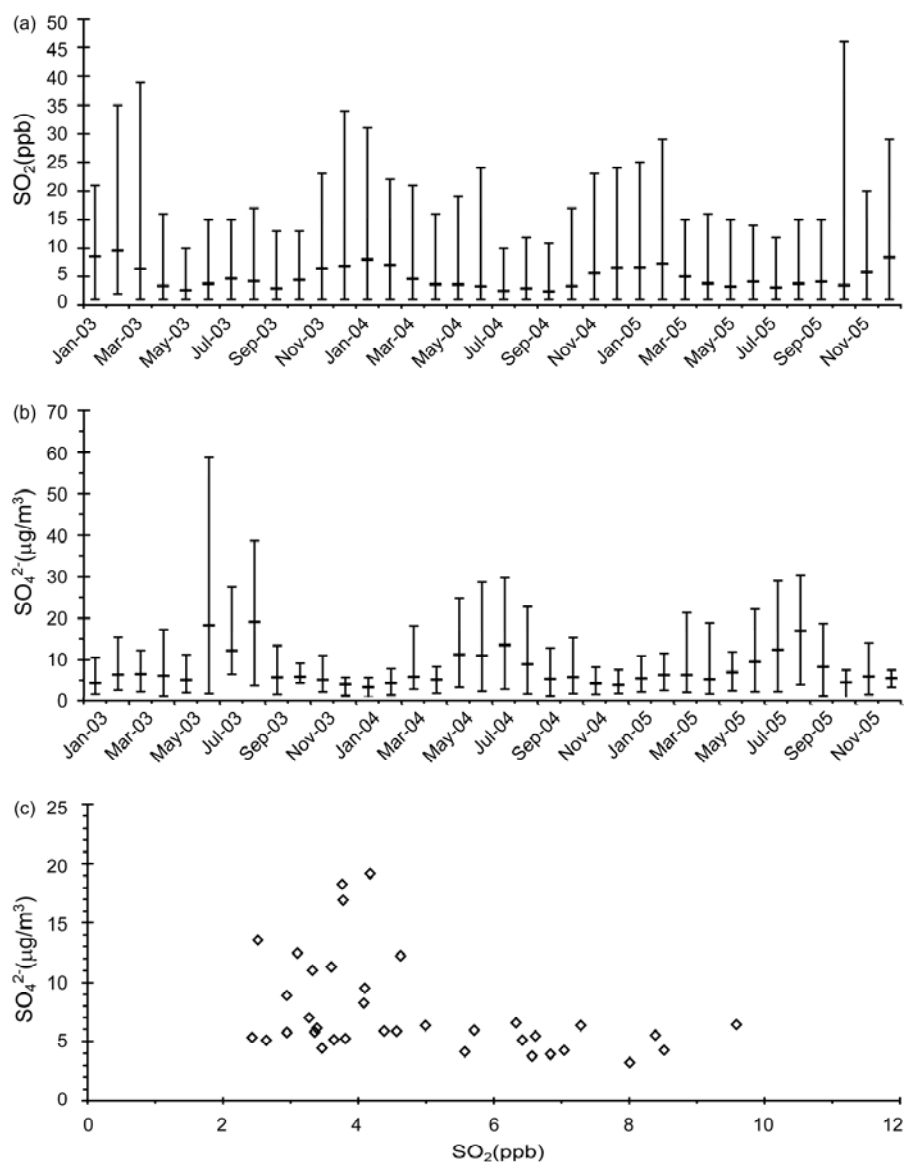
Figure 2-104. Philadelphia, 2003–2005. (a) Monthly mean, minimum, and maximum SO$_2$ concentrations. (b) Monthly mean, minimum, and maximum SO$_4^{2-}$ concentrations. (c) Monthly mean SO$_4^{2-}$ concentrations as a function of SO$_2$ concentrations.
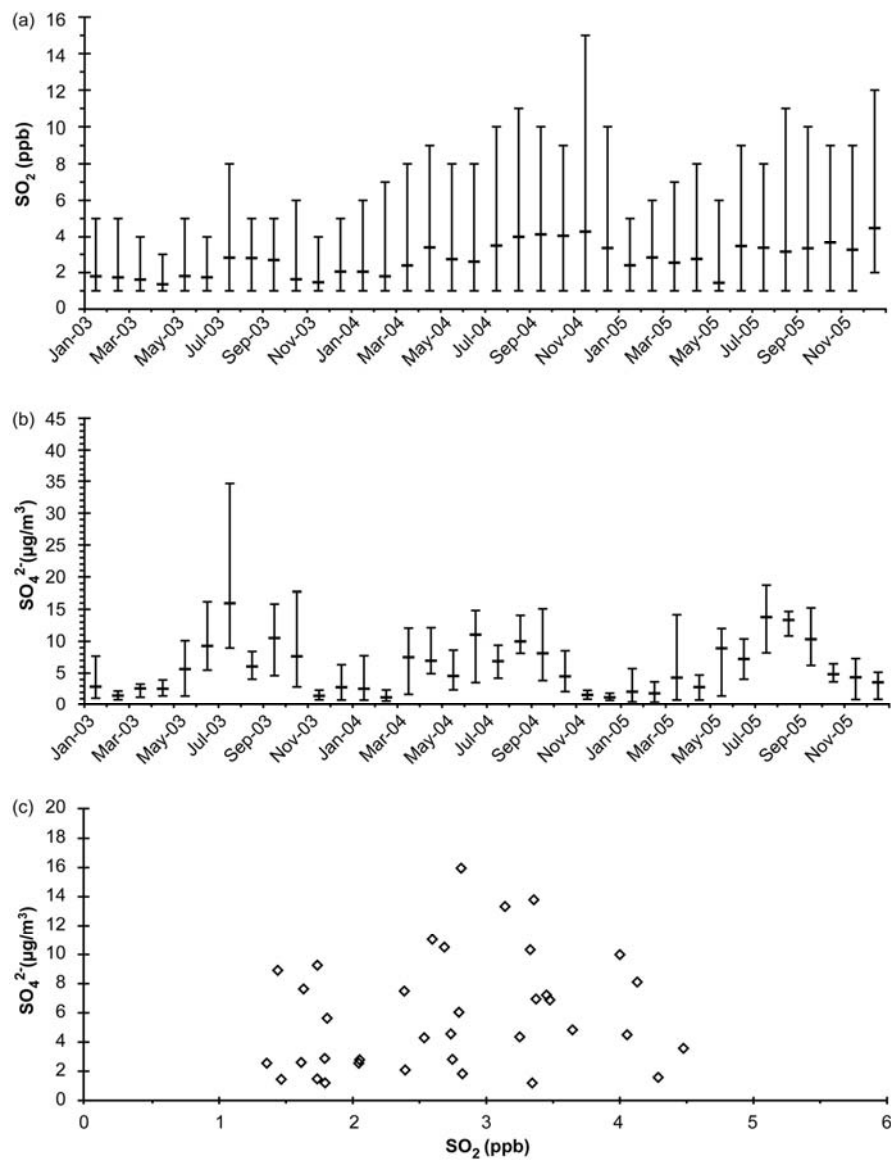
Figure 2-105. Los Angeles, 2003–2005. (a) Monthly mean, minimum, and maximum SO$_2$ concentrations. (b) Monthly mean, minimum, and maximum SO$_4^{2-}$ concentrations. (c) Monthly mean SO$_4^{2-}$ concentrations as a function of SO$_2$ concentrations.
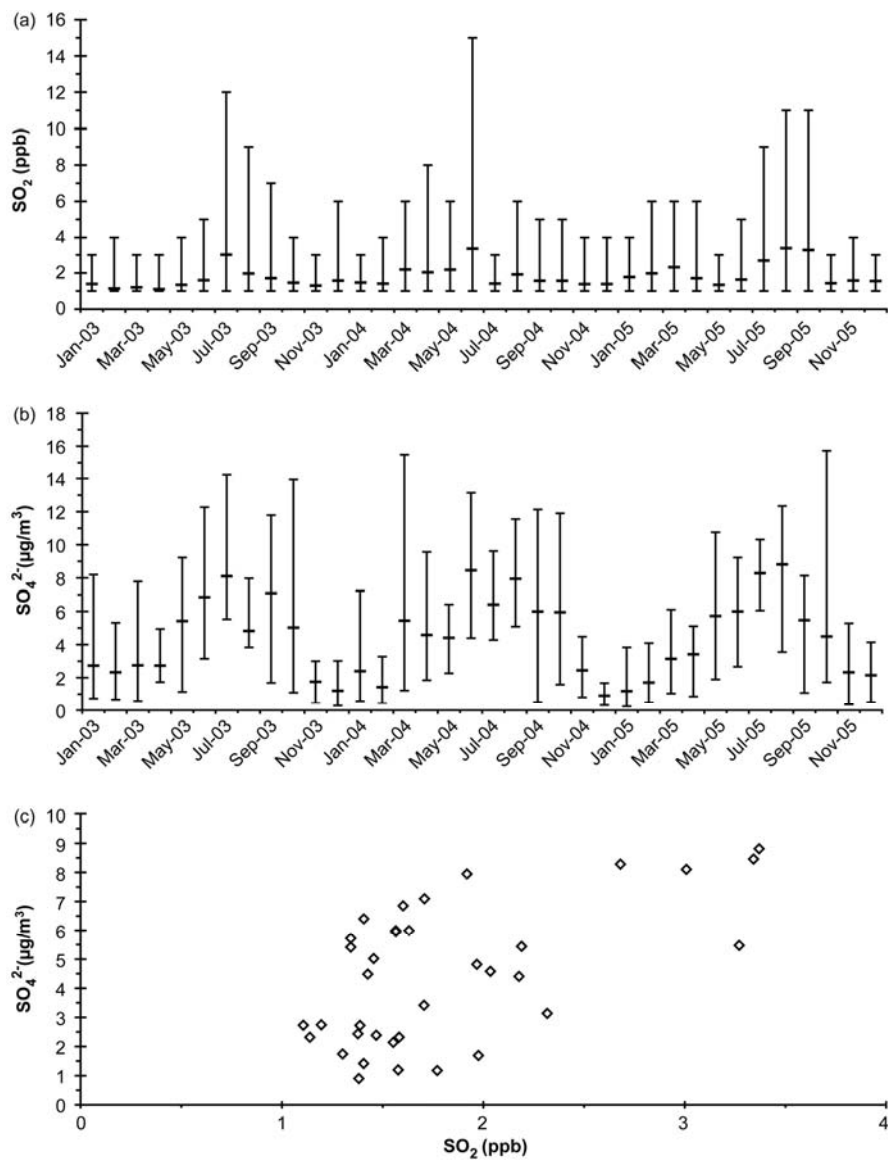
Figure 2-106. Riverside, CA, 2003–2005. (a) Monthly mean, minimum, and maximum SO_2 concentrations. (b) Monthly mean, minimum, and maximum SO_4^{2-} concentrations. (c) Monthly mean SO_4^{2-} concentrations as a function of SO_2 concentrations.
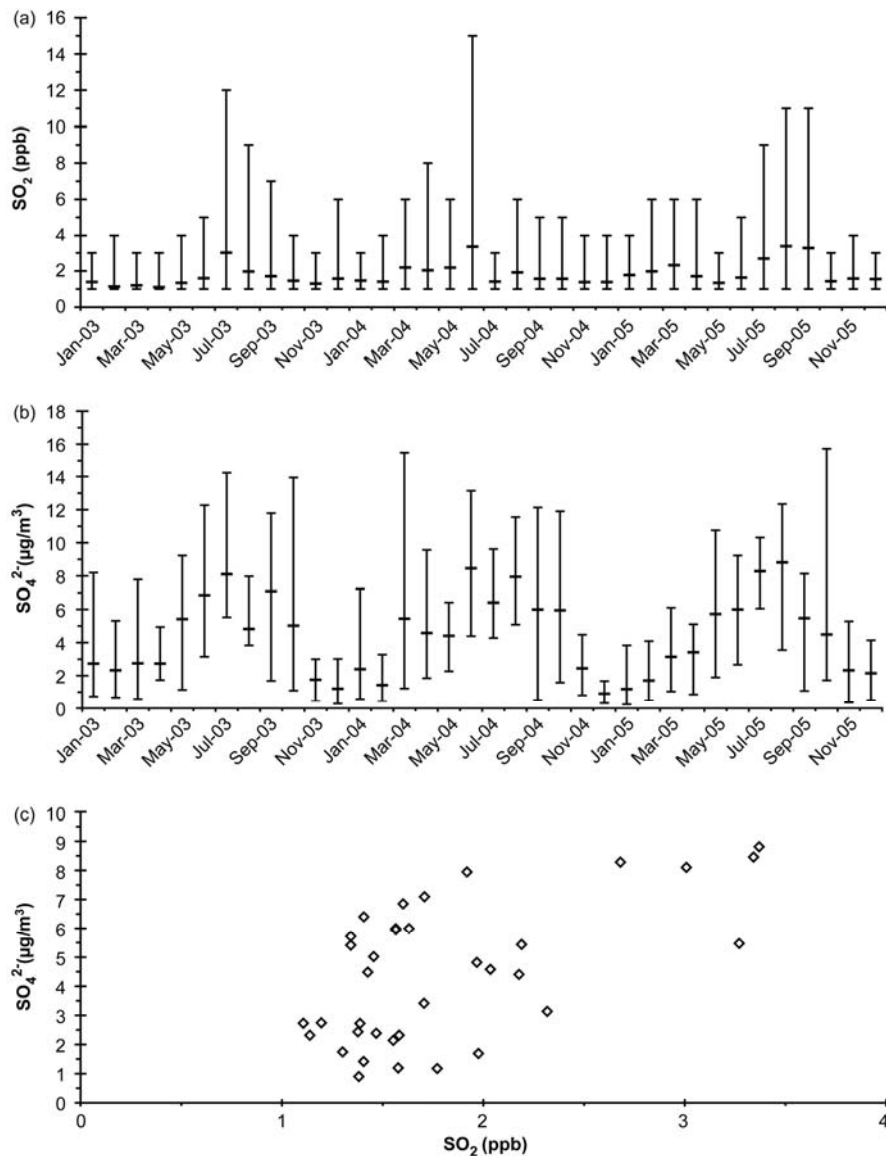
Figure 2-107. Phoenix, 2003–2005. (a) Monthly mean, minimum, and maximum SO_2 concentrations. (b) Monthly mean, minimum, and maximum SO_4^{2-} concentrations. (c) Monthly mean SO_4^{2-} concentrations as a function of SO_2 concentrations.

The Riverside, CA CMSA (Figure 2-106) presents the strongest example among the 12 examined for this study of correlation between SO_2 and SO_4^{2-}, though even here the R^2 value is merely 0.3. Seasonal peaks are obvious in summertime for SO_2 and SO_4^{2-}, both at roughly one-half the ambient concentrations seen in Los Angeles. This is very likely due to Riverside's geographic location just downwind of the regionally large electric generating utility sources near Los Angeles and the prevailing westerly winds in summer. Again, as with Los Angeles, the summertime peaks in SO_4^{2-} are most likely due to the combination of peaking SO_2 and favorable meteorological conditions allowing more complete oxidation.

Phoenix, AZ was the CMSA with the lowest monthly mean SO_2 and SO_4^{2-} concentrations examined here (Figure 2-107). In Phoenix, nearly all monthly mean SO_2 values were at or below the regulatory monitors' operating LOD of ~3 ppb. SO_4^{2-} concentrations were equivalently low, roughly one-half the concentrations seen in Riverside, CA, for example. The monthly mean data show strong summertime peaks for even these very low-level SO_4^{2-} observations, which, at ~1 to 3 μg/m^3, were generally one-half of those in Philadelphia. This suggests some seasonality in SO_2, though anticorrelated with SO_4^{2-}; however, the trend is very weak, as the correlation scatterplot shows.

2.9.6.2. SO_2 and SO_4^- in Rural and Remote Areas

The mean annual concentrations of SO_2 and SO_4^{2-} from CASTNet's long-term monitoring sites can be compared using two 3-year periods, 1989–1991 and 2003−2005, shown in Figure 2-108 for SO_2 and Figure 2-109 for SO_4^{2-}.

From 1989 through 1991 the highest ambient mean concentrations of SO_2 and SO_4^{2-} were observed in western Pennsylvania and along the Ohio River Valley: >20 μg/m^3 (~8 ppb) SO_2 and >15 μg/m^3 SO_4^{2-}. As with SO_2, in the years since the Acid Rain Program controls were enacted, both the magnitude of SO_4^{2-} concentrations and their areal extent have significantly decreased, with the largest decreases again along the Ohio River Valley.

IMPROVE monitors the major fine particle components including SO_4^{2-}, NO_3, crustal, elemental, and organic carbon plus coarse mass concentration defined as PM_{10} minus $PM_{2.5}$. An implicit assumption is that most of the pSO_4 is present as $(NH_4)_2SO_4$. Much of the information contained below is based on particulate elemental S used to infer the $(NH_4)_2SO_4$ levels. A discussion of IMPROVE S-to-pSO_4 history and trends is available (Eldred, 2001). As with data from IMPROVE used above for pNO_3, and except where noted, information in this section was derived form the IMPROVE IV Report (DeBell, 2006) with data displays created with data and tools available at http://vista.cira.colostate.edu/views/. Much of these data and conclusions are also to appear in Pitchford et al., 2008.

In contrast to results seen for pNO_3, additional monitoring sites in the U.S. Midwestern states produced no surprises for $(NH_4)_2SO_4$ concentration or areal extent. Figure 2-111 shows highest $(NH_4)_2SO_4$ concentrations in the mid-Atlantic and upper southern U.S. states where annual concentrations ranged from ~3 μg/m^3 to ~6 μg/m^3. The $(NH_4)_2SO_4$ concentrations in most western U.S. states was <~1 μg/m^3.

Combining IMPROVE and CSN data makes possible the comparison of urban pSO_4 to surrounding remote-area regional values. These are shown as paired color contours maps for IMPROVE and IMPROVE plus CSN in Figure 2-112. U.S. EPA (2004) used the pairing of IMPROVE and CSN monitoring sites at 13 selected areas to separate local and regional contributions to the major contributors of $PM_{2.5}$, as shown for pSO_4 in Figure 2-113.

As shown in Figures 2-112 and 2-113, annual-averaged urban pSO_4 concentrations were in general not significantly greater than the regional values, with urban excess pSO_4 generally <~0.5 μg/m^3. Exceptions to the general case appear in Texas and Louisiana where urban excess pSO_4 concentrations were >1μg/m^3. Urban contributions were a larger fraction of the total pSO_4 in western U.S. states because the regional levels were much lower there than in eastern ones. The small area decrease in pSO_4 evident on these maps between the two eastern high concentrations regions may not be real, but cannot be verified without speciation monitoring sites in southern Ohio, Kentucky, West Virginia, and Virginia. U.S. EPA (2004) estimates of the contribution of local sources to pSO_4 were made for the same cities included for pNO_3 shown above; see Figure 2-93. The east-west divide in both concentration and the regional contribution to pSO_4 is strongly apparent here.
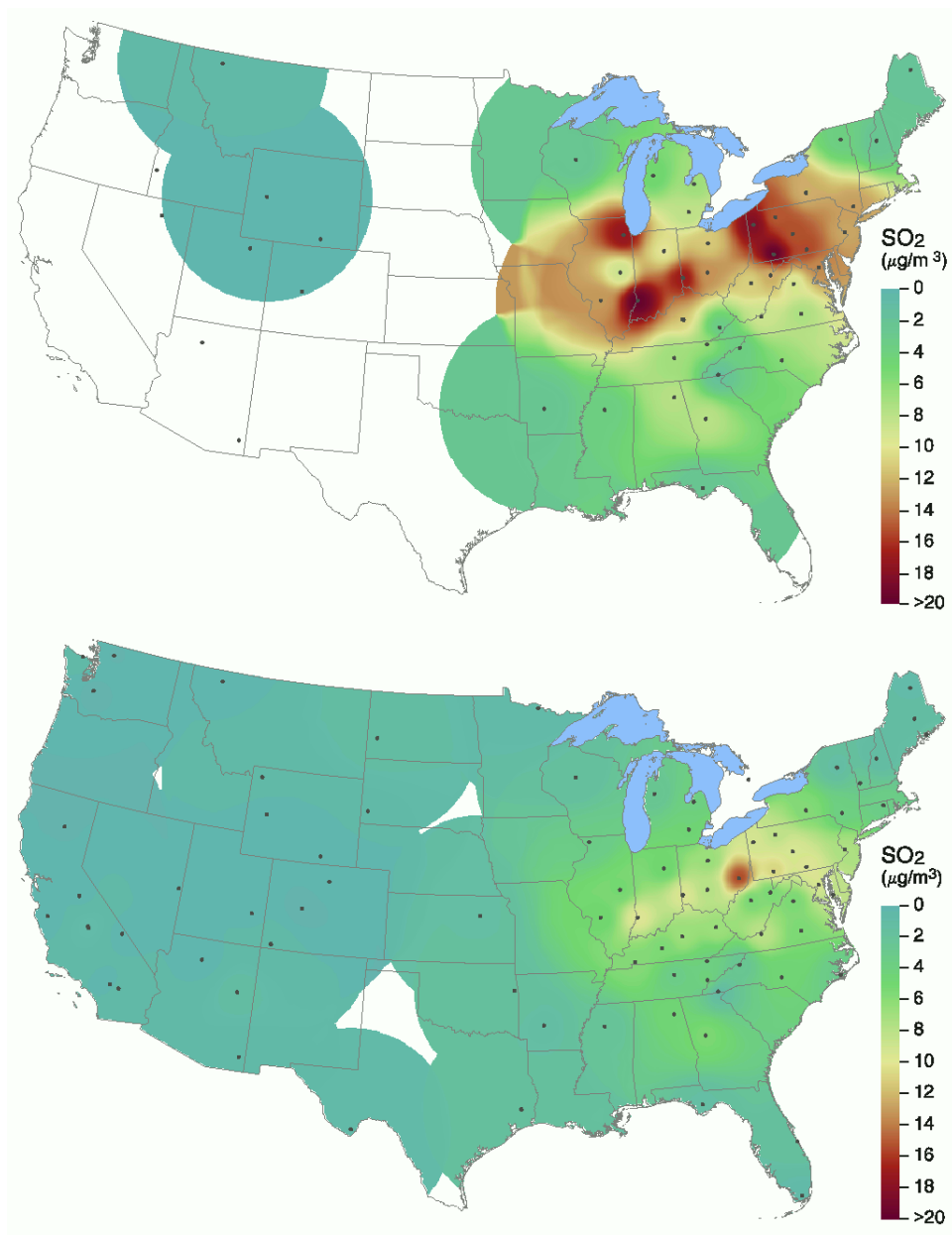
Figure 2-108. Annual mean ambient SO₂ concentration, 1989 through 1991 (top), and for 2003 through 2005 (bottom). White areas on the maps are areas where monitoring sites are absent and no information is available.
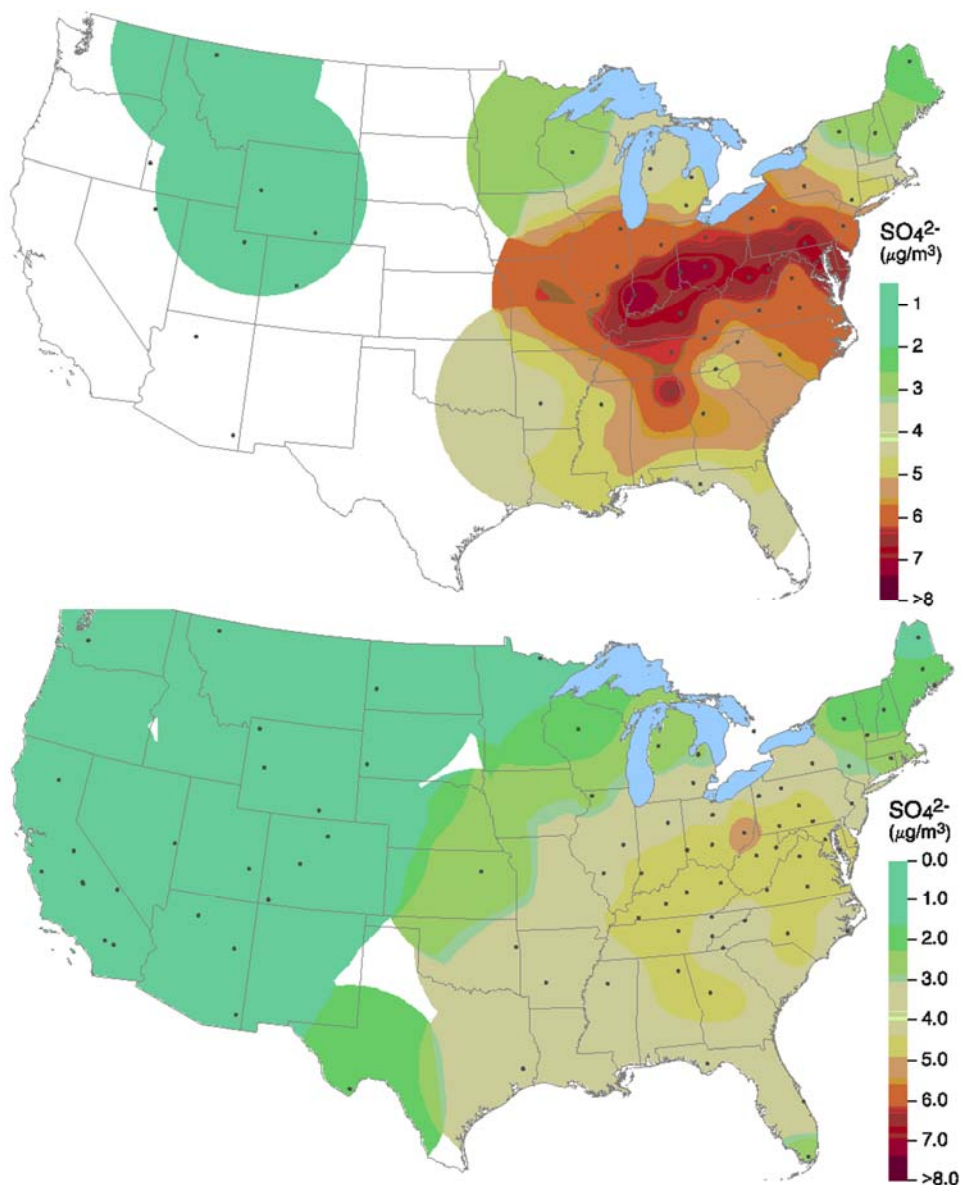
Figure 2-109. Annual mean ambient SO₄²⁻ concentration, 1989 through 1991 (top), and 2003 through 2005 (bottom). White areas on the maps are areas where monitoring sites are absent and no information is available.
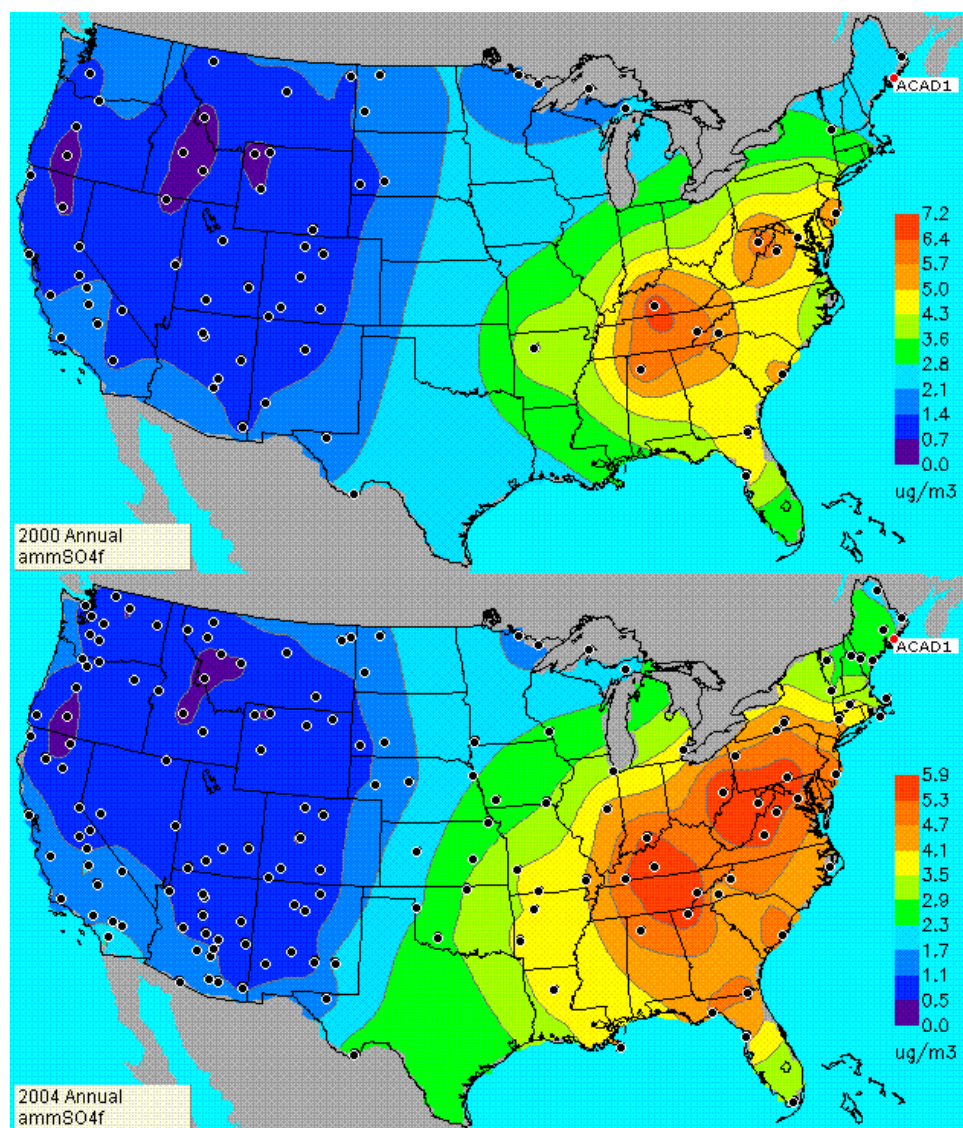
Figure 2-110.   IMPROVE network measured annual averaged pSO$_4$ concentration for 2000 (top) and for 2004 (bottom). Note difference in scale.
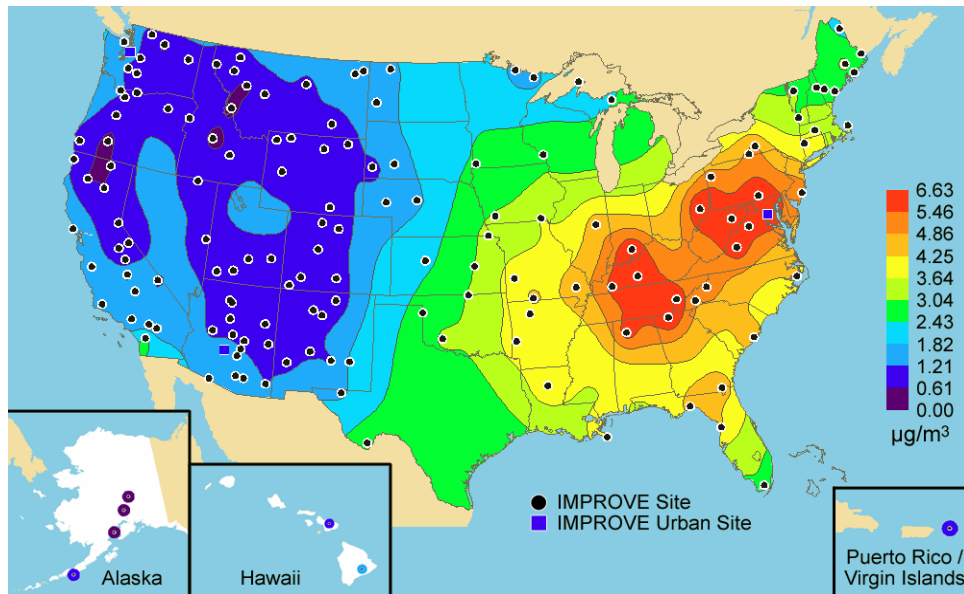
Figure 2-111.   IMPROVE mean (NH$_4$)$_2$SO$_4^{2-}$ concentrations for 2000 through 2004.
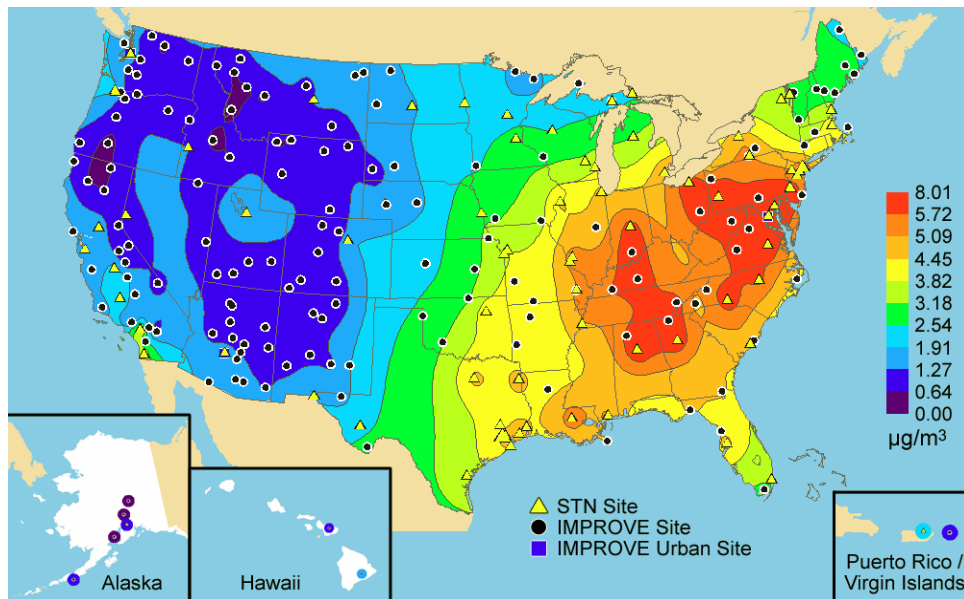
Figure 2-112.   IMPROVE and CSN (labeled STN) monitored mean (NH$_4$)$_2$SO$_4^{2-}$ concentrations for 2000 through 2004.
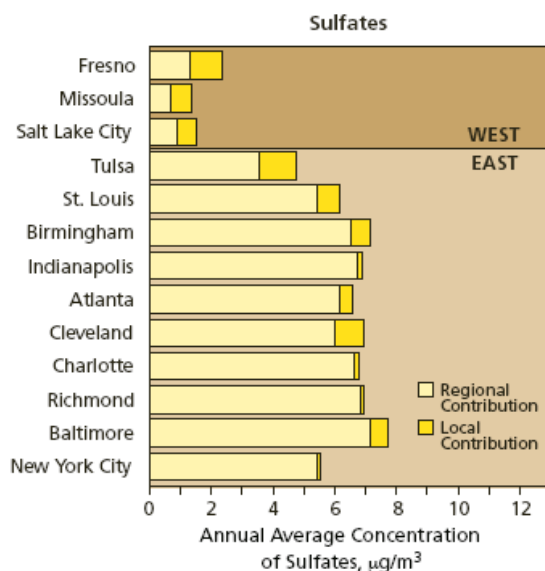
Figure 2-113. Regional and local contributions to annual average PM$_{2.5}$ by pSO$_4$ for select urban areas based on paired IMPROVE and CSN monitoring sites.

Source attribution of the pSO$_4$ contribution to haze at Big Bend NP, TX was a primary motivation for the BRAVO Study. Schichtel, et al. (2005) showed that during the four-month field monitoring study (July through October, 1999) SO$_2$ emissions sources in the U.S. and Mexico were responsible for ~55% and ~38% of the pSO$_4$ respectively. Among U.S. source regions, Texas was responsible for ~16%, eastern U.S. ~30%, and the western U.S. ~9%. A large coal fired power plant, the Carbón facility in Mexico just south of Eagle Pass, TX was responsible for about ~19%, making it the largest single contributor.

Modeling for a three-day pollution episode in September 1996 in the California South Coast Air Basin (SCAB) and for another episode in January 1996 in the San Joaquin Valley (SJV) by Ying and Kleeman (2006) has shown that ~80% of pSO$_4$ for both regions is derived from upwind sources, with most of the remaining local contributions associated with diesel and high-S fuel combustion. Kleeman, et al. (1999) used a combination of measurements and modeling to show that the upwind pSO$_4$ source region for the SCAB was over the Pacific Ocean, and this was confirmed by measurements on Santa Catalina Island. Moreover, these particles subsequently grew with accumulation of additional secondary aerosol material, principally NH$_3$NO$_3$, as they traversed the SCAB. Most the HNO$_3$ that forms pNO$_3$ in the SCAB is from diesel and gasoline combustion (~63%), while much of the NH$_3$ is from agricultural sources (~40%) and catalyst equipped gasoline combustion (~16%) and upwind sources (~18%). In the SJV most of the HNO$_3$ that forms pNO$_3$ is from upwind sources (~57%) with diesel and gasoline combustion contributing most of the rest (30%), while much of the NH$_3$ is from upwind sources (~39%) and a combination of area, soil and fertilizer sources (~52%).
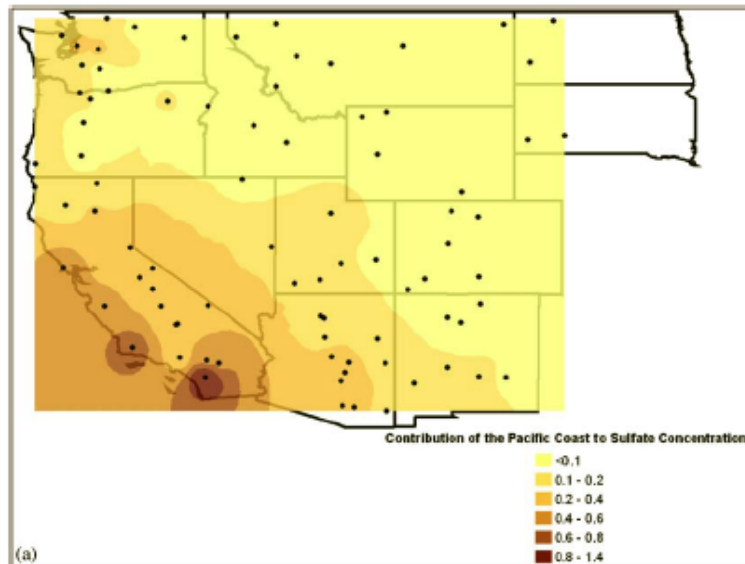
Figure 2-114. Contributions of the Pacific Coast area to the (NH₄)₂SO₄ (µg/m³) at 84 remote-area monitoring sites in western U.S. based on trajectory regression. Dots denote locations of the IMPROVE aerosol monitoring sites.

Using a regression analysis to find the dependence of pSO$_4$ concentration measured over a 3 year period (2000–2002) at 84 western IMPROVE monitoring sites on the modeled transport trajectories to the sites for each sample period, Xu et al. (2006) were able to infer the source regions that supplied pSO$_4$ in the western U.S. Among the source regions included in this analysis is the near-coastal Pacific Ocean (i.e. a 300 km zone off the coast of California, Oregon, and Washington states). Up to 50% of the pSO$_4$ measured at southern California monitoring sites is associated with this source region. As shown in Figure 2-114 the zone of impact from this source region includes large regions of California, Arizona, and Nevada, possibly owing to the high S-content fuel used in marine shipping and port emissions.

The SO$_4^{2-}$ attribution results of the WRAP air quality modeling (available from http://wrapair.org) are largely in line with these empirical results, finding that the Pacific Offshore source region contributed somewhat smaller amounts than reported by Xu et al., (2006) with concentrations at the highest affected site in California of ~45% compared to 50% by the regression analyses and even greater differences for more distant monitoring sites.
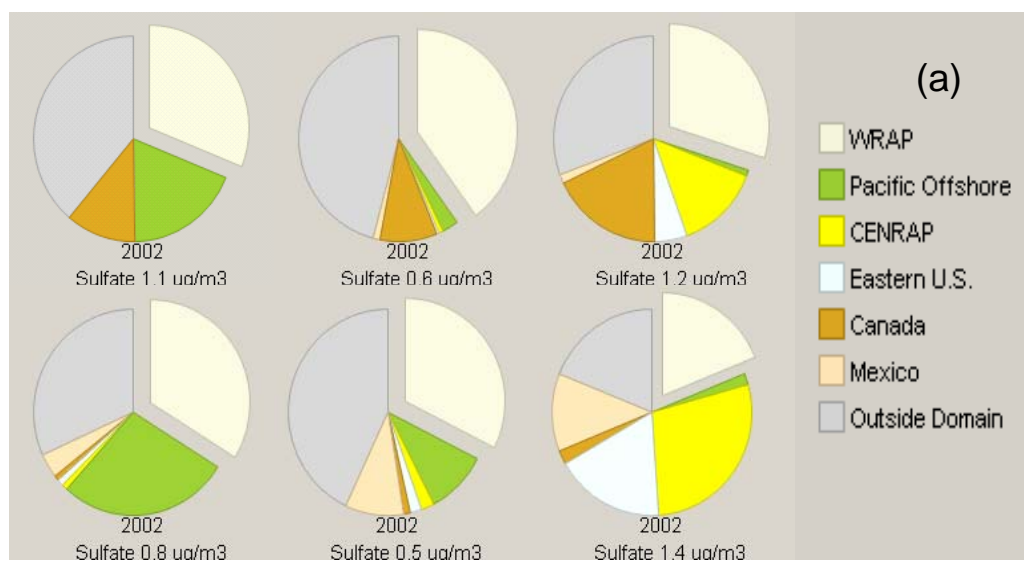
Figure 2-115. **pSO$_4$ source attribution by region using CAMx modeling for six western remote area monitoring sites. Top left to right Olympic NP, WA; Yellowstone NP, WY; Badlands NP, SD; bottom left to right San Gorgonio (W), CA; Grand Canyon NP, AZ; and Salt Creek (W), NM. WRAP includes North Dakota, South Dakota, Wyoming, Colorado, New Mexico and all states further west. CENRAP includes all states east of WRAP and west of the Mississippi River including Minnesota. Eastern U.S. includes all states east of CENRAP. The Pacific Offshore extends 300 km to the west of California, Oregon, and Washington. Outside Domain refers to the modeling domain, which extend hundreds of kilometers into the Pacific and Atlantic Oceans and from Hudson Bay Canada to just north of Mexico City.**

Several example monitoring locations distributed across the northern and southern portions of the western U.S. have been selected to illustrate the attribution results from the WRAP air quality simulation modeling by source region and source type for pSO$_4$. They include Olympic NP, WA; Yellowstone NP, WY; and Badlands NP, SD across the north, and San Gorgonio Wilderness (W), CA; Grand Canyon NP, AZ and Salt Creek W, NM across the south. Pie diagrams of the pSO$_4$ attribution results by source region for each of these sites are shown in Figure 2-115. Based on these sites, >50% of the pSO$_4$ in remote areas of the Pacific coastal states is from outside the U.S., Pacific Offshore and Outside of the Domain. The Outside of the Domain values are derived by simulating the fate of the boundary condition concentrations, which for the WRAP air quality modeling were obtained using output from the GEOS-CHEM global air quality model (Fiore et al., 2003). The pSO$_4$ fraction from the region labeled Outside of Domain is approximately uniform throughout the western U.S. with site-to-site variation in the fraction mostly caused by the variations in the total SO$_4^{2-}$ concentration. The more northerly sites have effects from Canadian emissions, while the southern sites have effects from Mexican emissions. Half of the Salt Creek, NM, pSO$_4$ is from the domestic source emissions further to the east (CENRAP and eastern U.S.), which also contribute ~20% to Badland pSO$_4$ concentrations. A breakout of the emission sources from within the WRAP region by source type (not shown) has most of the emissions from point sources, with the combination of motor vehicle, area and wildfire emissions contributing from a few percent at the furthest eastern sites to roughly half at San Gorgonio.

2.10. Deposition of Nitrogen and Sulfur Species Across the Landscape

As established in Sections 2.2 and 2.3 above, total emissions of NO_X and SO_X have decreased substantially in the last 35 years. Between 1970 and 2005, NO_X emissions fell from 26.9 million tons per year (Mt/yr) to 19 Mt/yr, and SO_2 emissions fell from 31.2 to 15 Mt/yr. These decreases in emissions led to correlative decreases in N and S concentrations, described just above in Section 2.9, and in atmospheric deposition of N and S species across the landscape; see the trends summarized in Figure 2-116. Importantly, however, these very recent decreases in deposition still leave current deposition amounts, which are a factor of 2 greater than in pre-industrial times for NO_3^- and NH_4^+, and a factor of 5 greater for SO_4^{2-}, according to modeling experiments by Luo et al. (2007).
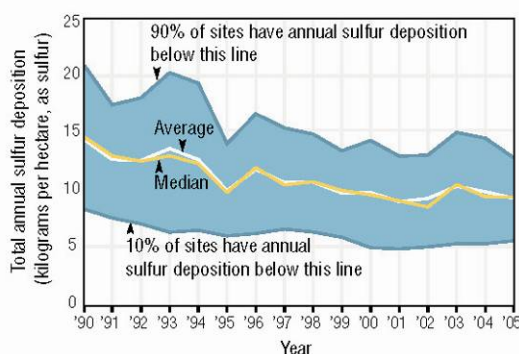
Coverage: 34 monitoring sites in the eastern United States.
Data source: MACTEC Engineering and Consulting, Inc., 2006

Figure 2-116. Trends, 1990–2005 in S (left) and N (right) deposition for 34 sites in the eastern U.S.

Deposition maps were developed by CASTNet to show the composition of dry deposition for N and S. The maps are labeled with inferred total deposition at each site, and a pie chart showing the relative proportion of wet and dry deposition or the chemical components of the deposition. Wet deposition is estimated from the interpolated concentration as measured by NADP multiplied by the measured rainfall at the site. Dry deposition is inferred from the measured ambient air concentrations of the chemical multiplied by the dry deposition rate obtained from an inferential model of linked resistances to derive species and location-dependent V_d. (See the CASTNet QAPP for more information on methods of computing their deposition totals). Note that NH_3 is not included in these total N estimates because it is not currently measured in these networks.

Data in this section are presented to show deposition across the landscape; finer-scale data and maps of sensitive and vulnerable regions and ecosystems are presented in other sections. Data presented in the maps and charts represent 3 year averages. For example, "89–91" is the average deposition of 1989, 1990, and 1991 for a given site. Only sites having valid total deposition for at least two of the three years are shown and in some instances sites only met this criterion for one of the two reporting periods. Because of differences like these, direct site-by-site comparisons are not possible everywhere.
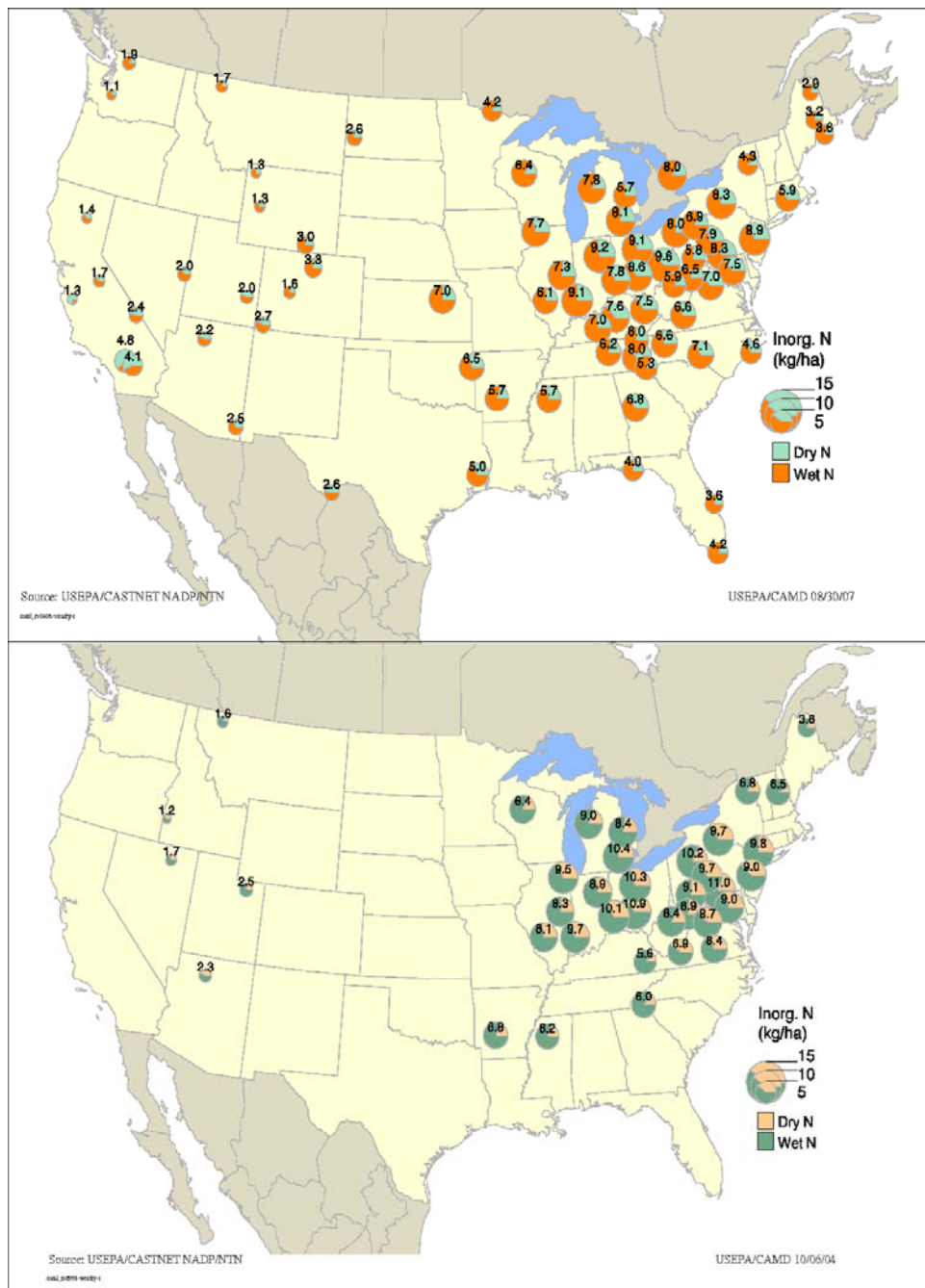
Figure 2-117.   Total average yearly wet and dry inorganic N deposition, excepting NH₃, for 2004–2006 (top) and 1989–1991 (bottom).
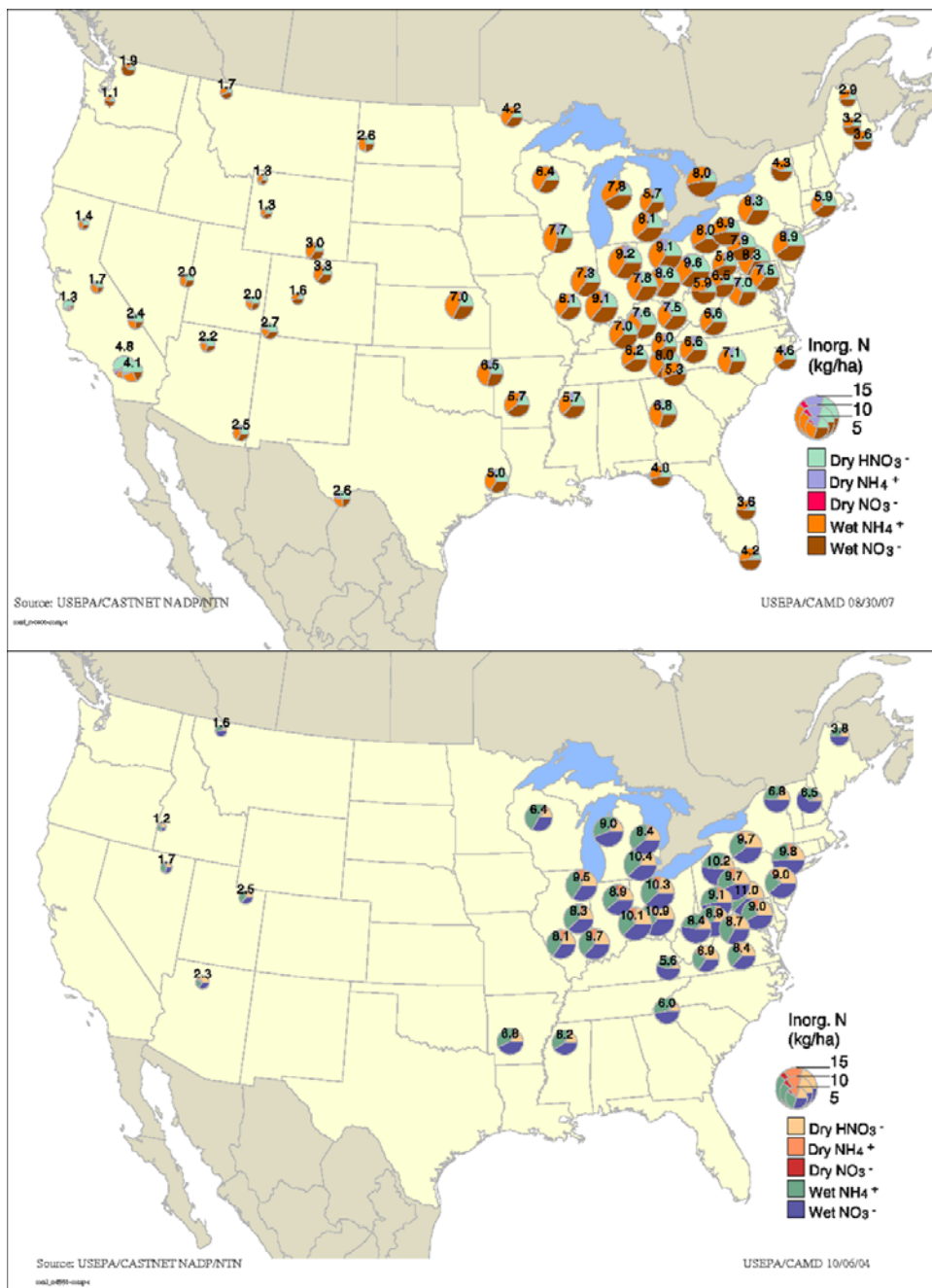
Figure 2-118. Total average yearly inorganic N deposition by species, excepting NH₃, for 2004–2006 (top) and 1989–1991 (bottom).

2.10.1. Nitrogen

For the years 2004–2006, mean N deposition was greatest in the Ohio River Valley, specifically in the states of Indiana and Ohio, with values as high as 9.2 and 9.6 kg N/ha/yr, respectively; see Figure 2-117. Recent work by Elliott et al. (2007) using $\delta^{15}N$ to trace deposition totals and isolate them to point to mobile source type shows that for 33 NADP/NTN sites in the East and Upper Midwest, spatial distributions of $\delta^{15}N$ concentrations were strongly correlated with NO_X emissions from point sources, and

that wet NO_3^- deposition at the 33 sites considered was strongly associated with NO_X emissions from the surrounding point sources. N deposition was lower in other parts of the East, including the Southeast and in northern New England. In the central U.S., Kansas and Oklahoma reported the highest deposition, 7.0 and 6.5 kg N/ha/yr, respectively. N deposition was generally much lower in the western U.S., where it was highest in urban areas in southern California and Denver, CO, 4.8 and 3.3 kg N/ha/yr, respectively. It should be noted, however, that large portions of the U.S. west of the Mississippi River are poorly covered by the current deposition monitoring networks as the location icons on these maps make clear. Hence, the actual degree of heterogeneity and magnitude of real deposition in much of the West is largely unknown.

Because NO_X emissions decreased by ~25% between 1990 and 2005, recent N deposition is lower compared with average deposition for the years 1989 to 1991. For 1989 to 1991, several recording stations in the Ohio River basin reported average annual deposition rates in excess of 10 kg N/ha/yr. Data are lacking, however, for much of the central and western U.S. and little can be said for changes between the two reporting periods in these areas for the reasons given above. The greatest mass of N deposition primarily occurred as wet NO_3^- and NH_4^+, followed in importance by dry HNO_3, dry NH_4^+, and dry NO_3^-; see Figure 2-118. Although most deposition for both reporting periods occurred as wet deposition, there were some exceptions, including parts of California where N deposition was primarily dry.

Figure 2-119 and Figure 2-120 show maps of wet deposition from NADP's data and IDW interpolation technique. pNO_3 concentration and wet deposition amounts track dry deposition in locations where the two monitoring networks overlap. Thus pNO_3 ambient concentration and deposition are highest in the upper Ohio River Valley, excepting the large reported pNO_3 deposition, in excess of 6 kg N/ha/yr where NADP has a substantial number of monitors but CASTNet does not; see the description of the Midwest NO_3 bulge in Section 2.9.6.2.
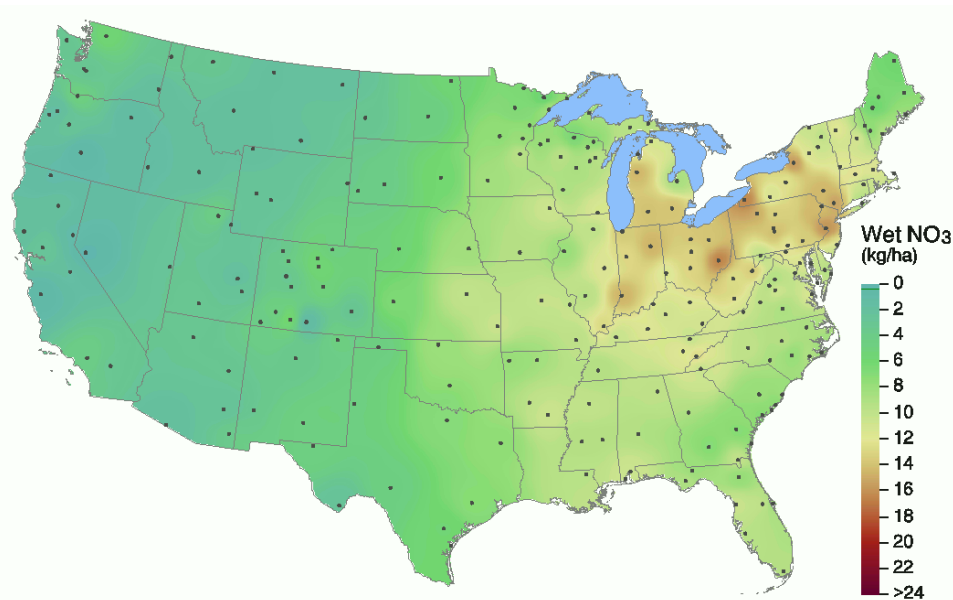
Figure 2-119. NO_3^- concentration in NADP wet deposition samples, 2004–2006.
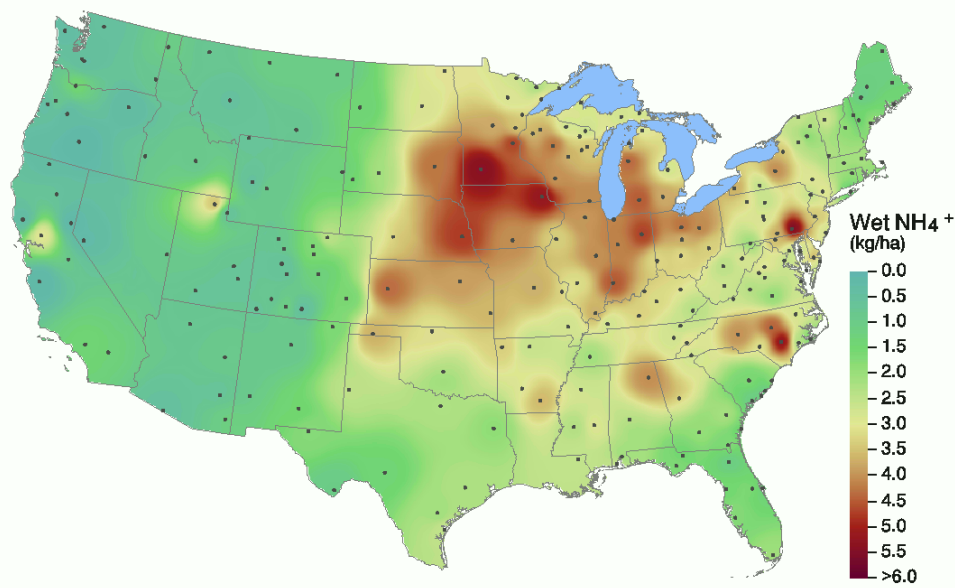
Figure 2-120. Average NO$_3^-$ concentration in NADP wet deposition samples, 2004–2006.

2.10.1.1. Example of NO$_2$ and HNO$_3$ Deposition and Flux Data from Harvard Forest

Harvard Forest is a rural site in central Massachusetts, where ambient NO$_X$, NO$_Y$, and other pollutant concentrations and fluxes of total NO$_Y$ have been measured since 1990 (Munger et al., 1996).

An intensive study in 2000 used a TDLAS to measure NO$_2$ and HNO$_3$. Absolute concentrations of HNO$_3$ were measured; and the flux inferred was based on the dry deposition inferential method that uses momentum flux measurements to compute a V_d and derives an inferred flux (Hicks et al., 1987; Wesely and Hicks, 1977). Direct eddy covariance calculations for HNO$_3$ were not possible because the atmospheric variations were attenuated by interaction with the inlet walls despite very short residence time and use of fluorinated silane coatings to make the inlet walls more hydrophobic. NO response was adequate to allow both concentration and eddy covariance flux determination. Simultaneously, NO and NO$_Y$ eddy covariance fluxes were determined with two separate O$_3$ CL detectors, one equipped with a H$_2$– gold catalyst at the inlet to convert all oxidized N compounds to NO. Additionally, the measurements include concentration gradients for NO, NO$_2$, and O$_3$ over several annual cycles to examine their vertical profiles in the forest canopy.

Overall, the results showed typical NO$_2$ concentrations of 1 ppb under clean-air conditions and mean concentrations up to 3 ppb at night and 1 ppb during daytime for polluted conditions. Net positive fluxes (emission) of NO$_2$ were evident in the daytime and negative fluxes (deposition) were observed at night (Figure 2-121). NO fluxes were negative during the daytime and near zero at night.
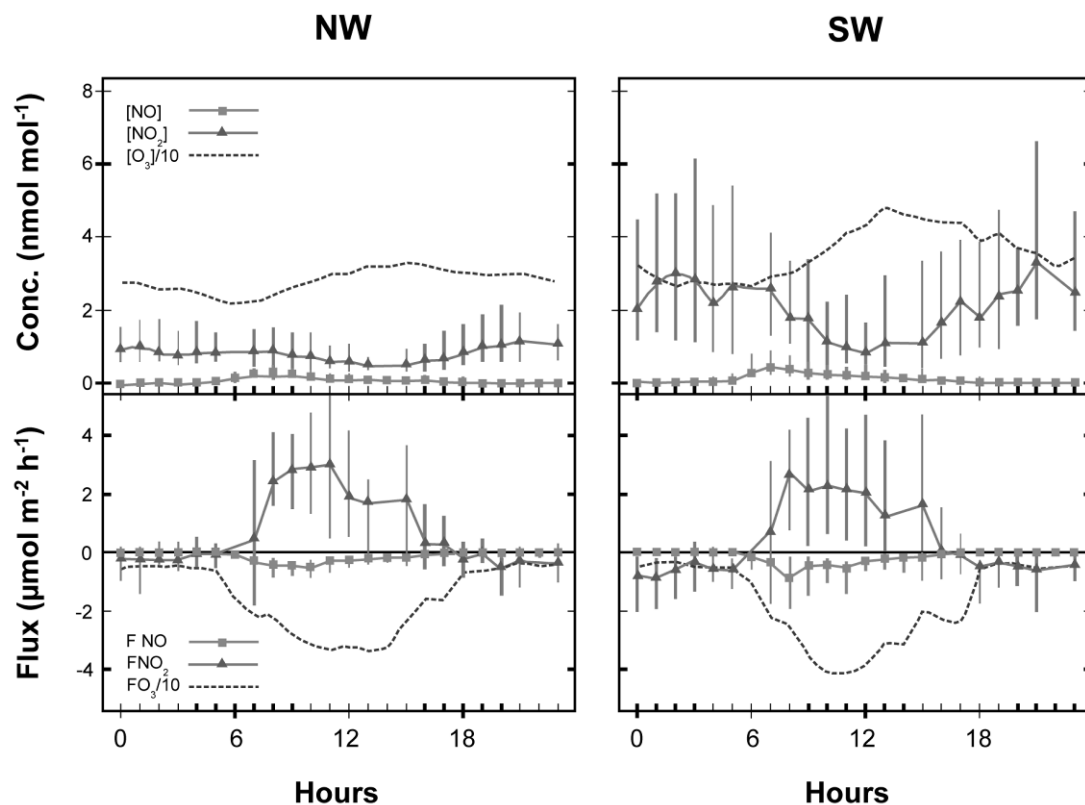
Figure 2-121. Diel cycles of median concentrations (upper panels) and fluxes (lower panels) for the northwest clean sector, left panels) and southwest (polluted sector, right panels) wind sectors at Harvard Forest, April-November, 2000, for NO, NO_2, and $O_3/10$. NO and O_3 were sampled at a height of 29 m, and NO_2 at 22 m. Vertical bars indicate 25th and 27th quartiles for NO and NO_2 measurements. NO_2 concentration and nighttime deposition are enhanced under southwesterly conditions, as are O_3 and the morning NO maximum.
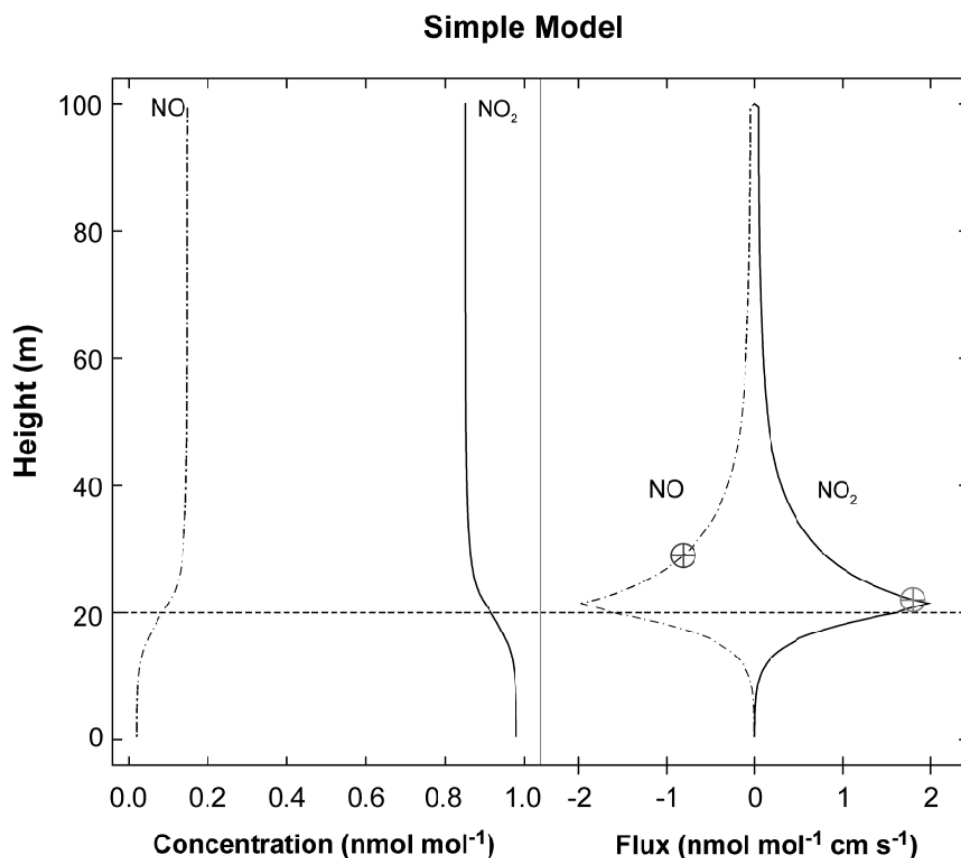
Simple Model

Figure 2-122. Simple NO_X photochemical canopy model outputs. Left panel, concentrations of NO (dashed) and NO_2 (solid); right, fluxes of NO (dashed) and NO_2 (solid). Symbols indicate measurement heights for NO (29 m) and NO_2 (22 m) at Harvard Forest. The model solves the continuity equation for NO concentration at 200 levels, d/dz(-Kc[dNO/dz]) = PNO⁻LNO, where PNO = [NO]/t1, LNO = [NO]/t2, and zero net deposition or emission of NO_X is allowed. NO_X (NO + NO_2) is normalized to 1 ppb. t1 = 70 s in this example. Due to the measurement height difference, observed upward NO_2 flux due to photochemical cycling alone should be substantially larger than observed downward NO flux attributable to the same process.

In part, the opposite NO and NO_2 fluxes are simply consequences of variable NO-to-NO_2 ratio distributions responding to vertical gradients in light intensity and O_3 concentration, which resulted in no net flux of NO_X (Gao et al., 1993). In the Harvard Forest situation, the NO and NO_2 measurements were not at the same height above the canopy, and the resulting differences derive at least in part from the gradient in flux magnitude between the two inlets (Figure 2-122).

$$\text{FNO}_2 \text{ (night)} = F_0 + V_0 \text{ [NO}_2] + a \text{ [NO}_2]^2$$
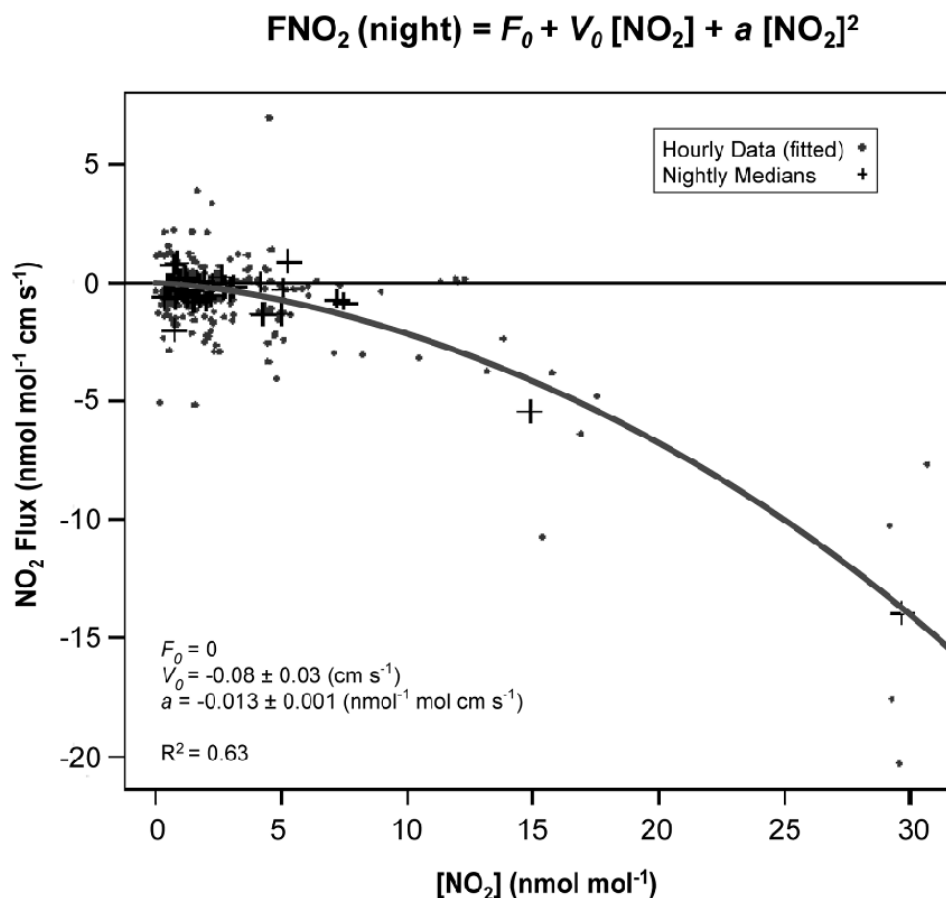
Figure 2-123. Hourly (dots) and median nightly (pluses) NO$_2$ flux vs. concentration, with results of least squares fit on the hourly data (curve).

At night, when NO concentrations are near zero due to titration by ambient O$_3$ there is not a flux of NO to offset NO$_2$ fluxes. Nighttime data consistently show NO$_2$ deposition (Figure 2-123), which increases with increasing NO$_2$ concentrations. Concentrations above 10 ppb were rare at this site, but the few high NO$_2$ observations suggest a nonlinear dependence on concentration. The data fit a model with V_d of -0.08 plus an enhancement term that was second order in NO$_2$ concentration. The presence of a second order term implies that NO$_2$ deposition rates to vegetation in polluted urban sites nearer to the prominent sources of NO$_2$ could be considerably larger than what was observed at this rural site.

After accounting for the time of the NO-NO$_2$ null cycle during the measurement-sampling period, the net NO$_X$ flux can be derived. Overall, there was a net deposition of NO$_X$ during the night and essentially zero flux in the day, with large variability in the magnitude and sign of individual flux observations. For the periods with NO$_2$ concentrations >2 ppb, deposition was always observed. These canopy-scale field observations are consistent with a finite compensation point for NO$_2$ in the canopy that offsets foliar uptake or even reverses it when concentrations are especially low. At concentrations above the compensation point, NO$_X$ is absorbed by the canopy. Examination of concentration profiles corroborates the flux measurements (Figure 2-124). During daytime for low-NO$_X$ conditions, there was a local maximum in the concentration profile near the top of the canopy where O$_3$ has a local minimum, which is consistent with foliar emission or light-dependent production of NO$_X$ in the upper canopy. Depletion was evident for both NO$_X$ and O$_3$ near the forest floor. Air reaching the ground has passed

through the canopy where uptake is efficient and the vertical exchange rates near the ground are slow. At night, the profiles generally decreased with decreasing height above the ground, showing only uptake. At higher concentrations, the daytime NO_X concentrations were nearly constant through the canopy; no emission was evident from the sunlit leaves.
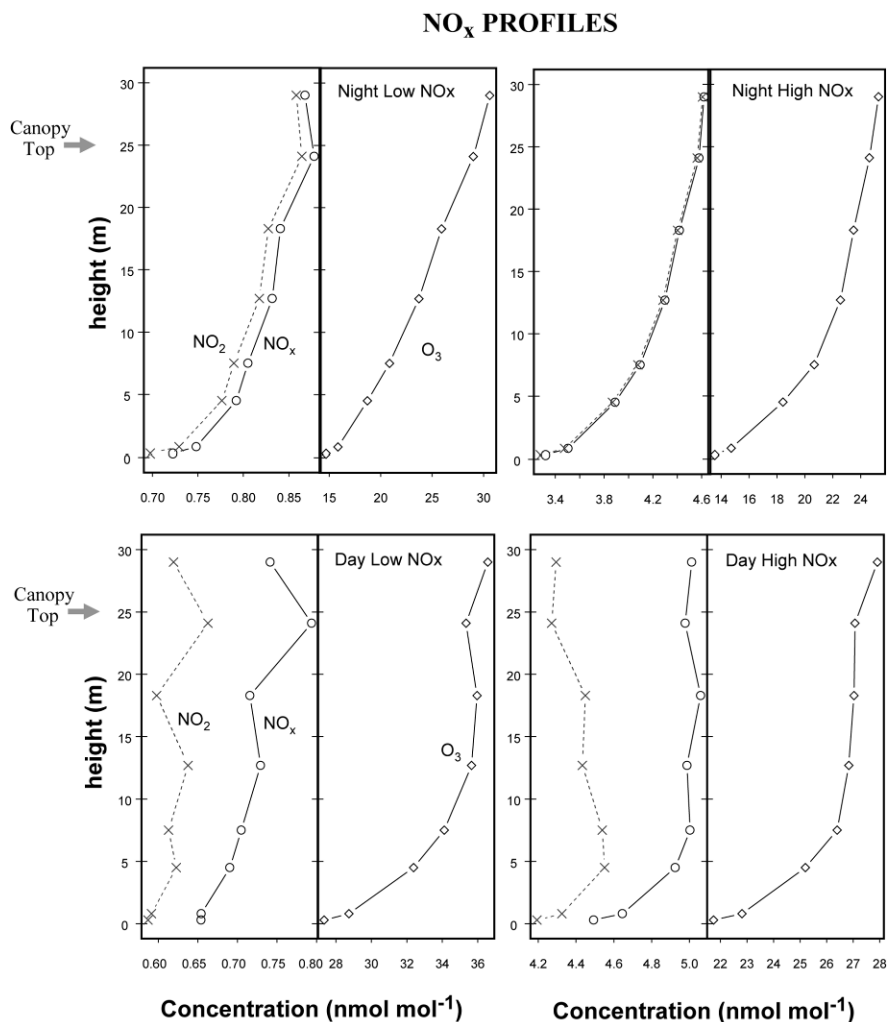
NO_X PROFILES

Source: Horii et al. (2004). Reprinted with permission.

Figure 2-124. Averaged profiles at Harvard Forest give some evidence of some NO_2 input near the canopy top from light-mediated ambient reactions, or emission from open stomates.

Figure 2-125 compares observed fluxes of all the observed species. The measured NO_X and estimated PAN fluxes were small relative to the observed total NO_Y flux. In clean air, HNO_3 accounted for nearly all the NO_Y flux and the sum of all measured species ws about equal to the NO_Y concentration. However, in polluted conditions, unmeasured species were up to 25% of the NO_Y, and HNO_3 fluxes cannot account for all the total NO_Y flux observed. These unmeasured NO_Y species likely are hydroxyalkyl nitrates and similar compounds rapidly deposited to surfaces but not routinely measured; see the descriptions of measurement techniques and challenges in Section 2.3. The deposition of HNO_3 and multifunctional $RONO_2$ were the largest elements of the measured N dry deposition budget.

Two key areas of remaining uncertainty were the production of HNO_2 over vegetation and the role of very reactive biogenic VOCs. HNO_2 is important because its photolysis is a source of OH radicals, and its formation may represent an unrecognized mechanism to regenerate photochemically active NO_X from NO_3 that had been considered terminally removed from the atmosphere; see the discussion in Section 2.3 above on the atmospheric chemistry of NO_X and the role of oxidized N compounds in atmospheric N transport.
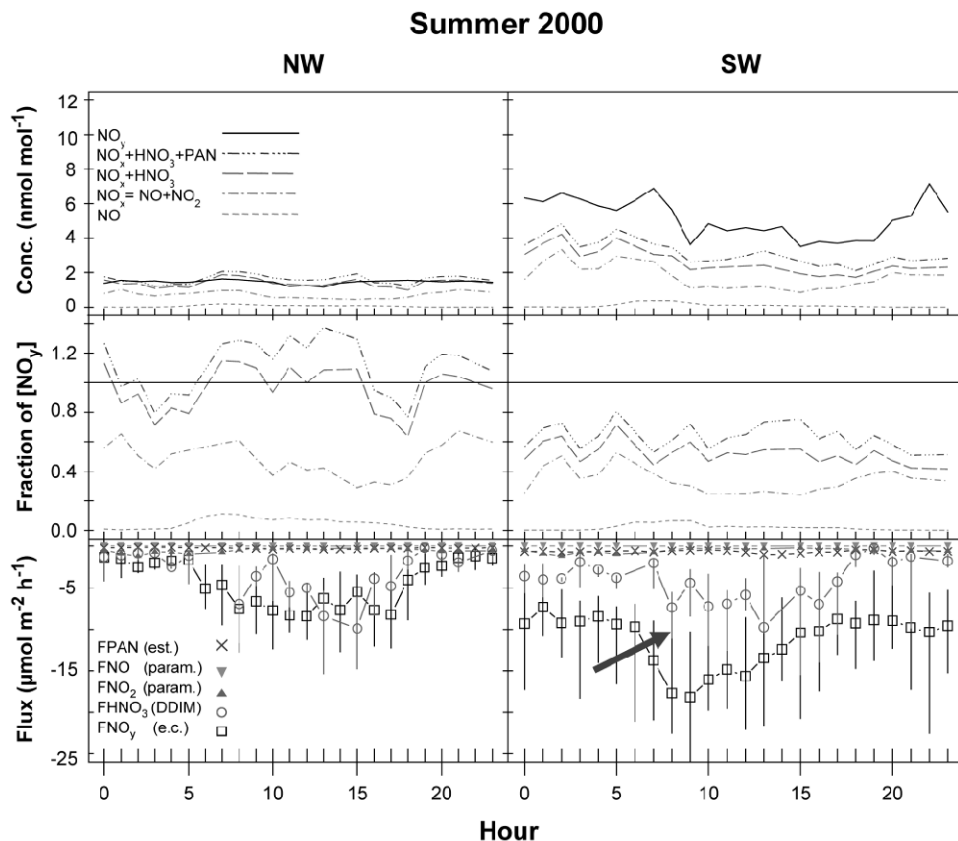
Figure 2-125. **Summer (June-August) 2000 median concentrations (upper panels), fractions of NO_Y (middle panels), and fluxes (lower panels) of NO_Y and component species separated by wind direction (northwest on the left and southwest on the right). Vertical lines in the flux panels show 25th and 75th quartiles of $F(NO_Y)$ and $F(HNO_3)$; negative fluxes represent deposition; $F(NO_X)$ is derived from eddy covariance $F(NO)$ and $F(NO_2)$ measurements (corrected for photochemical cycling), $F(HNO_2)$ is inferred, and $F(NO_Y)$ was measured by eddy covariance. The sum of NO_X, HNO_3, and PAN accounts for all of the NO_Y concentration and flux for northwesterly (unpolluted background) flows, whereas up to 50% of NO_Y and $F(NO_Y)$ under southwesterly flows are in the form of N_r species whose fluxes are not measured or estimated here.**

2.10.2. Sulfur

For the most recent 3-year reporting period available (2004 to 2006), mean S deposition was greatest in the eastern U.S. east of the Mississippi River, with the highest deposition of 21.3 kg S/ha/yr in the Ohio River Valley; see Figure 2-126. Most recording stations throughout the Ohio River Valley report 3-year total S deposition averages >10 kg S/ha/yr and many other stations in the East report deposition >5 kg S/ha/yr. Data are sparse for the central and west U.S. However, where available, data indicate lower values than in most of the East, ranging from 4.1 to 5.3 kg S/ha/yr. Total S deposition in the U.S. west of the 100th meridian is lower, with all recording stations reporting <2 kg S/ha/yr and many reporting <1.0 kg S/ha/yr. These values can also be compared to S deposition totals from 1989–1991 in Figure 2-126. Station-by-station comparisons between averaging periods are difficult because some stations do not have sufficient data to report a mean for the sampling period. There are, however, clear regional decreases in S deposition across the country. S deposition for 1989–1991 (the earliest 3-year reporting period available) is almost uniformly greater than for the most recent 3-year average (2004–2006). Deposition since 1989–1991 has declined throughout the Ohio River basin from a previous high of 25.4 kg S/ha/yr, and in New England, and the Mid-Atlantic regions, consistent with the ~48% decrease in SO_2 emissions nationwide between 1990 and 2005. Very little coverage for western and central U.S. was available for the 1989–2001 reporting period, but sites with data show a similar decrease. Figure 2-127 shows that for both the 1989–1991 and 2004–2006 reporting periods, S was primarily deposited as wet SO_4^{2-} followed by a smaller proportion as dry SO_2 and a much smaller proportion as dry SO_4^{2-}.
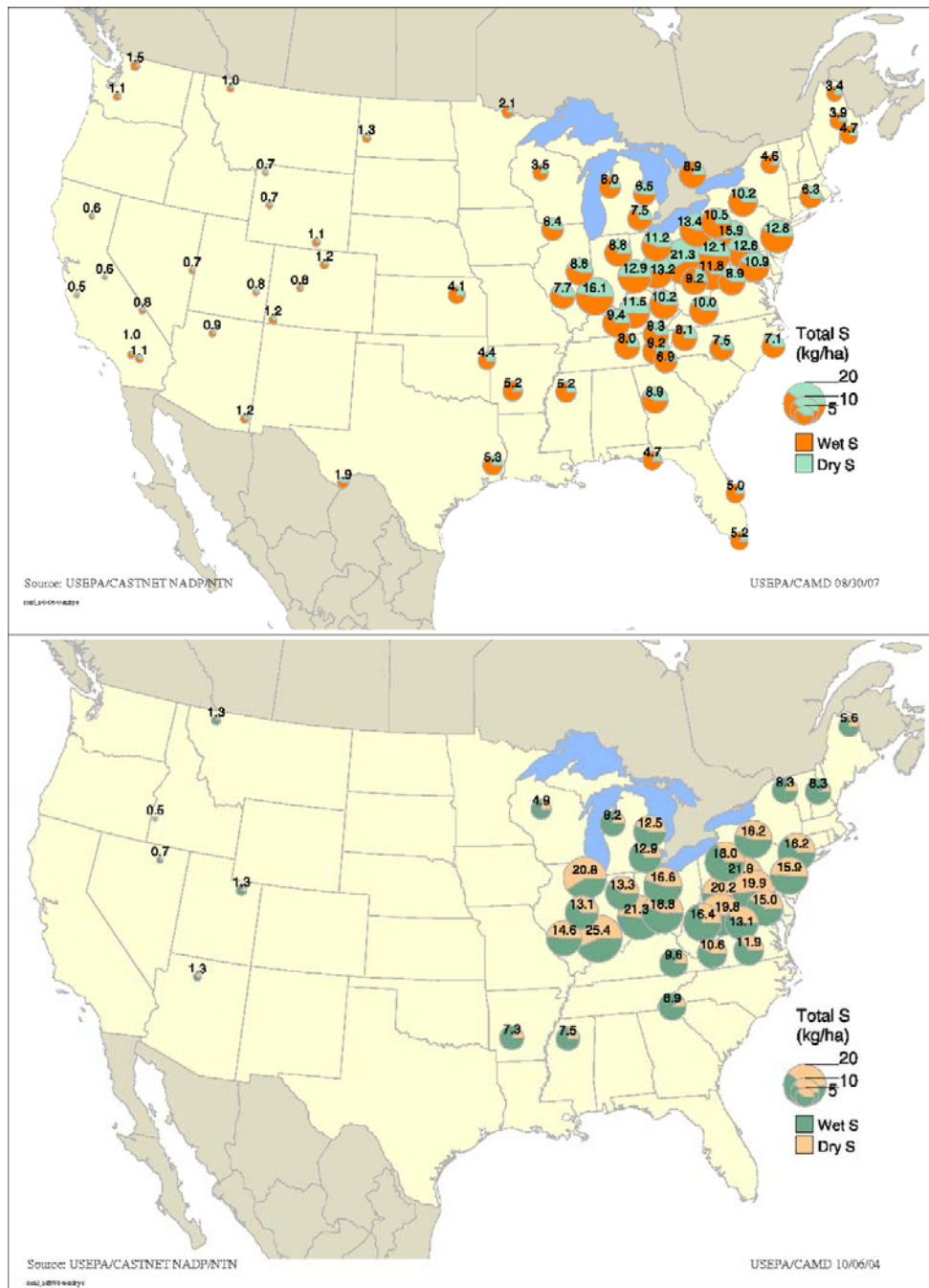
Figure 2-126. Total average yearly wet and dry S deposition for 2004–2006 (top) and 1989–1991 (bottom).
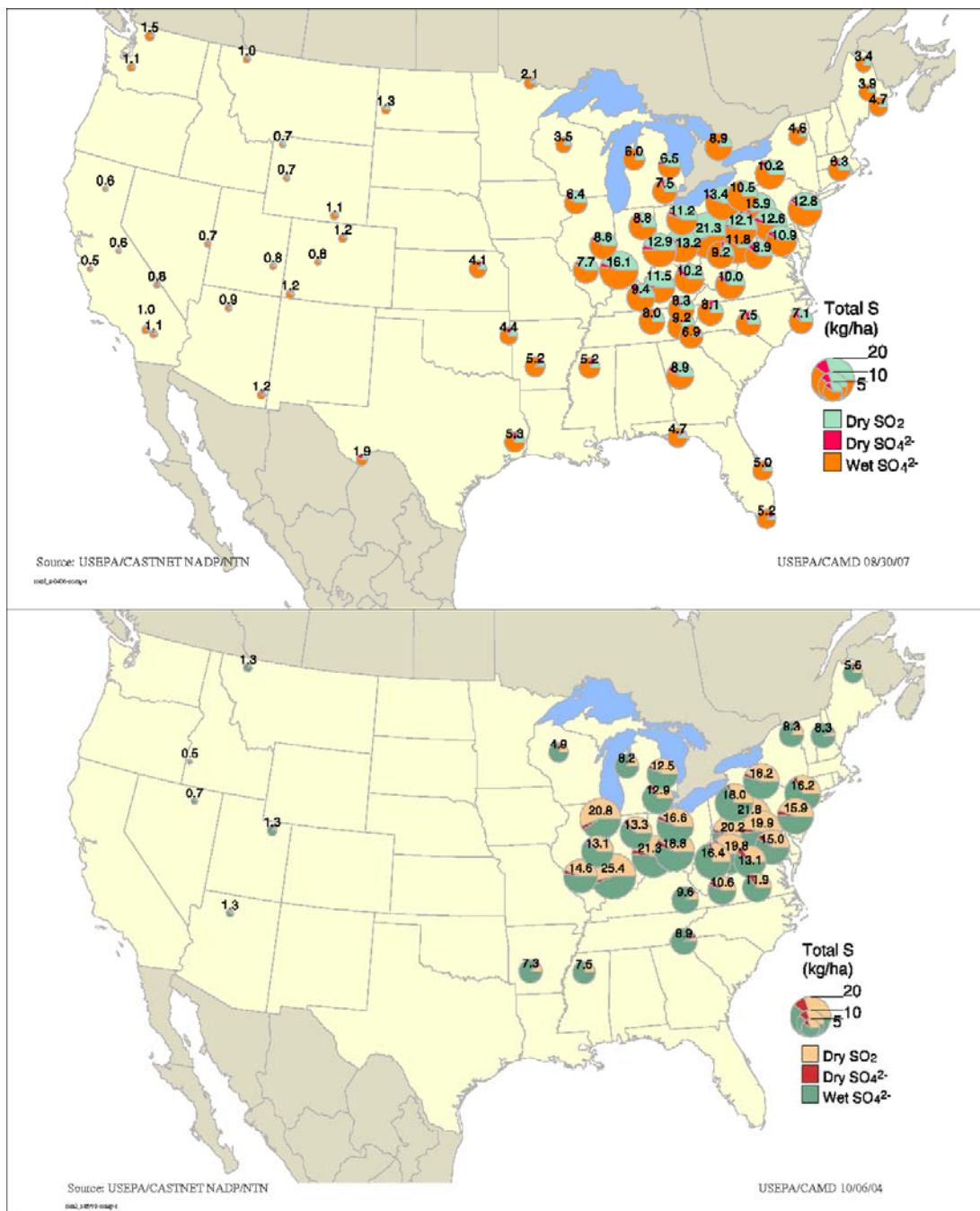
Figure 2-127. Total average yearly S deposition by species for 2004–2006 (top) and 1989–1991 (bottom).

2.11. Summary

2.11.1. Emissions and Atmospheric Concentrations

Total anthropogenic NO and NO_2 emissions in the U.S. in 2002 were 23.19 Tg. Combustion chemistry at EGUs contributed ~22% of this total, and transportation-related sources contributed ~56%. Ambient annual NO_X concentrations have decreased ~35% in the period 1990–2005 to current annual average concentrations of ~15 ppb.

Biogenic NO_X sources are substantially smaller than anthropogenic ones and include biomass burning, lightning, and soils. The NO and N_2O emitted from soils as intermediate products from denitrification can evolve either naturally or as stimulated by addition of N-containing fertilizers to crops and other soil management practices. N_2O, another member of the oxides of N family of compounds, is also a contributor to total U.S. GHG emissions: ~6.5% on a Tg CO_2e basis in 2005, and its U.S. emissions decreased ~3% in the period 1990–2005, though there remains considerable interannual variation in this value.

Concentrations of NO_2 in the CONUS from biogenic sources in the U.S., Canada, and Mexico and from all sources elsewhere in the world are defined as policy-relevant background concentrations. On an annual average basis, these concentrations are calculated to be <300 ppt over most of the CONUS and <100 ppt in the eastern U.S. where NO emissions are greatest. The 24-h ambient NO_2 levels in CMSAs where most of the regulatory monitors are located and where most anthropogenic emissions originate were, on average, <20 ppb with a 99% percentile value <50 ppb for the years 2003–2005. Annual-average NO_2 concentrations over the CONUS are calculated to be <5 ppb for nearly all urban and rural and remote sites.

On a national scale, energy production at EGUs accounted for ~66% of total SO_2 emissions in the U.S. in 2001–2002; ~5% of total SO_2 is emitted by transportation-related sources, with on-road vehicles accounting for ~40% of the transportation fraction and off-road diesel and marine traffic together accounting for the remainder. As with NO_X, emissions of SO_X have been significantly reduced in recent years: ambient annual SO_X concentrations have decreased ~50% in the period 1990–2005 and now stand at ~4 ppb for both aggregate annual and 24-h average concentrations nationwide.

Annual-average policy-relevant background SO_2 concentrations in the U.S. are <10 ppt over most of the CONUS, or <1% of observed SO_2 concentrations everywhere except areas in the Pacific Northwest where geogenic SO_2 sources are particularly strong.

NH_3 emissions are chiefly from livestock and from soils as stimulated by addition of N-containing fertilizers to crops and other soil management practices. Confined animal feeding operations and other intensified agricultural production methods over a period of many decades have resulted in greatly increased volumes of animal wastes high in N; 30 to 70% of these wastes may be emitted as NH_3. These increases in NH_3 emissions, and the consequent increases in ambient NH_3 concentrations and NH_4+ concentration and deposition, are highly correlated geospatially with the local and regional increases in agricultural intensity. However, estimates of total NH_3 emissions on national and sub-national scales range widely owing to three complex issues: the high spatial and temporal variability in NH_3 emissions; the high uncertainty in the magnitude of those emissions; and the lack of real-time, reliable, ambient NH_3 monitoring techniques. Nonetheless, U.S. national NH_3 emissions totals have been calculated, taking into account these three drivers of uncertainty; for 2001-2002 the national NH_3 emissions total from the NEI and as corrected by methods described in Section 2.5 was 4.08 Tg/yr.

2.11.2. Field Sampling and Analysis

The coverage of the networks is very thin over large expanses of the interior U.S. and especially so west of the 100th meridian. This lack of monitored sites increases the likelihood that significant exposure from N and S deposition is now occurring at current atmospheric concentrations where no measurements are available, as predicted in numerical experiments with large-scale, first-principles models of atmospheric chemistry and physics and deposition, and as measured at some few special experimental sites.

The instrumentation deployed at present in the routine monitoring networks for determination of gas-phase NO_2 and SO_2 concentrations is likely adequate for determining compliance with the current NAAQS. But in application for determining environmental effects, all these methods have important limitations, which make them inadequate for fully characterizing the state of the atmosphere at present, correctly representing the complex heterogeneity of N and S deposition across the landscape, and for realistically apportioning the contributions of reduced and oxidized forms of atmospheric N and S in driving observed biological effects at a national scale.

For example, routine NO_2 measurements by CL are contaminated by unknown and varying concentrations of higher-order oxidized N species, including gas-phase HNO_3, important in itself for N deposition to the biosphere and also as a precursor to pNO_3. Moreover, dry deposition of NO, NO_2, and PANs is not at present estimated in dry deposition networks, but could account for as much as 30% of total dry oxidized N deposition in areas near strong NO_X sources. This would include estuaries and other wetlands near large urban areas.

As concerns SO_2, the present-day ambient annual average SO_2 concentrations are very near or even below the operating LOD of most of the FRM monitors in the largest regulatory network. This produces irresolvable uncertainty in these data, which may be important for environmental effects from S compounds since they result in some cases from exposure at these current low concentrations.

Routine field sampling techniques for NH_3 are at present limited to integrated values from several days to one week because higher frequency semi-continuous methods are not yet sufficiently robust to deploy for routine operation in national networks although passive NH_3 samplers show excellent potential. Estimates for the contribution of NH_3 to the total N deposition budget range as high as 30% of total N, and are perhaps the dominant source of reduced N. Moreover, routine national-scale sampling and analysis for particulate-phase NO_3^-, SO_4^{2-}, and NH_4^+ are subject to positive and negative errors, chiefly from the loss or production of constituent species on the surface of the filter used for the long time-integrated measurement.

The aggregate effect of these uncertainties and errors very likely is to underestimate total N and S atmospheric deposition and subsequent biological exposures.

2.11.3. Nitrogen and Sulfur Deposition

Increasing trends in urbanization, agricultural intensity, and industrial expansion during the previous 100 years have produced a nearly 10-fold increase in N deposited from the atmosphere. NO_X, chiefly from fossil fuel combustion, often dominates total N pollution in the U.S. and comprises ~50 to 75% of the total N atmospheric deposition.

For the period 2004–2006, the routine monitoring networks report that the mean N deposition in the U.S. was greatest in the Ohio River Valley, specifically in Indiana and Ohio, with values as high as 9.2 and 9.6 kg N/ha/yr, respectively. N deposition was lower in other parts of the east, including the southeast and northern New England. In the central U.S., Kansas and Oklahoma reported the highest deposition: 7.0 and 6.5 kg N/ha/yr, respectively.

Table 2-25.   Regional changes in wet and dry N and S atmospheric concentrations and deposition, 1989-1991 and 2003-2005.

Measurement	Unit	Region	Average 1989–1991	Average 2003–2005	Percent Change*
Wet SO_4^{2-} deposition	kg/ha	Mid-Atlantic	27	20	-24
		Midwest	23	16	-32
		Northeast	23	14	-36
		Southeast	18	15	-19
Wet SO_4^{2-} concentration	mg/L	Mid-Atlantic	2.4	1.6	-33
		Midwest	2.3	1.6	-30
		Northeast	1.9	1.1	-40
		Southeast	1.3	1.1	-21
Ambient SO_2 concentration	µg/m³	Mid-Atlantic	13	8.4	-34
		Midwest	10	5.8	-44
		Northeast	6.8	3.1	-54
		Southeast	5.2	3.4	-35
Ambient SO_4^{2-} concentration	µg/m³	Mid-Atlantic	6.4	4.5	-30
		Midwest	5.6	3.8	-33
		Northeast	3.9	2.5	-36
		Southeast	5.4	4.1	-24
Wet inorganic N deposition	kg/ha	Mid-Atlantic	5.9	5.5	-8
		Midwest	6.0	5.5	-8
		Northeast	5.3	4.1	-23
		Southeast	4.3	4.4	+2
Wet NO_3 concentration	mg/L	Mid-Atlantic	1.5	1.0	-29
		Midwest	1.4	1.2	-14
		Northeast	1.3	0.9	-33
		Southeast	0.8	0.7	-9
Ambient NO_3^- concentration	µg/m³	Mid-Atlantic	0.9	1.0	+5
		Midwest	2.1	1.8	-14
		Northeast	0.4	0.5	+20
		Southeast	0.6	0.7	+17
Total ambient NO_3^- concentration (NO_3^- + HNO_3)	µg/m³	Mid-Atlantic	3.5	3.0	-14
		Midwest	4.0	3.5	-12
		Northeast	2.0	1.7	-13
		Southeast	2.2	2.1	-5

* Percent change is estimated from raw measurement data, not rounded; some of the measurement data used to calculate percentages may be at or below detection limits.
Source: CASTNet and the National Atmospheric Deposition Program / National Trends Network (NADP/NTN)

N deposition estimated from measurements primarily occurred in the form of wet NO_3^- and NH_4^+ followed with decreasing amounts of dry HNO_3, dry NH_4^+, and dry NO_3^-. Although deposition in most areas of the U.S. occurred in wet form, there were some exceptions, including parts of California where N deposition was primarily dry. Data are very sparse for the central U.S. between the 100th meridian and the

Mississippi River; but where available, N deposition values there were lower than in most of the eastern U.S., ranging from 4.1 to 5.3 kg N/ha/yr.

Estimates of total N loadings to estuaries, or to other large-scale elements in the landscape, are computed using the measurements of wet and dry N deposition (as reported above) where these are available, and then can be interpolated with or without a set of air quality model predictions to determine the relative contribution from the atmosphere of various species of reduced and oxidized N. Measurement and modeling experiments like these have shown that atmospheric inputs of N_r directly to the surface of some coastal waters are essentially equal to or greater than those contained in riverine flow in the absence of deposition and may contribute from 20 to >50% of external N loadings to these systems. For example, atmospheric N inputs to the northeast Atlantic coast of the U.S., the southeast Atlantic coast of the U.S., and the eastern Gulf of Mexico have been estimated to be 11, 5.6, and 5.6 kg N/ha/yr, respectively. More specifically and at finer spatial scales, atmospheric N loads to great waters and estuaries in the U.S. have been estimated to range from 2 to 8% for Guadalupe Bay, TX, on the lowest end, up to ~72% for the St. Catherine-Sapelo estuary at the highest end (Castro et al., 2003). At Chesapeake Bay, atmospheric N is estimated to contribute up to 30% of total N and 14% of the NH4 loadings to the Bay.

For the period 2004–2006, mean S deposition in the U.S. was greatest east of the Mississippi River with the highest deposition amount, 21.3 kg S/ha/yr, in the Ohio River Valley where most recording stations reported 3 year averages >10 kg S/ha/yr. Numerous other stations in the East reported S deposition >5 kg S/ha/yr. Total S deposition in the U.S. west of the 100th meridian was relatively low, with all recording stations reporting <2 kg S/ha/yr and many reporting <1 kg S/ha/yr.

S was primarily deposited in the form of wet SO_4^{2-} followed in decreasing order by a smaller proportion of dry SO_2 and a much smaller proportion of deposition as dry SO_4^{2-}. However, these annual S data in the western U.S., like those for N deposition, are derived from measurements in networks with many fewer nodes in the West than in the East and so cannot represent all subregions in the West.

Table 2-25 lists separate concentration and deposition totals for wet and dry N and S species in 4 sub-regions of the U.S. as annual averages for the years 1989–1991 and 2003–2005 as a summary of the foregoing data. Note that the U.S. West region is not present in this table owing to the dearth of annual-scale measured concentration and deposition data at a sufficient number of sites to compare to those in the eastern and Midwestern regions. Data on concentrations and deposition for individual years are available at some sites in the West, as described for those specific cases in Sections 2.9 and 2.10 above. In summary, measured N deposition in the West ranges from lows in the Pacific Northwest of between 1 and 2 kg N/ha/yr (N) (http://nadp.sws.uiuc.edu) to highs in the Sierra Nevada and San Bernardino Mountains in California of 20 to 40 kg N/ha/yr (total N) (Fenn et al., 2002 and 2003; Bytnerowicz et al., 2002), and may be higher in particular locations for some sub-annual seasons.

Chapter 3. Ecological and
Other Welfare Effects

This chapter is organized into four sections. The introduction (Section 3.1) frames the organizing principle of this chapter and several basic concepts of ecology. A discussion of acidification is presented in Section 3.2. N enrichment is discussed in Section 3.3. Lastly, other welfare effects are presented in Section 3.4, including interactions between S deposition and Hg methylation and direct gas-phase injury to vegetation.

3.1. Introduction to Ecological Concepts

3.1.1. Critical Loads as an Organizing Principle for Ecological Effects of Atmospheric Deposition

This chapter uses the critical loads concept as an organizing principle. The components that are necessary to develop a critical load provide a conceptual framework for linking atmospheric pollutants to ecological endpoints that indicate impairment. The generally accepted definition of a critical load of atmospheric pollutant deposition emerged from a pair of international workshops held in the late 1980s . The workshop participants defined a critical load as:

> "A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge."

The development of a quantitative critical load estimate requires a number of steps. An illustrative example of the eight general steps is shown in Table 3-1. A more detailed description of these steps is given in Annex D.

This chapter presents information with a focus on the following questions:

- What is the disturbance?

- What receptors are affected?

- What indicator organisms are (or previously were) present and observable?

- What chemical indicators are changing and can be measured?

- What atmospheric pollutant is driving the changes in the chemical indicators?

It is important to recognize that there is no single "definitive" critical load for a natural resource. Critical loads estimates reflect the current state-of-knowledge and policy priorities. Changes in scientific understanding may include, for example, new dose-response relationships; better resource maps and inventories; larger survey datasets; continuing time-series monitoring; and improved numerical models. Changes in the policy elements may include: new mandates for resource protection; focus on new pollutants; and inclusion of perceived new threats that may exacerbate the pollutant effects (e.g., climate change).

Table 3-1. An example of the matrix of information that must be considered in the definition and calculation of critical loads (see discussion in text). Note that multiple alternative biological indicators, critical biological responses, chemical indicators, and critical chemical limits could be used.

1) Disturbance	Acidification				Eutrophication	
2) Receptor	Forest		Lake		Grassland	Lake
3) Biological indicator	Sugar Maple	Norway Spruce	Brook trout	Fish species richness	Species diversity	Primary productivity
4) Critical biological response	Failure to reproduce	Seedling death	Presence absence	Species loss	Species loss	Excess productivity
5) Chemical indicator	Soil % Base Saturation	Soil Ca/Al ratio	Lakewater ANC	Lakewater ANC	Soil C/N ratio	Lakewater NO_3
6) Critical chemical limit	10%	1.0	0 µeq/L	50 µeq/L	20	10 µeq/L
7) Atmospheric pollutant	SO_4, NO_3, NH_4	SO_4, NO_3, NH_4	SO_4, NO_3, NH_4	SO_4, NO_3, NH_4	NO_3, NH_4	NO_3, NH_4
8) Critical pollutant load	???	???	???	???	???	???

This procedure can result in calculation of multiple critical loads for a given pollutant at a single location. The multiple solutions derive from the nested sequence of disturbances, receptors, and biological indicators that must be considered for a given pollutant. Multiple critical load values may also arise from an inability to agree on a single definition of "significant harm." Calculation of critical loads for multiple definitions of "harm" may be deemed useful in subsequent discussions of the analysis and in the decision-making steps that may follow critical load calculation.

Finally, there is the inescapable heterogeneity of all natural environments. Consider soils, for instance. The high spatial variability of soils almost guarantees that for any reasonably sized soil-based "receptor" that might be defined in a critical load analysis, there will be a continuum of critical load values for any indicator chosen. The range of this continuum of values may be narrow enough to be ignored; nevertheless, there is an a priori expectation in any critical load analysis that multiple values (or a range of values) will result from the analysis. Given the heterogeneity of ecosystems affected by N and S deposition, examples of published critical load values for a variety of endpoints and locations in the U.S. are presented here (see Section 3.3.7).

3.1.2. Ecosystem Scale, Function, and Structure

Information presented in this ISA was collected at multiple scales, ranging from the physiology of a given species to population, community, and ecosystem-level investigations. For this assessment, "ecosystem" is defined as a functional entity consisting of interacting groups of living organisms and their

abiotic (chemical and physical) environment. Ecosystems cover a hierarchy of spatial scales and can comprise the entire globe, biomes at the continental scale, or small, well-circumscribed systems such as a small pond.

Ecosystems have both structure and function. Structure may refer to a variety of measurements including the species richness, abundance, community composition and biodiversity as well as landscape attributes. Competition among and within species and their tolerance to environmental stresses are key elements of survivorship. When environmental conditions shift, for example, by the presence of anthropogenic air pollution, these competitive relationships may change and tolerance to stress may be exceeded. Function refers to the suite of processes and interactions among the ecosystem components and their environment that involve nutrient and energy flow as well as other attributes including water dynamics and the flux of trace gases. Plant processes including photosynthesis, nutrient uptake, respiration, and C allocation, are directly related to functions of energy flow and nutrient cycling. The energy accumulated and stored by vegetation (via photosynthetic C capture) is available to other organisms. Energy moves from one organism to another through food webs, until it is ultimately released as heat. Nutrients and water can be recycled. Air pollution alters the function of ecosystems when elemental cycles or the energy flow is altered. This alteration can also be manifested in changes in the biotic composition of ecosystems.

3.1.3. Ecosystem Services

Ecosystem structure and function may be translated into ecosystem services. Ecosystem services identify the varied and numerous ways that ecosystems are important to human welfare. Ecosystems provide many goods and services that are of vital importance for the functioning of the biosphere and provide the basis for the delivery of tangible benefits to human society. Hassan et al. (2005) define these to include supporting, provisioning, regulating, and cultural services:

- Supporting services are necessary for the production of all other ecosystem services. Some examples include biomass production, production of atmospheric O_2, soil formation and retention, nutrient cycling, water cycling, and provisioning of habitat. Biodiversity is a supporting service that is increasingly recognized to sustain many of the goods and services that humans enjoy from ecosystems. These provide a basis for three higher-level categories of services.

- Provisioning services, such as products (Gitay et al., 2001), i.e., food (including game, roots, seeds, nuts and other fruit, spices, fodder), fiber (including wood, textiles), and medicinal and cosmetic products (including aromatic plants, pigments).

- Regulating services that are of paramount importance for human society such as (a) C sequestration, (b) climate and water regulation, (c) protection from natural hazards such as floods, avalanches, or rock-fall, (d) water and air purification, and (e) disease and pest regulation.

- Cultural services that satisfy human spiritual and aesthetic appreciation of ecosystems and their components.

3.2. Ecological Effects of Acidification

This section describes the major effects of acidification on terrestrial and aquatic ecosystems resulting primarily from acidifying deposition. In this document, acidifying deposition includes gases and particles derived from SO_X, NO_X, and NH_X.

3.2.1. Effects on Major Biogeochemical Processes

Acidifying deposition has altered major biogeochemical processes in the U.S. by increasing the S (Figure 3-1) and N content of soils, accelerating SO_4^{2-} and NO_3^- leaching from soil to drainage water, depleting base cations (especially Ca and Mg) from soils, and increasing the mobility of Al. The extent of soil acidification is a critical factor that regulates virtually all acidification-related ecosystem effects from S and N deposition. Soil acidification occurs in response to both natural factors and acidifying deposition. To best integrate the effects of acidifying deposition, this assessment starts with a description of the effects on soils and major biogeochemical processes within ecosystems, then summarizes the chemical and biological effects on terrestrial, transitional, and aquatic ecosystems. More detailed information on acidification effects is provided in Annex B.
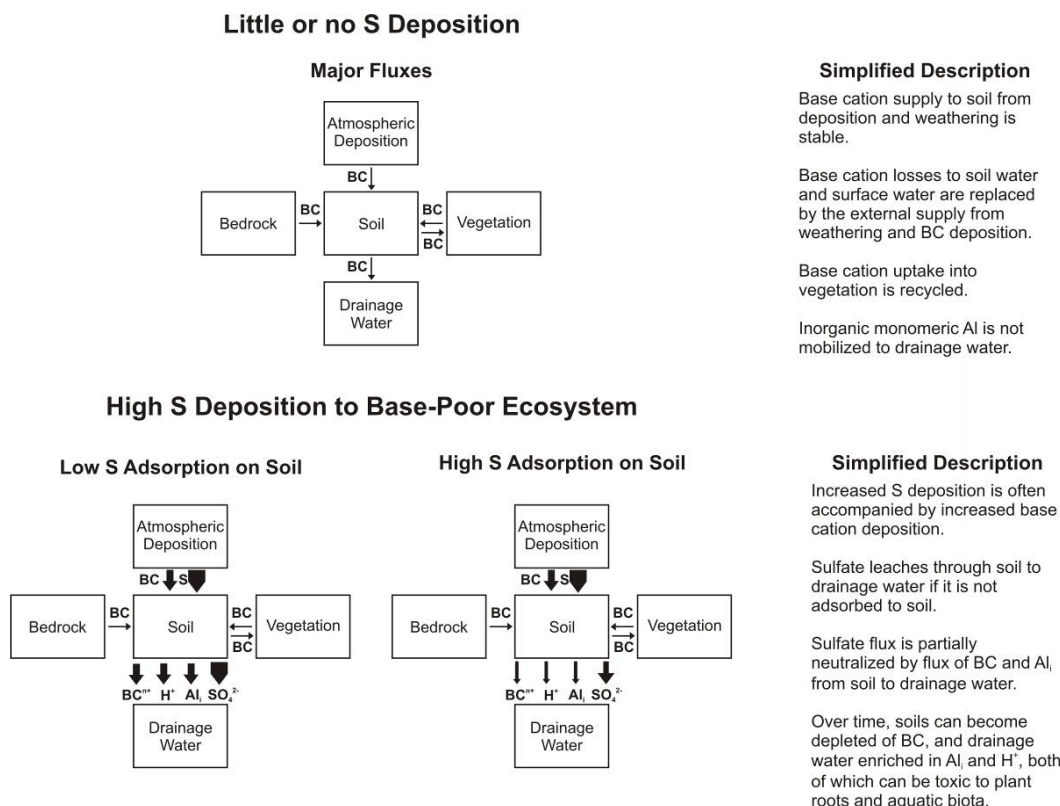
Figure 3-1. Illustration of major fluxes of ions associated with S-driven acidification of drainage water. The upper diagram represents ion fluxes in the absence of S deposition. The two lower diagrams illustrate changes to these fluxes in response to S deposition on two types of soils, without (left) and with (right) substantial S adsorption on soil. Effects are most pronounced under high deposition with little adsorption, and include increased leaching of base cations (contributes to soil acidification), H (reduced pH), and Al$_i$ (toxic to many plant roots and aquatic species). Larger fluxes are represented by thicker arrows.

3.2.1.1. Soil Acidification

Soil acidification is the loss of base cations plus the accumulation of acidic cations such as hydrogen ions (H^+) and aluminum ions (Al^{n+}) in the soil; this happens when a proton donor is added to the soil. Soil acidification is a natural process. Such natural acidity is contributed by carbonic acid, organic acids, and plant cation uptake (Charles, 1991; Turner et al., 1991). However, the donor can also be a mineral acid, such as HNO_3 and H_2SO_4, the common components of acid rain that result from NO_X and SO_X air pollution. Decreases in soil pH attributable to acidifying deposition have been documented in the U.S. (Bailey et al., 2005; Johnson et al., 1994a, b; Sullivan et al., 2006a). Effects in the eastern U.S. appear to have been limited mainly to the Northeast and portions of the Appalachian Mountains in both hardwood and coniferous forests. Soil acidification has also likely occurred in localized areas of mixed conifer forest and chaparral vegetation in, and near, the Los Angeles Basin, in response to locally high levels of atmospheric dry N deposition (Fenn et al., 2003a).

To evaluate soil acidification, the soil must be considered in terms of the surface organic layer (the primary rooting zone), of which the Oa horizon (or in some studies the O horizon, which combines the Oe and Oa horizons) is an important component (See Figure 3-2). In addition, the mineral soil including the A and/or B horizon, which lie below the Oa horizon and are primarily comprised of mineral matter, must be considered.

Acidifying deposition can have a direct effect on soil pH. However, net uptake of nutrient cations by vegetation can also generate acidity within the soil, and a considerable amount of natural organic acidity is produced in the Oa horizon through the partial decomposition of organic matter. This process can decrease the pH of soil water in the Oa horizon well below the lowest pH values measured in acidifying deposition (Krug et al., 1985; Lawrence et al., 1995). Oa-horizon soils under coniferous vegetation are strongly acidified by organic acids and are unlikely to have experienced a lowering of pH as a result of acidifying deposition (Johnson and Fernandez, 1992; Lawrence et al., 1995). Soils influenced by the growth of hardwood species tend to have surface horizons that are less acidic naturally and are, therefore, more susceptible to decreased pH in the Oa horizon from acidifying deposition. By taking up larger amounts of Ca from the soil, hardwoods can acidify lower soil horizons more than conifers even though they enrich surface horizons with Ca via litterfall (Alban, 1982).
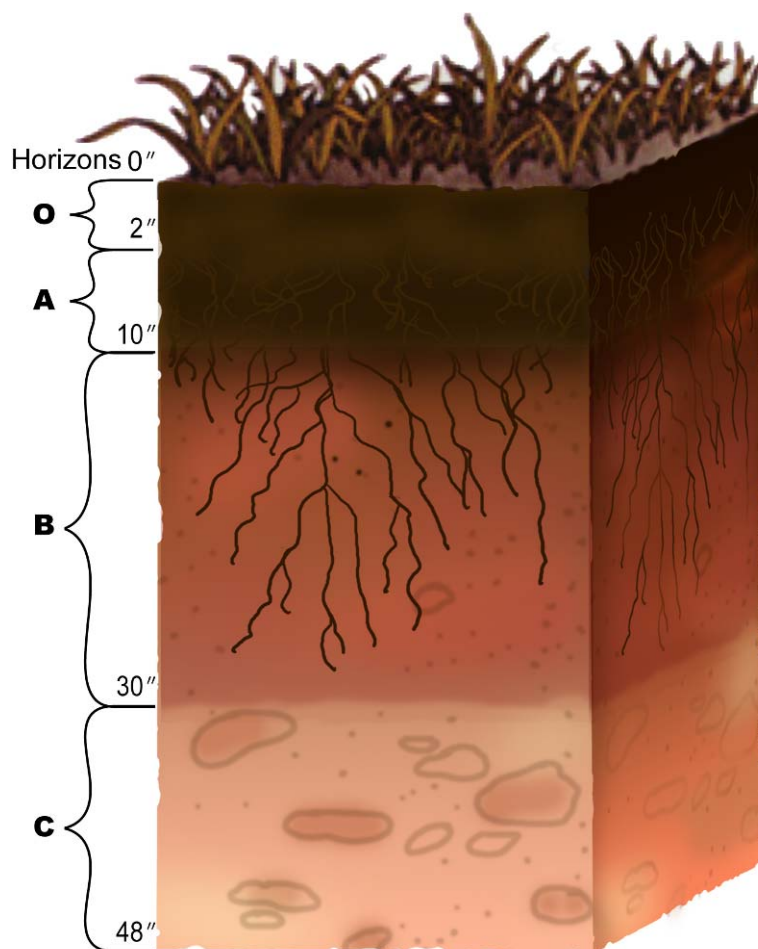
Figure 3-2.   **Diagram illustrates soil horizons commonly found. Each main horizon is denoted by a capital letter O) Organic matter: Litter layer of plant residues in relatively undecomposed form. A) Surface soil: Layer of mineral soil with most organic matter accumulation and soil life. This layer is depleted of iron, clay, aluminum, organic compounds, and other soluble constituents. B) Subsoil: This layer accumulates iron, clay, aluminum and organic compounds. C) Substratum: Layer of unconsolidated soil parent material. This layer may accumulate the more soluble compounds that bypass the "B" horizon.**

Several studies document declines in soil pH within the Oa/A horizons and the upper B horizon in sensitive regions of the U.S. over the past several decades (Bailey et al., 2005; Drohan and Sharpe, 1997; Johnson et al., 1994a, b; Warby et al. (2009). These declines have been attributed at least partly to acidifying deposition (Bailey et al., 2005).

In summary, soil acidification is a natural process, which is often exacerbated by acidifying deposition. Natural acidification is particularly pronounced in coniferous forests. Acidifying deposition can contribute to soil acidification, with consequent effects on the availability of nutrient cations in soil and the chemistry of drainage water that flows from soil into streams and lakes. Despite recent decreases in acidifying deposition and some improvement in surface water acid-base status, there are widespread observations of ongoing soil acidification such as decreases in soil exchangeable base cations (Bailey et al., 2005; Sullivan et al., 2006a, b; Warby et al., 2009) (See Section 3.2.1.4). More detailed descriptions of soil acidification are provided by Binkley and Richter (1987) and van Breemen et al. (1983).

3.2.1.2. Sulfur Accumulation and SO_4^{2-} Leaching

Most acidification-related consequences of atmospheric S and N deposition in the U.S. are caused by SO_4^{2-} (Driscoll et al., 2001b; Sullivan, 2000). The mobility within the watershed of SO_4^{2-}, derived from atmospheric S deposition, is a key factor governing many aspects of soil and water acidification at locations in the U.S. that are affected by acidifying deposition.

Upon deposition to the Earth's surface, S may be assimilated by vegetation or microbes, accumulate in the soil or act as a mobile ion and leach out of the soil. When a given area is affected by acidifying deposition, S deposition levels are typically much higher than plant demand for S and consequently almost all deposited S is transported to the soil where it may accumulate and is available for leaching as SO_4^{2-}. SO_4^{2-} acts as a mobile anion at many locations in the U.S. that receive high levels of S deposition, notably the glaciated Northeast and Upper Midwest, where much of the deposited S leaches through soils into streams and lakes. SO_4^{2-} leaching leads to most of the ecological effects from atmospheric S deposition because it is accompanied by leaching of cations, and this contributes to acidification of soil, soil water, and surface water.

Over time, sustained SO_4^{2-} leaching and associated soil acidification contributes to pronounced changes in soils in some areas. When S is transported from soils to surface waters in the form of SO_4^{2-}, an equivalent amount of cations, or countercharge, is also transported. When the countercharge is provided by base cations, the base saturation of the soil is reduced as the acidity of the soil water is neutralized. However, this process acidifies the soil, thereby decreasing the soil's capacity to neutralize additional acidity deposited from the atmosphere and prevent acidification of soil water, and by connection, surface water. As the base cations become depleted, the countercharge provided by acidic cations (H^+ and inorganic Al) increases, sometimes resulting in toxic conditions for plant roots and aquatic organisms (Charles, 1991; Turner et al., 1991).

In the U.S., there are some regional trends of soil accumulation, retention, and leaching of S that are discussed below.

Southeast

Accumulation of atmospherically deposited S in soil has resulted from anion adsorption and incorporation of S into organic matter through biological assimilation. Such retention of S can temporarily reduce SO_4^{2-} leaching and cause a delay in ecosystem recovery in response to decreases in S deposition, as some accumulated S is slowly released from the soil into drainage water. S adsorption on soil is especially pronounced in the southeastern U.S. Under continued loading of S deposition, it is expected that many southeastern watersheds will exhibit a gradual decrease in the extent of S adsorption in the future. This will likely contribute to further acidification of some streams, even under substantially reduced levels of S deposition (Elwood et al., 1991; Sullivan et al., 2004; Turner et al., 1991).

Northeast

In the Northeast, the accumulation of a portion of the historic legacy of atmospheric S deposition in soil was demonstrated by a positive relationship between wet deposition of SO_4^{2-} and concentrations of total S in the forest floor of 12 red spruce stands (Driscoll et al., 2001a). However, net loss of S from soils now appears to be occurring in a number of northeastern watersheds in response to decreased levels of atmospheric S deposition. The potential for net mineralization of stored S might affect recovery of drainage waters (Gbondo-Tugbawa et al., 2002; Likens et al., 2002; Novák et al., 2007). Where leaching of previously stored S occurs, it delays soil and surface water chemical recovery from acidification (Driscoll et al., 2001b).

Weathering contributes substantial S in some watersheds (Shanley et al., 2005). Uncertainties in estimates of ecosystem S fluxes, such as weathering and dry deposition, and the difficulty in discerning the effects of net SO_4^{2-} desorption and net S mineralization make it difficult to predict when S outputs in

the northeastern U.S. will no longer exceed inputs. Recent research results, based on experimental reduction of S inputs, suggest that this process will occur on a decadal timescale (Martinson et al., 2005; Mörth et al., 2005). The long-term role of C-bonded S adds further uncertainty because enhancement of S mineralization by a warming climate could also affect S retention and release from soil (Driscoll et al., 2001a; Knights et al., 2000),

In summary, atmospheric S deposition alters soil chemistry through the following mechanisms: sustained SO_4^{2-} leaching and associated changes in soil chemistry, and accumulation of S in the soil through physical/chemical adsorption and biological assimilation. The recent evidence of net loss of S from soils at a number of sites in the Northeast is a likely response to recent decreases in atmospheric S inputs (Driscoll et al., 2001b). The gradual loss of previously accumulated S is further contributing to continued SO_4^{2-} leaching and soil acidification.

3.2.1.3. Nitrogen Accumulation and NO_3^- Leaching

The scope of this section is the role of N deposition in the process of acidification. This assessment divides the effects of N deposition into the two broad categories of acidification and N nutrient enrichment effects. The latter is discussed in Section 3.3. N deposition may cause acidification of ecosystems via three main mechanisms: excess accumulation in soils followed by increased rates of nitrification by microbes; change in base cation status of soils caused by NO_3^- leaching; and increased growth of vegetation causing increased cation uptake.

Nitrification and Accumulation

Atmospherically deposited N accumulates in soil through incorporation of N into organic matter. Accumulation is either documented or suggested to occur across large areas of the U.S. (Aber et al., 2003). Direct evidence for such accumulation has been found in the northeastern U.S. and in Colorado. Increased accumulation of N in soil is suggested, for example, by a positive correlation between atmospheric deposition levels and total N concentration in the Oa soil horizon at red spruce sites in New York, Vermont, New Hampshire, and Maine (Driscoll et al., 2001b). Mass balance studies also show soil N retention (e.g., Campbell et al., 2004). Further evidence that atmospheric deposition has increased the availability of N in soil is provided by the strong negative correlation between atmospheric N deposition and the C:N ratio of the Oa soil horizon across the northeastern U.S. (Aber et al., 2003).

The nitrification process is mediated by autotrophic bacteria that derive energy by oxidizing NH_4^+ to NO_3^-. Nitrification produces acidity in the form of HNO_3 as a byproduct. The HNO_3 produced contributes to the acidification of soils and surface waters. If the C:N ratio of soils falls below about 20 to 25, nitrification is stimulated and net nitrification and associated production of acidity occurs in soils (Aber et al., 2003; Emmett et al., 1998). This process often results in elevated NO_3^- concentration in soil waters and surface waters (Aber et al., 2003; Ross et al., 2004). Thus, data collected from streams and lakes can yield important information about processes that occur in the soil. N saturation refers to the condition when N inputs from atmospheric deposition and other sources exceed the biological requirements of the ecosystem. Excess N supply reduces competition between plants and heterotrophic microbes for NH_4^+ to the point that net nitrification occurs (Aber et al., 1998, 2003).

Leaching

In many upland forested areas in the U.S., a large fraction of the N received in atmospheric deposition is retained in soil or in plant biomass. Nevertheless, elevated NO_3^- concentration in surface waters during the growing season is common and widespread in the U.S. (Charles, 1991). High concentrations of NO_3^- in lakes and streams, indicative of ecosystem N saturation in most natural systems, have been found at a variety of locations throughout the U.S. (Stoddard, 1994; U.S. EPA, 2004). In general, atmospheric deposition of 8 to 10 kg N/ha/yr or more, results in NO_3^- leaching to surface

waters in the eastern U.S. Lower N deposition levels (<5 kg N/ha/yr) may lead to NO_3^- leaching in the mountainous West because of colder temperatures, shorter growing season, little soil development, extensive exposed bedrock, and rapid melting of large snowpacks (Baron et al., 1994; Williams et al., 1996a).

NO_3^- leaching usually contributes to the leaching of base cations from soils to surface waters. Although concentrations of NO_3^- are typically less than SO_4^{2-} in drainage waters in most ecosystems in the U.S., concentrations of NO_3^- in some streams are high enough to suggest a substantial role for NO_3^- in base cation loss from soil, particularly during periods of high soil-water NO_3^- flux during the non-growing season (Cook et al., 1994; Van Miegroet et al., 1992).

The relationship between atmospheric N deposition and NO_3^- leaching from forest ecosystems is often modified by land-use history, current land-use, land disturbance, tropospheric O_3 levels, and climate. The N retention capacity of soils is highly dependent on land-use history and its effects on N cycling and pool sizes. For example, the removal of trees reduces the amount of N in the watershed and enhances the demand of vegetative regrowth for added N. This effect results in little or no NO_3^- leaching and can last for decades to more than a century (Goodale et al., 2000). NO_3^- leaching is also affected by current land use (U.S. EPA, 2006e). In the northeastern U.S., concentrations of N in streams of upland forested watersheds tend to be considerably lower than in streams draining watersheds with other land uses (Aber and Driscoll, 1997; Aber et al., 2003). Perhaps the most noteworthy effect of urban land use on processes of nutrient enrichment from N deposition concerns the transport of NO_3^- to N-limited estuarine and near-coastal waters. This topic is discussed in Section 3.3.2.4. In agricultural, and especially in forested areas, it is generally expected that most atmospherically deposited N is taken up by terrestrial vegetation. This is usually not the case in urban landscapes, although it is sometimes possible. Due to the relatively large impervious surface area in the urban landscape (e.g., buildings, roads, parking lots), a higher percentage of precipitation is routed directly to surface waters, with less opportunity for vegetative uptake of deposited N.

Climatic factors also play an important role in determining the extent of NO_3^- leaching. In particular, temperature and moisture have large effects on N cycling and NO_3^- leaching. Murdoch et al. (1998) found that, for at least one site, annual mean NO_3^- concentrations in stream water were not related to annual wet N deposition, but rather, were positively correlated with mean annual air temperature. This pattern was likely due partly to the fact that microbial processes responsible for NO_3^- production are very sensitive to temperature. Fluctuations in microbial immobilization and mineralization in response to climatic variability affect NO_3^- losses to drainage waters.

Long-term data sets also suggest that climate may affect patterns of NO_3^- loss. Many of the original (sampled periodically since the early 1980s) long-term monitoring lakes in the Adirondack Mountains showed increased NO_3^- leaching from terrestrial ecosystems throughout the 1980s, which was followed by a decline during the 1990s (Driscoll et al., 2003b, d). Decreasing stream NO_3^- concentrations during the 1990s were also observed in the Catskill Mountains and in New Hampshire (Driscoll et al., 2003b). There was not a substantial change in N emissions or deposition in the Northeast region over that period. Climatic factors, increases in atmospheric CO_2, and interactions with increasing availability of DOC have been proposed as possible contributing factors for regional decreases in NO_3^- in drainage water during the 1990s, but the driver of this decadal scale pattern remains under investigation. Snowmelt and rain-on-snow, along with soil freezing, can influence N cycling in cold climates (Campbell et al., 2005; Eimers et al., 2007; Park et al., 2003).

3.2.1.4. Base-Cation Leaching

Acidifying deposition has been shown to be an important factor causing decreases in concentrations of exchangeable base cations in soil. Loss of base cations from soil is a natural process. Under conditions of low atmospheric deposition of S and N the limited mobility of anions associated with naturally derived acidity (organic acids and carbonic acid) controls the rate of base cation leaching. Inputs

of S and N in acidifying deposition enhance inputs of strong acid anions that can accelerate natural rates of base-cation leaching (Cronan et al., 1978; Lawrence et al., 1999).

Leaching of base cations from watershed soils to surface waters is a mechanism that depletes essential plant nutrients from soil and limits the extent of surface water acidification in response to acidifying deposition. When SO_4^{2-} and NO_3^- leaching occur in equal magnitude to base cation leaching, the drainage water is not acidified. However, in the process of neutralizing the acidity of drainage water, base cation release from soil causes depletion of the base saturation of the soil. Soil base saturation expresses the concentration of exchangeable bases (Ca, Mg, potassium [K], sodium [Na]) as a percent of the total cation exchange capacity (which includes exchangeable H^+ and inorganic Al). Under conditions of low soil base saturation (<20%) and elevated concentrations of strong acid anions, Al is mobilized from soil to drainage water (Cronan and Schofield, 1990), with potentially harmful consequences for sensitive terrestrial plants and aquatic organisms throughout the food web.

In the 1990s, data were published supporting the occurrence of base cation depletion from soils in the U.S. (Lawrence and Huntington, 1999; Lawrence et al., 1995; 1997), although decreases in exchangeable Ca concentrations had earlier been identified in European soils through repeated sampling. Recent data revealed that decreases in concentrations of exchangeable base cations and base saturation in the Oa and B soil horizons have occurred over the past several decades in the eastern U.S. and most studies attribute this change to the effects of acidifying deposition. For example, a soil re-sampling study in the U.S. was conducted in northwestern Pennsylvania by Bailey et al. (2005). This study showed that between 1967 and 1997 pronounced decreases, attributed largely to acidifying deposition, were measured in exchangeable Ca and Mg concentrations in Oa/A horizons and throughout the B horizon (See also comments by Johnson [2005]). Data compiled by Sullivan et al. (2006a, b) suggested decreases in base saturation of B-horizon soils in the Adirondack Mountains between the mid-1980s and 2003. In another re-sampling study in the northeastern U.S. Warby et al. (2009) observed large decreases in exchangeable Ca and base saturation in the Oa horizons between 1984 and 2001, attributed to acidifying deposition. The greatest decreases in exchangeable Ca and base saturation were observed in the regions of central New England and Maine, where depletion of base cations was less apparent in 1984. Depletion of base cations contributes to soil acidification and influences the ability of watershed soils to support acid-sensitive vegetation and to neutralize acidity in future acidifying deposition. Both plant uptake of cations, for example via forest regrowth subsequent to logging or land use conversion, and acidifying deposition can acidify soils (Johnson and Todd, 1990; Richter and Markewitz, 2001; Trettin et al., 1999).

Upslope decreases in exchangeable soil base cation concentrations were found to be positively correlated with higher S deposition in the Catskill Mountains (Lawrence et al., 1999). Furthermore, declines in soil exchangeable pools of base cations have been documented in New Hampshire (Likens et al., 1996) and Norway (Kirchner and Lydersen, 1995). In summary, leaching of base cations associated with acidifying deposition is occurring in sensitive regions in the U.S. Base cation loss increases the sensitivity of the watershed to further acidifying deposition. Watersheds that were capable of fully neutralizing a particular level of acidifying deposition in the past may no longer be capable of fully neutralizing that level today or at some time in the future because of the cumulative effect of acidifying deposition on soil base saturation. Where the availability of exchangeable base cations is limited, the leaching of potentially toxic inorganic Al into soil and surface waters can result.

3.2.1.5. Aluminum Leaching

If soil base saturation is 20 to 25%, or lower, acidifying deposition can mobilize inorganic Al, which can lead to the leaching of this potentially toxic form of Al into soil waters and surface waters (Cronan and Schofield, 1990; Reuss and Johnson, 1985). This is an extremely important effect of acidifying deposition because some forms of inorganic monomeric Al, including Al^{3+} and various hydroxide species, are toxic to tree roots, fish, algae, and aquatic invertebrates (see Section 3.2.3). In fact, fish mortality in response to surface water acidification is usually attributable to Al toxicity. Increased

concentrations of exchangeable inorganic Al in the mineral soil have been identified through repeated sampling in the U.S. and Europe over periods ranging from 17 years to 41 years in studies by Billet et al. (1990), Falkengren-Grerup and Eriksson (1990), Bailey et al. (2005), and Lawrence et al. (1995). In areas of Europe with excessively high acidic deposition levels, evidence of Al depletion in the mineral soil has also been found (Lapenis et al., 2004; Mulder et al., 1989), but Al depletion has not been documented in the U.S.

Acidifying deposition is an important cause of increased mobilization of inorganic Al from soils to streams and lakes (Turner et al., 1991). Acidifying deposition introduces mineral acidity associated with anions that are more mobile than those from organic matter. If the release of base cations from the soil is insufficient to neutralize the inputs of sulfuric and nitric acid, then Al that had previously been deposited by normal soil development in the upper mineral soil is mobilized. Al may also be mobilized by organic acids. However, acidifying deposition mobilizes Al in inorganic forms, and in doing so increases the amount of exchangeable inorganic Al within the B horizon and results in transport of inorganic Al into soil waters and surface waters (Driscoll and Bisogni, 1984; Driscoll et al., 1985). Inorganic Al is minimally soluble at pH about 6.0, but solubility increases steeply at pH values below about 5.5. This distinction between organic and inorganic forms of Al is important because organic Al is not toxic, whereas inorganic Al is toxic to a variety of plants and aquatic organisms (Baker and Schofield, 1982; Baldigo and Murdoch, 1997; Joslin and Wolfe, 1988, 1989)(Section 3.2.3.1). Discussions in this document of inorganic Al in solution refer to dissolved, rather than particulate or colloidal, forms. These dissolved inorganic Al species are often collectively called inorganic monomeric Al (Driscoll, 1984).

Recovery of soil chemistry will require a decrease in exchangeable Al concentrations and Al leaching. Once acidified, it is unlikely that soil exchangeable Al concentrations will decline again unless soils are limed. Therefore, it is unclear what length of time would be required to decrease soil exchangeable Al concentrations to levels characteristic of unpolluted systems. Furthermore, in most cases it is unclear whether exchangeable Al concentrations are continuing to increase, remaining stable, or decreasing. Predictions of trends in exchangeable Al concentrations remain uncertain because of our incomplete understanding of mechanisms through which mineral matter and organic matter interact to control dissolved Al concentrations. Possible changes in the dynamics of soil organic matter that could be expected from climate change add further uncertainty to predictions of future change in exchangeable Al concentrations in soils.

In summary, the natural downward movement and deposition of Al within the upper soil profile is altered by acidifying deposition if the release of base cations is insufficient to buffer atmospheric inputs of acidity. Rather than be deposited as an alumino-organic complex, Al mobilized by acidifying deposition tends to remain in solution in inorganic forms that can be transported out of the soil and into surface waters. Depletion of exchangeable base cations generally precedes the mobilization of inorganic Al; therefore, as base cation concentrations in drainage water decrease, inorganic Al concentrations may increase. Increases in concentrations of inorganic Al have been documented at several locations in base-cation depleted soils in the U.S. and Europe. In soils with base saturation values less than about 15 to 20%, the ratio of exchangeable Ca to Al is typically low in upper mineral soils (Lawrence et al., 2005).

3.2.1.6. Episodic Acidification

The status of surface water chemistry can be examined and reported as chronic condition or episodic condition. Chronic condition refers to annual average conditions, which are often represented as summer and fall chemistry for lakes and as spring baseflow chemistry for streams. Episodic condition refers to conditions during rainstorms or snowmelt when proportionately more drainage water is routed through upper soil horizons, which tend to provide less neutralization of atmospheric acidity as compared with deeper soil horizons. Surface water chemistry exhibits lower pH and acid neutralizing capacity (ANC) during episodes than during baseflow conditions.

One of the most significant effects of acidifying deposition on surface water chemistry is the short-term change in chemistry termed "episodic acidification." While natural processes contribute to seasonal and short-term increases in the acidity of surface waters, research from several regions in the U.S. indicates that acidifying deposition likely has substantially increased the magnitude, frequency, and biological effects of episodic acidification events. Many streams that exhibit chemical conditions during base flow (relatively stable flows that occur between storms) that is suitable for aquatic biota, are subject to occasional episodic acidification with adverse consequences. During such episodes, both stream flow and water chemistry can change markedly (Figure 3-3). Episodic acidification can cause declines in pH and ANC, and most significantly, increases in inorganic Al concentrations in stream waters of the Northeast, Pennsylvania, and in the central Appalachian Mountain region (Charles, 1991). Episodic decreases in pH and ANC have been documented throughout the country (Wigington et al., 1990).

Episodes are generally accompanied by changes in at least two or more of the following chemical parameters: ANC, pH, base cations, SO_4^{2-}, NO_3^-, Al^{n+}, organic acid anions, and DOC (Sullivan, 2000). The U.S. EPA's Episodic Response Project (ERP) confirmed the chemical and biological effects of episodic pH depressions in lakes and streams in parts of the U.S. (Wigington et al., 1993). The ERP illustrated that episodic processes are mostly natural, that SO_4^{2-} and especially NO_3^- attributable to atmospheric deposition play important roles in the episodic acidification of some surface waters, and that the chemical response that has the greatest effect on biota is increased Al_i concentration. Similar findings had been reported elsewhere, especially in Europe, but the ERP helped to clarify the extent, causes, and magnitude of episodic acidification in portions of the U.S. (Sullivan, 2000a).

Aquatic biota vary greatly in their sensitivity to episodic decreases in pH and increases in inorganic Al in waters having low Ca concentration. Baker et al. (1990b) concluded that episodes are most likely to affect biota if the episode occurs in waters with pre-episode pH above 5.5 and minimum pH during the episode of less than 5.0. The most thorough characterization of episodic variation in stream chemistry in the U.S. was conducted through the ERP, in which 13 low-order streams (watershed areas less than 24 km^2) in the Adirondack and Catskill regions of New York and the Appalachian Plateau in Pennsylvania were monitored from 1988 to 1990 (Wigington et al., 1996). About 10% of the acid episodes involved decreases in ANC of up to 200 μeq/L, decreases in pH of up to one unit, and increases in concentrations of inorganic Al of up to 15 μM (Wigington et al., 1996). Results showed that acid episodes reduced the size of fish populations and eliminated acid-sensitive species if median high-flow pH was less than 5.2 and inorganic Al concentration exceeded 3.7 μM, despite the relatively short duration of episodes (Baker et al., 1996).

Results from the ERP demonstrated that episodic acidification can have long-term adverse effects on fish populations. Streams with suitable chemistry during low flow, but low pH and high inorganic Al levels during high flow, had substantially lower numbers and biomass of brook trout than were found in non-acidic streams (Wigington et al., 1996).

In many regions, the most severe acidification of surface waters generally occurs during spring snowmelt (Charles, 1991). Stoddard et al. (2003) found that, on average, the difference between spring and summer ANC during baseflow in New England, the Adirondacks, and the Northern Appalachian Plateau was about 30 μeq/L during the period 1990 to 2000 (see Figure 3-4). This implies that lakes and streams in these regions would need to recover to chronic ANC values above 30 μeq/L before they could, on average, be expected to not experience acidic episodes (Stoddard et al., 2003). However, the estimate of 30 μeq/L is certain to be low because the comparison was made with non-episodic sampling in spring, expressed as average spring ANC. ANC measured during episodic spring events would be expected to be lower than average ANC during spring.
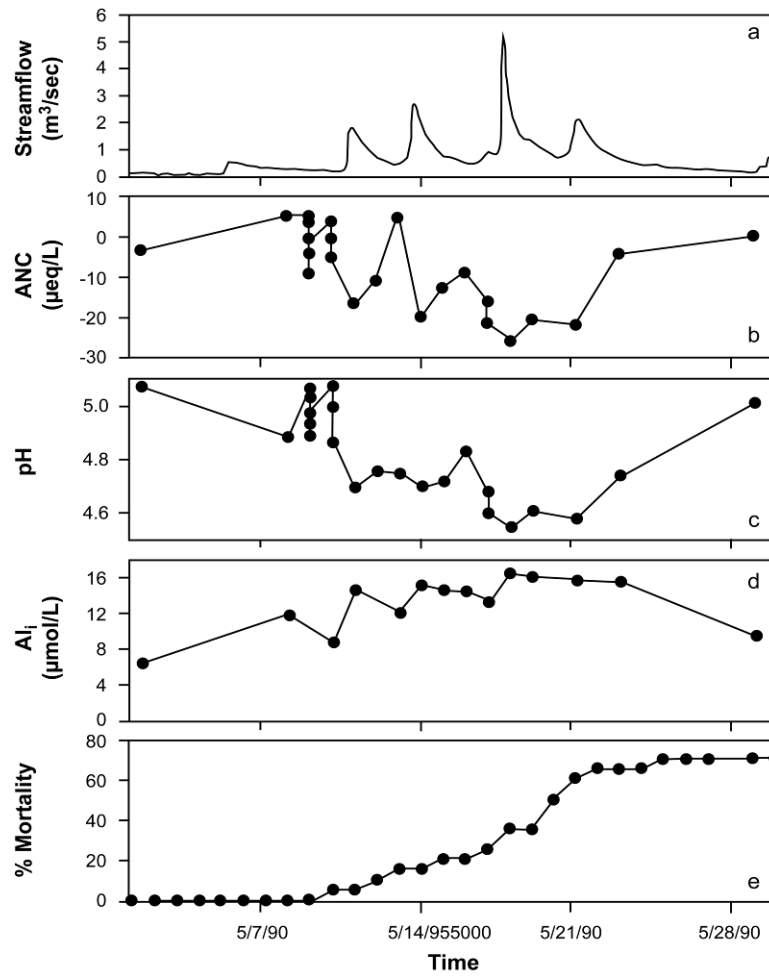
Figure 3-3. **Results of an in situ bioassay during a period of episodic acidification in Buck Creek, Adirondack Mountains, in spring 1990. (a) discharge, (b) acid neutralizing capacity, (c) pH, (d) concentration of inorganic monomeric aluminum, and (e) cumulative percentage of mortality of brook trout over time.**
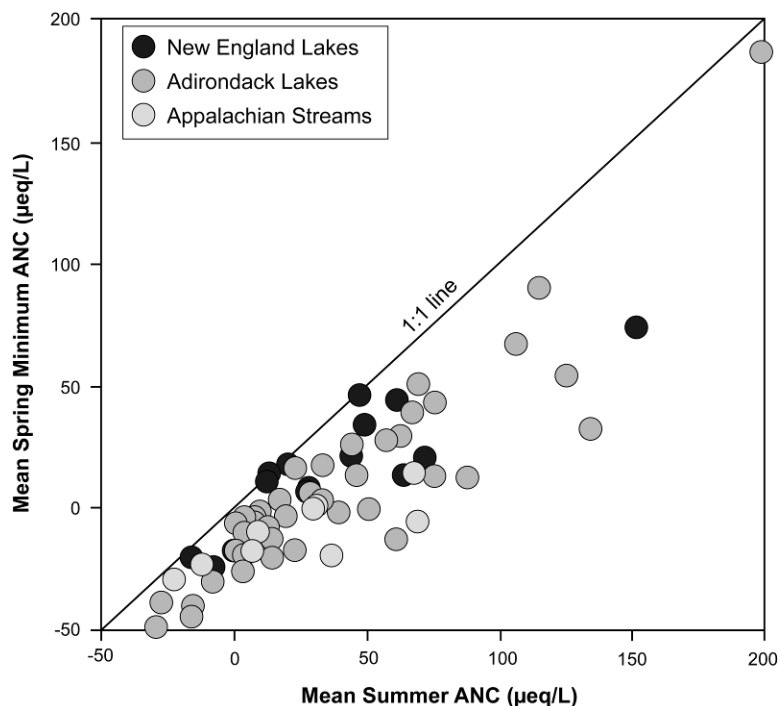
Figure 3-4. Relationship between mean summer acid neutralizing capacity (ANC) and the mean of minimum spring ANC values at long-term monitoring lake and stream sites in New England, the Adirondacks, and the Northern Appalachian Plateau.

The most important factor governing watershed sensitivity to episodic acidification is the pathway followed by snowmelt water and storm-flow water through the watershed. The routing of water as it flows through a watershed determines the degree of contact with acidifying or neutralizing materials and therefore influences (along with soils and bedrock characteristics) the amount of episodic acidification that occurs. In any given watershed, surface water ANC may vary in time depending upon the proportion of the flow that has contact with ANC supplying substrate; in general, the more subsurface contact, the higher the surface water ANC (Turner et al., 1991). This pattern can be attributed in part to higher base saturation and (in some watersheds) greater SO_4^{2-} adsorption capacity in subsurface soils. It may also relate to the accumulation in the upper soil horizons of acidic material derived from atmospheric deposition and decay processes (Lynch and Corbett, 1989; Turner et al., 1991).

Streams having acidic episodes show significantly higher fish mortality and other aquatic community changes as compared with streams in which ANC remains above 0 µeq/L (Wigington et al., 1993). Results from in situ bioassay studies from across the eastern U.S. show that acidic episodes (with associated low pH and elevated inorganic Al concentrations, and high streamwater discharge) caused rapid fish mortality under some conditions (Baker et al., 1996; Bulger et al., 1999; Driscoll et al., 2001b). For example, streams with suitable conditions during low flow, but moderate-to-severe episodic acidification during high flow, had higher fish mortality in bioassays, higher net downstream movement of brook trout during events, and lower brook trout abundance and biomass compared to streams that did not experience appreciable episodic acidification. These episodically affected streams lacked the more acid-sensitive fish species (blacknose dace and sculpin). Movement of trout into refugia (areas with

higher pH and lower inorganic Al) during episodes only partially mitigated the adverse effects of episodes (Baker et al., 1996).

Consideration of episodic acidification greatly increases the extent and degree of estimated effects for acidifying deposition on surface waters. In the Northeast, inclusion of episodically acidified water bodies in regional assessments substantially increases estimates of the extent of surface water acidification. For example, baseflow samples collected from 1991 to 1994 through the U.S. EPA Temporally Integrated Monitoring of Ecosystems (TIME) Program indicated that 10% of the 1,812 lakes larger than 1 ha surface area in the Adirondack region could be considered chronically acidic (fall index ANC values less than 0 µeq/L). However, an additional 31% of these lakes had fall index ANC values less than 50 µeq/L and were, therefore, estimated to be susceptible to episodic acidification (Driscoll et al., 2001b).

Lawrence (2002) estimated the extent of episodically acidified stream reaches in a Catskill, NY watershed (area = 85 km^2) using an index site at the base of the watershed that became episodically acidified at high flows. Upstream sites with a lower base flow ANC than the index site at the same date and time were found to have a high likelihood of becoming episodically acidified. Base flow sampling of 122 upstream sites indicated that approximately 16% of the total upstream reaches had chronic ANC less than 10 µeq/L, but that 66% of the stream reaches had episodic ANC less than 10 µeq/L.

In the Southeast, a recent study by Deviney et al. (2006) within Shenandoah National Park, Virginia used hourly ANC predictions over short time periods to compute recurrence intervals of annual water-year minimum ANC values for periods of 6, 24, 72, and 168 h. They extrapolated the results to the rest of the Shenandoah National Park catchments using catchment geology and topography to stratify watershed response patterns. On the basis of the models, they concluded that a large number of Shenandoah National Park streams had 6- to 168-h periods of low ANC values, which may stress resident fish populations (Deviney et al., 2006). Specifically, on the basis of a 4 year recurrence interval, approximately 23% of the land area (44% of the catchments) can be expected to have conditions that are classified with respect to brook trout response categories (Bulger et al., 1999) as indeterminate (ANC 20 to 50), episodically acidic (ANC 0 to 20) or chronically acidic (ANC less than 0) for 72 continuous hours. Many catchments were predicted to have successive years of ANC values sufficiently low as to potentially extirpate some aquatic species (Deviney et al., 2006). The authors of the study reported that smaller catchments are more vulnerable to episodic acidification than larger catchments underlain by the same bedrock. Results from a study of six intensively monitored sites in the Park demonstrated a clear pattern of larger episodic ANC depressions in streams having higher median ANC than in streams with lower ANC. However, streams with low median ANC typically experienced decreases that resulted in minimum ANC values associated with toxicity to biota. These low ANC conditions were more likely to occur in streams underlain by siliclastic bedrock than in those with granitic or basaltic bedrock.

In the West, episodic acidification is an especially important issue for surface waters throughout high-elevation areas. Where soils are sparse, as in alpine regions, most snowpack N is flushed to surface waters early in the snowmelt period. Even though there is evidence through use of isotopic tracers that much of the N was cycled microbially, snowpack N has been reported to cause temporary acidification of alpine streams (Campbell et al., 2002; Williams and Tonnessen, 2000). Snowmelt-related temporary acidification of alpine lakes and streams and associated effects have been reported in the Rocky Mountains (Brooks et al., 1996; Williams et al., 1996b) and Sierra Nevada (Johannessen and Henriksen, 1978; Stoddard, 1995).

There have been no studies in the U.S. to determine if either the severity or frequency of episodic acidification has lessened in response to recent decreases in acidifying deposition over the past three decades. In a study of two streams in Nova Scotia (Laudon et al., 2002) noticeable trends in ANC during different phases of storm hydrographs from 1983 to 1998 were generally not detected other than during the peak-flow phase of one stream (an increase of 0.87 µeq/L).

In summary, the vast majority of water chemistry data for acid-sensitive lakes and streams in the U.S. were collected at low stream flow. It is well known, however, that water chemistry changes with season and with weather. Altered water chemistry is most stressful to aquatic biota (lowest pH and ANC;

highest inorganic Al concentration) during high flow following snowmelt and rainstorms. During such conditions, stream chemistry can be toxic to species that thrive under chemical conditions more typical of base flow. The U.S. EPA ERP and other more localized studies have quantified the effects of episodes on fish. Episodes are driven by hydrological processes, but the acidification that occurs is largely a result of acidifying deposition, especially in cases where inorganic Al has been mobilized. Consideration of such variability in water chemistry is critical for accurate assessment of the extent, magnitude, and biological effects of surface water acidification. The biological effects of changes in surface water chemistry are discussed in greater detail in Section 3.2.3.3.

3.2.2. Terrestrial Ecosystems

The changes in major biogeochemical processes and soil conditions described above contribute to a series of effects on terrestrial ecosystems. These changes are manifest in both chemical and biological effects that can include reduced soil base saturation, altered key element ratios, changes in plant productivity, reduced stress tolerance of sensitive plant species, and in some cases, increased mortality of canopy trees. Specific chemical indicators of change can be used to assess sensitivity to, and effects from, acidifying deposition. In the U.S., terrestrial effects of acidification are best described for forested ecosystems, with supportive information on other plant communities, including shrubs and lichens.

3.2.2.1. Chemical Effects

There are several chemical indicators that provide useful information about the acid-base status of soils and its influence on terrestrial vegetation. These include soil base saturation; Ca:Al ratio; and C:N ratio (see Table 3-2). Each chemical indicator provides insight into the level to which the ecosystem has acidified and may be susceptible to associated biological effects. These chemical indicators may also be used to monitor the extent of acidification or recovery that occurs in forest ecosystems as deposition rates of S and N change. As such, several chemical indicators and possible effect thresholds have been developed and applied in conjunction with efforts to estimate critical loads. The critical loads approach is discussed in more detail in Section 3.1.1.

Table 3-2. **Examples of chemical indicators of effects from acidifying deposition to terrestrial ecosystems.**

Examples of Chemical Indicators	Example Possible Effect Threshold	References
Soil base saturation	10–20%	Lawrence et al. (2005); Driscoll et al. (2001b); Cronan et al. (1990)
Soil solution Ca:Al ratio	1.0	Cronan and Grigal (1995)
Soil C:N ratio	20–25	Aber et al. (2003)

Soil Base Saturation

In soils with a base saturation less than about 15 to 20%, exchange ion chemistry is dominated by Al (Reuss, 1983). Under this condition, responses to sulfuric and nitric acid inputs largely involve the release and mobilization of inorganic Al through cation exchange. This is the form of Al that interferes with uptake of Ca by plant roots and is also toxic to many forms of aquatic biota (Baker et al., 1990b; Cronan and Grigal, 1995).

The soil O horizon tends to have a much higher base saturation than the underlying mineral soil, despite having lower pH due to organic acidity. The base saturation of the B horizon is in a Spodosol can be sensitive to base cation depletion from leaching by SO_4^{2-} and NO_3^-, and is therefore useful for assessing base status with regard to acidifying deposition. Little direct work has been done to relate soil base saturation to forest health, but Cronan and Grigal (1995) determined that base saturation values below about 15% in the B horizon of forests in the northeastern U.S. could lead to effects from Al stress. Lawrence et al. (2005) also observed pronounced decreases in diameter growth of Norway spruce in northwestern Russia, where base saturation decreased from 30% to 20% in the upper 10 cm of the B horizon over a period of 37 years.

Base saturation values less than 10% predominate in the soil B horizon in the areas in the U.S. where soil and surface water acidification from acidifying deposition have been most pronounced, including conifer and hardwood forests in the Adirondack Mountains (Sullivan et al., 2006a), red spruce forests throughout the Northeast (David and Lawrence, 1996), hardwood forests in the Allegheny Plateau (Bailey et al., 2004), and conifer and hardwood forests in the southern Appalachian Mountains (Sullivan et al., 2003). In a study of sugar maple decline throughout the Northeast, Bailey et al. (2004) found threshold relationships between base cation availability in the upper B soil horizon and sugar maple mortality at Ca saturation less than 2%, and Mg saturation less than 0.5% (Bailey et al., 2004). The authors concluded that base saturation varied as a function of topography, geologic parent material, and acidifying deposition.

Aluminum Concentration in Soil Solution: Calcium to Aluminum Ratio

Al may be toxic to tree roots. Plants affected by high Al concentration in soil solution often have reduced root growth, which restricts the ability of the plant to take up water and nutrients, especially Ca (Parker et al., 1989) (Figure 3-5). Ca is well known as an ameliorant for Al toxicity to roots in soil solution, as well as to fish in a stream. However, because inorganic Al tends to be increasingly mobilized as soil Ca is depleted, elevated concentrations of inorganic Al tend to occur with low levels of Ca in surface waters. Mg, and to a lesser extent Na and K, have also been associated with reduced Al toxicity.

Dissolved Al concentrations in soil solution at spruce-fir study sites in the southern Appalachian Mountains frequently exceed 50 μM and sometimes exceed 100 μM (Eagar et al., 1996; Johnson et al., 1991; Joslin and Wolfe, 1992a). All studies reviewed by Eagar et al. (1996) showed a strong correlation between Al concentrations and NO_3^- concentrations in soil solution. They surmised that the occurrence of periodic large pulses of NO_3^- in solution were important in determining Al chemistry in the soils of southern Appalachian Mountain spruce-fir forests.

The negative effect of Al mobilization on Ca uptake by tree roots was proposed by Shortle and Smith (1988). Substantial evidence of this relationship has accumulated over the past two decades through field studies (Kobe et al., 2002; McLaughlin and Tjoelker, 1992; Minocha et al., 1997; Schlegel et al., 1992; Shortle et al., 1997) and laboratory studies (see review by Cronan and Grigal, 1995; Sverdrup and Warfvinge, 1993). Based on these studies, it is clear that high inorganic Al concentration in soil water can be toxic to plant roots. The toxic response is often related to the concentration of inorganic Al relative to the concentration of Ca, expressed as the molar ratio of Ca to inorganic Al in soil solution. As a result, considerable effort has been focused on determining a threshold value for the ratio of Ca to Al that could be used to identify soil conditions that put trees under physiological stress.

From an exhaustive literature review, Cronan and Grigal (1995) estimated that there was a 50% risk of adverse effects on tree growth if the molar ratio of Ca to Al in soil solution was as low as 1.0. They

estimated that there was a 100% risk for adverse effects on growth at a molar ratio value below 0.2 in soil solution.
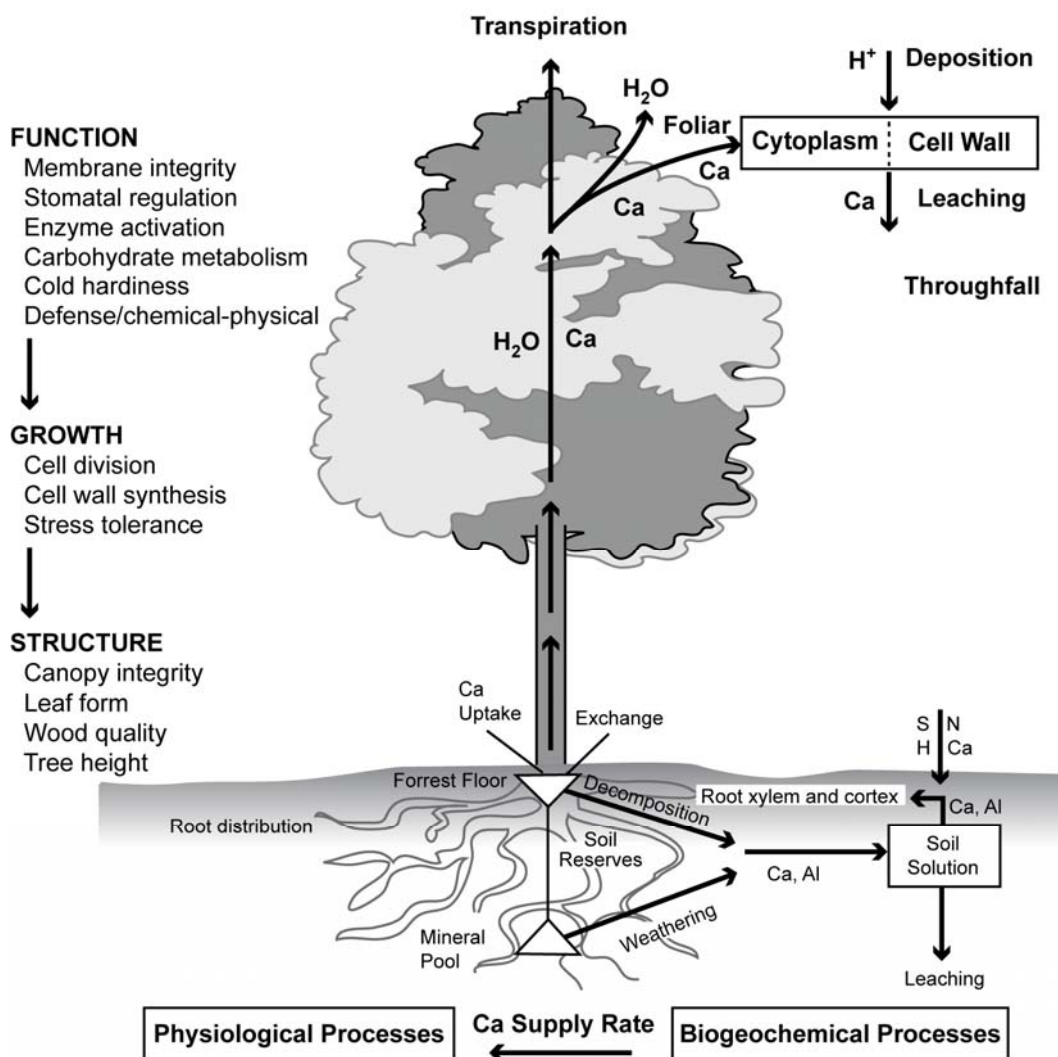
Figure 3-5. **Diagram based on Fenn et al. (2006) shows indicators of forest physiological function, growth and structure that are linked to biogeochemical cycles through processes that control rates of Ca supply. Calcium affects plant physiological processes that influence growth rates and the capacity of plants to resist environmental stresses such as extremes of temperature, drought, insects, and diseases. Therefore, acidifying deposition, which can deplete soil Ca or interfere with Ca uptake through mobilization of soil Al, is a concern for maintenance of forest health.**

The information available to define levels of risk for the Ca:Al ratio is complicated by differences in natural soil conditions and differences between tree species. As a result of these complications, the risk levels for the ratio defined in laboratory experiments have not necessarily been successfully applied to field conditions. For example, Johnson et al. (1994a, b) reported Ca:Al ratios above 1.0 through most of 4

years in the Oa and B horizons of a high-elevation red spruce stand experiencing high mortality. In the 3−yr study of De Witt et al. (2001), Al additions lowered molar Ca to inorganic Al ratios in soil solutions of a Norway spruce stand below 0.5, but the authors found no response other than reduced Mg concentrations in needles in the third year, which was a possible precursor to damage.

In summary, a molar ratio of Ca to Al in soil solution can be used as a general index that suggests an increasing probability of stress to forest ecosystems as the ratio decreases. The ratio value of 1.0 is proposed as a general damage threshold, but cannot be interpreted as a universally applicable threshold in all natural systems. Tree species vary widely in their sensitivity to Al stress (See Annex Table B-20). In addition, Al concentrations in soil solution often exhibit pronounced spatial and temporal variability that is difficult to relate to root activity. Finally, the form of Al present in solution plays an important role in determining toxicity. For example, organically complexed Al, which predominates in upper, organic-rich soil horizons, is essentially nontoxic (Baker and Schofield, 1982; Cronan and Grigal, 1995).

Soil N: Carbon to N Ratio

Mechanisms of retention and release of N in forest ecosystems are not fully understood, but the adverse effects of nitrification and associated acidification and cation leaching have been consistently shown to occur only in soils with a C:N ratio below about 20 to 25 (Aber et al., 2003; Ross et al., 2004). This observation makes the C:N ratio especially useful because N mineralization and nitrification rates are difficult to measure directly under natural conditions. All available measurement approaches disturb the soil and often cause artificially high rates. Therefore, field measurement provides a relative index rather than a realistic quantitative rate (Ross et al., 2004). Approaches for measuring N mineralization and nitrification also are subject to high degrees of variability, both temporally (hourly to seasonal) and spatially (down to the sub meter level). Measurements of total OC and N however, are less variable in space and time and are therefore more straightforward to document than N mineralization and nitrification rates. Also, ratios of C to N in the forest floor are inversely related to acidifying deposition levels, although the relationship is stronger for hardwood stands than conifer stands (Aber et al., 2003). In summary, these factors make the C:N ratio a reliable and relatively straightforward measure for identifying forest ecosystems that may be experiencing soil acidification and base leaching as a result of N input and increased nitrification.

DOC leaching

Over the past two decades, increased DOC concentrations in soils and surface waters were widely reported across North America and Europe (Findlay 2005; Evans et al., 2006; Roulet and Moore 2006; Monteith et al., 2007). It is very likely DOC levels will continue to rise, leading to an increase in C export from the relative stable pool (soil) to the labile pool (riverine and marine) (Roulet and Moore 2006; Monteith et al., 2007). Although there have been arguments about the mechanism responsible for producing the high DOC concentration, changes in S and N atmospheric deposition both appears to play key roles in this trend (Driscoll et al., 2003c; Findlay 2005; Evans et al., 2006; Roulet and Moore 2006; Monteith et al., 2007). Through an assessment of time series data from 522 remote lakes and streams in North American and Europe, Monteith et al. (2007) found that DOC concentrations had increased in proportion to the rates at which atmospheric S and sea salt deposition declined. Numerous laboratory and field studies showed that the solubility of SOM increases with decreasing soil acidity (Kalbitz et al., 2000). Declining S deposition may increase soil DOC concentration by increasing soil pH. Decreasing S deposition may also result in lower ionic strength by decreasing the concentrations of a suite of multivalent ions, such as SO_4^{2-} and aluminum. The coagulation of DOC decreases under low ionic strength, leading to higher DOC export rates. (Monteith et al., 2007).

Chronically high N deposition has been proposed as another significant factor that influences DOC production and transportation. Increases in DOC concentrations were often observed in both experimental sites which received chronic N addition (Pregitzer et al., 2004; Sinsabaugh et al., 2004; Adams et al., 2005), and natural ecosystems which experienced high rates of N deposition, such as Hudson River and

several European peatlands (Findlay 2005; Bragazza et al., 2006). Although N deposition contributes to the acidification of soils, it may increase DOC export by increasing litter input and decreasing DOC degradability (Roulet and Moore 2006). However, the mechanism behind the association between N deposition and DOC production is not yet well understood (Pregitzer et al., 2004; DeForest et al., 2005; Findlay 2005).

3.2.2.2. Summary of Biogeochemistry and Chemical Effects

The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in biogeochemistry related to terrestrial ecosystems. The strongest evidence for a causal relationship comes from studies of forested ecosystems, with supportive information on other plant communities, including shrubs and lichens; grasslands are likely less sensitive to acidification than forests. Soil acidification occurs in response to inputs of sulfuric acid (H_2SO_4) and nitric acid (HNO_3); the effect can be neutralized by weathering or base cation exchange. Soil acidification is a natural process, but is often accelerated by acidifying deposition. Acidifying deposition is important in decreasing concentrations of exchangeable base cations in soils. Despite recent decreases in acidifying deposition, there are widespread observations of ongoing soil acidification such as decreases in soil exchangeable base cations (Bailey et al., 2005, Sullivan et al. 2006a, 2006b, Warby et al., 2009). The limited mobility of anions associated with naturally derived acidity (organic acids and carbonic acid) controls the rate of base cation leaching from soil under conditions of low atmospheric deposition of S and N. Because inputs of S and N in acidifying deposition provide anions that are more mobile in the soil environment than anions of naturally derived acids, these mineral acid anions can accelerate natural rates of base-cation leaching.

Nitrification is mediated by autotrophic bacteria that derive energy by oxidizing NH_4^+ to NO_3^-. Nitrification produces acidity in the form of HNO_3 as a byproduct. The HNO_3 produced contributes to the acidification of soils and surface waters.

There are three useful indicators of chemical changes and acidification effects on terrestrial ecosystems, showing consistency and coherence among multiple studies: soil base saturation, Al concentration in soil water, and soil C:N ratio.

- Soil base saturation is the concentration of exchangeable bases as a percent of the total soil cation exchange capacity. Once base saturation decreases to a critical level (approximately 15–20%), inputs of H_2SO_4 and HNO_3 result in exchange of inorganic Al.

- Inorganic Al is toxic to some tree roots. Plants affected by high inorganic Al concentrations in soil solution often have reduced root growth, which restricts the ability of the plant to take up water and nutrients, especially calcium (Ca) (Parker et al., 1989).

- The C:N ratio of soil is used to indicate alterations to the N biogeochemical cycle. If the C:N ratio of soils falls below about 20 to 25, nitrification is stimulated resulting in net nitrification and increased acidity.

3.2.2.3. Biological Effects

Acidifying deposition can affect terrestrial ecosystems via direct effects on plant foliage and indirect effects associated with changes in soil chemistry. Biological effects of acidification on terrestrial ecosystems are generally attributable to Al toxicity and decreased ability of plant roots to take up base cations (especially Ca) and water from the soil (Cronan and Grigal, 1995). Acidifying deposition to acid-sensitive soils can cause soil acidification, increased mobilization of inorganic Al from soil to drainage water, and depletion of the pool of exchangeable base cations in the soil. Effects on the soil and direct effects of acidifying deposition on foliage can influence the response of plants to climatic stresses such as

drought and cold temperature. They can also influence the sensitivity of plants to other stresses, including insect pests and disease (Joslin et al., 1992).

The combined effects of acidifying deposition and other stressors on terrestrial vegetation are typically measured using indices such as percent dieback of canopy trees, dead tree basal area (as a percent), crown vigor index, and fine twig dieback (see Table 3-3). Each of these variables has a rating system used to quantify forest condition and relate the variables to foliar and soil nutrient concentrations.

Table 3-3.   Example biological effects indicators in terrestrial ecosystems.

Indicator Species	Example of Health Indices	References
Red spruce	Percent dieback of canopy trees	Shortle et al. (1997) DeHayes et al. (1999)
Sugar maple	Basal area dead sugar maple (as %) Crown vigor index Fine twig dieback	Bailey et al. (1999) Drohan and DeWalle (2002)

The effects of acidifying deposition on the health, vigor, and productivity of terrestrial ecosystems in the U.S. are best documented in spruce-fir and northern hardwood forests of the eastern U.S. Some information is also available for individual species such as red spruce, sugar maple, and some species of lichen. In the western U.S., the health of Ponderosa pine and Jeffrey pine has been affected by air pollution, but such effects have largely been attributed to ozone exposure, not acidifying deposition.

Health, Vigor, and Reproduction of Tree Species in Forests

Both coniferous and deciduous forests throughout the eastern U.S. are experiencing gradual losses of base cation nutrients from the soil due to accelerated leaching from acidifying deposition. This change in base cation nutrient availability may reduce the quality of forest nutrition over the long term. Evidence suggests that red spruce and sugar maple in some areas in the eastern U.S. have experienced declining health as a consequence of acidifying deposition. Existing information regarding the effects of acidifying deposition on these two forest tree species is summarized below and reference is made to specific health indicators where such information is available.

Red Spruce

Red spruce (*Picea rubens*) is a conifer that occurs mainly in the northeastern U.S. and at scattered high-elevation sites in the Appalachian Mountains (see Figure 3-6). Red spruce dieback or decline has been observed across high elevation landscapes of the northeastern, and to a lesser extent, southeastern U.S. At high elevations in the Adirondack and Green Mountains, more than 50% of the canopy red spruce trees died during the 1970s and 1980s. In the White Mountains, about 25% of the canopy spruce died during that same period (DeHayes et al., 1999). Dieback of red spruce has also been observed in mixed hardwood-conifer stands at relatively low elevations in the western Adirondack Mountains, an area that receives high inputs of acidifying deposition (Shortle et al., 1997); acidifying deposition has been implicated as a causal factor (DeHayes et al., 1999). The frequency of freezing injury to red spruce needles has increased over the past 40 years, a period that coincided with increased emissions of S and N oxides and increased acidifying deposition (DeHayes et al., 1999).

From the 1940s to 1970s, red spruce growth also declined at high elevation in the southeastern U.S. (Cook and Zedaker, 1992; Eagar et al., 1996; McLaughlin et al., 1987} as emissions of both NO_X and SO_2

increased to maxima of about 25 and 30 million tons/yr, respectively. The growth decline in Great Smoky Mountains National Park in North Carolina and Tennessee started earlier at higher elevations (around the 1940s and 1950s) and was steeper, while the growth decline developed at lower elevation sites 20 years later. After the 1980s, red spruce growth increased substantially at both the higher- and lower-elevation sites, corresponding to a decrease in SO_2 emissions in the U.S. (to about 20 million tons/yr by 2000), while NO emissions held fairly steady (at about 25 million tons/yr). Annual emissions of S plus NO_X explained about 43% of the variability in red spruce tree ring growth between 1940 and 1998. Climatic variability accounted for about 8% of the growth variation for that period. At low elevation, changes in radial growth could be explained by climatic variables only, and there was no correlation with national S plus nitrogen oxide emissions trends. Recent reductions in S oxide emissions may have changed growth trajectories (Webster et al., 2004).
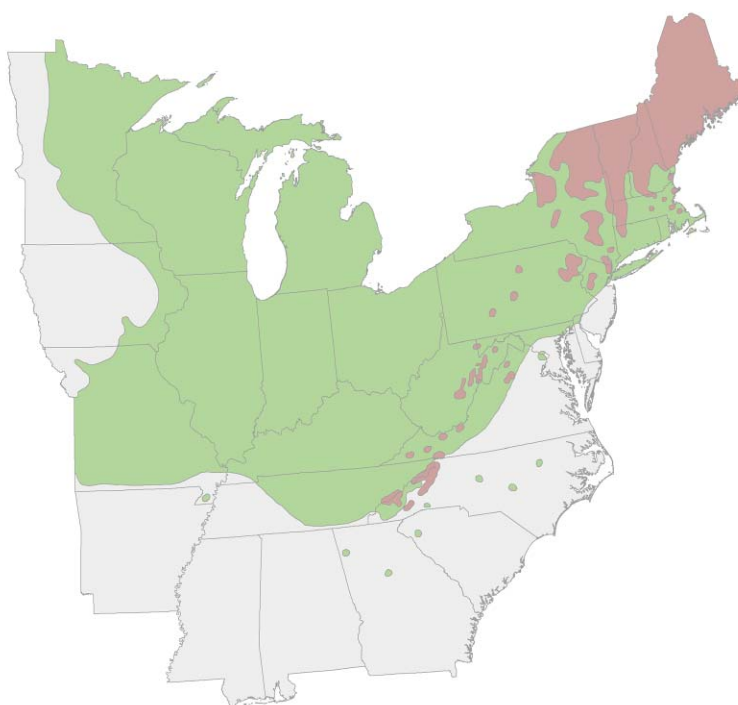
<div align="right">Source: Little (1971)</div>

Figure 3-6. **Distribution of red spruce (rose) and sugar maple (green) in the eastern U.S. These two tree species have experienced adverse effects in portions of their ranges that have been attributed to acidification from acidifying deposition. Tree distribution data were obtained from Little's Atlas.**

The observed dieback in red spruce has been linked, in part, to reduced cold tolerance of red spruce needles, caused by acidifying deposition. Results of controlled exposure studies showed that acidic mist or cloud water reduced the cold tolerance of current-year red spruce needles by 3 to 10 ºC (DeHayes et al., 1999). There is a significant positive association between cold tolerance and foliar Ca in trees that exhibit foliar Ca deficiency. The membrane-associated pool of Ca, although a relatively small fraction of the total foliar Ca pool, strongly influences the response of cells to changing environmental conditions. The plant plasma membrane plays an important role in mediating cold acclimation and low-temperature injury (U.S. EPA, 2004). The studies of DeHayes et al. (1999) suggested that direct acidifying deposition on red spruce needles preferentially removes membrane-associated Ca. More recently, a link has been

established between availability of soil Ca and winter injury (Hawley et al., 2006) based on an experimental addition of Ca at the Hubbard Brook Experimental Forest, New Hampshire. This study demonstrated that Ca depletion from soil was associated with winter injury of red spruce foliage during 2003 when winter injury was unusually high throughout the region (see Figure 3-7).
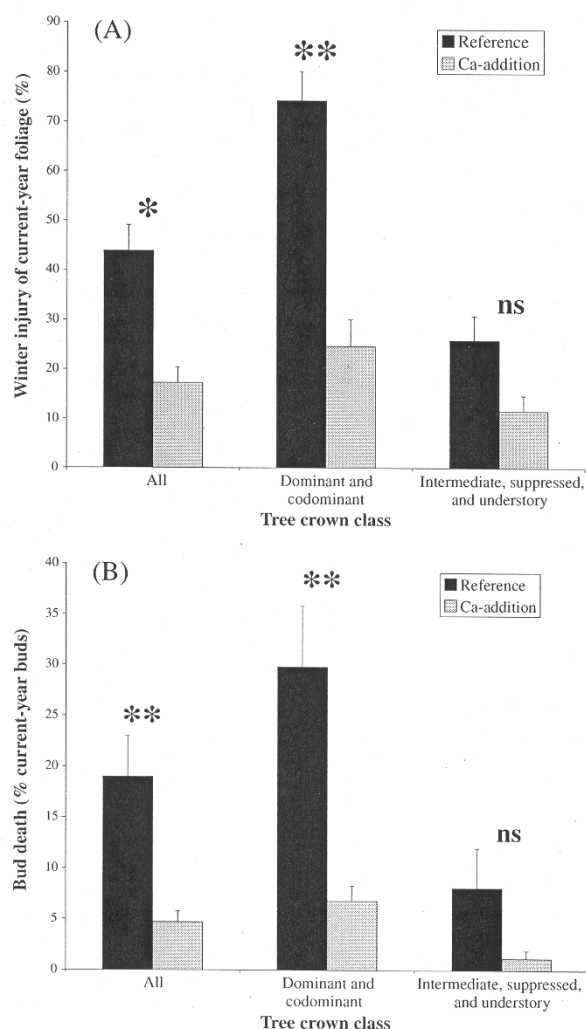
Figure 3-7. **Mean (+ standard error bars) of current-year red spruce needle winter injury in reference and calcium-addition watersheds and among crown classes, expressed as foliar injury (A) and bud mortality (B). Watershed means were either not significantly different (ns) or statistically different at p <0.05 (*) or p <0.01 (**) based on nested analyses of variance.**

In summary, the weight of evidence suggests that changes in soil chemistry have contributed to high mortality rates and decreasing growth trends of red spruce trees in some areas over the past three decades (Sullivan et al., 2002). In forests where this has occurred, which are mainly located at high elevation, changes in red spruce growth rates are attributable, at least in part, to base cation deficiencies related to decreased availability of Ca and increased availability of Al as a result of acidifying deposition

effects on soils. Important factors appear to include depletion of base cations in upper soil horizons by acidifying deposition, Al toxicity to tree roots, and accelerated leaching of base cations from foliage as a consequence of acidifying deposition. Recent studies also show improvements in red spruce growth with decreasing emissions of SO_2 in the U.S. (Webster et al., 2004).

Sugar Maple

Sugar maple (*Acer saccharum*) is the deciduous tree species of the northeastern U.S. that is most commonly associated with adverse acidification-related effects of S and N deposition, though other base cation accumulating hardwoods may also be at risk (Driscoll et al., 2001b). Sugar maple is distributed throughout the northeastern U.S. and central Appalachian Mountain region as a component of the northern hardwood forest Figure 3-6.

A conceptual view of the interactions of acidifying deposition and other stressors in sugar maple decline is provided in Figure 3-8. Several studies, mainly in Pennsylvania, have hypothesized that sugar maple decline is linked to the occurrence of relatively high levels of acidifying deposition and base-poor soils (Bailey et al., 2004; Hallett et al., 2006; Horsley et al., 2000; Moore and Ouimet, 2006; St. Clair et al., 2005).

Acidifying deposition may be contributing to episodic dieback of sugar maple in the Northeast through depletion of nutrient cations from marginal soils (Figure 3-8). Horsley et al. (2000) found that dieback at 19 sites in northwestern and north central Pennsylvania and southwestern New York was correlated with combined stress from defoliation and soil deficiencies of Mg and Ca. Dieback occurred predominately on ridgetops and on upper slopes, where soil base cation availability was much lower than occurred in the deeper soils found on middle and lower slopes (Bailey et al., 2004). A long-term decrease in soil pH since 1960 (0.78 pH unit decrease in the O horizon, and 0.23 pH unit decrease in the A horizon) in Pennsylvania hardwood forests has been documented, along with decreases in soil Ca and Mg concentrations. Declining sugar maples were shown to be deficient in foliar Ca and Mg (Drohan and Sharpe, 1997). More recent research has strengthened understanding of the role of cation nutrition in sugar maple health at a regional scale across a broad range of conditions (Hallett et al., 2006).

Drohan et al. (2002) investigated differences in soil conditions in declining versus non-declining sugar maple plots in northern Pennsylvania from the U.S. Department of Agriculture (USDA) Forest Service's Forest Inventory and Analysis (FIA) program. Soils in plots with declining sugar maple tended to have lower base cation concentrations and pH, and Ca:Al ratio less than 1. Regressions between foliar and soil chemistry showed that foliar nutrition was highly correlated with the chemistry of the upper 50 cm of soil (Drohan et al., 2002).

Juice et al. (2006) added Ca to watershed 1 (W1) at HBEF in October 1999 sufficient to raise the pH of the Oie soil horizon from 3.8 to 5.0 and the O_a horizon from 3.9 to 4.2. Subsequently, they measured the response of sugar maples to the Ca fertilization. Foliar Ca of canopy sugar maples increased markedly and foliar Mn declined. By 2005, crown condition was much healthier then in the untreated reference watershed (W6). The density of sugar maple seedlings increased significantly following high seed production in 2000 and 2002. In addition, sugar maple germinants were 50% larger on W1 and mycorrhizal colonization of seedlings was much higher in the treated watershed (22.47% of root length) as compared with the reference watershed (4.4%) (Juice et al., 2006).

In general, evidence indicates that acidifying deposition in combination with other stressors is a likely contributor to the decline of sugar maple trees that occur at higher elevation, on geologies dominated by sandstone or other base-poor substrate, and that have base-poor soils having high percentages of rock fragments (Drohan et al., 2002). Such site conditions are representative of the kinds of conditions expected to be most susceptible to adverse effects of acidifying deposition because of probable low initial base cation pools and high base cation leaching losses.
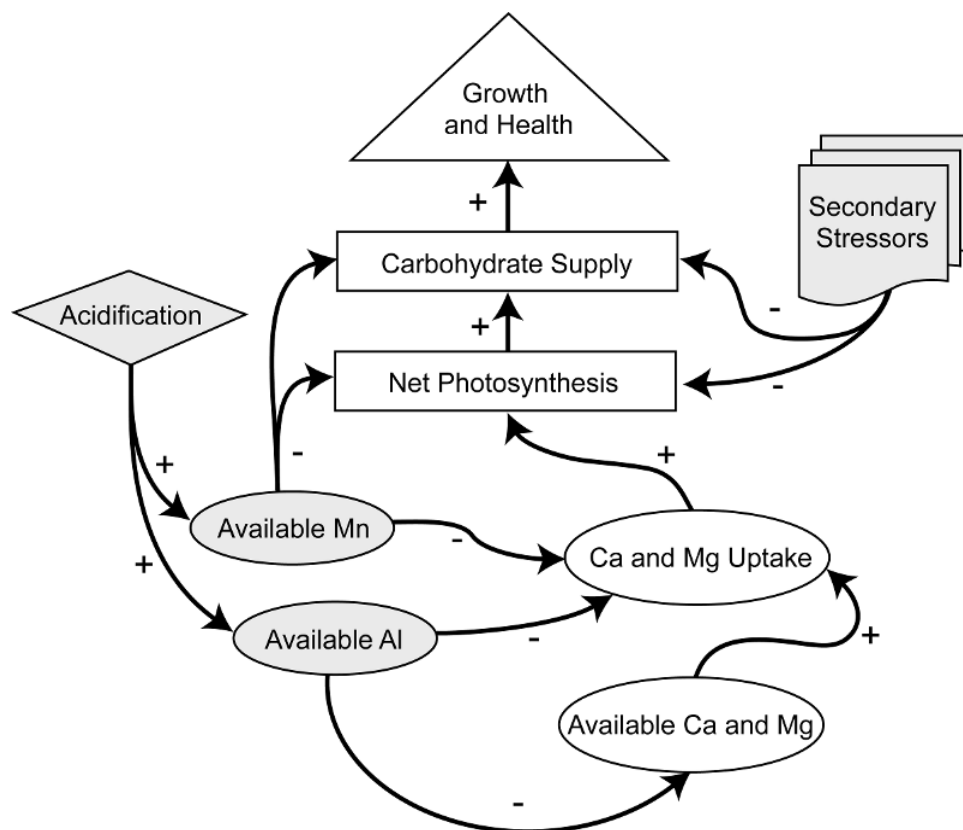
Figure 3-8. **Conceptual diagram outlining the current understanding of sugar maple decline. Positive and negative signs indicate the nature of the correlative relationship between variables.**

Other Forest Ecosystems

Loss of base cations, specifically Ca^{2+}, has also been implicated in increased susceptibility of flowering dogwood (*Cornus florida*) to its most destructive disease, dogwood anthracnose (Figure 3-9). Flowering dogwood is a dominant understory species of hardwood forests in the eastern U.S. (Holzmueller et al., 2006), with important ecosystem functions as a food source for numerous species of animals, and as a large contributor to available Ca in forest litter. It is also recognized as a significant cultural and aesthetic resource throughout its range. Since dogwood anthracnose, a mostly fatal disease, was first reported in 1976 in New York State, it has spread over a large portion of the species' range, generally resulting in mortality greater than 90% in affected stands. Pacific dogwood (*Cornus nutallii*) is similarly affected, but because its abundance within its range was much lower before the disease first appeared, the effect has received less notice. Susceptibility to the disease, and disease severity in stands, appear dependent on several factors, including acid deposition and various edaphic characteristics and meteorological conditions.
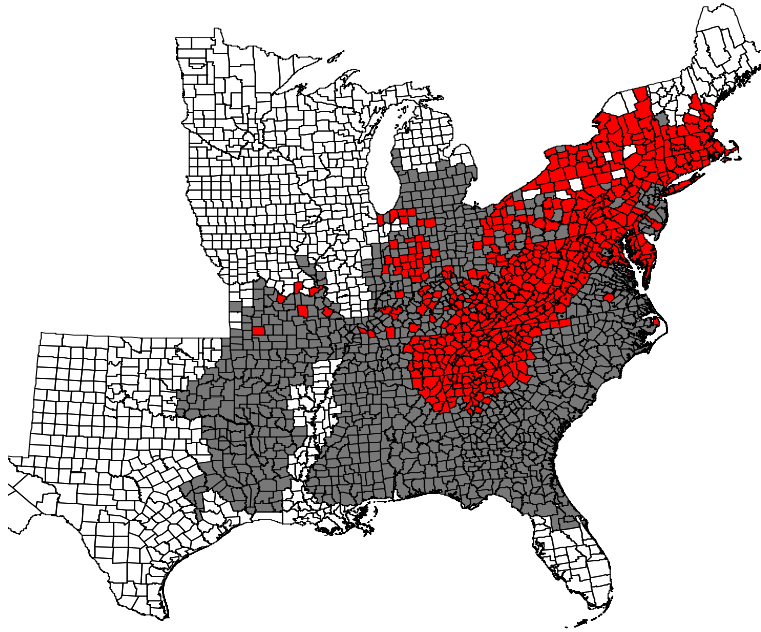
Figure 3-9.   Native range of flowering dogwood (*Cornus florida*) (dk. gray) and the documented range of dogwood anthracnose in the eastern U.S. (red). 2002 data from the U.S. Forest Service.

In 1990 and 1991, Britton et al. (1996) exposed 200 potted dogwood plants to simulated acid rain (SAR) at 4 levels of pH between 2.5 and 5.5. The plants were then placed among natural stands showing symptoms of the disease. In both years, there was a fourfold increase in percentage of leaf area affected from the plants treated with SAR at a pH of 5.5 to those treated with SAR at a pH of 2.5. In 1992 and 1993, four combinations of SAR with a pH of 2.5 or 5.5 were applied separately to the foliage and the soil before inoculation. The percent of leaf area affected was approximately two to four times greater for plants grown in soil treated with acidic SAR, regardless of foliar treatment, suggesting that the worsening of anthracnose damage by acid deposition occurs mostly through soil effects.

In a study of the effects of Ca, K, and Mg on dogwood density in forest stands, and on resistance to anthracnose in containerized dogwood plants, (Holzmueller et al., 2007) found a strong relation between soil available cations, particularly Ca^{2+}, and dogwood density in Great Smoky Mountains National Park, where dogwood anthracnose has resulted in significant damage. The mortality of potted dogwood plants fertilized with solutions varying in Ca^{2+}, K^+, or Mg^{2+} concentration, and exposed to anthracnose, was both greatest and most rapid when Ca^{2+} was deficient, but not when K^+ and Mg^{2+} were deficient.

Data on the possible effects of S and N deposition on the acid-base characteristics of forests in the U.S., other than the spruce-fir and northern hardwood forest ecosystems, are limited. Ponderosa pine (*Pinus ponderosa*) seedlings exposed to acidic precipitation (pH 5.3, 4.4, 3.5 of 1:1 NHO_3:H_2SO_4) showed no significant changes in growth (Temple et al., 1992). Fenn et al. (2003a) reported that deposition of 20 to 35 kg N/ha/yr contributed to increased NO_3^- leaching and soil acidity and decreased base saturation in southern California forest ecosystems, but they did not report quantitative measures of growth. Baron et al. (2000) showed that small differences in the N deposition between the east (3 to 5 kg N/ha/yr) and the west (1 to 2 kg N/ha/yr) side of the Rocky Mountains were associated with significant declines in foliar Mg levels and increased foliar N:Mg and N:Ca ratios in old-growth stands of Engelmann spruce (*Picea engelmanii*). It is not known if such changes in nutrient ratios affect the health or growth of these forests.

Despite the evidence for effects of acidifying deposition on the health and vigor of some terrestrial plant communities, few studies are available that have directly documented species loss, reduced biodiversity, or adverse effects on threatened and endangered species. A notable exception is the effect of acidifying deposition on lichen abundance and diversity within forest communities (See discussion below). In eastern North America and central Europe, areas that receive relatively high levels of acidifying deposition and high atmospheric concentrations of SO_2, N oxides, and reduced N have experienced noticeable reductions in cyanolichen abundance on both coniferous and deciduous trees (Richardson and Cameron, 2004). Effects on lichen species biodiversity are also likely (McCune, 1988; van Haluwyn and van Herk, 2002). In London, epiphyte diversity, including a majority of the lichen taxa, declined in areas where NO exceeded 40 $\mu g/m^3$ and total N oxides exceeded 70 $\mu g/m^3$.

Health and Biodiversity of Other Plant Communities

Shrubs

Forest trees are not the only vascular plants that are potentially sensitive to acidifying deposition. Available data suggest that it is possible, or perhaps likely, that a variety of shrub and herbaceous species are sensitive to base cation depletion and/or Al toxicity. However, conclusive evidence is generally lacking.

Research in Europe has illustrated a shift from shrub to grass dominance in heathlands in response to acidifying deposition. However, such effects are probably more related to the nutrient enrichment effects of N deposition than to the acidification effects of S and N deposition. (See further discussion in Section 3.3.3.1.) In summary, whereas some evidence suggests that effects on shrubs and perhaps herbaceous plants are possible, data in the U.S. are insufficient to support the use of shrub or herbaceous plant species as indicators of the acidification-related effects of acidifying deposition at this time.

Lichens

Typically, lichens and bryophytes are among the first components of the terrestrial ecosystem to be affected by acidifying deposition. Vulnerability of lichens to increased N input is generally greater than that of vascular plants (Fremstad et al., 2005). Even in the Pacific Northwest, which receives uniformly low levels of N deposition, changes from acid-sensitive and N-sensitive to pollution-tolerant and nitrophillic lichen taxa are occurring in some areas (Fenn et al., 2003a). Lichens remaining in areas affected by acidifying deposition were found by Davies et al. (2007) to contain almost exclusively the families Candelariaceae, Physciaceae, and Teloschistaceae.

Effects of SO_2 exposure on lichens includes reduced photosynthesis and respiration, damage to the algal component of the lichen, leakage of electrolytes, inhibition of N fixation, reduced K absorption, and structural changes (Farmer et al., 1992; Fields, 1988). In response to reductions after the 1970s in SO_2 exposure and acidifying deposition in London, lichen diversity increased dramatically (Hawksworth, 2002). However, the recovery of lichens in response to reduced S and N inputs is inconsistent. Improvement for bryophytes has been reported to occur in 1 year by Power et al. (2006) and Mitchell et al. (2004), 5 years by Gordon et al. (2001), and 49 years by Strengbom et al. (2001).

Scott (1989a, 1989b) concluded that the S:N exposure ratio was as important as pH in causing toxic effects on lichens, based on experiments on *Cladina rangiferina and C. stellaris*. Thus, it is not clear to what extent acidity may be the principal stressor under high levels of air pollution exposure. The toxicity of SO_2 to several lichen species is greater under acidic conditions than under neutral conditions. The effects of excess N deposition to lichen communities are discussed in Section 3.3.5.1.

Grasslands

Due to structural differences and their lower canopy, grasslands are thought to be less sensitive to acidification than woodlands (Blake et al., 1999; Kochy and Wilson, 2001). Among grasslands, those with calcareous soils will be less sensitive than those with acidic soils (Bobbink et al., 1998). Most literature on the effects of atmospheric S and N deposition on grasslands documents effects of fertilization from N deposition, not acidification. Such fertilization effects are discussed in Section 3.3.5.1.

Arctic and Alpine Tundra

The possible effects of acidifying deposition on arctic and alpine plant communities are also of concern. Especially important in this regard is the role of N deposition in regulating ecosystem N supply and plant species composition. (See further discussion of such effects in Section 3.3.5.1.) Soil acidification and base cation depletion in response to acidifying deposition have not been documented in arctic or alpine terrestrial ecosystems in the U.S. Such ecosystems are rare and spatially limited in the eastern U.S., where acidifying deposition levels have been high. These ecosystems are more widely distributed in the western U.S. and throughout much of Alaska, but acidifying deposition levels are generally low in these areas. Key concerns are for listed threatened or endangered species and species diversity. However, for most rare, threatened, or endangered herbaceous plant species, little is known about their relative sensitivities to acidification from atmospheric deposition inputs. Although plant species diversity of arctic and alpine ecosystems is highly valued, it is difficult to document changes in this parameter in response to acidifying deposition.

3.2.2.4. Summary of Biological Effects

The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in terrestrial biota. The strongest evidence for a causal relationship comes from studies of terrestrial systems exposed to elevated levels of acidifying deposition that show reduced plant health, reduced plant vigor, and loss of terrestrial biodiversity. Consistent and coherent evidence from multiple species and studies shows that acidifying deposition can affect terrestrial ecosystems by causing direct effects on plant foliage and indirect effects associated with changes in soil chemistry. Biological effects of acidification on terrestrial ecosystems are generally attributable to Al toxicity and decreased ability of plant roots to take up base cations. There are several indicators of stress to terrestrial vegetation (see Table 3-3) including percent dieback of canopy trees, dead tree basal area (as a percent), crown vigor index, and fine twig dieback.

Species Level

- Changes in soil chemistry (depletion of soil base cations, Al toxicity to tree roots, leaching of base cations into drainage water) have contributed to high mortality rates and decreasing growth trends of red spruce trees (*Picea rubens*) in some areas of the eastern U.S. over the past three decades.

- Acidifying deposition, in combination with other stressors, is a likely contributor to the decline of sugar maple (*Acer saccharum*) trees that occur at higher elevation, in some portions of the eastern U.S., on geologies dominated by sandstone or other base-poor substrate, and that have base-poor soils.

- Lichens and bryophytes are among the first species affected by acidifying deposition in the terrestrial ecosystem. Effects of SO_2 on lichens include reduced photosynthesis and respiration, damage to the algal component of lichen, leakage of electrolytes, inhibition of N fixation, reduced potassium (K) absorption and structural changes.

- Data are insufficient to draw general conclusions for other species.

Community Level

- Species loss and reduced biodiversity of forests, shrubs, and meadow plant communities may occur, but has not been clearly demonstrated in the U.S.

3.2.3. Aquatic Ecosystems

3.2.3.1. Chemical Effects

The changes in major biogeochemical processes and soil conditions caused by acidifying deposition have significant ramifications for the water chemistry and biological functioning of associated surface waters. Surface water chemistry indicates the adverse effects of acidification on the biotic integrity of fresh water ecosystems. Because surface water chemistry integrates the sum of soil and water processes that occur upstream within a watershed, it also reflects the results of watershed-scale terrestrial effects, including N saturation, forest decline, and soil acidification (Stoddard et al., 2003). Thus, water chemistry integrates and reflects changes in soil and vegetative properties and biogeochemical processes.

The effects on aquatic ecosystems can be described by changes in several chemical effects indicators such as SO_4^{2-} concentration, NO_3^- concentration, base cation concentration, pH, ANC, and inorganic Al. All of these are of interest, and each can provide useful information regarding both sensitivity to surface water acidification and the level of acidification that has occurred. Importantly, these chemical changes can occur over both long- and short-term timescales. Short-term (hours or days) episodic changes in water chemistry have perhaps the most significant biological effects. The acidification effects on aquatic biota are most commonly evaluated using either Al or pH as the primary chemical indicator (Table 3-4). ANC is also used because it integrates overall acid status and because surface water acidification models do a better job projecting ANC than pH and inorganic Al concentrations. However, ANC does not relate directly to the health of biota. The usefulness of ANC lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, Ca, and inorganic Al. The base cation surplus (Lawrence et al., 2007) is an alternate index that integrates acid-base status. It is based on a measurement of ANC (calculated from the charge balance of ionic concentrations in water) and also accounts for the influence of natural organic acidity.

A synoptic illustration of the national patterns of surface water alkalinity in the conterminous U.S. is provided in Figure 3-10. Alkalinity is the most readily available measure of the sensitivity of lakes and streams to acidifying deposition. Although the actual sensitivity of a water body depends on many watershed characteristics and processes, the low-alkalinity areas on the map indicate where sensitive surface waters are most likely to be found. The map is based on data from approximately 39,000 lake and stream sites and the associations of the data values with factors such as land use, physiography, geology, and soils.

Table 3-4. Examples of chemical indicators of effects from acidifying deposition to aquatic ecosystems.

Chemical Indicator	Examples of Potential Thresholds	Reference
Surface water pH	5.0–6.0	Baker et al. (1990b)
Surface water ANC	0–50 µeq/L	Bulger et al. (1999)
Inorganic Al	2–4 µmol/L	Baldigo et al. (2007); Driscoll et al. (2001b); Wigington et al. (1996)
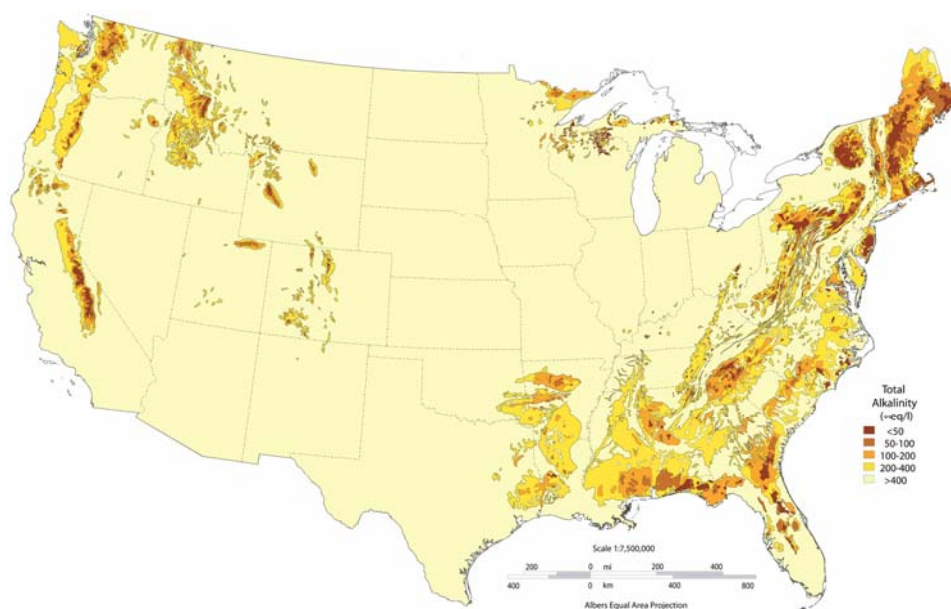
Source: Omernik et al. (1983).

Figure 3-10. Surface water alkalinity in the conterminous U.S. Shading indicates the range of alkalinity within which the mean annual values of most of the surface waters of the area fall.

Surface Water SO_4^{2-}

Measurements of SO_4^{2-} concentration in surface water provide important information on the extent of cation leaching in soils and how SO_4^{2-} concentrations relate to ambient levels of atmospheric S deposition. Assessments of acidifying deposition effects dating from the 1980s to the present have shown SO_4^{2-} to be the primary anion in most, but not all, acid-sensitive waters in the U.S. (Driscoll and Newton, 1985; Driscoll et al., 1988; 2001b; Webb et al., 2004). In an analysis representative of over 10,000 acid-sensitive lakes in the Northeast, inorganic anions represented most negative (anionic) charge in 83% of the lakes, and in this group of lakes, 82% of the total negative charge was due to SO_4^{2-} (Driscoll et al., 2001b). In contrast, naturally derived organic anions represented an average of 71% of total negative charge in the 17% of lakes in which organic anions predominated (Driscoll et al., 2001b).

Atmospheric deposition of S is widely acknowledged as causing changes in concentrations of SO_4^{2-} in surface water. No long-term data sets exist to document changes in SO_4^{2-} in surface waters since the onset of the Industrial Revolution. One of the longest-running monitoring programs exists at the Hubbard Brook Experimental Forest in New Hampshire. Surface water data from this Long-Term Ecological Research site have been used to develop historic estimates of SO_4^{2-} concentrations using the Photosynthesis and EvapoTranspiration-BioGeoChemical (PnET-BGC) model (Gbondo-Tugbawa et al., 2002). Results from Hubbard Brook suggest that acidifying deposition has contributed to a nearly four-fold increase in stream SO_4^{2-} concentration between 1850 and 1970 (Driscoll et al., 2001b).

Long-term data in other regions suggest similar trends in some cases. For example, a study of seven streams in the Catskill region of New York, Stoddard (1991) identified increasing trends in SO_4^{2-} concentrations from 1952–54 to 1970 in three streams and no trend in the four other streams.

As emissions and deposition of S have declined over approximately the last 30 years, surface water concentrations of SO_4^{2-} have decreased in most regions in the eastern U.S. For example, Stoddard et al. (2003) found that surface waters monitored in the U.S. EPA Long-Term Monitoring program showed consistent decreases in SO_4^{2-} concentrations from 1990 to 2000 in New England lakes (1.77 µeq/L/yr), Adirondack lakes (2.26 µeq/L/yr), Appalachian streams (2.27 µeq/L/yr) and Upper Midwest lakes (3.36 µeq/L/yr). The only exception to the pattern of decreasing SO_4^{2-} concentration in surface waters during this period was for streams in the Blue Ridge Mountain region of Virginia, which showed a significant increase in SO_4^{2-} concentrations (0.29 µeq/L/yr) during this period. The increasing trend in Virginia streams is presumably the result of decreased S adsorption on soils and net desorption from the soil in response to decreased S deposition.

In summary, available data indicate a pattern of increasing concentrations of SO_4^{2-} in surface waters before the year of peak S emissions in the early 1970s, followed by widespread decreasing trends in SO_4^{2-} concentrations after the peak (with the only exception being the Blue Ridge Mountain region in Virginia). On this basis, continued decreases in S emissions would be expected to result in further decreases in SO_4^{2-} concentrations in surface waters, although the rate of response is variable and some model results suggest that recovery may be delayed as accumulated S leaches from watersheds, even as emissions and deposition decline.

Surface Water NO_3^-

As described in the previous section, the acidification potential of atmospherically deposited S is primarily a function of the extent of SO_4^{2-} anion mobility in watershed soils and drainage waters. Similarly, acidification of soil water and surface water from atmospheric N deposition is largely governed by the mobility of the NO_3^- anion. Both oxidized and reduced N deposition can contribute to the NO_3^- flux in drainage water. Once N is deposited, processes within the N cycle, including microbial assimilation, plant uptake, and loss to denitrification act to limit the extent of NO_3^- leaching. In contrast, processes such as mineralization, nitrification, fixation, and atmospheric deposition contribute to the NO_3^- flux and increase the likelihood that substantial leaching of NO_3^- in drainage water will occur. Such leaching of NO_3^- is required in order for N deposition to cause N saturation, surface water acidification, or base cation leaching and depletion. Ultimately, the balance of these processes in the N cycle will determine the extent to which such effects will be manifested.

Whereas SO_4^{2-} is generally considered the dominant agent of surface water acidification in most affected regions of the U.S., NO_3^- plays a large role in acidification of surface waters in some regions, particularly during snowmelt and rainstorms. Before the mid-1980s, atmospheric deposition effects research in the U.S. focused almost exclusively on S. Within the 1980 to 1990 (NAPAP) research program, relatively little attention was paid to N research.

Release of NO_3^- from soil to surface waters may affect nutrient relationships and biological neutralization processes in aquatic ecosystems (Bukaveckas and Shaw, 1998; Kelly et al., 1987; Momen et al., 2006). Driscoll and Newton (1985) found that NO_3^- concentrations in 20 lakes in the early 1980s in the Adirondack region of New York averaged 12% of SO_4^{2-} concentrations, whereas Lovett et al. (2000)

found that baseflow NO_3^- concentrations in 1994–97 were an average of 37% of SO_4^{2-} concentrations in 39 streams in the Catskill region of New York. Murdoch and Stoddard (1993) demonstrated the importance of NO_3^- during high-flow conditions in Catskill streams in which concentrations periodically equaled or exceeded SO_4^{2-} concentrations. Concentrations of NO_3^- in most southeastern streams tend to be considerably less than SO_4^{2-} concentrations (Webb et al., 2004). However, Cook et al. (1994) documented very high NO_3^- concentrations in stream water at high elevation in the Great Smoky Mountains in North Carolina.

Surface water NO_3^- concentrations have changed over time and these trends vary by region. Several regions in the northeastern U.S. showed increased NO_3^- concentrations during the 1980s. For example, in the Catskill Mountains of New York all 16 streams for which data were available showed increasing trends in NO_3^- concentration during that period. A similar increase in NO_3^- concentration was reported for Adirondack lakes in the 1980s (Stoddard et al., 1999). These increasing trends in NO_3^- concentration were initially attributed to N saturation in response to atmospheric deposition (Aber et al., 1998).

More recent information on NO_3^- trends during the 1990s, when atmospheric N deposition was relatively stable, suggest that the relationship between atmospheric N deposition and surface water NO_3^- concentrations is complex. During the 1990s, the only significant change occurred in the two regions with the highest ambient surface water NO_3^- concentrations: lakes in the Adirondack Mountains and streams in the Northern Appalachian Plateau (Figure 3-11). Both exhibited small but significant downward trends in NO_3^- concentration during the 1990s. The long-term record of dissolved inorganic N (which is largely NO_3^-) concentrations at the Hubbard Brook Experimental Forest showed a similar pattern: high concentrations in the late 1960s and 1970s, followed by decreases to minimum values in the mid-1990s (Aber et al., 2002). Across New England and the Upper Midwest, where ambient surface water concentrations are much lower than in the Adirondack Mountains and Northern Appalachian Plateau (Figure 3-11), NO_3^- concentrations in surface waters were unchanged during the 1990s. The Ridge/Blue Ridge province registered a small, but significant, decrease in NO_3^- concentration during the 1990s, but interpretation of trends for NO_3^- in this region was complicated by gypsy moth defoliation, which caused large increases in the concentration of NO_3^- in soil water and stream water (Eshleman et al., 1998).

Efforts to explain the complex patterns in NO_3^- concentrations under conditions of reasonably stable atmospheric N deposition have focused on both terrestrial and aquatic N cycling. Goodale et al. (2003) reported that lower NO_3^- concentrations measured in the 1990s at streams in New Hampshire could not be accounted for by differences in stream flow or forest succession, but inter-annual climate variation was proposed as a possible cause. In the Adirondacks, Driscoll et al. (2007a) proposed that increased concentrations of atmospheric CO_2 may have resulted in a fertilization effect that increased N assimilation. Studies by Mitchell et al. (1996) and Murdoch et al. (1998) provide some evidence of climate effects on trends in NO_3^- concentrations in surface waters in the Northeast. In particular, a region-wide spike in NO_3^- concentrations followed an unusually cold December that may have disrupted soil N cycling processes (Mitchell et al., 1996). Murdoch et al. (1998) also found that mean annual air temperatures were strongly related to average annual NO_3^- concentrations during most years in a Catskill watershed with elevated NO_3^- concentrations in stream water.

Regional Trends, 1990-2000
(in lakes and streams)
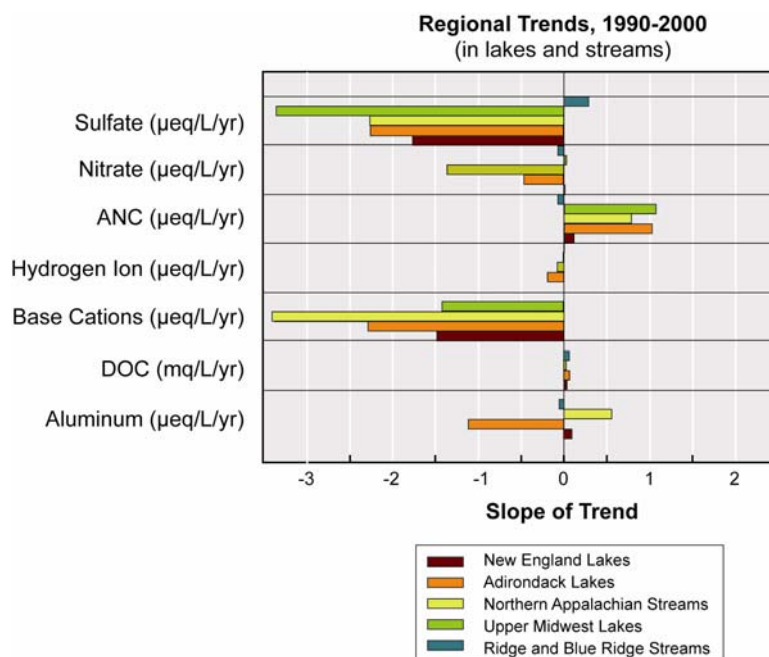
Source: Stoddard et al. (2003)

Figure 3-11.   Summary of regional trends in surface water chemistry from 1990 to 2000 in regions covered by the Stoddard et al. (2003) report.

Processes within lakes may have also played a role in the measured trends in Adirondack lakes (Ito et al., 2005; 2007). In a study of 30 of the 48 long-term monitoring lakes investigated by (Driscoll et al., 2003d; 2007a) and Momen et al. (2006) found that concentrations of dissolved NO_3^- were inversely correlated with concentrations of chlorophyll *a* (Chl *a)* in 11 lakes, and that Chl *a* was increasing in concentration in 9 lakes. The increase in pH observed in most of these lakes may have stimulated productivity so that N assimilation by plankton increased (Momen et al., 2006).

In summary, NO_3^- contributes to the acidity of many lakes and streams in the eastern U.S. that have been affected by acidifying deposition, especially during spring months and under high-flow conditions. Nevertheless, there is little or no apparent relationship between recent temporal trends in N deposition and trends in NO_3^- concentrations in surface waters in the eastern U.S. This observation is in sharp contrast to observed responses for S deposition and SO_4^{2-} concentrations. These results likely reflect the complexities of N use within terrestrial and aquatic ecosystems. Uptake of atmospherically deposited N by plants and microorganisms in the terrestrial environment precludes drainage water acidification and base cation leaching that would be caused if excess N leached as NO_3^- from the terrestrial to aquatic ecosystems. While great uncertainty exists, and the timescales of N saturation may be longer than previously considered (e.g., centuries rather than decades), the long-term retention of N deposited in forested regions and consequent dampening of deposition effects on surface waters is unlikely to continue indefinitely (Aber et al., 2003). Moreover, spatial patterns of NO_3^- concentrations in surface water across the northeastern U.S. are consistent with atmospheric N deposition values although there is considerable variation in these concentrations based upon watershed attributes.

Surface Water Base Cations

The results from several studies in the eastern U.S. suggest that base cation concentrations in surface waters increased during the initial phases of acidification into the 1970s. This trend reversed and base cations decreased in response to decreasing SO_4^{2-} and NO_3^- concentrations. For example, Likens

et al. (1996) evaluated trends in base cation concentrations in stream water in relation to long-term trends in SO_4^{2-} plus NO_3^- for the Hubbard Brook Experimental Forest. This record showed an approximately linear increasing relationship between concentrations of base cations and SO_4^{2-} plus NO_3^- from 1964 to 1969, then a reversal in 1970 and a decreasing trend up to 1994. The slope of the phase with increasing cation concentrations was steeper than the slope for the phase with decreasing cation concentrations. Regional declines in base cation concentrations were measured in the Long-Term Monitoring project from 1990 to 2000 for lakes in New England, the Adirondack Mountains, and the Upper Midwest (Figure 3-11). Lawrence et al. (1999) showed decreased concentrations of base cations at a rate that exceeded decreases in (SO_4^{2-} plus NO_3^-) in Catskill Mountain streams from 1984 to 1997. Within western Virginia and in Shenandoah National Park, concentrations of base cations in streams did not exhibit significant temporal trends from 1988 to 2001, perhaps due to the influence of S adsorption to soil on stream water SO_4^{2-} concentrations.

In some surface waters, interpretation of the effects of, and changes in, the concentration of base cations and ANC is complicated by the influence of naturally occurring organic acidity. The base cation surplus provides an approach for distinguishing between the effects of organic acidity and acidifying deposition (Lawrence et al., 2007). Base cation surplus is defined as the difference between the summed concentrations of base cations (Ca, Mg, Na, K) and strongly acidic inorganic anions (SO_4^{2-}, NO_3^-, chloride), plus an estimate of the strongly acidic organic anions estimated from dissolved organic C and an assumed charge density. These strongly acidic organic anions are dissociated at low pH, and function essentially as mineral acid anions in terms of their effect on ANC. The calculated base cation surplus is similar to the calculated ANC, but explicitly accounts for strongly acidic organic acids. When the base cation surplus is plotted against inorganic Al concentration, a distinct threshold for Al mobilization occurs at a base cation surplus value that closely approximates 0, regardless of the DOC concentration (Figure 3-12) (Lawrence et al., 2007). This threshold provides an unambiguous reference point for evaluating the effects of acidifying deposition on mobilization of inorganic Al. To date, this calculated variable has only been used in one large-scale assessment of acidifying deposition effects on surface waters (Lawrence et al., 2007).

In summary, decreases in base cation concentrations in surface water in the eastern U.S. over the past two to three decades are ubiquitous and are closely tied to trends in SO_4^{2-} concentrations. In most regions, rates of decrease for base cations have been similar to those for SO_4^{2-} plus NO_3^-, with the exception of streams in western Virginia and in the Shenandoah National Park, which are affected by decreases in SO_4^{2-} adsorption in soils. Decreasing trends of base cation concentrations do not necessarily indicate further acidification or recovery of surface waters, but may indicate either lower base cation leaching rates in soils or depletion of base cations from the soil system.

Surface Water pH

Surface water pH is a commonly used as an indicator of acidification. In addition, pH correlates with other biologically important components of surface water acid-base chemistry, including ANC, inorganic Al, Ca concentration, and organic acidity. Low pH can have direct toxic effects on aquatic species (Driscoll et al., 2001b). Threshold pH levels for adverse biological effects have been summarized for a variety of aquatic organisms (Baker et al., 1990b; Haines and Baker, 1986). Common reference values for pH, below which adverse biological effects are anticipated, are 6.0, 5.5, and 5.0 (Driscoll et al., 2001b). Only the most acid tolerant fish species can survive below pH 5.0, and Kretser et al. (1989) found that half the total number of fish species that occur in the Adirondack region were present in lakes with pH less than 6.0. A pH value of 6.0 is often considered the level below which biota are at risk from acidification (Driscoll et al., 2001b). The effects of low pH are specific to the study organism and depend also upon the concentrations of other chemicals in the water, notably inorganic Al and Ca. Species-specific effects are discussed in more detail in Section 3.2.3.3.

Long-term past changes in surface water pH have been inferred for lakes in the Adirondacks through paleolimnological studies (Charles et al., 1989; Cumming et al., 1992; 1994; Sullivan et al.,

1990). These studies of algal remains in lake sediments for regionally representative Adirondack lakes suggested that about 25 to 35% of the Adirondack lakes that are larger than 4 ha have acidified since preindustrial time. An estimated 80% of the Adirondack lakes that had ambient pH less than 5.2 in the mid-1980s were inferred to have experienced declines in pH and ANC since the previous century. About 30 to 45% of the lakes with ambient pH between 5.2 and 6.0 have also acidified. The results suggest that the low-ANC lakes of the southwestern Adirondacks acidified more compared to other lakes in the Adirondacks since preindustrial time.
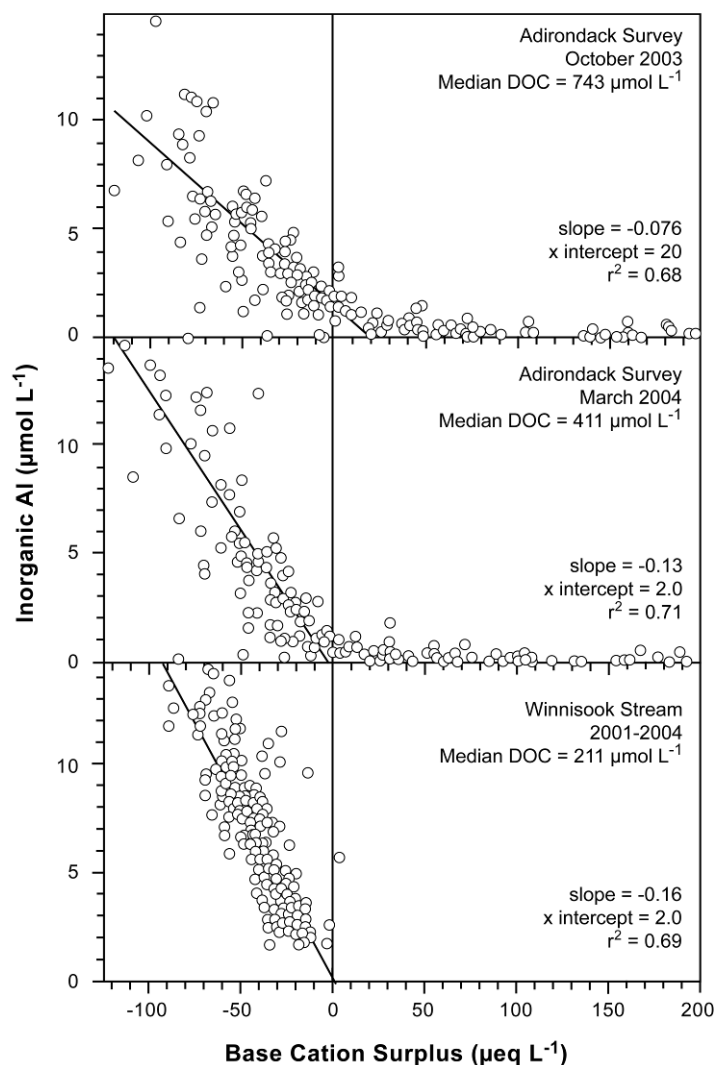
Figure 3-12. **Concentration of inorganic Al in Adirondack streams as a function of the calculated base cation surplus.**

Additional information regarding long-term changes in surface water pH has been gained through site-specific dynamic modeling. For example, by applying the PnET-BGC model to the long-term stream chemistry record at the Hubbard Brook Experimental Forest, (Gbondo-Tugbawa et al., 2002) estimated that past stream pH (circa 1850) was probably about 6.3, compared with values just above 5.0 in 2000 (Driscoll et al., 2007c).

In recent decades, measurements of pH have been routinely collected in surface waters in the U.S. where effects of acidifying deposition have been monitored, but there has been a long-standing reliance on titrated ANC as the primary chemical measurement for evaluation of surface water acidification. Overall, between 1980 and 2000 most studies reported slight increases in surface water pH, including lakes in the Adirondack Mountains (rate variable) (Driscoll et al., 2007a) and southern New England (0.002 pH units per year) (Warby et al., 2005), and streams in the Catskill/Poconos region of New York and Pennsylvania (0.008 pH units per year) (Warby et al., 2005).

Through frequent monitoring from 1990 to 2000, Stoddard et al. (2003) found a decrease in hydrogen ion (0.19 µeq/L/yr) that was similar to the rate of change observed in the same Adirondack lakes by Driscoll et al. (2007a) from 1992 to 2004 (0.18 µeq/L/yr). Stoddard et al. (2003) also reported an increase in the hydrogen ion concentration of Appalachian streams (0.08 µeq/L/yr) and Upper Midwest lakes (0.01 µeq/L/yr); no trends were found in New England lakes in this study (see Figure 3-11).

In summary, increasing trends in pH (decreasing hydrogen ion concentration) in surface waters in the northeastern U.S. were common through the 1990s up to 2004, but many exceptions occur, and overall, the rates of change have been small. Driscoll et al. (2001a, 2001b; 2007c) attributed the limited pH recovery of lakes in acid-sensitive regions to three factors: (1) the levels of acid-neutralizing base cations in surface waters have decreased markedly because of the depletion of available base cations from the soil, and to a lesser extent, a reduction in atmospheric inputs of base cations; (2) as forests mature, their requirements for N decrease, and they are expected to increasingly lose NO_3^- as forests develop; and (3) sulfur has accumulated in the soil under previous conditions of high atmospheric S deposition and is now being gradually released to surface water as SO_4^{2-}, even though S deposition has decreased.

Surface Water ANC

The most widely used measure of surface-water acidification is ANC, which is often determined by Gran titration (titrated ANC). This measurement is the primary chemical indicator for assessing past effects of acidifying deposition, and the recovery expected from decreasing atmospheric deposition (Bulger et al., 2000; Stoddard et al., 2003). Titrated ANC is useful because it reflects the ANC of the complete chemical system, which is typically decreased by acidic deposition in acid-sensitive landscapes. Surface water pH is a common alternative to ANC as an indicator of acidification. However, at pH values above about 6.0, pH is not a good indicator of either sensitivity to acidification or level of effect. In addition, pH measurements (especially at these higher values) are sensitive to levels of dissolved CO_2 in the water. In contrast, ANC is more stable and it reflects sensitivity and effects of acidification in a linear fashion across the full range of ANC values. Therefore, ANC is the preferred indicator variable for surface water acidification. Both titrated and calculated ANC values are commonly determined in studies aimed at resource characterization or long-term monitoring.

Bulger et al. (1999) defined ANC response categories for brook trout in Virginia as less than zero (chronic damage likely), 0 to 20 µeq/L (episodic damage likely), 20 to 50 µeq/L (likelihood of damage not determined), and greater than 50 µeq/L (brook trout not sensitive). Baker et al. (1990b) used ANC cutoffs of 0, 50, and 200 µeq/L for reporting on national lake and stream population estimates. ANC less than 0 µeq/L is of significance because waters at or below this level have limited capacity to neutralize acid inputs. Surface waters with ANC <50 µeq/L have been termed "extremely acid sensitive" (Schindler, 1988), are prone to episodic acidification in some regions (DeWalle et al., 1987; Eshleman, 1988), and may be susceptible to future chronic acidification at current or increased rates of acidifying deposition.

In assessing changes in surface water ANC, it is important to distinguish between acidic waters and acidified waters. "Acidic" describes a condition that can be measured (i.e., Gran ANC less than or equal to 0). It may be due either to the effects of acidifying deposition, or to other causes such as the presence of organic acidity or the oxidation of chemically reduced S-containing minerals in the watershed. "Acidified" refers to the consequences of the process of acidification (a decrease in ANC observed through time). It does not require that the water body be acidic, and does not imply a particular cause for

the change in chemistry. The term "anthropogenically acidified" implies that human activity was responsible for the increase in acidity that occurred.

Some of the most detailed studies of ANC have been conducted in the Adirondack Mountains. Model simulations suggested that none of the lakes in the Adirondack target lake population identified by the U.S. EPA (EMAP) were chronically acidic or had ANC less than 20 µeq/L under preindustrial conditions, but that by 1980 there were hundreds of such lakes (Table 3-5). Many lakes were estimated to have had preindustrial ANC below 50 µeq/L, but this estimate more than doubled by 1990. Based on MAGIC model outputs extrapolated to the regional population of Adirondack lakes larger than 1 ha that currently have ANC below 200 µeq/L, maximum past acidification occurred by about 1980 or 1990, with median ANC of the lake population of about 61 µeq/L (reduced from a median of 92 µeq/L estimated for the preindustrial period). Changes in ANC produced an increase in not only the percentage of lakes that were chronically acidic, but also in those that were deemed likely to experience episodic acidification and its associated short-term changes in water chemistry (Sullivan et al., 2008).

Table 3-5. **Estimates of change in number and proportion of acidic surface waters in acid-sensitive regions of the North and East, based on applying current rates of change in Gran ANC to past estimates of population characteristics from probability surveys.**

Region	Results of Regional Survey				Results of Monitoring during 1990s			
	Population Size	Number Acidic[1]	% Acidic[2]	Time Period of Estimate	Rate of ANC change[3]	Estimated Number Acidic in 2000	% Acidic in 2000	% Change in Number of Acidic Systems
New England	6,834 lakes	386 lakes	5.6%	1991–94	+0.3	374 lakes	5.5%	−2%
Adirondacks	1830 lakes	238 lakes	13.0%	1991–94	+0.8	149 lakes	8.1%	−38%
N. Appalachians	42,426 km	5,014 km	11.8%	1993−94	+0.7	3,600 km	8.5%	−28%
Ridge/Blue Ridge	32,687 km	1,634 km	5.0%	1987	−0.0	1,634 km	5.0%	0%
Upper Midwest	8,574 lakes	251 lakes	2.9%	1984	+1.0	80 lakes	0.9%	−68%

[1] Number of lakes/length of streams with Gran ANC <0 in past probability survey by the U.S. EPA (data collected at "Time Period of Estimate," in column 5).
[2] Percent of population (from Column 2) with Gran ANC <0 in past probability survey (data collected at "Time Period of Estimate," in column 5).
[3] Based on regional trends presented in the Stoddard et al. (2003) report, in µeq/L/yr, for the 1990s.

In other regions, responses to reduced levels of acidifying deposition required by the CAA and other emissions control legislation were reported by Stoddard et al. (2003). They found tendencies during the 1990s toward increasing surface water Gran ANC in all of the glaciated regions of the eastern U.S. (i.e., New England, Adirondacks, and Northern Appalachian Plateau) and Upper Midwest, and decreasing Gran ANC in the Ridge/Blue Ridge province. Changes in ANC were relatively modest compared with observed reductions in SO_4^{2-} concentrations in surface waters. The regional increases in the Adirondacks, Northern Appalachian Plateau, and Upper Midwest were statistically significant (Table 3-6). Median increases of about +1 µeq/L/yr in the Northern Appalachian Plateau, Adirondacks, and Upper Midwest represent significant trends towards ecological recovery from acidification (Stoddard et al., 2003). Estimated change in the number of acidic surface waters decreased during the 1990s in all regions investigated by Stoddard et al. (2003), except the Ridge and Blue Ridge Provinces in the mid-Appalachian Mountains (Table 3-5). For other regions, the change in number of acidic systems ranged from −2% in New England to −68% in the Upper Midwest.

Table 3-6. Regional trend results for long-term monitoring lakes and streams for the period 1990 through 2000.

Region	SO_4^{2-} (µeq/L/yr)	NO_3^- (µeq/L/yr)	Base Cations [Ca + Mg] (µeq/L/yr)	Gran ANC (µeq/L/yr)	Hydrogen (µeq/L/yr)	DOC (mg/L/yr)	Aluminum (µg/L/yr)
New England Lakes	−1.77**	+0.01ns	−1.48**	+0.11ns	−0.01ns	+0.03*	+0.09ns
Adirondack Lakes	−2.26**	−0.47**	−2.29**	+1.03**	−0.19**	+0.06**	−1.12**
Appalachian Streams	−2.27*	−1.37**	−3.40**	+0.79*	−0.08*	+0.03ns	+0.56ns
Upper Midwest Lakes	−3.36**	+0.02ns	−1.42**	+1.07**	−0.01*	+0.06**	−0.06ns
Ridge/Blue Ridge Streams	+0.29**	−0.07**	−0.01ns	−0.07ns	+0.01ns	NA	NA

Values are median slopes for the group of sites in each region. Regional trend not significant (p >0.05) * p <0.05 ** p <0.01. NA = insufficient data.

In summary, ANC is the most widely used measure of acid sensitivity, acidification, and chemical recovery of surface waters in response to changes in acidifying deposition. Lake and stream ANC values decreased throughout much of the 20th century in a large number of acid-sensitive lakes and streams throughout the eastern U.S. This effect has been well documented in monitoring programs, paleolimnological studies, and model simulations. Since about 1990 the ANC of many affected lakes and streams have shown some increase, but such increases have been relatively modest.

Surface Water Aluminum

The concentration of inorganic Al in surface waters is an especially useful indicator of acidifying deposition effects because (1) it is widely toxic, and (2) it generally does not leach from the terrestrial soils to surface waters in the absence of acidifying deposition (Driscoll et al., 1988; Lawrence et al., 2007) with exceptions such as acid mine drainage and relatively rare geologic deposits. Lawrence et al. (2005) showed that strong organic acid anions can contribute to the mobilization of inorganic Al in combination with SO_4^{2-} and NO_3^-, but in the absence of geologic S, the presence of inorganic Al in surface waters is an ambiguous indication of acidifying deposition effects.

Considerable work was done to define pH sensitivity ranges for a wide variety of aquatic organisms, but when pH values fall below approximately 5.5, inorganic Al generally becomes the greater health risk to biota. Although organically complexed Al (organic Al) can occur in surface waters as a result of natural soil and hydrologic processes, this form of Al is not harmful to aquatic life (Gensemer and Playle, 1999). Inorganic Al, however, has been found to be toxic to plant and animal species throughout the food web (Gensemer and Playle, 1999).

Earlier studies demonstrated reduced growth and survival of various species of fish (Baker and Schofield, 1982; Baker et al., 1996) at inorganic Al concentrations between approximately 2 and 7.5 µmol/L. Most recently, 20% mortality of young-of-the year brook trout was documented in situ during a 30–day period with a median inorganic Al concentration of 2 µmol/L (Baldigo et al., 2007). This study estimated that 90% mortality would occur over 30 days with a median inorganic Al concentration of 4.0 µmol/L.

The development of methods to fractionate Al into organic and inorganic forms (Driscoll, 1984; Sullivan et al., 1986) resulted in collection of a considerable amount of data on Al concentrations in surface waters in the 1980s. However, most of this sampling was done either once or for a limited period of time (Cronan et al., 1990; Driscoll and Newton, 1985; Driscoll et al., 1987b; Lawrence et al., 1987). Available long-term trend information for inorganic Al is limited. In Adirondack lakes, inorganic Al

concentrations decreased slightly (e.g., by 0.02 μM/yr to 0.18 μM/yr) (Driscoll et al., 2007a) or remained unchanged between 1982 and 2004 (Driscoll et al., 2007a; Stoddard et al., 2003). There was no trend in inorganic Al for this period in New England lakes, Appalachian streams, or Midwest lakes. Monthly stream chemistry monitoring at the Hubbard Brook Experimental Forest showed decreases in inorganic Al concentrations at four locations along the reference stream for the experimental forest from 1982 to 2000, but no trends at two other locations along this stream (Palmer et al., 2004).

Most recently, Lawrence et al. (in press) found that 49 of 195 streams (25%) in the western Adirondack region had inorganic Al concentrations above 2.0 μM during August base flow. Although there is not a clear benchmark value above which inorganic Al is toxic to aquatic biota, 2 μM is generally recognized as a reasonable threshold for biological effects at a variety of trophic levels (Baldigo et al., 2007; Driscoll et al., 2001b).

In summary, inorganic Al is an important chemical indicator of the effects of acidifying deposition on surface water. It has well-documented effects on aquatic biota at specific thresholds. Limited data suggest that acid-sensitive regions of the northeastern U.S. have elevated inorganic Al concentrations which have been induced by years of acidifying deposition and which pose a threat to aquatic life. Concentrations have decreased slightly in some surface waters in the northeastern U.S. during the last two decades in response to decreased levels of acidifying deposition.

Quantification of Acidification

Changes in the acid-base status of soils and drainage waters operate on different time scales. Most temperate forest soils have high exchangeable acidity, and relatively small changes in the acidity of precipitation input would not be expected to have a large effect on soil acidity (Krug and Frink, 1983; Turner et al., 1990). Therefore, projected recovery of soil acid-base chemistry in response to future decreases in acidifying deposition is expected to be limited (Gbondo-Tugbawa and Driscoll, 2002; Sullivan et al., 2006b). In contrast, changes in the chemistry of drainage water in response to changes in acidifying deposition can occur more rapidly. This is because drainage water can become acidified by the leaching of a mobile acid anion such as SO_4^{2-} or NO_3^- even if the acidity of the soil is not measurably affected (Reuss and Johnson, 1986; Seip, 1980; Turner et al., 1990). In areas (including the northeastern U.S.) where S adsorption on soils is minimal, and therefore where SO_4^{2-} is highly mobile, changes in S deposition input have been shown to cause changes in the ANC and base cation concentrations in lakes and streams over a time period of years to decades (c.f., Driscoll et al., 2003).

One way to quantify acidification dose-response relationships is to calculate the changes in various ionic constituents in solution that occur in response to changes in mineral acid anion (SO_4^{2-} and NO_3^-) concentrations due to changes in acidifying deposition input. As $SO_4^{2-} + NO_3^-$ concentration increases or decreases in solution, equivalent changes must also occur in the concentrations of other anions (i.e., bicarbonate [HCO_3^-], organic acid anion [$RCOO^-$]) or cations (i.e., H^+, Al^{n+}, sum of base cations [SBC]) to maintain the charge balance. Typically, the largest counteracting change is in SBC. It is generally assumed that most of the base cation change is due to Ca^{2+} and Mg^{2+}. In acid-sensitive waters, additional changes can occur in ANC (which can be expressed as [$HCO_3^- - H^+$]), Al^{n+}, and/or $RCOO^-$) (Husar and Sullivan, 1991). Henriksen (1984) presented evidence for Norwegian lakes, suggesting that base cation release accounted for up to a maximum of 40% of the added mineral acid anions. This proportional change in base cations relative to SO_4^{2-} or [$SO_4^{2-} + NO_3^-$] is called the F-factor:

$$F = \frac{\Delta SBC}{\Delta[\,SO_4^{2-} + NO_3^-\,]}$$

Subsequently, diatom reconstructions for Adirondack lakes suggested higher F-factors, generally ranging from 0.4 to greater than 1.0 (Sullivan et al., 1990).

Sullivan and Eilers (1994) compiled available data on proportional changes in SBC, ANC, and Al^{n+}, relative to the observed or estimated change in [$SO_4^{2-} + NO_3^-$]. Their analysis included: 1) measured

short-term (<20 year) changes in drainage water chemistry in response to ambient or experimental increases or decreases in S deposition loading, 2) results of space-for-time substitution analyses, 3) results of diatom inferences of past lake chemistry, and 4) MAGIC model hindcast and forecast simulations. Results indicated a wide range in the estimated proportional changes in SBC as a percent of change in $[SO_4^{2-} + NO_3^-]$. Estimated F-factors generally ranged from about 0.5 to 1.0, although some watersheds in Norway and in the western U.S. showed F-factors as low as about 0.25. The estimated proportional change in ANC was typically less than 0.3, and change in Al^{n+} was smaller. Quantitative data were not available for the organic acid anion response, but this response is also expected to generally be relatively small. More recent PnET-BGC simulations for Adirondack lakes were in close agreement with the diatom results in Figure 3-13 (Zhai et al., 2008), ranging from about 0.4 to 1.0.

The plot shows F-factor on the y-axis (0.0 to 1.5) versus ANC (μeq/L) on the x-axis (-50 to 250), with a fitted curve and the equation:

$$F = -10^{-5} * ANC^2 + 0.005 * ANC + 0.52$$
$$R^2 = 0.62$$
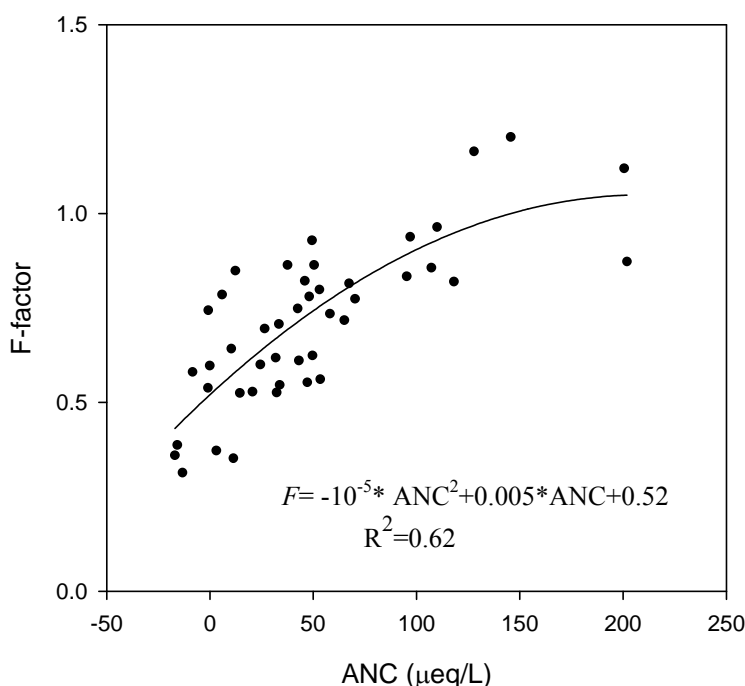
Figure 3-13.   F-factors calculated from PnET-BGC model results for the period 1850 to 1980 as a function of simulated ANC in 1980 for 44 EMAP lakes in the Adirondack region of New York.

Measured, modeled, and inferred changes in surface water chemistry in areas that have experienced relatively short-term (less than three decades) changes in acid deposition loading are available from many sources. Process model hindcasts and paleolimnological reconstructions of pre-industrial surface water chemistry provide insight into the extent to which individual lakes and streams have acidified over the longer term (Sullivan et al., 2006b). Evaluation of acidification effects from assessment of current conditions is generally not helpful. This is because lakes and streams vary with respect to their expected chemistry (i.e., ANC or pH) in the absence of acidifying deposition. In many regions, pre-disturbance lake and stream ANC values below 50 μeq/L and pH below 6.0 appear to have been common; in some cases, ANC below 0 and pH below 5.0 also occurred (Sullivan et al., 2006b). The common occurrence of lakes and streams that were naturally low in ANC and pH before the advent of acidifying deposition is further complicated by the fact that disturbances other than air pollution have contributed to further changes in acid-base status, including both ANC and pH increases and decreases. Such disturbances have included

logging, fire, forest regrowth, erosion, road-building, forest insect infestation and disease, and other land-disturbing activities and events. Current surface water chemistry is a complex function of inherent sensitivity (which to some degree was reflected in pre-disturbance chemistry), levels of acidifying deposition (historic and current), and the effects of other disturbances.

Dose-response functions may in some cases be similar from water body to water body within a defined region. For example, model simulations conducted for the NAPAP Integrated Assessment (NAPAP 1991) reported by Sullivan et al. (1992) found that, although substantial variability was found in projected future change in ANC among the modeled Adirondack watersheds, there was a highly consistent relationship between median change in acidifying deposition and projected median change in ANC over 50 years. Each 1 kg S/ha/yr change in future S deposition caused approximately a 3.5 µeq/L change in simulated lakewater ANC (see Figure 3-14). Results of MAGIC model hindcast simulations suggested that all of the Adirondack lakes modeled for NAPAP (1991) had acidified (decreased in pH or ANC) since pre-industrial times. The median and range of estimated changes in ANC were -46 µeq/L and -31 to -84 respectively. None of the lakes were inferred to have been acidic (ANC ≤ 0) in pre-industrial times. The minimum simulated pre-industrial values were pH 5.4 and ANC = 30 µeq/L (Sullivan and Eilers, 1994).

Historical changes in Adirondack lakewater chemistry inferred from measurements in diatoms suggested somewhat more conservative estimates of historical acidification. From these data, Sullivan (1990) concluded:

- the "median" Adirondack lake had not acidified;

- acidification was generally limited to lakes that had ambient ANC during the 1980s less than about 50 µeq/L (or pH less than about 6.0);

- approximately 15% of the Adirondack lakes were inferred to have acidified by more than 0.28 pH units;

- the median historical acidification (expressed as Δ ANC − Δ Al$_i$) of lakes that were acidic (ANC <0) at the time of sampling was -37 µeq/L;

- approximately 3% of the Adirondack lakes were acidic in pre-industrial times, compared to 14% in the 1980s.
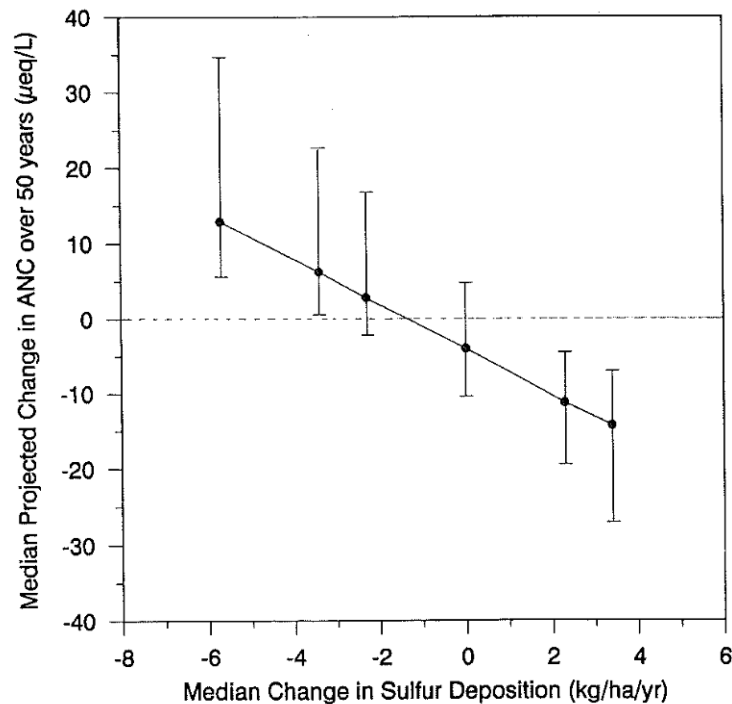
Figure 3-14. **Median and range of projected change in ANC (µeq/L) of Adirondack lakes for 50-year MAGIC simulations versus median future change in sulfur deposition (kg S/ha/yr) for each deposition scenario. Points on each line correspond to -50%, -30%, -20%, 0%, +20%, +30% change from current deposition.**

These paleolimnological estimates suggested that Adirondack lakes that were acidic in the 1980s had decreased a median of about 4 µeq/L in [$ANC_G - Al_i$] for each kg S/ha/yr change in S deposition. This was slightly more than one-half of the median historical rate of acidification projected by MAGIC (7 µeq/L of calculated ANC for each kg S/ha/yr) for acidic Adirondack lakes (Sullivan et al., 1992).

In comparing estimates, derived from different approaches, of past and future changes in Adirondack lakewater chemistry in response to acidifying deposition, it is important to consider several factors (Sullivan et al., 1992):

- Chemical changes estimated from paleolimnology or monitoring data incorporate all influences on the acid-base chemistry of lakewater, including land use, disturbances, and climatic differences. Model estimates commonly include only postulated or estimated changes in acidifying deposition as having influenced the lakewater chemistry. Because watershed disturbances generally cause an increase in surface water ANC, they may partially explain the more conservative estimates of diatom-inferred acidification compared with MAGIC model estimates of acidification.

- The use of a process-based model for hindcasting requires assumptions regarding historical deposition of all major ions. In addition to uncertainties regarding historical sulfur deposition levels, base cation deposition has also likely changed by an unknown amount, and the degree to which sulfur and base cation deposition have been coupled is unclear (Chen and Gomez, 1989; Driscoll et al., 1989).

- Organic acids may have exerted a greater influence on lakewater pH during pre-industrial times than they do currently because DOC and organic acid anion concentrations may have decreased in response to increased organic acid protonation and increased concentrations of Al (Almer et al., 1974; Davis et al., 1985; Kingston and Birks, 1990; Krug and Frink, 1983). Data sets from different points in time are often not directly comparable because of differences in ANC definition or pH measurement. For example, the calculated ANC used by MAGIC differs from titrated ANC (ANC_G) used to calibrate paleolimnological transfer functions and reported in surveys. The differences are due to the partially counteracting influences of Al and organic acids on ANC_G and their omission from calculated ANC. These differences can be appreciable for acidic and low-ANC waters (Sullivan et al., 1989).

There is not a clear definable relationship between atmospheric S deposition and ecological effects. A given amount of S deposition can cause a wide range of ecological responses, from no ecological effect to varying levels of adverse ecological effect. These can include changes in community composition, loss of sensitive species, reduced biological diversity, and altered ecosystem functions. Such effects can occur in both aquatic and terrestrial ecosystems. The observed wide range of responses within and among regions is attributable to varying ecosystem sensitivity. Some soils (notably in many watersheds in the southeastern U.S.) have the capacity to adsorb substantial quantities of S, with essentially no acidification of drainage water. Nevertheless, there is a finite limit to this S adsorption capacity, and under continual high S deposition loading, the adsorptive capacity of soil will eventually become depleted.

In addition to differences in S adsorption capacity of soils, watersheds also differ in their sensitivity to acidification effects as a consequence of differing sensitivity of the species that make up the local biological community. Some species of fish, aquatic insects, and mollusks, for example, are highly sensitive to adverse effects from low pH and high inorganic Al concentrations; others are less sensitive. Finally, watersheds differ in the size of the soil base cation pool available to neutralize deposited mineral acidity. Some watersheds have sufficient quantities of base cations in their soils such that drainage waters will remain well buffered, even under relatively high S deposition loads, for many decades or longer. Other watersheds had relatively low base cation supply during preindustrial times due to low weathering rates of the underlying geology, and the base cation supply may have been further depleted by past acidifying deposition.

As a consequence of these, and other, differences in sensitivity to S inputs, watersheds differ in the extent to which they acidify in response to a given amount of S deposition and they also differ in the extent to which that acidification translates to biological effects. Thus, one cannot specify a level of S deposition that would be likely to cause adverse effects across the landscape. Sensitivity differs from watershed to watershed.

Despite these differences in watershed sensitivity to acidification, it is possible to place bounds on the amount of acidification that has occurred in response to a given change in S deposition. Such quantitative estimates of acidification have been derived using watershed models of acidification response. Modeling results summarized in Table 3-7 illustrate a wide range in the model estimates of past acidification of acid-sensitive lakes and streams in the eastern U.S.

Table 3-7. Model projections of surface water SO_4^{2-} and associated ANC, shown as changes between dates, for Adirondack and Shenandoah streams.

Region	Water Bodies	Dates	Model	Pollution Scenario	Change in Median Surface Water SO_4^{2-} (µeq/L)	Change in Median Surface Water ANC (µeq/L)	Reference
HINDCASTS							
Adirondacks, NY	38 lakes	1850 to 2003	PnET-BGC		+72.9	-39.9	Zhai et al. (2008)
Adirondacks, NY	37 lakes	1850 to 1984	PnET-BGC		+107	-77.8	Chen et al. (2005)
Adirondacks, NY	44 potentially acid-sensitive lakes	1850 to 1990	MAGIC		+77.8	-38.3	Sullivan et al. (2006b)
			PnET-BGC		+57.3	-29.5	
FORWARD PROJECTIONS							
Shenandoah NP, VA	5 streams on siliciclastic bedrock	1990 to 2040	MAGIC	constant deposition	+13	-11.6	Sullivan et al. (2008)
				mild reduction	-21	+6.2	
				medium reduction	-23	+7.2	
				strong reduction	-40	+24.2	
				very strong reduction	-44	+27.2	
Shenandoah NP, VA	4 streams on granitic bedrock	1990 to 2040	MAGIC	constant deposition	+22	-8	Sullivan et al. (2008)
				mild reduction	+11	-5	
				medium reduction	+11	-5	
				strong reduction	+3	-2	
				very strong reduction	+2	-2	
Shenandoah NP, VA	5 streams on basaltic bedrock	1990 to 2040	MAGIC	constant deposition	+33	-5	Sullivan et al. (2008)
				mild reduction	+12	0	
				medium reduction	+11	+1	
				strong reduction	-4	+5	

Region	Water Bodies	Dates	Model	Pollution Scenario	Change in Median Surface Water SO$_4^{2-}$ (µeq/L)	Change in Median Surface Water ANC (µeq/L)	Reference
				very strong reduction	-9	+6	
Adirondacks, NY	44 potentially acid-sensitive lakes	1990 to 2050	MAGIC	current and expected controls	-42.4	+5.89	Sullivan et al. (2006b)
				moderate emission controls	-58.9	+18.6	
				aggressive emission controls	-64.6	+22.6	
Adirondacks, NY	44 potentially acid-sensitive lakes	1990 to 2050	PnET-BCG	current and expected controls	-18	-3.7	Sullivan et al. (2006b)
				moderate emission controls	-32.2	+1.8	
				aggressive emission controls	-38.3	+9.3	

3.2.3.2. Summary of Biogeochemistry and Chemical Effects

The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in biogeochemistry related to aquatic ecosystems. The strongest evidence for a causal relationship comes from studies of changes in surface water chemistry including concentrations of SO_4^{2-}, NO_3^-, inorganic Al, and Ca, surface water pH, sum of base cations, ANC, and base cation surplus. Surface water chemistry integrates the sum of upstream soil and water processes and reflects the results of watershed-scale terrestrial effects of S and N deposition including, N saturation, forest decline, and soil acidification (Stoddard et al., 2003). In many cases, surface water chemistry indicates the effects of acidification on biotic species and communities found in fresh water ecosystems.

Surface water chemistry can be examined and reported as chronic chemistry or episodic chemistry. Chronic chemistry refers to annual average conditions, which are often represented as summer and fall chemistry for lakes and as spring baseflow chemistry for streams. Episodic chemistry refers to conditions during rainstorms or snowmelt when proportionately more drainage water is routed through upper soil horizons, which tend to provide less neutralizing of atmospheric acidity as compared with deeper soil horizons. Surface water chemistry has lower pH and ANC during storm runoff or snowmelt than during baseflow conditions. One of the most important effects of acidifying deposition on surface water chemistry is the short-term change in chemistry that is termed "episodic acidification." Some streams may have chronic or average chemistry that is suitable for aquatic biota, but be subject to occasional episodic acidification with lethal consequences. Episodic declines in pH and ANC are nearly ubiquitous in

drainage waters throughout the eastern U.S. caused partly by acidifying deposition and partly by natural processes.

Acidification effects on aquatic biota are often evaluated using measures of either inorganic Al or pH. ANC is also used because it is an indicator of acid base status (although ANC does not relate directly to the health of biota). The usefulness of ANC lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, Ca, and inorganic Al.

SO_4^{2-}, NO_3^-, and Base Cations

Changes in water chemistry resulting from acidifying deposition typically include changes in SO_4^{2-}, NO_3^-, and base cation concentrations. Each plays an important role in the acid-base chemistry of water, but none are directly toxic at concentrations commonly encountered in natural waters.

- SO_4^{2-} is the primary inorganic anion found in most acid sensitive waters. Continued decreases in S emissions should cause further decreases in SO_4^{2-} concentrations in surface waters. However, the rate of decrease in surface water SO_4^{2-} concentrations may be delayed as accumulated S leaches from watershed soils in some regions of the country, especially the Blue Ridge Mountains.

- The importance of NO_3^- as an agent of acidification varies by region, but it is particularly important during periods of high hydrologic flow from soils to streams such as those that occur during snowmelt and rain events. The relationship between N deposition and surface water NO_3^- concentration is complex and involves the terrestrial and aquatic cycling of N and other elements. NO_3^- contributes to the acidity of many lakes and streams in the eastern U.S., but there is no apparent relationship between recent trends in N deposition and trends in NO_3^- concentrations in these surface waters (in contrast to observed responses for S deposition and SO_4^{2-} concentrations). This suggests that the time scales of N saturation may be longer than previously considered (e.g., centuries rather than decades). Nevertheless, long-term retention of N deposited in forested regions and consequent dampening of deposition effects on surface waters is unlikely to continue indefinitely (Aber et al., 2003).

- Decreases in base cation concentrations in eastern U.S. surface waters over the past two to three decades are ubiquitous and are closely tied to trends in SO_4^{2-} concentrations. Rates of base cation depletion have been similar to those for SO_4^{2-} plus NO_3^- in most areas (Shenandoah National Park is a notable exception). Decreasing trends in base cation concentrations do not necessarily indicate further acidification or recovery of surface waters, but may indicate either lower base cation leaching rates in soils or depletion of base cations from the soil system.

pH, Acid Neutralizing Capacity, and Aluminum

Acidification of surface water causes changes in pH, ANC, and inorganic aluminum concentration. Low pH and high inorganic Al concentration can be directly toxic to aquatic biota.

- The pH of freshwater streams and lakes is a common measure used to link acidification to adverse effects on aquatic biota. Decreases in pH below values of 6.0 typically result in species loss of benthic invertebrates, plankton species, and fish. A number of synoptic surveys indicated loss of species diversity and absence of several fish species in the pH range of 5.0 to 5.5. If pH decreases to lower values, there is a greater likelihood that more aquatic species could be lost without replacement, resulting in decreased richness and diversity. (See the following discussion on biota).

- ANC reflects the difference between base cations and anions of strong acids in solution and is the most widely used measure of acid sensitivity, acidification, and chemical recovery of surface waters in response to changes in acidifying deposition. Acidic waters are defined as those having ANC equal to or below zero. Waters with ANC of <50 µeq/L are considered "extremely acid sensitive" (Schindler, 1988) and are vulnerable to episodic acidification (DeWalle et al., 1987; Eshleman, 1988). Lake and stream ANC values decreased throughout much of the 20th century in a large number of acid-sensitive lakes and streams throughout the eastern U.S. Since about 1990, the ANC of many affected lakes and streams has increased slightly. The number of acidic surface waters has decreased in some areas of the Northeast, but not in the mid-Appalachian Mountains.

- Dissolved inorganic Al is an important chemical indicator of the effects of acidifying deposition on surface water because it is toxic to aquatic life and generally does not leach from soils in the absence of acidification. When pH falls below approximately 5.5, inorganic Al generally becomes a greater health risk to biota. Limited data suggest that acid-sensitive regions of the northeastern U.S. have elevated inorganic Al concentrations in surface waters induced by years of acidifying deposition, posing a threat to aquatic life. Concentrations have decreased slightly in some surface waters in the northeastern U.S. during the last two decades in response to decreased levels of acidifying deposition.

3.2.3.3. Biological Effects

Aquatic effects of acidification have been well studied in the U.S. and elsewhere at various trophic levels. These studies indicate that aquatic biota have been affected by acidification at virtually all levels of the food web in acid sensitive aquatic ecosystems. Effects have been most clearly documented for fish, aquatic insects, other invertebrates, and algae.

Biological effects are primarily attributable to a combination of low pH and high inorganic Al concentration. Such conditions occur more frequently during rainfall and snowmelt that cause high flows of water and less commonly during low-flow conditions, except where chronic acidity conditions are severe. Biological effects of episodes include reduced fish condition factor, changes in species composition, and declines in aquatic species richness across multiple taxa, ecosystems and regions. These conditions may also result in direct mortality as was shown from results of in situ bioassays (Van Sickle et al., 1996). High concentrations of Ca, and to a lesser extent other base cations, can lessen the toxicity of low pH and high inorganic Al concentration where they occur (Baker et al., 1990a).

Biological effects in aquatic ecosystems can be divided into two major categories: effects on health, vigor, and reproductive success; and effects on biodiversity. The first category includes changes in biological indicators such as individual condition factor and recruitment success. The latter can be described by changes in species composition and taxonomic richness.

The following sections define concepts used to measure and evaluate acidification-related effects on aquatic biota. Measures are presented of changes in health, vigor, and reproductive success; and biodiversity for fish. Finally, the general effects literature is summarized for phytoplankton, zooplankton, benthic invertebrates, amphibians, and fish-eating birds. Specific reference is made to the biological indicators outlined above where such information exists.

Measures of Health, Vigor, and Reproductive Success

There are few measures of the effects of acidification on the health, vigor, and reproductive success of aquatic species. Condition factor is one measure of sublethal acidification stress that has been used to quantify effects of acidification on an individual fish. Condition factor is an index that describes the relationship between fish weight and length. Expressed as fish weight/length[3], multiplied by a scaling constant, this index reflects potential depletion of stored energy (Dennis and Bulger, 1995; Everhart and Youngs, 1981; Goede and Barton, 1990). Condition factor is interpreted as depletion of energy resources

such as stored liver glycogen and body fat in response to increased stress at sublethal levels (Goede and Barton, 1990). Fish with higher condition factor are more robust than fish having low condition factor. Field studies have shown lower condition factor in fish found in more acidic streams (Dennis and Bulger, 1995).

Measures of Biodiversity

Species composition refers to the mix of species that are present in a particular ecosystem. Acidification alters species composition in aquatic ecosystems. There are a number of species common to many oligotrophic waters that are sensitive to acidifying deposition and that cannot survive, compete, or reproduce in acidic waters. In response to small to moderate changes in acidity, acid-sensitive species are often replaced by other more acid-tolerant species, resulting in changes in community composition, but little or no change in total community abundance or biomass. The extent of alteration of surface water biological community composition increases as surface waters become more acidic. There is also a common pattern of lower community diversity with increased acidification.

One important tool that aids in the determination of effects on species composition is the ASI developed by (Baker et al., 1990b). This index uses fish bioassay survival data to predict the probability of fish survival expressed as a percent mortality. Separate ASI models were developed for tolerant, intermediate, and sensitive fish species.

Taxonomic richness is a metric that is commonly used to quantify the effects of an environmental stress on biota. It can be applied at various taxonomic levels. For example, the number of fish species present in a lake or stream can be used as an index of acidification (Bulger et al., 1999). Similarly, acidification effects on aquatic insects can be evaluated on the basis of the number of families or genera of mayflies (order Ephemeroptera) (Sullivan et al., 2003). In the latter cases, the mayfly order was selected for study because it includes a number of genera and species having varying degrees of sensitivity to acidification.

Decreases in ANC and pH and increases in inorganic Al concentration have been shown to contribute to declines in species richness and abundance of zooplankton, macroinvertebrates, and fish (Keller and Gunn, 1995; Schindler et al., 1985). Species richness is positively correlated with pH and ANC (Baker et al., 1990b; Rago and Wiener, 1986) primarily because of the elimination of acid-sensitive species at lower pH and ANC (Schindler et al., 1985). Interpretation of species richness can be difficult because more species tend to occur in larger lakes and streams as compared with smaller ones, irrespective of acidity (Sullivan et al., 2003). Nevertheless, decreases in species richness have been observed for all major trophic levels of aquatic organisms (Baker et al., 1990b), even after adjusting for lake size (Frenette et al., 1986; Harvey and Lee, 1982; Matuszek and Beggs, 1988; Rago and Wiener, 1986; Schofield and Driscoll, 1987).

Health, Vigor, and Reproductive Success of Fish

Fish populations in acidified streams and lakes of Europe and North America have declined, and some have been eliminated as a result of atmospheric deposition of acids and the resulting changes in water quality (Baker et al., 1990b). A variety of water chemistry variables, including inorganic Al, DOC, and Ca, along with the timing and magnitude of episodic fluctuations in toxic acid and inorganic Al concentrations, are related to the degree to which surface water acidification influences fish survival in natural systems (Baker et al., 1990b; Baldigo and Murdoch, 1997; Gagen et al., 1993; Siminon et al., 1993; Van Sickle et al., 1996).

The effects of acidification on the health, vigor, and reproductive success are manifested through a range of physiological effects on individual life stages and fish species. The primary mechanism for the toxic effects of low pH and elevated inorganic Al on fish involves disruption of normal ion regulation at the gill surface, resulting in increased rates of ion loss and inhibition of ion uptake (Bergman et al., 1988; Leivestad, 1982; McWilliams and Potts, 1978; Wood and McDonald, 1987). Additional effects might include disruption of Ca metabolism (Gunn and Noakes, 1987; Peterson and Martin-Robichaud, 1986;

Reader et al., 1988); and decreased hatching success (Gunn and Noakes, 1987; Haya and Waiwood, 1981; Peterson et al., 1980; Reader et al., 1988; Runn et al., 1977; Waiwood and Haya, 1983).

There is marked variability among species, and among life stages within species, in the specific levels of pH and inorganic Al that produce measurable responses. In general, early life stages are more sensitive to acidic conditions than the young-of-the-year, yearlings, and adults (Baker and Schofield, 1985; Baker et al., 1990b; Johnson et al., 1987). Also, small fish, especially swim-up fry, are probably less mobile and less able to avoid exposure to adverse chemical conditions than the relatively larger adults (Baker et al., 1996). Here, effects are described by life stage. Several studies have shown that the earliest reproductive stages are highly sensitive to low pH. The processes of oogenesis and fertilization in fish are especially sensitive (Havas et al., 1995; Muniz, 1991), most likely due to adverse effects on the female spawner. For instance, Beamish (1976) reported that reduced serum and plasma Ca in female fish in acidified Canadian lakes caused a higher probability of failure in producing viable eggs. Depletion of Ca from bone and increased numbers of females with unshed eggs have also been linked to acidification at this life stage (cf. Muniz, 1991; Rosseland, 1986).

After fertilization, the embryo seems to be susceptible to acidic waters throughout the whole period of development, although periods shortly after fertilization and before hatching seem to be most critical (Rosseland, 1986). The susceptibility of the embryo can be the result of direct exposure to elevated H^+ concentrations and to the toxic effects of inorganic Al at intermediate pH-values. Low pH in the surrounding water also results in pH-depression inside the egg, leading to either prolongation of hatching or to reduced hatching success (Rosseland, 1986). Eggs lying in gravel on stream and lake beds are, to some extent, protected from exposure to rapid changes in pH (Gunn and Keller, 1984b; Lacroix, 1985). Nevertheless, they can experience high mortality during periods of acid runoff, such as snowmelt (Gunn and Keller, 1984a). Yellowstone cutthroat trout (*O. c. bouveri*) were exposed to 7–day pH depressions by Farag et al. (1993). Of the four life stages studied, eggs were most sensitive to low pH. Eggs exposed for seven days to pH 5.0 test water showed a statistically significant reduction in survival compared with eggs exposed for seven days to pH 6.5 test water. Survival of alevin and swim-up larvae was significantly reduced from near 100% at pH 6.5 to near 0% at pH 4.5. Intermediate pH values (6.0, 5.5) in all cases showed reduced survival compared with the control (6.5), but not by statistically significant amounts (p >0.05).

Emergent alevins show susceptibility to the adverse effects of inorganic Al and H^+ that increases with age (Baker and Schofield, 1982; Wood and McDonald, 1982). Rosseland (1986) indicated that this increasing sensitivity results from changes that take place in the respiratory system. Shortly after hatching, alevins still respire through their skin but gradually gills become the primary organ of gas and ion exchange. Gills are the locus for interference of hydrogen ion and inorganic Al with iono-regulatory exchange.

Woodward et al. (1989) exposed cutthroat trout (*Oncorhynchus clarki*) from the Snake River in Wyoming to pH depressions from pH 4.5 to 6.5 in the laboratory and found that reductions in pH from 6.5 to 6.0 in low-Ca water (70 µeq/L) did not affect survival, but did reduce growth of swim-up larvae. The eggs, alevin, and swim-up larval stages showed significantly higher mortality at pH 4.5 than at pH 6.5. Mortality was also higher at pH 5.0 than at pH 6.5, but only statistically higher for eggs. The authors concluded that the threshold for effects of acidity on greenback cutthroat trout in the absence of inorganic Al was pH 5.0 (Woodward, 1991).

In juvenile, young-of-year and adult fish there is an energy cost in maintaining physiological homeostasis; the calories used to respond to stress are a part of the fish's total energy budget and are unavailable for other functions, such as growth and reproduction (Schreck, 1981, 1982; Wedemeyer et al., 1990). Observed differences in condition factor may occur because maintenance of internal chemistry in the more acidic streams would require energy that otherwise would be available for growth and weight gain (Dennis and Bulger, 1999; Sullivan et al., 2003). The energy costs to fish for active iono-osmoregulation can be substantial (Bulger, 1986; Farmer and Beamish, 1969).

Prominent physiological disturbances to fish exposed to acid waters are iono- and osmoregulatory failure, acid-base regulatory failure, and respiratory and circulatory failure. Most of these effects can be

directly attributed to effects on gill function or structure. The acute toxicity of low pH in acidic waters results in the loss of Ca from important binding sites in the gill epithelium, which reduces the ability of the gill to control membrane permeability (Exley and Phillips, 1988; Havas, 1986; McDonald, 1983). Al has been shown to accumulate on the gill surface when fish are exposed to water having high inorganic Al concentration.

Cumulative sublethal physiological effects can be expressed by changes in condition factor. Condition factor has been developed and applied mainly for blacknose dace. This fish species is widely distributed in Appalachian Mountain streams and is moderately tolerant of low pH and ANC, relative to other fish species in the region. However, the condition factor concept is probably applicable to other species as well. Condition factor may be a useful metric for many species in aquatic ecosystems that are only marginally affected by acidification. Bulger et al. (1999) observed a positive relationship between dace condition factor and pH in streams in Shenandoah National Park. Dennis and Bulger (1995) found a reduction in the condition factor for blacknose dace in waters near pH 6.0. The four populations with the lowest condition factor had mean habitat pH values within or below the range of critical pH values at which Baker and Christensen (1991) estimated that negative population effects are likely for the species. The mean condition factor of fish from the study stream with the lowest ANC was about 20% lower than that of the fish in best condition. In addition to effects on blacknose dace, condition factor, reduced growth rates have been also attributed to acid stress in a number of other fish species, including Atlantic salmon (*Salmo salar*), Chinook salmon (*Oncorhynchus tshawytscha*), lake trout (*Salvelinus namaycush*), rainbow trout (*Oncorhynchus mykiss*), brook trout, brown trout (*Salmo trutta*), and arctic char (*Salvelinus alpines*) (Baker et al., 1990b).

In summary, some studies have been conducted on changes in the health, vigor, and reproductive success of fish exposed to water having low pH and high inorganic Al concentration. Blacknose dace have been most thoroughly studied regarding the sublethal effects of acidity on fish condition. Effects tend to vary by life stage; early life stages tend to be particularly sensitive. Adverse effects often involve disruption of gill function, partly due to Al toxicity.

Fish Biodiversity

Biodiversity loss is a predictable consequence of acidification and there are abundant examples of this in North America and Europe, mostly focused on fish (Bulger et al., 2000). Population-level fish response to acidification is primarily through recruitment failure, a result of increased mortality of early life stages or indirect effects through the food chain (loss of prey species). Changes in inorganic Al, pH, and Ca most likely have the greatest influence on fish community structure. These changes in water chemistry can alter species composition and species richness, both of which are components of biodiversity.

By 1990, it was well established that changes in pH in the range of 4.0 to 6.5 could cause significant adverse biological effects on fish community composition. As described above, the toxicity of low pH was, in most cases, the result of impaired body salt regulation. Decreased water pH inhibited the active uptake of Na^+ and Cl^- and stimulated the passive loss of these ions from the bloodstream (Baker et al., 1990b). Species vary in terms of their sensitivity to such disruptions of physiological condition.

The response of fish to pH, ANC, and inorganic Al is not uniform across species. A number of synoptic surveys indicated loss of species diversity and absence of several fish species in the pH range of 5.0 to 5.5. If pH is lower, there is a greater likelihood that more fish species could be lost without replacement, resulting in decreased richness and diversity. In general, populations of salmonids are not found at pH levels less than 5.0, and smallmouth bass (*Micropterus dolomieu*) populations are usually not found at pH values less than about 5.2 to 5.5. Bioassay experiments using brook trout eggs and fry have demonstrated greater mortality in chronically acidic stream water as compared to water having higher ANC.

The ASI is an index of acidification that uses fish bioassay survival data fitted to a regression model of exposure to water chemistry (pH, Al, and Ca) to predict the probability of fish survival.

Approximate ASI reference levels were reported by (Baker et al., 1990b) for various fish species, based on logistic regression of fish presence as a function of the sensitive, intermediate, and tolerant ASI values for brown bullhead (*Ameiurus nebulosus*), brook trout, lake trout, and common shiner (*Luxilus cornutus*).

Fish species richness is an important indicator of acidification response, in part because the public tends to place relatively high value on fisheries. As discussed in the previous section, lakes and streams having pH below about 5.0 or ANC below about 0 generally do not support fish. There is often a positive relationship between pH and number of fish species, at least for pH values between about 5.0 and 6.5, or ANC values between about 0 and 50 to 100 µeq/L (Bulger et al., 1999; Cosby et al., 2006; Sullivan et al., 2006a). Such observed relationships are complicated, however, by the tendency for smaller lakes and streams, having smaller watersheds, to also support fewer fish species, irrespective of acid-base chemistry. This pattern may be due to a decrease in the number of available niches as stream or lake size decreases. Nevertheless, fish species richness is relatively easily determined and is one of the most useful indicators of biological effects of surface water acidification.

Some of the most in-depth studies of the effects of acid stress on fish species richness have been conducted in the streams in Shenandoah National Park, Virginia and the lakes in the Adirondack Mountains, New York. These regions are examined in detail below. However, note that effects on fish species richness have also been documented in acid-sensitive streams of the Catskill Mountains of southeastern New York (Stoddard and Murdoch, 1991) and the Appalachian Mountains from Pennsylvania to Tennessee and South Carolina ((SAMAB), USDA 1996; Bulger et al., 1999; 2000).

The Shenandoah National Park Fish in Sensitive Habitats (FISH) Project evaluated the effects of streamwater acidification on fish communities in streams in Shenandoah National Park (Bulger et al., 1995; Dennis and Bulger, 1995; Dennis et al., 1995; MacAvoy and Bulger, 1995). A statistically robust relationship between stream ANC and fish species richness was documented. Numbers of fish species were compared among 13 Shenandoah National Park streams spanning a range of pH and ANC conditions. There was a highly significant (p <0.0001) relationship between stream acid-base status (during the 7–year period of record) and fish species richness among the 13 streams. The streams with the lowest ANC hosted the fewest species (Figure 3-15). The 3−year FISH study of stream acidification demonstrated negative effects on fish from both chronic and episodic acidification (Bulger et al., 1999). Bulger et al. (1999) concluded that the most important cause of the observed decline in species richness with decreasing ANC was acid stress from acidification. However, an additional causal factor may have been a decrease in the number of available aquatic niches when moving from downstream locations (which are seldom low in pH and ANC) to upstream locations (which are often low in pH and ANC in this region)(Sullivan et al., 2003).

South of Shenandoah National Park, the effects of surface water acidification on fish species richness have been studied in some detail in the St. Marys River in Virginia. Fish species richness was closely associated with surface water acid-base chemistry. The number of fish species in the St. Marys River within the wilderness declined from 12 in 1976 to 4 in 1998. Three of the four species present in 1998 (brook trout, blacknose dace, fantail darter [*Etheostoma flabellare*] are tolerant of low pH and are typically the only fish species present in streams having similar levels of acidity in nearby Shenandoah National Park (Bulger et al., 1999).

Dynamic water chemistry model projections have been combined with biological dose-response relationships to estimate declines in fish species richness with acidification. A relationship derived from the Shenandoah National Park data was used by Sullivan et al. (2003), along with stream ANC values predicted by the MAGIC model to provide estimates of the expected number of fish species in each of the modeled streams for the past, present and future chemical conditions simulated for each stream. Results suggest that historical loss of species had been greatest in the streams located on the most sensitive geological class (siliciclastic bedrock; 1.6 species lost), with fewer lost species on granitic bedrock and basaltic bedrock (average of 0.4 species lost).
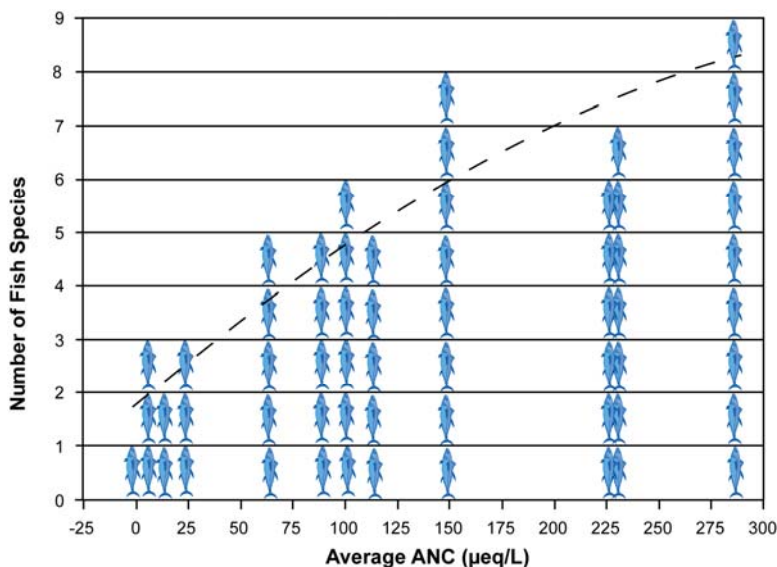
Figure 3-15.   Number of fish species as a function of mean stream ANC among 13 streams in Shenandoah National Park, Virginia. Values of ANC are means based on quarterly measurements, 1987– 1994. The regression analysis showed a highly significant relationship (p <0.0001) between mean stream ANC and number of fish species. Streams having ANC consistently <50 µeq/L had three or fewer species.

In the Adirondack Mountains, lakewater acidification and the associated elevated concentrations of inorganic Al have adversely affected fish populations and communities in sensitive areas (Baker and Schofield, 1982; Baker et al., 1990a; Johnson et al., 1987; Schofield and Driscoll, 1987; Siminon et al., 1993). Of the 53 fish species recorded in Adirondack lakes by the Adirondack Lakes Survey Corporation, about half (26 species) were absent from lakes with pH below 6.0. Among the absent species were several important recreational species (Baker et al., 1990a), plus ecologically important minnows that serve as forage for sport fish. Fully 346 of 1,469 lakes surveyed supported no fish at all at the time of the survey. These lakes were significantly lower in pH, dissolved Ca, and ANC, and had higher concentrations of inorganic Al than lakes hosting one or more species of fish (Gallagher and Baker, 1990). Among lakes with fish, there was an unambiguous relationship between the number of fish species and lake pH, ranging from about one species per lake for lakes having pH less than 4.5 to about six species per lake for lakes having pH higher than 6.5 (Baker et al., 1990a; Driscoll et al., 2001b).

High-elevation lakes are more likely to be fishless than larger lakes at low elevation (Gallagher and Baker, 1990). This observation has been attributed to the fact that high elevation lakes tend to have poor access for fish immigration, poor fish spawning substrate, or low pH, or they may be susceptible to

periodic winter kills. Small, high-elevation Adirondack lakes with fish also had significantly higher pH compared with fishless high-elevation lakes; acidity is likely to play an important role in the absences of fish from such lakes (Driscoll et al., 2001a).

Sullivan et al. (2006b) developed a relationship between fish species richness and ANC class for Adirondack lakes. Under chronically acidic conditions (summer index or annual average ANC <0 µeq/L), Adirondack lakes are generally without fish. There was a marked increase in mean species richness with increases in ANC up to values of approximately 50 to 100 µeq/L (Figure 3-16). The asymptote for the fish species equation was 5.7 species. This analysis suggests that there could be loss of fish species with decreases in ANC below approximately 50 to 100 µeq/L. The response functions from Shenandoah National Park (Figure 3-15) and the Adirondack Mountains (Figure 3-16) are generally similar at low ANC values, below about 100 µeq/L. Fish species richness was somewhat higher in Shenandoah National Park at higher ANC values. The reasons for this difference are not known.
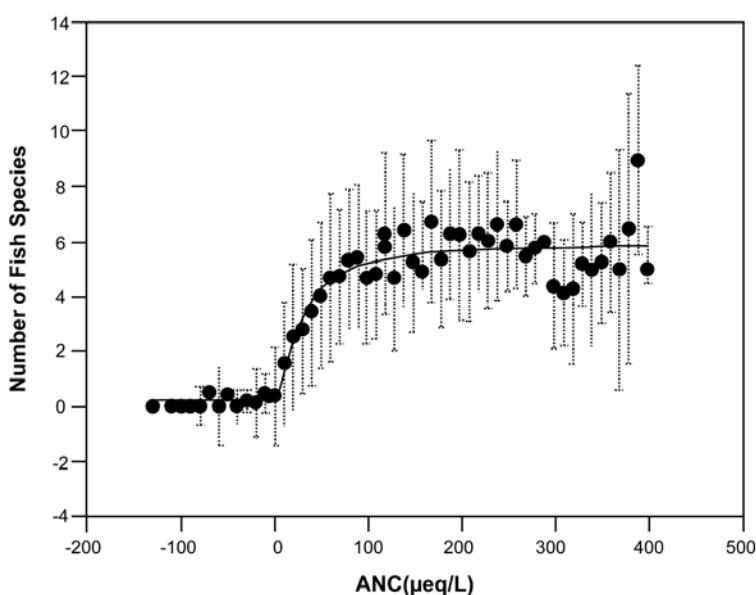
Source: Sullivan et al. (2006b).

Figure 3-16. Number of fish species per lake versus acidity status, expressed as ANC, for Adirondack lakes. The data are presented as mean (filled circles) and range (bars) of species richness within 10 µeq/L ANC categories, based on data collected by the Adirondack Lakes Survey Corporation.

The absence of fish from a given lake or stream in an area that experiences surface water acidification does not necessarily imply that acidification is responsible for the absence of fish. For example, results of fisheries research in the Adirondacks have indicated that many Adirondack lakes always had marginal spawning habitat for brook trout (Schofield, 1993). However, multivariate regression of the presence or absence of brook trout in Adirondack waters produced a ranking of factors that appeared to influence the presence of brook trout when biological factors (stocking, presence of associated species, presence of competitors) were excluded from the analysis. Among contributing factors, including silica (Si), ANC, DOC, substrate type, and distance to the nearest road, pH ranked first as a predictor of brook trout presence. The results of this analysis supported the conclusion that 1990 levels of pH and related variables restricted the distribution of fish in some Adirondack lakes.

In summary, acidic conditions characterized by low pH, low ANC, and high inorganic Al exert considerable influence on the fish species composition of sensitive surface waters, particularly in the eastern U.S. Low pH and ANC, and high inorganic Al concentrations, contribute to loss of the most acid-sensitive fish species. Species richness is a common indicator used to reflect the effects of water acidification on aquatic biota. This index is most often applied to fish. Few or no fish species are found in lakes and streams that have very low ANC (near zero) and low pH (near 5.0). The number of fish species generally increases at higher ANC and pH values. This relationship is complicated, to some extent, by the tendency of smaller lakes and streams (which are more likely to have low ANC and pH) to host fewer fish species, regardless of acid-base chemistry. Nevertheless, available data strongly suggest that acid stress is a major factor governing the observed relationship between fish species richness and surface water acidity.

3.2.3.4. Summary of Biological Effects

The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in aquatic biota. The strongest evidence for a causal relationship comes from studies of aquatic systems exposed to elevated levels of acidifying deposition that support fewer species of fishes, macroinvertebrates, and diatoms. Although there are few studies of the response of higher trophic levels to pH changes resulting from acidifying deposition, piscivorous birds are known to be affected by acidifying deposition (see Table 3-9). Consistent and coherent evidence from multiple species and studies shows that acidification can result in the loss of acid-sensitive species, and more species are lost with greater acidification. Biological effects are linked to changes in water chemistry including ANC, pH, and inorganic Al. Decreases in ANC and pH and increases in inorganic Al concentration contribute to declines in taxonomic richness of zooplankton, macroinvertebrates, and fish. Chemical changes can occur over both long- and short-term time scales, with additional effects on biological systems. Short-term (hours or days) episodic changes in water chemistry can have biological effects, including reduced fish condition factor, changes in species composition, and declines in aquatic species richness across multiple taxa, ecosystems and regions.

Species

- High levels of acidification (to pH values below 5) virtually eliminate all mayflies, crustaceans, and mollusks from some streams.

- In general, populations of salmonid fish are not found at pH levels less than 5.0, and smallmouth bass (Micropterus dolomieu) populations are usually not found at pH values less than 5.5 to 5.2.

- Twenty percent mortality of young-of-the year brook trout was documented during a 30–day period with a median inorganic Al concentration of 2 µmol/L (Baldigo et al., 2007). It was estimated that 90% mortality would occur over 30 days with a median inorganic Al concentration of 4.0 µmol/L.

Community

Community-level effects were observed in two well-studied ares, the Adirondacks and the Shenandoah National Park, where taxonomic richness is lower in lakes and streams having low ANC and pH.

- Decreases in pH and increases in inorganic Al concentrations have reduced the species richness of plankton, invertebrates, and fish in acid-affected surface waters.

- Invertebrate taxa that are most sensitive to acidification include mayflies, amphipods, snails, and clams.

- In the Adirondacks, a positive relationship exists between the pH and ANC in lakes and the number of fish species present in those lakes. A number of synoptic surveys indicated suggested loss of species diversity and absence of several sensitive fish species in the pH range of 5.0 to 6.0.

- In Shenandoah National Park streams, the fish species richness decreased with decreasing stream ANC. On average, richness is lower by one fish species for every 21 μeq/L decrease in ANC.

- Short-term episodes of acidification are particularly harmful to aquatic biota. Early life stages are more sensitive to acidic conditions than the young-of-the-year, yearlings, and adults. Episodes are most likely to affect biota if the water had pre-episode pH above 5.5 and minimum pH during the episode of less than 5.0. Episodic acidification can have long-term adverse effects on fish populations.

3.2.4. Most Sensitive and Most Affected Ecosystems and Regions

3.2.4.1. Characteristics of Sensitive Ecosystems

The principal factor governing the sensitivity of terrestrial and aquatic ecosystems to acidification from S and N deposition is geology (particularly surficial geology). Geologic formations having low base cation supply generally underlie the watersheds of acid-sensitive lakes and streams. Bedrock geology has been used in numerous acidification studies (Bricker and Rice, 1989; Stauffer, 1990; Stauffer and Wittchen, 1991; Vertucci and Eilers, 1993; Sullivan et al., 2007b). Other factors contribute to the sensitivity of soils and surface waters to acidifying deposition, including topography, soil chemistry, land use, and hydrologic flowpath.

Several studies have confirmed the importance of geology in regulating terrestrial and aquatic ecosystem sensitivity to acidification, and highlighted other key factors responsible for terrestrial and aquatic sensitivity to acidifying deposition throughout the southeastern U.S. Sensitive terrestrial ecosystems include high-elevation spruce-fir forests dominated by relatively nonreactive bedrock in which base cation production via weathering is limited (Elwood et al., 1991). Soils in such areas tend to have thick organic horizons, high organic matter content in the mineral horizons, and low pH (Joslin et al., 1992). Because of the largely nonreactive bedrock, base-poor litter and organic acid anions produced by the conifers, high precipitation, and high leaching rates, soil base saturation in these high-elevation forests tends to be below about 10% and the soil cation exchange complex is generally dominated by Al (Eagar et al., 1996; Johnson and Fernandez, 199).

Galloway (1996) further attributed forest soil sensitivity to acidification in the southeastern U.S. to atmospheric deposition level, soil age, weathering rate, and S adsorption capacity. Moncoulon et al. (2004) suggested that forest ecosystem sensitivity to acidification varies mainly with weathering rate. In a review of 241 ecosystem types in France (classified by pedologic and geologic characteristics), the ecosystems most susceptible to acidification were those with low weathering rates and thus limited buffering capacity (Moncoulon et al., 2004).

In hardwood forests, species nutrient needs, soil conditions, and additional stressors work together to determine sensitivity to acidifying deposition. Stand age and successional stage also can affect the susceptibility of hardwood forests to acidification effects. In northeastern hardwood forests, older stands exhibit greater potential for Ca depletion in response to acidifying deposition than younger stands. Thus, with the successional change from pin cherry (*Prunus pensylvanica*), striped maple (*Acer pensylvanicum*), white ash (*Fraxinus americana*), yellow birch and white birch (*Betula papyrifera*) in younger stands to

beech and red maple in older stands, there is an increase in sensitivity to acidification (Hamburg et al., 2003).

Land use influences watershed sensitivity to acidification mainly through disturbance and consequent exposure of S-bearing minerals to oxidation, loss of base cations through erosion and timber harvesting, and change in N status of the forest through timber management. Each of these types of activity can influence the relative availability of mobile mineral acid anions (SO_4^{2-}, NO_3^-) in soil solution and base cations (Ca, Mg, K, Na) on the soil ion exchange sites and in drainage water.

The movement of water through the soils into a lake or stream, and the interchange between drainage water and the soils and sediments, strongly regulate the type and degree of watershed response to acidic inputs (Sullivan, 2000a). Surface waters in the same setting can have different sensitivities to acidification depending on the relative contributions of near-surface drainage water and deeper groundwater (Chen et al., 1984; Driscoll et al., 1991; Eilers et al., 1983).

Movement of a strong acid anion, such as SO_4^{2-} or NO_3^-, through an acidic soil can mobilize H^+ and Al^{3+} because these cations are available on soil exchange sites. There is no time lag in this exchange reaction and it is instantly reversible if input of strong acid anions is ceased (Turner et al., 1991). It is necessary, however, for appreciable mobilization of H^+ and Al^{3+} that the soil be acidic, either naturally or because of soil acidification from acidifying deposition.

In summary, lakes and streams in the U.S. that are sensitive to episodic and chronic acidification in response to SO_X, and to a lesser extent NO_X, deposition tend to occur at relatively high elevation in areas that have base-poor bedrock, high relief, and shallow soils. For example, in the Southern Appalachian region (Sullivan et al., 2002a, 2007b) determined that underlying bedrock geology dominated by sandstone or related rock types and elevations greater than 1000 m (3250 ft) could be used to identify landscapes in the region most likely to contain acidic streams.

3.2.4.2. Extent and Distribution of Sensitive Ecosystems

Surface Waters

Several regions of the U.S. contain appreciable numbers of lakes and streams with low ANC (less than about 50 µeq/L), including portions of the Northeast (especially New England, the Adirondacks, and the Catskill Mountains), Southeast (the Appalachian Mountains and northern Florida), Upper Midwest, and western U.S. (Charles, 1991). The Adirondack and Appalachian Mountains, and to a lesser extent the Upper Midwest, include many acidified surface waters that have been affected by acidifying deposition. Portions of northern Florida also contain many acidic and low-ANC lakes and streams, although the role of acidifying deposition in these areas is less clear. The western U.S. contains many of the surface waters most susceptible to potential acidification effects, but with the exception of the Los Angeles Basin and surrounding areas, the levels of acidifying deposition in the West are low in most areas, acidic surface waters are rare, and the extent of chronic surface water acidification that has occurred to date has likely been very limited.

Several national assessments were conducted to estimate the distribution and extent of surface water acidity in the U.S. During summer baseflow of 2004, the U.S. EPA conducted a National Wadeable Stream Assessment (WSA) survey of 1,392 randomly selected sites across the conterminous 48 U.S. to assess the ecological condition of wadeable streams (U.S. EPA, 2006d). Because this sampling was conducted during baseflow in the summer (which exhibits the least acidic conditions of the year), only the most chronically acidified streams were identified as acidic. Therefore, the extent of potential seasonal acidification was underestimated by this approach (Lawrence et al., 2008). Overall, less than 1% of the 1,020,000 km of stream in the target population (based on the 1:100,000–scale U.S. Geological Survey (USGS) map blue line network) was acidic due to acidifying deposition. No acidic streams were observed in the Mountainous West, Xeric West, Upper Midwest, Northern Plains, Southern Plains, or Temperate Plains ecoregions. Acidic streams attributable to acidifying deposition were found in the Northern Appalachians (2.8% of 96,100 km of stream), and the Southern Appalachians (1.8% of 287,000 km). Very

low ANC (0–25 µeq/L) streams likely exposed to episodic acidification were found in the Northern Appalachians (2.7% of 96,100 km of stream), the Coastal Plain (6.3% of 119,000 km), and the Mountainous West (0.6% of 204,000 km).

Even though the WSA had over 1,300 sample sites, it was still a very coarse sample of the nation's streams with respect to acidifying deposition effects, which are only observed in spatially restricted subpopulations. More precise survey estimates of the effects of surface water acidification were made in the National Surface Water Survey (NSWS) in the mid 1980s. By statistically selecting representative lakes and streams in each surveyed region, the NSWS estimated chemical conditions of 28,300 lakes and 56,000 stream reaches (Baker et al., 1990b). The NSWS concluded that 4.2% of lakes larger than 4 ha and 2.7% of stream segments in the acid-sensitive regions of the eastern U.S. were acidic. The NSWS documented the status and extent of surface water acid-base chemistry during probability surveys of lakes and streams conducted from 1984 through 1988 in the major acid sensitive regions of the U.S. (Kaufmann et al., 1988; Landers et al., 1987; Linthurst et al., 1986a).

The stream component of the NSWS, the National Stream Survey (NSS), was focused in the northern and southern Appalachians and Coastal Plain of the eastern U.S. (Kaufmann et al., 1991). The NSS included 500 stream reaches selected from 1:250,000 scale USGS topographic maps using a systematic, randomized sample. Study reaches were sampled at both the upstream and downstream end of each selected reach. Population estimates were made for chemistry at both reach ends and for stream length by interpolating chemical results between reach ends.

Overall, out of the estimated 57,000 stream reaches in the NSS, after excluding streams acidic due to acid mine drainage, 6.2% of the upstream and 2.3% of the downstream reach ends were acidic during spring baseflow (Kaufmann et al., 1991). After interpolation, this corresponded to 2.7% of the 201,000 km of stream in the study region. In acidic and low-ANC NSS reaches, ANC usually increased with downstream distance. Acidic (ANC ≤ 0) streams were located in the highlands of the Mid-Atlantic Region (southern New York to southern Virginia, 2320 km), in coastal lowlands of the Mid-Atlantic (2530 km), and in Florida (461 km). Acidic streams were rare (less than 1%) in the highlands of the Southeast and Piedmont. Inorganic monomeric Al concentrations were highest in acidic streams of the Mid-Atlantic Highlands, where over 70% of the acidic streams had inorganic Al greater than 3.7 µM (100 µg/L), a concentration above which deleterious biological effects have frequently been reported.

Anion composition of the NSS stream samples was examined to evaluate the most probable sources of stream acidity in acidic and low-ANC sites (Baker et al., 1991b; Herlihy et al., 1991). Acidic streams that had minimal organic influence (organic anions constituted less than 10% of total anions), and SO_4^{2-} and NO_3^- concentrations indicative of evaporative concentration of atmospheric deposition, were classified as acidic due to acidifying deposition. These acidic streams were located in small (<30 km^2) forested watersheds in the Mid-Atlantic Highlands (an estimated 1980 km of stream length) and in the Mid-Atlantic Coastal Plain (1250 km). Acidic streams affected primarily by acidifying deposition but also influenced by naturally occurring organic anions accounted for another 1210 km of acidic stream length and were mainly located in the New Jersey Pine Barrens, plateau tops in the Mid-Atlantic and Southeast Highlands, and the Florida Panhandle. The total length of streams that were identified as acidic due to acid mine drainage in the NSS (4590 km) was about the same as the total length of acidic streams likely affected by acidifying deposition (4455 km). Acidic streams whose acid anion composition was dominated by organics were mainly located in Florida and the Mid-Atlantic Coastal Plain. In Florida, most of the acidic streams were organic-dominated, whereas about half of the acidic streams in the Mid-Atlantic Coastal Plain were organic-dominated. Organic-dominated acidic streams were not observed in the Mid-Atlantic or Southeast Highlands.

Stoddard et al. (2003) presented a map of acid-sensitive regions of the eastern U.S. where lakes and streams occur that are likely to be affected by acidifying deposition (Figure 3-17). The map shows considerable overlap with the areas of high interest identified by Baker et al. (1990b). Surface waters in most other regions of the U.S. are not sensitive to the effects of acidification due largely to the nature of the local geology (Stoddard et al., 2003). An exception is the region surrounding the Los Angeles Basin,

which receives high N deposition (>20 kg N/ha/yr in some areas) and includes streams with very high NO_3^- concentrations (>50 µeq/L; Bytnerowicz and Fenn, 1996; Fenn and Poth, 1999, 2001).

Acid Sensitive Regions of the Northern and Eastern United States
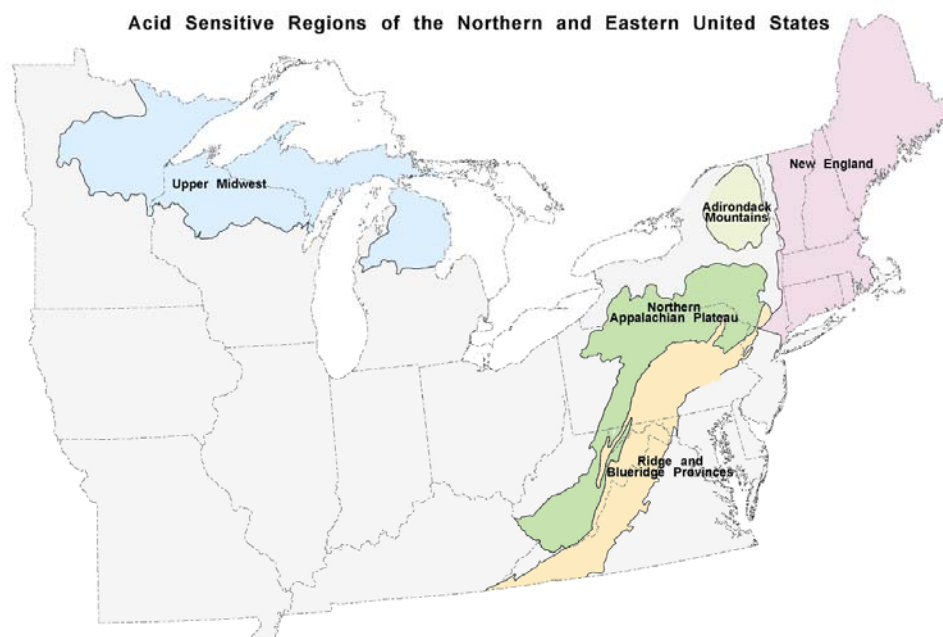
Figure 3-17.   Regions of the northern and eastern U.S. that contain appreciable numbers of lakes and streams that are sensitive to acidification from acidifying deposition.

In addition to the large water chemistry databases developed by the U.S. EPA, which help to identify the spatial distribution of acid-sensitive and acid-affected surface waters in the U.S., there are also some important supplemental regional databases in New England, the Adirondacks, the mid-Appalachian region, the Florida Panhandle, the Upper Midwest, and the western U.S. Results from these studies are summarized in the following paragraphs.

New England

For the New England region, results from the U.S. EPA TIME program indicate that 5.6% of the regional lake population (386 lakes) in New England exhibited ANC <0 µeq/L during the period 1991 to 1994. This result is similar to the EMAP findings, which indicate that 5% of lakes in New England had ANC values less than 0 µeq/L. The EMAP survey was a probability based survey representative of lakes with surface area greater than 1 ha (1,812 lakes). The survey was conducted during low-flow summer conditions, and the results therefore likely reflect the highest ANC values for the year. The EMAP analysis also estimated that an additional 10% of the population had low ANC values, between 0 and 50 µeq/L, and were probably sensitive to episodic acidification (Driscoll et al., 2001b).

Adirondacks

A study by Driscoll, et al. (2001b) used EMAP data from 1991 to 1994 to evaluate the extent of acidic lakes in the Adirondacks for that period. Results from the survey indicate that 10% of the population of Adirondack lakes were chronically acidic (ANC values of less than 0) and 31% were

sensitive to episodic acidification (ANC values between 0 and 50) during the study period (Driscoll et al., 2001b).

The Adirondack Lake Survey Corporation conducted a comprehensive survey of Adirondack lakes greater than 0.2 ha in surface area between 1984 and 1987 (Baker et al., 1990a). Of the 1,489 lakes surveyed, 24% had summer pH values below 5.0, 27% were chronically acidic (ANC <0) and an additional 21% were probably susceptible to episodic acidification (ANC between 0 and 50; Driscoll et al., 2007a).

Mid-Appalachian Region

A compilation of survey data from the mid-Appalachians yields a consistent picture of the acid-base status of streams. In the subpopulation of upland forested streams, which comprises about half of the total stream population in the mid-Appalachian area, data from various local surveys showed that 5% to 20% of the streams were acidic and about 25 to 50% had ANC <50 µeq/L (Herlihy et al., 1993). NSS estimates for the whole region showed that there were 2330 km of acidic streams and 7500 km of streams with ANC <50 µeq/L. In these forested reaches, 12% of the upstream reach ends were acidic and 17% had pH ≤ 5.5. SO_4^{2-} from atmospheric deposition was the dominant source of acid anions in acidic mid-Appalachian streams.

Cosby et al. (2006) provided a detailed characterization of streamwater acid-base chemistry in Shenandoah National Park, Virginia, which has been the most thoroughly studied area within the mid-Appalachian Mountain region with respect to acidification from acidifying deposition. Based on MAGIC model simulations and extrapolation using landscape characteristics, Cosby et al. (2006) developed maps showing the distribution of streamwater conditions in the Park for the preindustrial past, current conditions, and anticipated future conditions.

Florida Panhandle

According to the U.S. EPA eastern lakes survey conducted in 1984, 75% of the Florida Panhandle lakes were acidic at that time, as were 26% of the lakes in the northern peninsula. Most of the acidic lakes were clear water (DOC <400 µM) seepage lakes in which the dominant acid anions were chloride and SO_4^{2-}. Most of the acidic and low-ANC lakes were located in the Panhandle and north central lake districts. Acidic streams were located in the Panhandle, were mildly acidic (mean pH 5.0), and extremely dilute, with very low sea salt-corrected sum of base cations (mean 21 µeq/L) and sea salt-corrected SO_4^{2-} concentrations (mean 16 µeq/L). One-fourth of these acidic Panhandle streams were organic-dominated but the remaining sites all had DOC <2 mg/L. Inorganic monomeric Al concentrations in these acidic streams were very low (mean 11 µg/L). In these low DOC, low ANC Panhandle streams, it was suggested that the degree of SO_4^{2-} and NO_3^- retention in soil was an important control on streamwater ANC (Baker et al., 1990b).

Upper Midwest

Based on the eastern lakes survey, the Upper Midwest has a large population of lakes having ANC ≤ 200 µeq/L, (Linthurst et al., 1986a; 1986b); only 6% of the lakes had ANC ≤ 50 µeq/L. Groundwater recharge lakes (those having Si concentration less than 1 mg/L, indicating little groundwater input) constituted 71% of the seepage lakes in the Upper Midwest, and were more frequently low in pH and ANC. Five percent were acidic and 9% had pH ≤ 5.5. Nearly 90% of Upper Midwestern lakes that had ANC ≤ 50 µeq/L were in the groundwater recharge category (Baker et al., 1991b). Such lakes tend to be susceptible to acidification from acidifying deposition.

Acidic lakes in the Upper Midwest are primarily small, shallow, seepage lakes that have low concentrations of base cations and Al and moderate SO_4^{2-} concentrations. Organic anions, estimated by both the Oliver et al. (1983) method and the anion deficit, tend to be less than half the measured SO_4^{2-}

concentrations in the acidic lakes (Eilers et al., 1988), but much higher in many of the drainage lakes that are less sensitive to acidification from acidifying deposition.

West

Landers et al. (1987) identified subregions in the West with acid-sensitive lakes, based on results of the U.S. EPA Western Lakes Survey. The surface water chemistry data for the West indicate that the Sierra Nevada and Cascade Mountains constitute the mountain ranges with the greatest number of sensitive lake resources. Surface waters in this region are among the most poorly buffered surface waters in the U.S. (Landers et al., 1987; Melack and Stoddard, 1991). The hydrologic cycle is dominated by the annual accumulation and melting of a dilute, mildly acidic snowpack.

Many Cascade and Rocky Mountain lakes are highly sensitive to potential acidifying deposition effects (Nelson, 1991; Turk and Spahr, 1991). It does not appear that chronic acidification has occurred to any significant degree, although episodic acidification has been reported for lakes in the Colorado Front Range (Williams and Tonnessen, 2000).

Along the eastern edge of the Continental Divide in Colorado and southeastern Wyoming, Musselman et al. (1996) conducted a synoptic survey of surface water chemistry in the mountainous areas that are exposed to relatively high (by western standards) deposition of N. A total of 267 high-elevation lakes situated in watersheds having a high percentage of exposed bedrock or glaciated landscape were selected for sampling. None of the lakes were chronically acidic (ANC <0), although several had ANC <10 µeq/L, and more than 10% of the lakes had ANC <50 µeq/L.

Forest Ecosystems

No systematic national survey of terrestrial ecosystems in the U.S. has been conducted to determine the extent and distribution of terrestrial ecosystem sensitivity to acidifying deposition. The scarcity of information on sensitive terrestrial ecosystems is due in part to sparse soils data. In general, forest ecosystems of the Adirondack Mountains of New York, Green Mountains of Vermont, White Mountains of New Hampshire, the Allegheny Plateau of Pennsylvania, and high-elevation forests in the southern Appalachians are considered to be the regions most sensitive to terrestrial acidification effects from acidifying deposition.

One national and a few regional efforts have been undertaken to characterize forest sensitivity to acidifying deposition using a critical loads approach. In this context, acid-sensitive soils are those which contain low levels of exchangeable base cations and low base saturation. On a broad national scale, McNulty et al. (2007) used a simple mass balance equation and available national databases to estimate forest soil critical acidic loads (for wet and dry deposition of S and N) and exceedances for forest soils. Exceedances are pollutant loads that are greater than the estimated critical load for that location. They found that approximately 15% of forest soils in the U.S. receive acidifying deposition that exceeds the estimated critical load of wet and dry deposition of S and N by more than 250 eq ha/yr (McNulty et al., 2007). The areas where exceedances reach this level could be considered to represent those areas that are likely most sensitive to continued high levels of acidifying deposition. Thus, there is not a national survey of soil sensitivity to acidification, but there are approaches available with which to identify areas likely to include sensitive soils.

Note that the McNulty et al. (2007) paper represents the beginning of an iterative process to identify more precise critical loads for terrestrial acidity. The authors note that the actual area in exceedance of the forest soil critical acid load may be higher than the mapped estimates for several reasons (McNulty et al., 2007). First, their estimated total deposition did not include cloud deposition. Second, base cation deposition to near-coastal areas was not corrected for marine aerosol contributions. Third, the 1–km squared grid size of the mapping resulted in averaging of soil and deposition data, which removed extreme values from the analysis (McNulty et al., 2007). The authors take care to describe their results as "preliminary" and note that a more systematic analysis of model-predicted and measured forest

soil critical acid load exceedance is needed before this approach can be used as a tool for identifying areas of potential forest health concern (McNulty et al., 2007). For these reasons, and because of the significant uncertainty associated with many of the large national databases used in the analysis, the appropriate use of this information is not for the actual determination of critical loads at specific locations or for predictions of forest health effects, but rather for increased understanding of relative differences in forest soil sensitivity at a national scale. In general, the Northeast, the Southern Appalachians, parts of Florida and the Upper Midwest have the highest proportion of soils that exceed the estimated critical acid loads by at least 250 eq ha/yr and therefore could be termed vulnerable. Where the exceedances are highest, forest soils are likely most sensitive to continued effects from acidifying deposition.

At a regional scale, Pardo et al. (2007) calculated critical loads of S and N deposition to forests in Great Smoky Mountains National Park (GSMNP) based on available data. A simple mass balance model and the Very Simple Dynamic model (VSD) were used to calculate a critical load for acidity (N+S) and N nutrient. The authors concluded that current deposition exceeded the critical load at all four sites evaluated (2 high elevation spruce-fir sites, a mid-high elevation beech site, and a lower elevation mixed hardwood site). The exceedance for S + N deposition ranged from 150 eq/ha/yr for the low elevation mixed hardwood site to 2300 eq/ha/yr at the upper spruce-fir site. The maximum acceptable deposition of N ranged from 200 eq/ha/yr (3 kg N/ha/yr) for the low elevation mixed hardwood site to 500 eq/ha/yr (7 kg N/ha/yr) at the upper spruce-fir site.

Another approach to identification of sensitive forest lands is to map the distribution of tree species thought to be most sensitive to adverse effects. The effects of acidifying deposition are particularly well documented for red spruce trees (Cronan and Grigal, 1995; Johnson and Lindberg, 1992; Johnson et al., 1994b; Joslin et al., 1992) that occur in the northeastern U.S. and southern Appalachian Mountains (Figure 3-6 shows the distribution). In the Northeast, red spruce grows at elevations from near sea level to about 1,400 m. In the Appalachian Mountains, spruce-fir forests are generally found at relatively high elevation, for example above about 1400 m in the southern portion of the range (SAMAB, 1996). Northern hardwood forests have also been identified as forest resources experiencing air pollution effects. Effects are best documented for sugar maples, which are broadly distributed across the northern hardwood forests in the northeastern U.S. (Figure 3-6 shows the distribution). The areas where sugar maples appear to be at greatest risk are along ridges and where this species occurs on nutrient-poor soils.

Model Simulations

In the eight-state Southern Appalachian Mountains region, Sullivan et al. (2005) modeled future effects of atmospheric S and N deposition on aquatic resources. Modeling was conducted with the MAGIC model for 40 to 50 sites within each of three physiographic provinces, stratified by stream water ANC class. The model runs were based on three emissions control strategies (A2, B1, and B3). A2 is the base case that represents best estimates for air emission controls under regulations for which implementation strategies were relatively certain at the time of the study (about the year 2000). This A2 strategy includes the acid rain controls under Title IV of the 1990 Amendments to the CAA, the 1-h ozone (O_3) standard, NO_X reductions required under the U.S. EPA call for revised State Implementation Plans (SIPs), and several highway vehicle and fuel reductions. The B1 and B3 strategies assumed progressively larger emissions reductions, targeted only to the eight states in the southern Appalachian Mountains region, but covering all emissions sectors.

The results for the portion of the region south of Virginia and West Virginia suggest that the percentages of streams having ANC below zero and below 20 µeq/L will actually increase through the year 2040 under all except the most restrictive emissions control strategies (Sullivan et al., 2005). Most simulated changes in stream water ANC from 1995 to 2040 were rather modest, given the very large estimates of future decrease in S deposition. Few modeled streams showed projected change in ANC of more than about 20 µeq/L (Sullivan et al., 2005). Some of the largest changes were simulated for some of the streams that were most acidic in 1995. For such streams, however, even relatively large increases in

ANC would still result in stream water having negative ANC, and therefore little biological improvements would be expected from the simulated improvement in chemistry (Sullivan et al., 2005).

Sullivan et al. (2002b) used the NuCM model to evaluate potential changes in soil chemistry in response to acidifying deposition in the southern Appalachian Mountains. The results suggest that spruce-fir forests in the region are likely to experience decreased Ca:Al ratios in soil solution under virtually all strategies of reduced future acidifying deposition considered. This result was partly because SO_4^{2-} adsorption in soils is likely to decline, even with dramatically reduced S deposition. In addition, many spruce-fir forests in the region are N-saturated, and continued N deposition at moderate or high levels would be expected to contribute to elevated NO^{3-} concentrations in soil water, which could further enhance base cation leaching and mobilization of Al from soils to soil solution.

In the Adirondacks, model results produced by several studies suggest that the trend of increasing lakewater ANC for the most acid-sensitive lakes might not continue in coming decades. These results are discussed above in the Adirondack case study.

In a regional application of PnET-BGC, Chen and Driscoll (2005) analyzed 60 DDRP (Direct Delayed Response Project) lake watersheds within northern New England under three future emissions reduction scenarios. Most of the lakes had surface water ANC values greater than 50 µeq/L in 1984, and were therefore not considered chronically acidic. The authors reported that ANC was projected to increase under all three scenarios, with greater rates of recovery occurring with deeper emissions reductions. Soil improvements were slow and modest under all scenarios. Simulations suggested that 80% of the northern New England sites and 60% of the Maine sites will have soil base saturation below 20% in 2050 (Chen and Driscoll, 2005). They concluded that the decreases in SO_4^{2-} and NO_3^- concentrations in surface water were coupled with nearly stoichiometric decreases in base cation concentrations. Simulated improvements in ANC in response to reduced acidifying deposition were minor. Therefore, while further declines in atmospheric deposition in S and N will bring some improvements, most ecosystems in the study were not expected to recover to background conditions by 2050.

Bulger et al. (2000) developed model-based projections using the MAGIC model to evaluate the potential effect of reductions in S deposition of 40% and 70% from 1991 levels using data from streams in and near Shenandoah National Park. Projections were based on four brook trout stream categories: Suitable, ANC >50 µeq/L; Indeterminate, ANC 20 to 50 µeq/L; Marginal, ANC 0 to 20 µeq/L; and Unsuitable, ANC <0 µeq/L. Three scenarios of future acidifying deposition were modeled: constant deposition at 1991 levels, 40% reduction from 1991 deposition levels, and 70% reduction from 1991 deposition levels. Based on observed 1991 ANC values, approximately 30% of all trout streams in Virginia were marginal or unsuitable for brook trout because they were either episodically (24%) or chronically (6%) acidic. In addition, another 20% of the streams were classified as indeterminate, and brook trout in these streams may or may not have been affected. Based on the model simulations, 82% of these streams would not have been acidic before the onset of acidifying deposition and would likely have been suitable for brook trout.

The model projections suggested that neither the 40% nor the 70% reductions in acidifying deposition would increase the number of streams that were suitable for brook trout above the ambient 50%. In fact, the results suggested that a 70% reduction in deposition would be needed in the long term just to maintain the number of streams that were considered suitable for brook trout. Because of the length of time required to restore buffering capacity in watershed soils, most of the marginal or unsuitable streams were expected to remain marginal or unsuitable for the foreseeable future.

Results of modeling studies for lakes and streams in the Adirondack Mountains and in Shenandoah National Park are presented in the case study sections of this report.

3.2.4.3. Levels of Deposition at Which Effects are Manifested

The effects of S and N deposition are manifested at a range of deposition levels, depending on the inherent sensitivity of the natural resources, as described in the previous sections, and the historical

deposition loading. The intersection among current deposition loading, historic loading, and sensitivity defines the ecological vulnerability to the adverse effects of acidification. Few studies in the U.S. have defined deposition levels that are associated with effects over large areas.

Some degree of surface water acidification, and perhaps also of soil acidification, can occur at very low levels of S deposition (only a few kg S/ha/yr). These highly sensitive areas are characterized by very low levels of exchangeable base cations and soil base saturation. Water pathways and soil depth can also limit the capacity of these areas to neutralize acidifying deposition. These areas provide limited neutralization of acidic drainage water.

Effects levels for N deposition can be established based on changes to stream and soil chemistry that signal alteration of nutrient cycling, causing NO_3^- leaching. Analyses have been conducted in the northeastern U.S. and Europe to examine the relationships between N deposition and NO_3^- leaching to surface waters. The relationship between measured wet deposition of N and streamwater output of NO_3^- was evaluated by Driscoll et al. (1989) for sites in North America (mostly eastern areas), and augmented by Stoddard (1994). The resulting data showed a pattern of N leaching at wet inputs greater than approximately 5.6 kg N/ha/yr. Aber et al. (2003) concluded that loss of NO_3^- to surface waters during the growing season in forested watersheds often occurs above a threshold of total (wet plus dry) atmospheric N deposition of about 8 to 10 kg N/ha/yr.

The effects of N addition on forests have been shown to be wide-ranging. Additions of 25 kg N/ha/yr to spruce plots in Vermont (ambient bulk deposition 5.4 kg N/ha/yr), in which net nitrification did not occur before treatment, triggered net nitrification in the second year of treatment (McNulty et al., 1996). Similar results were seen in Colorado, where additions of 25 kg N/ha/yr to old-growth spruce plots in Loch Vale watershed (ambient bulk deposition 4 to 5 kg N/ha/yr) doubled N mineralization rates and stimulated nitrification. In marked contrast to these results, concentrations of NO_3^- plus NH_4^+ were not detected until the seventh year in hardwood plots in Harvard Forest, Massachusetts, which received additions of 150 kg N/ha/yr (Magill et al., 2004). Concentrations of NO_3^- plus NH_4^+ in hardwood plots receiving 50 kg N/ha/yr were not yet detectable in the 15th year of treatment.

Many of the changes in plant species composition, species diversity, and nitrification and mineralization rates in response to atmospheric N deposition are associated with nutrient N fertilization, rather than acidification. They are discussed in more detail in Section 3.3.

Chemical Response

As discussed in Section 3.2.1.6., surface water chemistry has responded to changes in emissions and deposition of S over the past two to three decades and most recently also decreases in N. Monitoring data collected within the U.S. EPA Long-Term Monitoring (LTM) and TIME projects, as well as other monitoring programs, has been key to understanding chemical responses. See discussion of major monitoring programs in Annex B. Surface water chemistry monitoring data generated through TIME and LTM (Stoddard et al., 2003) suggest that the following important changes in lake and stream chemistry have occurred over the past one to two decades in the eastern U.S.:

- SO_4^{2-} concentration has decreased as a percentage of total ion concentration in surface waters.

- ANC has increased modestly in three of the five regions studied.

- DOC and associated natural organic acidity increased, perhaps toward more natural pre-disturbance concentrations, as surface water acidity contributed from acidifying deposition has decreased.

- Inorganic Al concentrations appear to have decreased slightly in some sensitive aquatic systems.

The significant decreases in surface water SO_4^{2-} concentration, which have been observed in many areas, have not necessarily brought large changes in the acidity of lakes and streams. For example, the decline in Adirondack lakewater SO_4^{2-} during the 1980s was charge-balanced by a nearly equivalent decrease in concentrations of base cations in many of the low-ANC lakes, and this limited the increase in

ANC and pH that occurred in response to lower SO_4^{2-} concentrations. Overall, improvements in lakewater acid-base chemistry since 1990 have been measurable but modest. Similar patterns have been observed in most other regions. There are currently no data in the U.S. that indicate increases in soil pH associated with recent declines in acidifying deposition levels.

Declines in SO_2 and NO_X emissions have brought about measurable improvements in streamwater chemistry in sensitive regions of the U.S. since 1990. However, model forecasts suggest that a reversal in chemical recovery could occur in many sensitive ecosystems under current emissions and deposition levels and that further reductions beyond those required by the 1990 Amendments to the CAA may be needed to prevent continued adverse effects and to support biological recovery of terrestrial and aquatic ecosystems (see discussion in Section 3.2.4.5.).

Biological Response

Biological recovery can occur only if chemical recovery is sufficient to allow survival and reproduction of acid-sensitive plants and animals. The time required for biological recovery is uncertain. For terrestrial ecosystems, it may be decades after soil chemistry is restored because of the long life of many plant species and the complex interactions of soil, roots, microbes, and soil biota. For aquatic systems, research suggests that stream macroinvertebrate populations may recover relatively rapidly (within approximately 3 years), whereas lake populations of zooplankton recover more slowly (Gunn and Mills, 1998).

Table 3-8 contains a general summary of pH levels at which biological changes are typically manifested. Nevertheless, for aquatic ecosystems, there is currently no theoretical basis on which to predict the pathway and timing of biological recovery. Biological recovery of previously acidified surface waters can lag behind chemical recovery because of such factors as limits on dispersal and recolonization; barriers imposed by water drainage patterns (Jackson and Harvey, 1995); the influence of predation (McNicol et al., 1995); and other environmental stressors (Gunn et al., 1995; Havas et al., 1995; Jackson and Harvey, 1995; McNicol et al., 1995; Yan et al., 1996a, 1996b). Full biological recovery may take decades from the onset of chemical recovery. The results of biological recovery research from the Sudbury region of Canada and several experimental lakes is summarized below.

Table 3-8. **General summary of biological changes anticipated with surface water acidification, expressed as a decrease in surface water pH.**

pH Decrease	General Biological Effects
6.5 to 6.0	Small decrease in species richness of plankton and benthic invertebrate communities resulting from the loss of a few highly acid-sensitive species, but no measurable change in total community abundance or production.
	Some adverse effects (decreased reproductive success) may occur for highly acid-sensitive fish species (e.g., fathead minnow, striped bass).
6.0 to 5.5	Loss of sensitive species of minnows and dace, such as fathead minnow and blacknose dace; in some waters, decreased reproductive success of lake trout and walleye, which are important sport fish species in some areas.
	Visual accumulation of filamentous green algae in the near-shore zone of many lakes and in some streams.
	Distinct decrease in species richness and change in species composition of plankton and benthic invertebrate communities, although little if any change in total community abundance or production.
	Loss of some common invertebrate species from zooplankton and benthic communities, including many species of snails, clams, mayflies, and amphipods, and some crayfish.

5.5 to 5.0	Loss of several important sport fish species, including lake trout, walleye, rainbow trout, and smallmouth bass, as well as additional nongame species such as creek chub.
	Further increase in the extent and abundance of filamentous green algae in lake near-shore areas and streams.
	Continued shift in species composition and decline in species richness of plankton, periphyton, and benthic invertebrate communities; decreases in total abundance and biomass of benthic invertebrates and zooplankton may occur in some waters.
	Loss of several additional invertebrate species common in surface waters, including all snails, most species of clams, and many species of mayflies, stoneflies, and other benthic invertebrates.
	Inhibition of nitrification.
5.0 to 4.5	Loss of most fish species, including most important sport fish species such as brook trout and Atlantic salmon. A few fish species are able to survive and reproduce in water below pH 4.5 (e.g., central mud minnow, yellow perch, and in some waters, largemouth bass).
	Measurable decline in the whole-system rates of decomposition of some forms of organic matter, potentially resulting in decreased rates of nutrient cycling.
	Substantial decrease in number of species of plankton and benthic invertebrates and further decline in species richness of plankton and periphyton communities; measurable decrease in total community biomass of plankton and benthic invertebrates of most waters.
	Loss of additional species of plankton and benthic invertebrate species, including all clams and many insects and crustaceans.
	Reproductive failure of some acid-sensitive species of amphibians, such as spotted salamanders, Jefferson salamanders, and the leopard frog.

The Sudbury region of Ontario, Canada has been important for studying both the chemical and biological effects of S deposition. Mining and smelting of copper-nickel ore began in the 1880s. By the 1950s and 1960s, SO_2 emissions from the mining and smelting operations peaked at over 5,000 tons/day and extensive acidification of nearby surface waters was documented (Beamish and Harvey, 1972). Emissions of SO_2 then decreased during the 1970s to less than one-third of the peak values. S emission reductions resulted in improved water quality in many lakes (Keller and Pitblado, 1986; Keller et al., 1986), and some fisheries recovery was also documented (Gunn and Keller, 1990; Keller and Yan, 1991). Griffiths and Keller (1992) found changes in the occurrence and abundance of benthic invertebrates that were consistent with a direct effect of reduced lakewater acidity. A more recent assessment of recovery of ecosystems in Canada provided further evidence of biological recovery, but also showed that the spatial extent of recovery was limited to lakes that had been severely acidified by the Sudbury smelter (Jeffries et al., 2003). Research at Sudbury clearly documented that chemical recovery of lakes was possible upon reduced emissions and deposition of S, and that biological recovery, involving multiple trophic levels, could follow. Major findings of the research at Sudbury and elsewhere are summarized below.

Phytoplankton

Studies of phytoplankton recovery from experimental acidification indicate that there is an increase in phytoplankton species richness and diversity as pH increases. In Lake 223 in the Experimental Lakes area of Ontario, there was little increase in phytoplankton diversity as pH changed from 5.0 to 5.8 but a strong recovery of diversity at pH above 6 (Findlay and Kasian, 1996). In Lake 302S, profound change began at pH 5.5; phytoplankton assemblages at pH below 5.5 resembled acidified lakes.

Zooplankton

Zooplankton recovery in response to experimental de-acidification has been reported for lakes in Ontario, Canada and Minnesota. Zooplankton recovery in experimentally acidified Lake 223 as pH returned back to 6.1 was reported by Malley and Chang (1995). Species diversity that had been reduced during the acidification phase had partially returned to pre-acidification levels. Rotifers had recovered less than crustaceans.

One decade after cessation of the experimental acidification of Little Rock Lake in Wisconsin, recovery of the zooplankton community was complete (Frost et al., 2006). Recovery did not follow the same trajectory as the initial acidification, however, indicating a substantial hysteresis in zooplankton community recovery. About 40% of the zooplankton species in the lake exhibited a lag of 1 to 6 years to recover to levels that occurred in the neutral reference basin.

Benthic Invertebrates

There has been some research conducted on the recovery of benthic invertebrate communities in surface waters exhibiting chemical recovery from acidification. In Scotland, Soulsby et al. (1995) reported an increase in acid-sensitive mayflies in some streams that showed recent ANC increases. However, no increases in invertebrates were observed in the most acidic streams despite observed increases in ANC. They suggested that further reductions in acidic deposition and sufficient time for reversal of soil acidification may be required before aquatic biotic recovery can occur. The extent to which benthic invertebrates in streams in the U.S. may have recovered in response to any recent increases that may have occurred in stream ANC and pH is not known.

Fish

Fish populations have recovered in acidified lakes when the pH and ANC have been increased through liming or reduction of acidifying deposition (Beggs and Gunn, 1986; Dillon et al., 1986; Gunn et al., 1988; Hultberg and Andersson, 1982; Keller and Pitblado, 1986; Kelso and Jeffries, 1988; Raddum et al., 1986). The timing of fish recovery is uncertain and probably depends heavily on dispersion. Stocking could accelerate fish population recovery (Driscoll et al., 2001a). Limitations on dispersal and recolonization can hamper biological recovery from acidification.

Continued periodic episodic acidification might hamper biological recovery of a lake or stream that is experiencing improvement in chronic chemistry. If fish move into refugia during episodes of low pH and then return, behavioral avoidance would reduce the overall effect of episodic acidification on fish populations. If fish move out of the stream system in response to acidic episodes, as suggested by Baker et al. (1996), and do not return or return in smaller numbers, then the population level effects of episodic acidification would be greater than predicted based on mortality tests alone.

Table 3-9. Studies that either did or did not yield evidence that acidifying deposition affected certain species of birds.

Species	Diet/Foraging YES	Diet/Foraging NO	Breeding Distribution YES	Breeding Distribution NO	Reproductive Measures YES	Reproductive Measures NO	Reference
Common loon	x		x	x	x	x	Alvo et al. (1988); Blair (1990); Blancher and McNicol, (1991); DesGranges and Houde (1989); Wayland and McNicol (1990); Parker (1988)
Arctic loon						x	Eriksson (1987)
Common merganser			x		x		McNicol et al. (1987)
Belted kingfisher			x				Goriup (1989)
Osprey	x		x		x		Eriksson (1983, 1986)
Black duck	x		x		x[b]		DesGranges and Darveau (1985); Harasmis and Chu (1987); Hunter (1986); Rattner (1987)
Common goldeneye			x[b]				DesGranges and Darveau (1985); McNicol et al. (1987)
Ring-necked duck	x				x		McAuley and Longcore (1988a); McAuley and Longcore (1988b)
Eurasian dipper	x		x		x		Ormerod et al. (1985, 1986); Ormerod and Tyler (1987)
Eastern kingbird				x	x		Glooschenko et al. (1986)
Tree swallow	x			x	x		Blancher and McNicol (1988, 1991); St. Louis et al. (1990)

[b] Effect was beneficial

　　Baker et al. (1990a) used field-based models to test the potential for biological recovery. For each species considered, the current presence or absence of the species was analyzed as a function of the water quality variables associated with acidification (e.g., pH, Al, Ca, ANC, and DOC) using maximum likelihood logistic regression (Reckhow et al., 1987). The results from the various models were compared to their prediction of the change in the number of Adirondack lakes with unsuitable acid-base chemistry, given a 50% decrease or a 30% increase in S deposition relative to the existing conditions at the time of the eastern lakes survey (1984). Most of the models provided similar results and suggest that a 30% increase in S deposition would increase the unsuitable fish habitat in Adirondack DDRP lakes by 15% to 28% for brook trout, lake trout, and common shiner. A 50% decrease in S deposition was projected to increase suitable habitat by 8% to 18%.

Waterfowl

　　Few studies have been conducted on the recovery of higher trophic level organisms such as birds (Table 3-9). However, breeding distribution for the common goldeneye (*Bucephala clangula*), an insectivorous duck, may be affected by changes in acidifying deposition (Longcore and Gill, 1993).

Similarly, reduced prey diversity and quantity have been observed to create feeding problems for nesting pairs of loons on low-pH lakes in the Adirondacks (Parker, 1988).

Logistic regression modeling with measured pH and species occurrence data for acid-sensitive lakes in the Algoma region of Ontario showed that the occurrences of fish, common loons, and common mergansers were positively related to lake water pH (McNicol, 2002). Predictions of common loon and merganser recovery for this area were made using the Waterfowl Acidification Response Modeling System (WARMS) under varying S emissions control scenarios targeted for 2010 (McNicol, 2002). The number of lakes projected to be suitable for supporting breeding pairs and broods increased with Lake pH and stricter emissions controls (McNicol, 2002). Marginal improvements in fish-eating bird habitat were predicted to occur by 2010, with more significant improvements expected under hypothetical S emissions reductions of 50% and 75% for lakes with pH below 6.5 (McNicol, 2002). Fundamental to the predicted improvement of these fish-eating bird populations is the expected increase in food availability with lake pH recovery.

3.2.4.4. Acidification Case Study #1: Adirondack Region of New York

In this and the following section, case studies are presented for two of the most thoroughly studied regions of the U.S. that are known to have been affected by acidification from atmospheric S and N deposition. Studies in these regions have focused on both chemical and biological effects, and have included extensive model simulations of past acidification and projections of the likelihood of future recovery as deposition levels decline. The Adirondack Mountain region is perhaps the most thoroughly studied region in the world with respect to surface water acidification. Large numbers of Adirondack lakes have been acidified over the past century, and many of those now show signs of chemical recovery. Shenandoah National Park contains many acidified and acid-sensitive streams. Sensitivity in this region is strongly controlled by geology and the extent to which deposited S is adsorbed to soils. These two case studies are intended to be illustrative of the types of research that has been conducted and what that research has revealed.

General Description of Region

The Adirondack Mountains are in northeastern New York State and are densely forested, have abundant surface waters, and have 46 peaks that extend up to 1600 m in elevation. The Adirondack Park has long been a nationally important recreation area for fishing, hiking, boating, and other outdoor activities.

The Adirondacks, particularly the southwestern Adirondacks, are sensitive to acidifying deposition because they receive high precipitation, have shallow base-poor soils, and are underlain by igneous bedrock with low weathering rates . The Adirondacks are among the most severely acid-affected regions in North America (Driscoll et al., 2003b; Landers et al., 1988) and have long been used as an indicator of the response of forest and aquatic ecosystems to U.S. policy on atmospheric emissions of SO_2 and NO_X (GAO, 2000; NAPAP, 1998; U.S. EPA, 1995a).

Rates of Acidifying Deposition

Current rates of wet deposition of S and N in the western Adirondacks remain among the highest in the nation. Spatial patterns in wet deposition of S and N from 1988 to 1999 were developed by Ito et al. (2002), using data from 24 precipitation and 4 wet deposition monitoring stations. Results from this effort suggest that wet S deposition ranged from 2.3 to 12.9 kg S/ha/yr and wet NO_3-N deposition rates ranged from 1.7 to 5.1 kg N/ha/yr (Ito et al., 2002) (Figure 3-18). In general, deposition rates are highest in the southwestern Adirondacks and decrease to the northeast. Rates of dry deposition are less well known, but probably constitute 25% to 50% or more of total wet deposition (Sullivan et al., 2006b).

Deposition trends have changed with the implementation of federal and state emissions control regulations. For example, by 1990 average wet S deposition in the Adirondack region had declined by approximately 30% from its peak in the 1970s (Sullivan et al., 1990). Deposition of S has continued to decline (Figure 3-19) and (Figure 3-20) in response to implementation of the CAAA of 1990. Until recently, wet N deposition had been fairly consistent over the previous two decades. N deposition now appears to be decreasing (http://nadp.sws.uiuc.edu/).
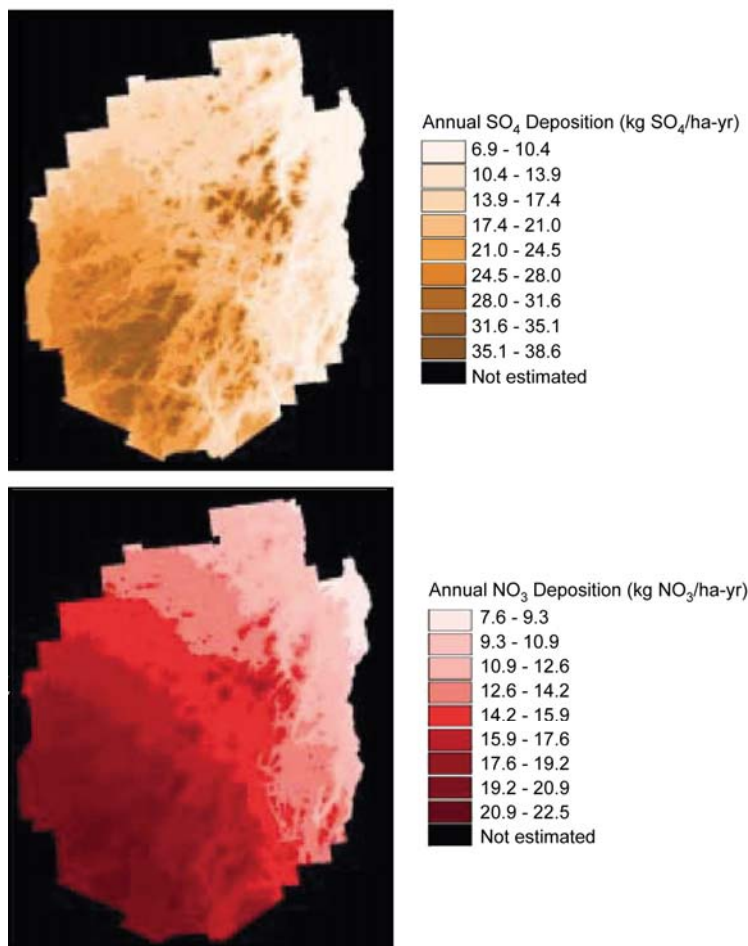
Figure 3-18. **Spatial patterns in predicted wet SO_4^{2-} and NO_3^- deposition in the Adirondack Park during the period 1988 to 1999.**

Soil Retention and Leaching of Sulfur and Nitrogen

As discussed in Section 3.2.4.4, acidifying deposition has resulted in the accumulation of S and N in Adirondack soils. Although input-output budgets for S developed in the 1980s suggested that the amount of S exported was approximately equal to the S inputs from atmospheric deposition, more recent studies show that watershed loss of SO_4^{2-} now exceeds atmospheric S deposition inputs (Driscoll et al., 1998). This pattern suggests that decades of atmospheric S deposition have resulted in the accumulation of S in forest soils. With recent declines in atmospheric S deposition and a possible warming-induced enhancement of S mineralization from soil organic matter, previously retained S is gradually being

released to surface waters (Driscoll et al., 1998). This release of SO_4^{2-} from soils could contribute to a delay in the recovery of surface waters in response to SO_2 emissions controls.

N dynamics are quite different from those of S. Because N is a growth-limiting nutrient for many forest plants, retention in forest ecosystems under low levels of air pollution is generally high and NO_3^- loss to streams is relatively low (Aber et al., 2003). However, recent research suggests that N has accumulated in soils over time in the Adirondacks and that some forests have exhibited increasing retention of N inputs (Driscoll et al., 2003a, c). The result has been increased leaching of NO_3^- to surface waters. The extent and degree of leaching appear to be linked to climatic variation, land-use history, and vegetation type (see Section 3.2.1.3).
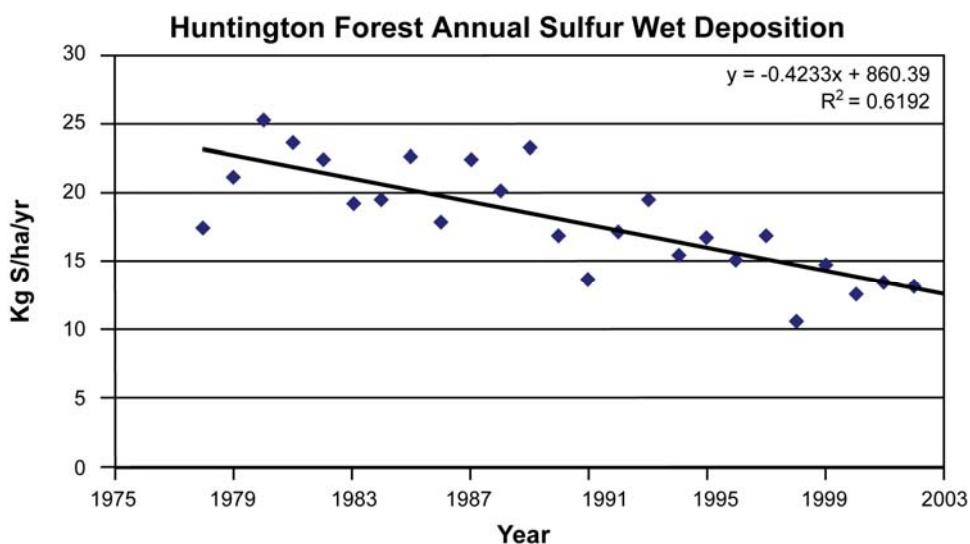
Figure 3-19.   Measured wet deposition of sulfur at the Huntington Forest NADP/NTN monitoring station.

The leaching of both SO_4^{2-} and NO_3^- into drainage water has contributed to the displacement of cations from soil, acidification of surface waters (Driscoll et al., 2001b), and the associated chemical and biological effects discussed below.

Soil Acidification and Base Cation Depletion

Atmospherically deposited hydrogen ions can directly affect soil pH. Net uptake of nutrient cations by vegetation can also generate acidity within the soil, and a considerable amount of natural organic acidity is produced in the Oa horizon through the partial decomposition of organic matter and uptake of nutrient cations. In the only repeated soil sampling in the U.S. in which the original sampling predated acidifying deposition, (Johnson et al., 1994b) found significantly higher soil pH values in 1930 than in 1984 in the Oa horizon of Adirondack soils that had an initial pH of 4.0–5.5, but no decrease in pH in soils with an initial pH of <4.0. (Johnson et al., 1994b) also documented a decrease in exchangeable Ca concentrations in both the O (combined Oa and Oe horizons) and B horizons from 1930 to 1984. The decrease in soil pH and Ca concentrations was attributed to a combination of acidifying deposition and changing vegetation dynamics.
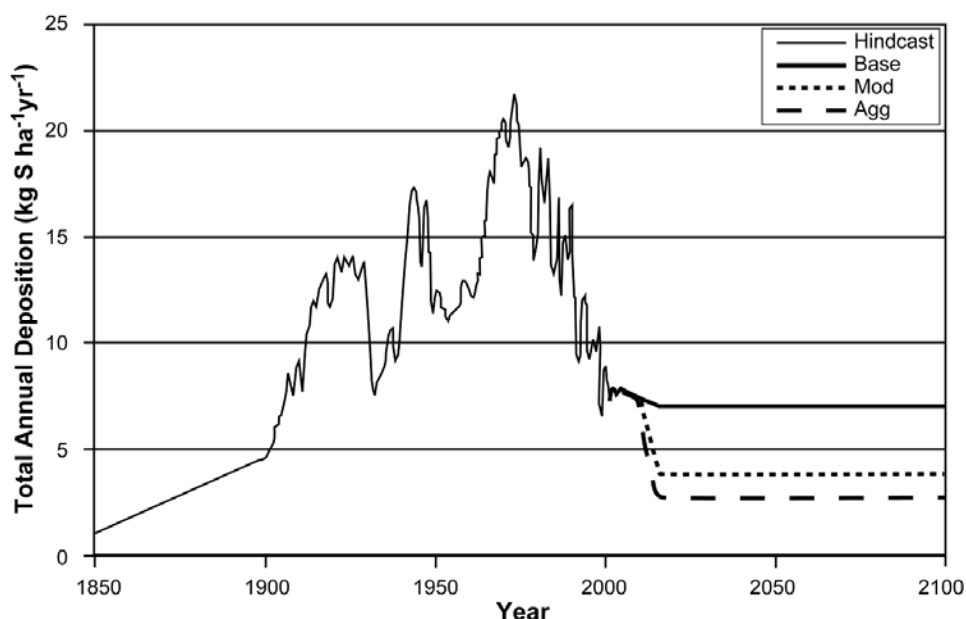
Figure 3-20. **Estimated time series of S deposition at one example watershed in the southwestern Adirondack Mountains. Table used by Sullivan et al. (2006a) as input to the MAGIC model for projecting past and future changes in lakewater chemistry attributable to acidifying deposition. Future deposition estimates were based on three emissions control scenarios (Base Case [solid line], Moderate Additional Controls [dotted line], Aggressive Additional Controls [dashed line]).**

In a statistically based regional assessment of changes in soil-exchange chemistry, Sullivan et al. (2006a) found that base saturation and exchangeable Ca concentrations in the Adirondack region appeared to have decreased in the B horizon between the mid 1980s and 2003 in watersheds of lakes with acid-neutralizing capacity less than 200 µeq/L. Although this study did not involve repeated sampling of the same sites, the comparison could be made on a regional basis because the sampling locations were selected randomly in both the mid 1980s and in 2003, and a large and similar number of sites were included in both samplings.

Effects of Acidifying Deposition on Adirondack Surface Water Chemistry

The Adirondack Lake Survey Corporation conducted a comprehensive survey of Adirondack lakes greater than 0.2 ha in surface area between 1984 and 1987 (Baker et al., 1990a). Of the 1,489 lakes surveyed, 24% had summer pH values below 5.0, 27% were chronically acidic (ANC <0) and an additional 21% were probably susceptible to episodic acidification (ANC between 0 and 50; Driscoll et al., 2007a).

In addition to low pH and ANC, many acidic surface waters in the Adirondacks are characterized by high concentrations of inorganic Al. For example, a study of 12 sub-basins in the watershed of the North Branch of the Moose River by (Driscoll et al., 1987a) determined that the concentration of inorganic Al in lakewater was higher in lakes having pH below 6.0. Recently, Lawrence et al. (2007) determined that 66% of 188 streams sampled in the western Adirondack region during snowmelt in 2004 had measurable concentrations of inorganic Al, an indicator of acidification by acidifying deposition.

Historical changes in lakewater chemistry from the mid-1800s to recent times have been estimated for the Adirondacks using paleolimnological techniques. Fossil remains of diatoms and chrysophytes in

sediment cores have been used to reconstruct chemical histories. The PIRLA I and II projects (Paleoecological Investigation of Recent Lake Acidification) used the remains of diatoms preserved in lake sediments to estimate historical changes in lakewater chemistry across the Adirondack region. The PIRLA-II project focused on lakes that are 4 ha or larger that represented a subpopulation of 675 Adirondack lakes. The results from these analyses suggest that nearly all lakes with estimated preindustrial pH less than 6.0 had acidified between 0.3 and 1.0 pH units during the 20th century. Based on an analysis of data from Cumming et al. (1992) and (Baker et al., 1990a), low-pH lakes were uncommon or rare in the preindustrial Adirondacks; the number of lakes with pH less than 5.5 had at least doubled by the mid 1980s and the number with pH less than 5.0 had increased by 5 to 10 times.

The PIRLA results are generally consistent with projections from model hindcasts. (Sullivan et al., 2006b) modeled past changes in the acid-base chemistry of 70 Adirondack lake watersheds. These included 44 that were statistically selected to be representative of the approximately 1,320 Adirondack lake watersheds that have lakes larger than 1 ha and deeper than 1 m and that have ANC ≤ 200 μeq/L. Model hindcasts were constructed using both the MAGIC and PnET-BGC models. Based on MAGIC model outputs, maximum past acidification occurred by about 1980 or 1990, with a median ANC for the study population of about 61 μeq/L (reduced from a median of 92 μeq/L estimated for the preindustrial period). By 1990, 10% of the population target lakes had decreased in ANC to below -16 μeq/L and 25% had ANC <28 μeq/L. The model simulations coupled with population-level extrapolations suggest that none of the target lakes were chronically acidic (had ANC <0 μeq/L) under preindustrial conditions, but that by 1980 there were about 204 chronically acidic Adirondack lakes.

PnET-BGC model simulations generated output that was generally similar to results provided by MAGIC model simulations. Results from PnET-BGC suggest that none of the lakes in the Adirondack population had preindustrial ANC below 20 μeq/L. By 1990, there were 289 lakes having ANC <20 μeq/L and 217 chronically acidic (ANC ≤ 0 μeq/L) lakes according to PnET-BGC simulations. There were 202 lakes in the population simulated to have had preindustrial ANC below 50 μeq/L, and this number increased 2.8 times by 1980 under the PnET-BGC simulations.

Zhai et al. (2008) reported PnET-BGC hindcasts for the 44 EMAP lakes. They report that simulated median values of pH, ANC, and soil percent base saturation were 6.63, 67.7 μeq/L, and 12.3%, respectively, in 1850 compared to current measured values of 5.95, 27.8 μeq/L, and 7.9%. They also calculated F factors for the PnET-BGC model projections of historical acidification. The F-factor (Henriksen, 1984; Husar and Sullivan, 1991) reflects the proportion of the increase in lakewater SO_4^{2-} plus NO_3^- concentration that is charge balanced by an equivalent increase in base cation concentrations. The remaining proportion (1–F) is attributed to increase in the potentially toxic cations, hydrogen ions and inorganic Al. Based on PnET-BGC hindcast simulations, F-factors for the EMAP lakes ranged from 0.3 to slightly over 1.0, with a mean value of 0.7 (Figure 3-13). The F-factor increased with ambient lakewater ANC. These results are in close agreement with paleolimnological analyses reported by Sullivan et al. (1990), which showed historic F-factors for Adirondack lakes ranging from about 0.5 to above 1.0.

While there were differences for some variables (i.e., MAGIC showed greater soil acidification) and clear lake-to-lake differences, Sullivan et al. (2006b) observed that the population-level projections with both models represent robust indicators of the extent and magnitude of changes in lake chemistry associated with historical inputs of acidic deposition. The differences observed in the nature of acidification between the two models may be linked to model structural differences. In MAGIC, soil water is assumed to be in equilibrium with an aluminum trihydroxide mineral at all times (Cosby et al., 1985a, b). Inputs of strong acids, therefore, drive the mobilization of Al. This Al strongly displaces exchangeable base cations from the soil exchange complex. In PnET-BGC, the soilphase is in equilibrium only when solutions are oversaturated with the aluminum trihydroxide solid phase. As a result, there is less Al available in PnET-BGC to displace exchangeable soil base cations and greater acidification of the solution is realized. Backward and forward projections of population-level estimates of lake water and soil chemistry for the Adirondacks are presented as cumulative distribution functions in Figure 3-21.
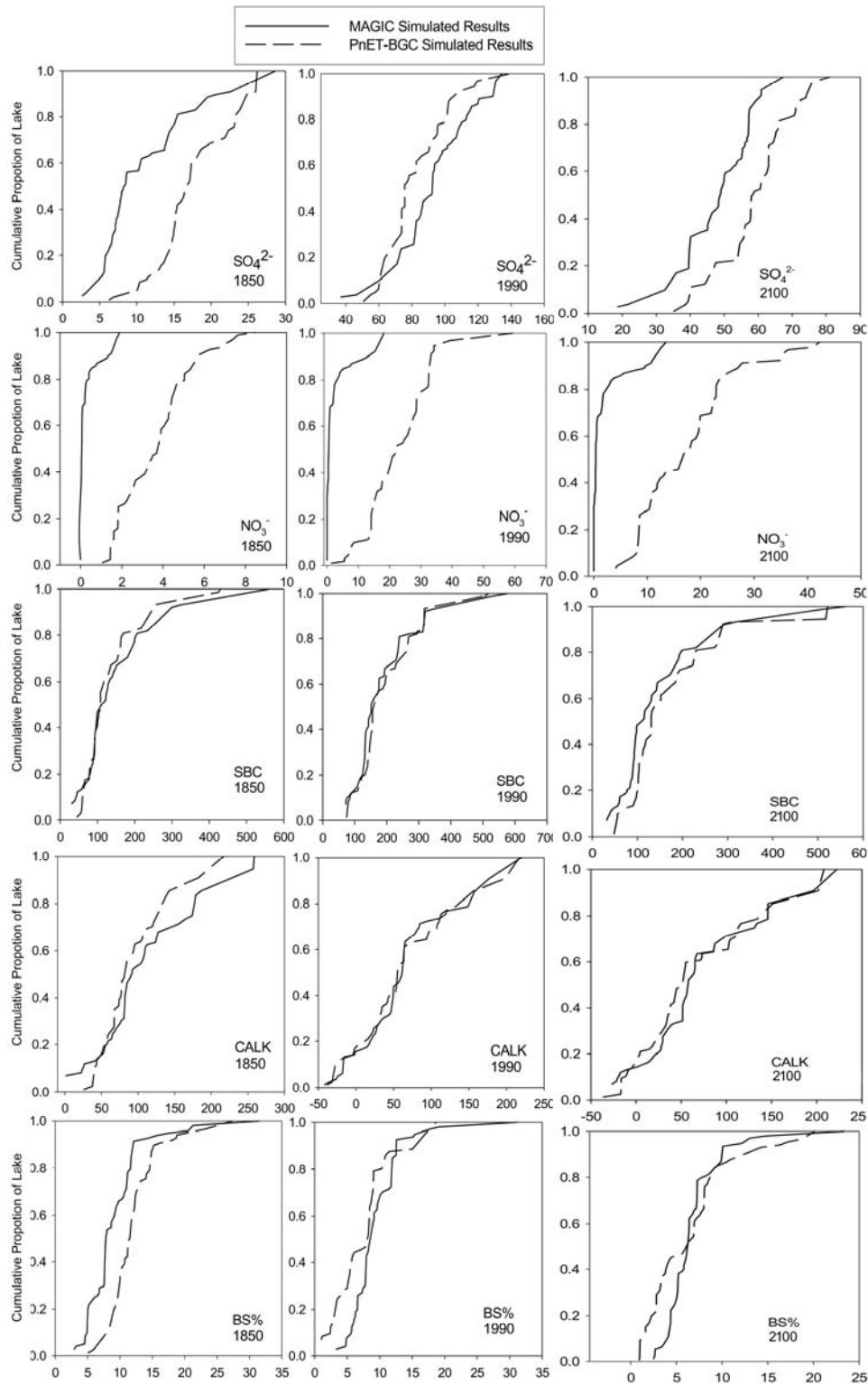
Source: Sullivan et al. (2006b)

Figure 3-21.   Cumulative distribution functions of selected major ions (µeq/L), calculated ANC of lakewater (µeq/L), and B horizon soil % base saturation for the MAGIC and PnET-BGC models. Results are shown for 1850, 1990, and 2100.

Biological Effects

The Adirondack region has a rich aquatic biota dataset from which to examine relationships among lake water chemistry and species abundance, composition, and richness. In general, there tends to be a negative relationship in Adirondack lakes between pH, ANC, and inorganic Al chemical variables and the diversity and abundance of fish (Baker and Laflen, 1983; Baker et al., 1990a; Havens et al., 1993) (Figure 3-16), phytoplankton, and zooplankton (Confer et al., 1983; Siegfried et al., 1989) (Table 3-10).

Table 3-10.   **Observed relationships between zooplankton species richness and lakewater ANC in the Adirondack Mountains.**

Taxonomic Group	Equation	R^2	p
Total zooplankton	Richness = 15.65 + 0.089 ANC	0.46	0.001
Crustaceans	Richness = 6.35 + 0.028 ANC	0.47	0.001
Rotifers	Richness = 9.04 + 0.053 ANC	0.30	0.001
Large Cladocerans	Richness = 1.95 + 0.017 ANC	0.41	0.001

Source: Sullivan et al. (2006b).

Through the Adirondack Lakes Survey, 1,469 lakes were sampled between 1984 and 1987, representing 80% of the estimated population of Adirondack lakes larger than 1 ha in area (Whittier et al., 2002). The goal of the survey was to characterize the biological, physical, and chemical characteristics of the lakes and evaluate the relationships between fish communities and water chemistry. The major results were reported by (Baker et al., 1990a). Key findings are:

- Seventy-six percent of the lakes had fish; 24% (346 lakes) were fishless.

- The most common fish caught were native acid-tolerant species: brown bullhead, brook trout, and white sucker.

- As pH decreases, fish diversity also decreases. The average number of fish species declines from six fish species in lakes with pH higher than 6.5 to two or fewer fish species in lakes with pH of 5.0 or less.

- As pH decreases, the number of fishless lakes increases. Few lakes with pH of 5.5 or higher are fishless. Below pH 5.0, approximately 75% of the lakes are fishless.

Researchers in the Adirondacks were among the first in the U.S. to demonstrate that fish mortality increases during acid episodes, which are common to lakes and streams in the Adirondacks during spring runoff. (Driscoll et al., 1987b) documented surface water chemistry changes associated with periods of high flow. They found that pH and ANC decreased substantially during hydrological episodes and inorganic Al concentrations commonly exceeded thresholds harmful to fish. These relationships were further documented by the Episodic Response Project as shown in the example for Bald Mountain Brook in the Adirondacks (Wigington et al., 1996). Work by Van Sickle et al. (1996) and others linked these chemical changes to fish mortality in small streams. They determined that blacknose dace were highly sensitive to low pH and could not tolerate inorganic Al concentrations above about 3.7 µM for extended periods of time. After 6 days of exposure to high inorganic Al, dace mortality increased rapidly to nearly

100% (Van Sickle et al., 1996). Brook trout were less sensitive, but still showed high mortality during many acid episodes.

Several efforts have been made to link changes in fish populations with historical changes in water chemistry associated with acidifying deposition. Among the most widely cited is the work of (Baker et al., 1990a; 1996). They analyzed 988 Adirondack Lake Survey lakes for which data existed for the period before 1970 and for the 1980s. Of the 2,824 fish populations confirmed by pre-1970 surveys, 30% had apparently been lost by the 1980s (Baker et al., 1990a). An estimated 23% of the fish population losses were related to acidifying deposition. This relationship was strengthened by evidence from the PIRLA projects. In the 32 lakes that had both historic fish data and paleolimnological chemical reconstructions, the lakes that had acidified the most or that were originally the most acidic were the same ones that were judged to have lost fish populations (Baker et al., 1996).

Recent Trends in Surface Water Chemistry and Projections of Future Change

Several studies have been conducted to analyze trends in lake chemistry in the Adirondacks. (Driscoll et al., 2003c) evaluated changes from 1982 to 2000 in the original 16 Adirondack LTM lakes and from 1992 to 2000 in the complete set of 48 Adirondack LTM lakes. They found that nearly all study lakes showed marked decreases in SO_4^{2-} concentration over the period of record and several lakes showed declines in NO_3^- concentration. Data for one example monitoring lake are given in Figure 3-22. They found that 7 of the 16 original monitoring lakes showed a statistically significant increase in ANC (Figure 3-22), with a mean rate of increase of 0.78 µeq/L/yr (Driscoll et al., 2003c). Twenty-nine of the group of 48 lakes showed increasing ANC trends from 1992 to 2000 with a mean rate of increase of 1.60 µeq/L/yr (Driscoll et al., 2003b). The authors attributed this recent increase in ANC to declines in both SO_4^{2-} and NO_3^- concentrations (Driscoll et al., 2003c).

Despite these recent improvements in lake water chemistry in the Adirondack Long-Term Monitoring lakes, 34 of the 48 lakes still had mean ANC values less than 50 µeq/L in 2000, including 10 lakes with ANC less than 0 µeq/L. Thus, current chemistry data suggest that most of these lakes exhibit chemical conditions that continue to pose a risk to aquatic biota. Model projections of future acid-base chemistry of lakes in the Adirondack Mountains under three scenarios of future atmospheric emissions controls were presented by (Sullivan et al., 2006a) to evaluate the extent to which lakes might be expected to continue to increase in ANC in the future. Estimated levels of S deposition at one representative watershed are shown in Figure 3-20 for the hindcast period and in the future under the three emissions control scenarios. Model simulations for 44 statistically selected Adirondack lakes using the MAGIC and PnET-BGC models were extrapolated to the regional lake population. Cumulative distribution frequencies of ANC response projected by MAGIC are shown in Figure 3-24 for the past (1850), peak acidification period (approximately 1990), and future (2100). Results for the future are given for each of the scenarios.

Forecasting results suggested that the ongoing trend of increasing lakewater ANC for the most acid-sensitive lakes would not continue under future emissions and deposition levels anticipated as of 2003 (Base Case Scenario). The numbers of Adirondack lakes having ANC below 20 and below 50 µeq/L were projected to increase between 2000 and 2100 under that scenario, and the number of chronically acidic Adirondack lakes (i.e., ANC less than 0) was projected to stabilize at the level reached in 2000. Thi3s projected partial reversal of chemical recovery of acid-sensitive lakes was due to a continuing decline in the simulated pool of exchangeable base cations in watershed soils. Simulations suggested that re-acidification might be prevented with further reductions in emissions and deposition.

Chen and Driscoll (2004) applied the PnET-BGC model to DDRP lake watersheds in the Adirondacks. The model was applied to three future emissions scenarios: base case, moderate emissions reductions, and aggressive emissions reductions. A case study for Indian Lake in the Adirondacks illustrated that larger reductions in deposition caused greater decreases in SO_4^{2-} and base cation concentrations in lake water and greater recovery in pH and ANC. Within the full population of lake-watersheds, some showed decreasing ANC and pH values from 1990 to 2050 even under the moderate and aggressive reduction scenarios. By 2050 to 2100, however, nearly all lakes were simulated to

experience increasing ANC and pH. The modeled soil base saturation increased very slowly over the modeled time period compared to changes in surface water chemistry. For 95% of the lake-watersheds studied, simulated soil base saturation remained below 20% in 2100 under all emissions scenarios.
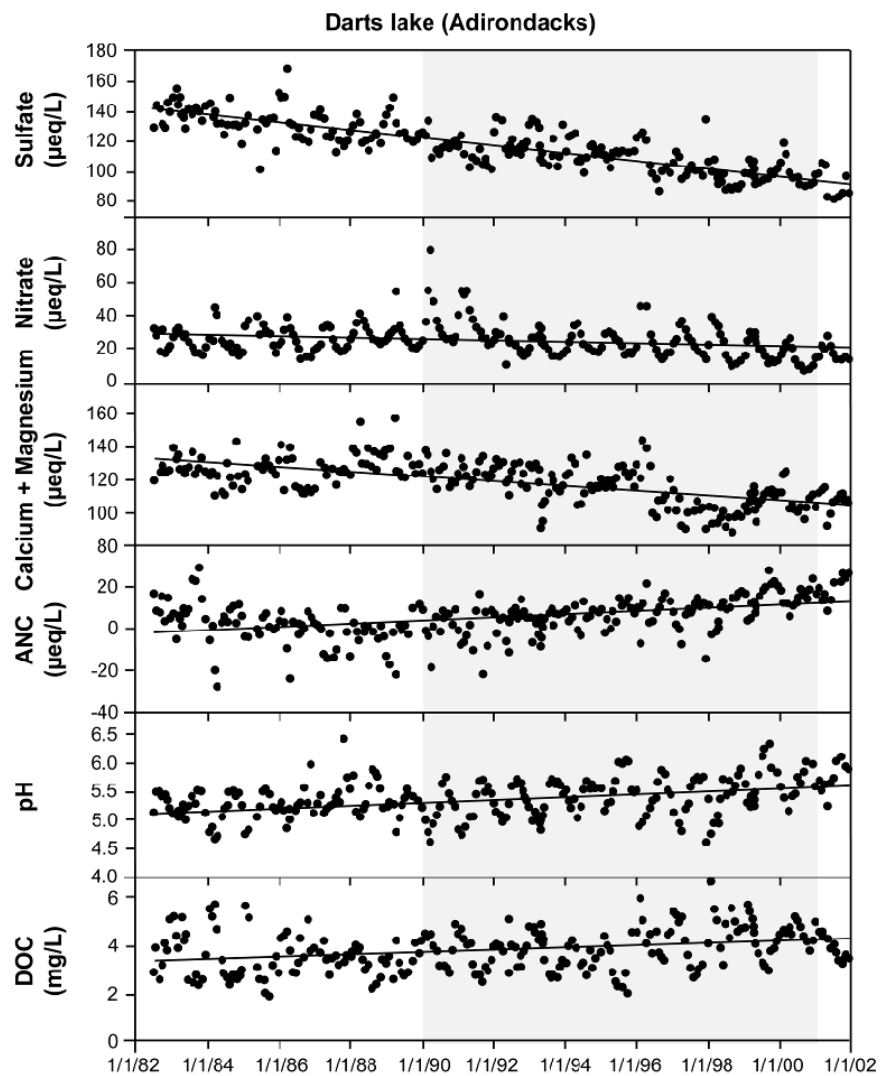
Source: Stoddard et al. (2003)

Figure 3-22. Time series data for SO_4^{2-}, NO_3^-, base cations [Ca plus Mg], Gran ANC, pH, and DOC in one example of long-term monitoring in Darts Lake in the Adirondack Park. Shaded box indicates time period of analyses reported by Stoddard et al. (2003).
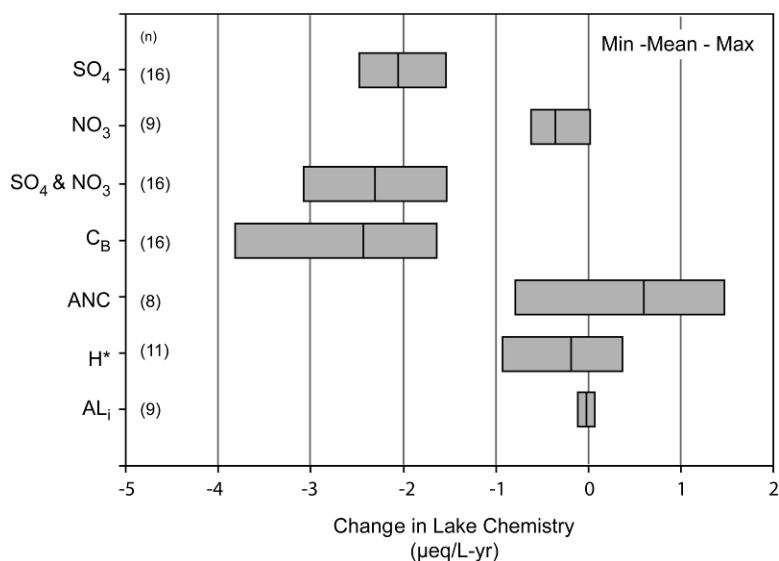
Source: Driscoll et al. (2003b)

Figure 3-23. **Mean rates of change in solute concentration in 16 lakes of the Adirondack Long-Term Monitoring (ALTM) program from 1982 to 2000. Minimum, mean, and maximum changes in concentrations and number of lakes showing significant trends are shown. All values are in µeq/L/yr, except for concentrations of inorganic monomeric aluminum (Al$_i$), which are expressed in µM/yr.**

Multipollutant Interaction: Biological Mercury Hotspots in the Adirondacks

The Adirondacks has been identified as a region at risk from the combined effects of acidifying deposition and Hg deposition (Driscoll et al., 2007a). The relationship between atmospheric deposition of S and enhanced Hg methylation is discussed in Section 3.4. In general, the solubility of Hg increases with increasing sulfide concentrations in anoxic waters through complexation reactions, potentially increasing the pool of Hg available for methylation (Benoit et al., 2003; Driscoll et al., 2007a). Evers et al. (2007) identified a biological Hg hotspot in the western Adirondacks based on Hg concentrations in yellow perch and common loons. Mean yellow perch Hg concentrations in the Adirondack hotspot were 1.5 to 2.5 times higher than the U.S. EPA and U.S. Food and Drug Administration's reference dose used for fish consumption advisories (Evers et al., 2007). The authors hypothesized that the occurrence of the biological hotspot was due in part to the combination of high Hg deposition and sensitive water chemistry, such as low ANC and pH, which is associated with both natural acidity and the long-term effects of acidifying deposition (Evers et al., 2007). Driscoll et al. (2007a) concluded that watersheds sensitive to Hg deposition tend to be forested, have an abundance of wetlands, contain shallow hydrologic flow paths and low nutrient concentrations, and are affected by acidifying deposition.

MAGIC Model Estimates of ANC Distribution
Adirondack Lakes with ANC < 200 µeq/L

Legend:
- 1850
- 1990
- 2100-Aggresive
- 2100-Base
- 2100-Moderate

X-axis: Predicted ANC (µeq/L)
Y-axis: Cumulative Proportion of Lakes
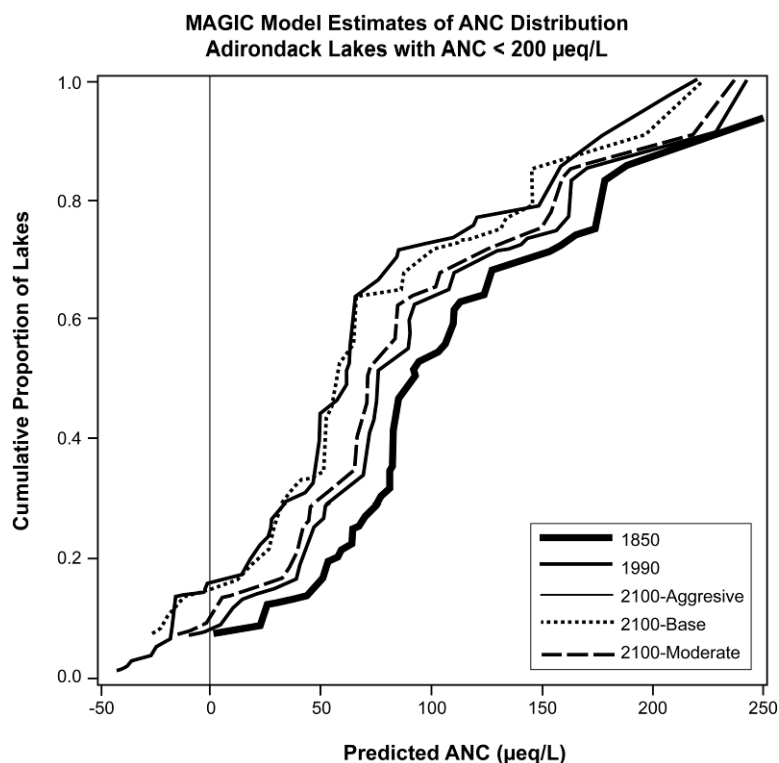
Figure 3-24. **Simulated cumulative frequency distributions of lakewater ANC at three dates for the population of Adirondack lakes, based on MAGIC model simulations reported by Sullivan et al., 2006b. Conditions for the year 2100 are presented for three emissions control scenarios: Base Case, Moderate Additional Controls, and Aggressive Additional Controls. (See Figure 3-15)**

3.2.4.5. Acidification Case Study #2: Shenandoah National Park, Virginia

Shenandoah National Park is located along the crest of the Blue Ridge Mountains in Virginia. Air pollution within Shenandoah National Park, including S and N deposition and O_3 concentration, is higher than in most other national parks in the U.S. Measured wet S deposition in the park has ranged from 8 to 10 kg S/ha/yr in the early 1980s to near 6 kg S/ha/yr since 2000 (Figure 3-25). Dry S deposition may be nearly as high as wet deposition (Sullivan et al., 2003). Most acidification effects in the park have been linked with S deposition.

The sensitivity of streams in the park to acidification from acidifying deposition is determined mainly by the types of rocks found beneath the stream and the characteristics of the watershed soils that surround it. If the underlying geology is Si-based (siliclastic lithology), the soil and water in the watershed generally have poor ability to neutralize acids deposited from the atmosphere. About one-third of the streams in the park are located on this type of geology. Model estimates using the MAGIC model suggest that such streams have typically lost most of their natural ANC, largely in response to a century of industrial emissions and acidifying deposition. As a consequence, stream pH values in many streams are low, especially during winter and spring. Before human-caused air pollution, most streams in Shenandoah National Park probably had pH above about 6. Many park streams on siliclastic lithology currently have pH as low as about 5 (Cosby et al., 2006; Sullivan et al., 2003). Other predominant lithologies in the park include granite-based (granitic) lithologies typically characterized by intermediate ANC streams, and

basalt-based (basaltic) lithologies typically characterized by relatively high stream ANC (Cosby et al., 2001; Sullivan et al., 2004, 2007, 2008).

The effects of acidifying deposition on Shenandoah National Park streams have been studied for over 25 years by the Shenandoah Watershed Study, the longest-running watershed study program in any of the national parks (Cosby et al., 2006; see http://swas.evsc.virginia.edu). This program has determined that the high rate of atmospheric deposition of S, combined with naturally low contributions from some rock types of Ca and other base cations (that serve to neutralize acidity), are the most important causes of low streamwater ANC in many park streams. Some park streams can also become temporarily acidic for short periods (hours to days) during rainstorms or snowmelt.
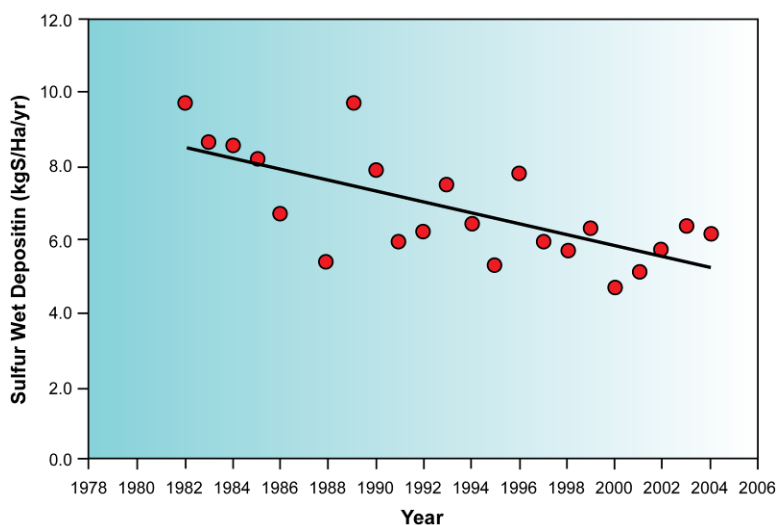
Figure 3-25. **Wet sulfur deposition for the period of record at the Big Meadows NADP/NTN monitoring station in Shenandoah National Park.**

The acidification of streams in the Park is linked to effects that are occurring in the watershed soils. Over time, the ability of soils to adsorb S, thereby effectively negating sulfur's potential to acidify water, is decreasing due to the long term accumulation of SO_4^{2-} on soil adsorption sites in response to a legacy of acidifying deposition. In addition, the amount of stored Ca and Mg in the soil is gradually declining in response to acidifying deposition. Therefore, streams are expected to acidify more in the future than they have so far, relative to the amount of acidifying deposition received. This prognosis is consistent with recent analysis of national lake and stream response to reductions in air pollution emissions (Stoddard et al., 2003). Unlike a number of other regions of the country, streams in the region that includes Shenandoah National Park are generally not recovering from acidification.

A great deal of research has been conducted in the park on the effects of S and N deposition on soil and water acidification. This park was a major site of early research on acidification processes (Galloway et al., 1983). This early work provided much of the foundation for development of the MAGIC model (Cosby et al., 1985c), which has been the most widely used dynamic watershed acid-base chemistry model worldwide for the past two decades.

Although research on many aspects of acidification effects science has been conducted in the park, it has been particularly noteworthy for studies on episodic acidification; biological effects of stream acidification; and dynamic modeling of acidification, recovery, and critical loads. Research within Shenandoah National Park on each of these topics is discussed below.

Episodic Acidification

A number of studies of episodic acidification have been conducted in streams within Shenandoah National Park. Eshleman and Hyer (2000) estimated the contribution of each major ion to observed episodic ANC depressions in Paine Run, Staunton River, and Piney River during a 3−year period. During the study, 33 discrete storms were sampled and water chemistry values were compared between antecedent baseflow and the point of minimum measured ANC (near peak discharge). The relative contribution of each ion to the ANC depressions was estimated using the method of Molot et al. (1989), which normalized the change in ion concentration by the overall change in ANC during the episode. At the low-ANC (~0 μeq/L) Paine Run site on siliciclastic bedrock, increases in NO_3^- and SO_4^{2-}, and to a lesser extent organic acid anions, were the primary causes of episodic acidification. Increases in base cations tended to compensate for most of the increases in acid anion concentration. ANC declined by 3 to 21 μeq/L (median 7 μeq/L) during the episodes studied.

At the intermediate-ANC (~60 to 120 μeq/L) Staunton River site on granitic bedrock, increases in SO_4^{2-} and organic acid anions, and to a lesser extent NO_3^-, were the primary causes of episodic acidification. Base cation increases compensated these changes to a large degree, and ANC declined by 2 to 68 μeq/L during the episodes (median decrease in ANC was 21 μeq/L).

At the high-ANC (~150 to 200 μeq/L) Piney River site on basaltic (69%) and granitic (31%) bedrock, base cation concentrations declined during episodes (in contrast with the other two sites where base cation concentrations increased). SO_4^{2-} and NO_3^- concentrations usually increased. The change in ANC during the episodes studied ranged from 9 to 163 μeq/L (median 57 μeq/L) (Eshleman and Hyer, 2000). Changes in base cation concentrations during episodes contributed to changes in the ANC of Paine Run, had little effect in Staunton River, and contributed to decreases in ANC in Piney River.

The most acidic conditions in Shenandoah National Park streams occur during high-flow periods, in conjunction with storm or snowmelt runoff. There are several different mechanisms of episodic acidification in operation in these streams, depending at least in part on the bedrock geology of the stream watershed. The relative importance of the major processes that contribute to episodic acidification varies among the streams, in part as a function of baseflow streamwater ANC which is largely controlled by bedrock geology. S-driven acidification was an important contributor to episodic loss of ANC at all three study sites, probably because S adsorption by soils occurs to a lesser extent during high-flow periods. This is due, at least in part, to diminished contact between drainage water and potentially adsorbing soil surfaces along the shallow flow paths. Dilution of base cation concentrations during episodes, which is an acidifying process, was most important at the high-ANC site.

Thus, episodic acidification of streams in Shenandoah National Park can be attributed to a number of causes, including dilution of base cations and increased concentrations of sulfuric, nitric, and organic acids (Eshleman et al., 1995; Hyer et al., 1995). For streams having low pre-episode ANC, episodic decreases in pH and ANC and increases in toxic Al concentrations can have adverse effects on fish populations. However, not all of the causes of episodic acidification are related to acidifying deposition. Base-cation dilution and increase in organic acid anions during high-flow conditions are natural processes. At least for streams in the Shenandoah National Park. the contribution of N, indicated by increased NO_3^- concentrations, evidently has been related to forest defoliation by the gypsy moth (Eshleman et al., 1998; Webb et al., 1995). Significant contributions of H_2SO_4, indicated by increased SO_4^{2-} concentrations during episodes in some streams, is an effect of atmospheric deposition and the dynamics of S adsorption on soils (Eshleman and Hyer, 2000).

A recent study by Deviney et al. (2006) used hourly ANC predictions over short time periods to compute recurrence intervals of annual water-year minimum ANC values for periods of 6, 24, 72, and 168 h. They extrapolated the results to the rest of the catchments using catchment geology and topography. On the basis of the models, they concluded that many streams in the park have 6- to 168-h periods of low ANC values, which may stress resident fish populations (Deviney et al., 2006). Specifically, on the basis of a 4–year recurrence interval, approximately 23% of the land area (44% of the catchments) can be expected to have conditions for 72 continuous hours that are indeterminate with

respect to brook trout suitability (ANC 20 to 50), episodically acidic (ANC 0 to 20), or chronically acidic (ANC less than 0). Many catchments were predicted to have successive years of low-ANC values potentially sufficient to extirpate some species (Deviney et al., 2006). The authors of the study reported that smaller catchments are more vulnerable to adverse effects of episodic acidification than larger catchments underlain by the same bedrock. Catchments with similar topography and size are more vulnerable if underlain by less basaltic and carbonate bedrock.

Biological Effects of Acidification

A robust relationship between acid-base status of streams and fish species richness was documented in Shenandoah National Park in the 3−year Fish in Sensitive Habitats (FISH) study (Bulger et al., 1999). Numbers of fish species were compared among 13 streams spanning a range of pH and ANC conditions. There was a highly significant (p <0.0001) relationship between stream acid-base status (during the 7 year period of record) and fish species richness among the 13 streams. The streams with the lowest ANC hosted the fewest species (Figure 3-15). This study demonstrated biological differences in low- versus high-ANC streams, including species richness, population density, condition factor, age, size, and field bioassay survival. Of particular note was that both episodic and chronic mortality occurred in young brook trout exposed in a low-ANC stream, but not in a high-ANC stream (MacAvoy and Bulger, 1995), and that blacknose dace (*Rhinichthys atratulus*) in low-ANC streams were in poor condition relative to blacknose dace in higher-ANC streams (Dennis et al., 1995; Dennis and Bulger, 1995).

Bulger et al. (1999) observed a positive relationship between condition factor and pH in streams in Shenandoah National (Figure 3-26). Dennis and Bulger (1995) also found a reduction in condition factor for blacknose dace in waters near pH 6.0. The four populations depicted in (Figure 3-26) with the lowest condition factor had mean habitat pH values within or below the range of critical pH values at which Baker and Christensen (1991) estimated that negative population effects for blacknose dace are likely for the species. The mean condition factor of fish from the study stream with the lowest ANC was about 20% lower than that of the fish in best condition. Comparisons with the work of Schofield and Driscoll (1987) and Baker et al. (1990b) suggest that pH values in the low-pH streams are also near or below the limit of occurrence for blacknose dace populations in the Adirondack region of New York (Sullivan et al., 2003).

MacAvoy and Bulger (1995) used multiple bioassays over 3 years in one of the low-ANC streams as part of the FISH project to determine the effect of stream baseflow and acid episode stream chemistry on the survival of brook trout eggs and fry. Simultaneous bioassays took place in mid- and higher-ANC reference streams. Acidic episodes, with associated low pH and elevated inorganic Al concentrations and high streamwater discharge, caused rapid fish mortality in the low-ANC stream, while the test fish in the higher-ANC stream survived (Bulger et al., 1999).

$$y = 1.194x + 1.519, r^2 = .777$$
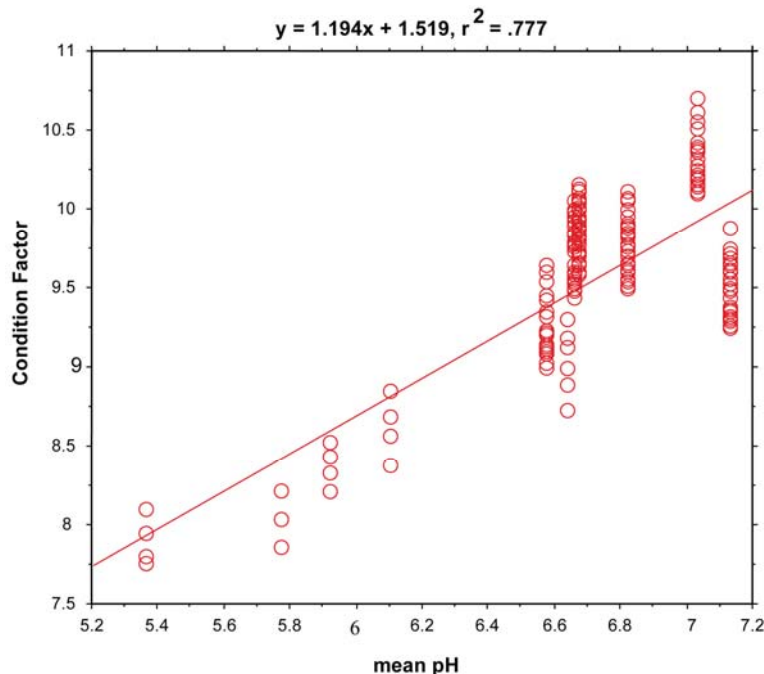
Figure 3-26. **Length-adjusted condition factor (K), a measure of body size in blacknose dace (Rhinichthys atratulus) compared with mean stream pH among 11 populations (n = 442) in Shenandoah National Park. Values of pH are means based on quarterly measurements, 1991–1994; K was measured in 1994. The regression analysis showed a highly significant relationship (p <0.0001) between mean stream pH and body size, such that fish from acidified streams were less robust than fish from circumneutral streams.**

Modeling of Acidification, Recovery, and Critical Loads

Dynamic models have been used in Shenandoah National Park to help determine whether the changes in surface water chemistry that have occurred over the past one to two decades will continue and whether they will reach levels needed to support biological recovery. The most commonly used models are described in Annex B and details of these analyses are discussed below. In general, model forecasts indicated that under base case conditions (those expected under existing or anticipated emissions controls) surface water ANC in the southern Appalachians (and in parts of the Adirondacks) would be likely to decline in the future. In terms of soil chemistry, projected future improvements in both regions appear to be slow and in most cases do not reach a base saturation of 20% or more within the next 100 years.

MAGIC model simulations for streams in Shenandoah National Park by Sullivan et al. (2003) suggested that acidifying deposition would have to be decreased substantially to improve and maintain acid-sensitive streams at levels of ANC that would be expected to protect against ecological harm. In addition, it took a long time for these streams to acidify in the past; because of complexities related to soil conditions, it would take even longer for them to recover in the future. To protect against chronic acidity in the year 2100, with associated probable lethal effects on brook trout, the authors predicted that S deposition to the most geologically sensitive siliciclastic lithology watersheds in the park would have to be kept below about 9 kg S/ha/yr for the next 100 years (Sullivan et al., 2007a). Before the Industrial Revolution, most streamwater in the Park had ANC higher than about 50 μeq/L. To promote ANC recovery to 50 μeq/L in the future, to protect against general ecological harm, S deposition to Si-based (siliciclastic) watersheds in the park would have to be kept below about 6 kg S/ha/yr. Finally, the authors

predicted that some watersheds will likely not recover streamwater ANC to values above 50 μeq/L over the next century even if S deposition is reduced to zero (Sullivan et al., 2007a).

Simulation and mapping of watershed responses to historical changes in acidifying deposition (from preindustrial to current) by Cosby et al. (2006) suggest that large areas of Shenandoah National Park have suffered deterioration of both soil and stream conditions. The changes in soil condition have been relatively modest up to the present time, with areas in the southern district of the park moving from classification of "moderate concern" (watershed average mineral soil percent base saturation 10% to 20%; the historical baseline) to "elevated concern" (average mineral soil percent base saturation 5% to 10%) as a result of leaching of base cations from the soils in response to S deposition. Simulation results indicated that deterioration in stream conditions has been more severe than for soil conditions, with large areas in the southern district and some smaller areas in the central and northern districts moving from "moderate concern" (average stream ANC 50 to 100 μeq/L) to "elevated concern" (average stream ANC 0 to 50 μeq/L). Neither soil nor stream conditions have shown any improvement from 1980 to the present in response to the decline in acidifying deposition over the last 25 years.

Simulation and mapping of watershed responses to predicted future changes in acidifying deposition by Cosby et al. (2006) were developed following U.S. EPA methods for preparation of emissions inventory inputs into air quality modeling for policy analysis and rule making purposes. These alternate emissions scenarios were based on existing emission control regulations and several proposed alternatives. The model output suggested that the responses of soil conditions to changes in S deposition are expected to be relatively slow. In the short term (by the year 2020), neither improvement nor further deterioration is likely to be observed in soil condition regardless of the future deposition scenario considered. However, model results suggested that constant deposition at 1990 levels would produce worsening soil conditions in the park by the year 2100 with the development of areas of "acute concern" (average percent soil base saturation below 5%) in the southern district. Although the scenarios of possible reduced future deposition did not produce worsening soil conditions, neither did they indicate any improvement in soil condition, even in the long term.

Simulated responses of stream conditions were more rapid than those of soils. In the short term (by the year 2020), constant deposition at 1990 levels would likely produce further deterioration in stream condition. The scenarios of future deposition reductions failed to reverse the deterioration of stream condition that has occurred during the last century. In the long term (by year 2100), the effects of the deposition reduction scenarios begin to diverge. The moderate S deposition reduction scenario (69% reduction from 1990 values) did not produce improvement in stream chemistry relative to current conditions. The larger deposition reduction scenario (75%), by contrast, produced modest improvements in stream chemistry by 2100. However, even the relatively large S deposition reductions of this scenario did not result in a simulated return of stream conditions to the preindustrial state.

To develop projections of probable past and future responses of aquatic biota to changing S deposition in Shenandoah National Park, the MAGIC model was coupled by Sullivan et al. (2003) with several empirical models that linked biological response to past and future model projections of water quality. Unlike MAGIC, which is a geochemical, process-based model, the biological effects estimates were based on observed empirical relationships rooted in correlation and expressed as linear relationships. Correlation does not necessarily imply causality, but an observed pattern of covariation between variables does provide a quantitative context for extrapolation. In this case, the projections did not require extrapolation beyond the observed ranges of observations, and therefore the projections were statistically robust. To the extent that the observed empirical relationships used in the coupled models do in fact reflect the effects of acid stress on aquatic biota, the projections were also biologically robust.

Dynamic water chemistry model projections were combined with biological dose-response relationships to estimate declines in fish species richness with acidification. A relationship derived from the data in Figure 3-15 was used by Sullivan et al. (2003) with stream ANC values predicted by the MAGIC model to provide estimates of the expected number of fish species in each of the modeled streams for the past, present and future chemical conditions simulated for each stream. The coupled geochemical and biological model predictions were evaluated by comparing the predicted species

richness in each of the 13 streams with the observed number of species that occur in each stream. The agreement between predicted and observed species numbers was good, with a root mean squared error in predicted number of species across the 13 streams of 1.2 species. The average error was 0.3 species, indicating that the coupled models were unbiased in their predictions. Model reconstructions of past species richness in the streams suggested that historical loss of species had been greatest in the streams located on the most sensitive geological class (siliciclastic). The average number of species lost from streams on the three bedrock types examined was estimated as 1.6 species on siliciclastic bedrock, 0.4 species on granitic bedrock, and 0.4 species on basaltic bedrock. In the case of the siliciclastic streams, the projected past changes were much larger than the average error and root mean squared error of the coupled models, suggesting that the projections were reasonably robust.

3.2.5. Ecosystem Services

The evidence reviewed in this ISA supports that acidification of ecosystems is primarily driven by NO_X, NH_X and SO_X. Ecosystem services, as defined by Hassan et al. (2005), are broadly grouped into four main categories (see Section 3.1.3). The specific effects of ecosystem acidification may be grouped into these categories as follows.

- **Supporting**: altered nutrient cycling, decreased biodiversity, decline of productivity

- **Provisioning:** decline in the richness, abundance, and/or health of fish, other aquatic species and some terrestrial trees

- **Regulating:** decline in water and soil quality

- **Cultural**: decline in forest aesthetics, fishing, ecotourism and cultural heritage values related to ecosystem integrity and biodiversity

There are few publications that directly evaluate the ecological effects of acidification in terms of valuation. Even though acidification is well documented in the scientific literature, the lack of valuation studies related to them limits full assessments of terrestrial damages from NO_X and SO_X pollution. As noted in the case study (see Section 3.2.4.4.), the Adirondack Park in New York is among the best documented of all areas affected by acidic deposition in the U.S. This park has been the subject of numerous valuation studies in recent decades on cultural ecosystem services (Morey and Shaw 1990; Mullen and Menz 1985; Englin et al., 1991; Cameron and Englin 1997; Banzhaf et al., 2006). There are currently no studies on the valuation of supporting or regulating ecosystem services.

3.3. Nutrient Enrichment Effects from Nitrogen Deposition

The ecological effects caused by atmospheric deposition of N_r are the main focus of this section. As discussed previously, the scope of this ISA includes assessment of all forms of N compounds that contribute to nutrient enrichment. The various chemical forms of N can be broadly divided into two groups: nonreactive (N_2 gas) and N_r. Nonreactive N_2 gas composes 80% of the total mass of the Earth's atmosphere, but it is not biologically available until transformed into reactive forms of N. N_r includes all biologically and chemically active N compounds in the Earth's atmosphere and biosphere (Galloway et al., 2003). The N_r group includes inorganic reduced forms (e.g., NH_3 and NH_4^+), inorganic oxidized forms (e.g., NO_X, HNO_3, N_2O, NO_3^-), and organic N compounds (e.g., urea, amine, proteins, nucleic acids) (Galloway et al., 2003). Atmospheric N deposition may be composed of numerous chemical species besides oxides, all of which contribute to ecosystem nutrient enrichment. The ISA evaluates the nutrient effects of NO_X in combination with all other forms of N_r deposition for which information is

available. Agricultural lands are excluded from this discussion because crops are routinely fertilized with amounts of N (100 to 300 kg N/ha) that exceed air pollutant inputs even in the most polluted areas (U.S. EPA, 1993a). These high rates of fertilization can contribute to ground water NO_3^- contamination and eutrophication of some surface waters, especially estuaries. However, the environmental effects of agricultural N fertilization is beyond the scope of this assessment.

Organisms in their natural environment are commonly adapted to a specific regime of nutrient availability. Change in the availability of one important nutrient, such as N, may result in imbalance in ecological stoichiometry, with effects on ecosystem processes, structure and function (Sterner and Elser, 2002). In general, ecosystems that are most vulnerable to nutrient enrichment from atmospheric N deposition are those that receive high levels of deposition relative to non-anthropogenic N loading, those that are N-limited, or those that contain species that have evolved in nutrient-poor environments. The most common experimental designs to quantify the effects of N deposition on ecosystems are N addition, N gradient, or observation correlated to changing pollution levels over time. N addition experiments often use NH_4NO_3 or $(NH_4)_2SO_4$ additions to simulate the chemical species in atmospheric N_r deposition. Deposition gradient experiments often only measure oxidized and reduced forms of N and therefore do not adequately identify all components of N_r deposition. Therefore, publications addressing N additions or deposition gradients often do not include data on all components of N_r.

The following discussion of N-nutrient deposition begins with the N cascade, which provides a conceptual foundation for discussing the effects of N on the structure and function of ecosystems. Subsequent sections include the effects of N deposition on: N cycling, C cycling, biogenic GHG emissions, biodiversity, as well as the characterization of sensitive ecosystems and regions in the U.S. Information is presented for ecosystems in which atmospheric deposition dominates total N_r input (i.e. many non-managed terrestrial ecosystems) and ecosystems in which atmospheric deposition constitutes a proportion of total N_r load (e.g., some wetlands and estuarine ecosystems).

3.3.1. Reactive Nitrogen and the Nitrogen Cascade

N_r is one of the most important nutrients in practically all ecosystems (Vitousek and Howarth, 1991). N_r is required by all organisms because it is a major constituent of both the nucleic acids that determine the genetic character of all living things and the enzymes and proteins that drive the metabolism of every living cell (U.S. EPA, 1993a; Galloway, 1998; Galloway and Cowling, 2002). It is of critical importance in plant metabolism and it often governs the utilization of P, K and other nutrients.
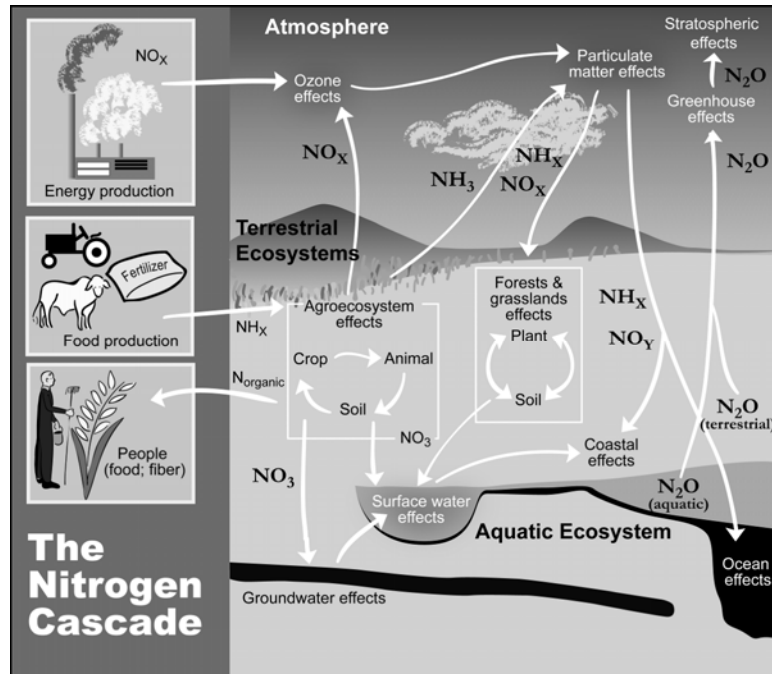
Figure 3-27. Illustration of the N cascade showing the movement of the human-produced N_r as it cycles through the various environmental reservoirs in the atmosphere, terrestrial ecosystems, and aquatic ecosystems.

An increase in global N_r has occurred over the past century, largely due to three main causes: widespread cultivation of legumes, rice, and other crops that promote conversion of N_2 gas to organic N through biological N fixation; combustion of fossil fuels, which converts both atmospheric N_2 and fossil N to NO_X; and synthetic N fertilizer production via the Haber-Bosch process, which converts nonreactive N_2 to N_r to sustain food production and some industrial activities (Galloway and Cowling, 2002 Galloway et al., 2003). Food production accounts for much of the conversion from N_2 to N_r, and accounts for geographic redistribution of N as food is shipped to meet population demands and often returned to the environment via waste water.

N_r accumulates in the environment on local, regional, and global scales (Galloway, 1998; Galloway and Cowling, 2002; Galloway et al., 2003). This accumulation occurs in the atmosphere, soil, and water (Galloway and Cowling, 2002), with a multitude of effects on humans and ecosystems (Galloway, 1998; Rabalais, 2002; Van Egmond et al., 2002; Townsend et al., 2003). The sequence of transfers, transformations, and environmental effects is referred to as the "N cascade" (Galloway and Cowling, 2002; Galloway et al., 2003)(Figure 3-27).

In general, the results of the N cascade and the various transformations in the N cycle can be both beneficial and detrimental to humans and to ecosystems (Galloway and Cowling, 2002; Galloway and Aber, 2003). Among the most important effect of atmospheric N deposition are aquatic eutrophication, changes in the structure of terrestrial plant communities, disruptions in nutrient cycling, increased soil emissions of nitrous oxide (N_2O; a potent greenhouse gas), accumulation of N compounds in the soil, soil-mediated effects of acidification (see Section 3.2), and increased susceptibility of plants to stress factors (Aber et al., 1989, 1998; Bobbink, 1998; Driscoll et al., 2003c; Fenn et al., 1998).

3.3.2. Nitrogen Enrichment Effects on N Cycling

Given the complexity of the N cycle, a broadly applicable and well-tested predictive model of these interactions has not yet been developed. There is scientific information with which to make generalizations about how ecological and biogeochemical processes respond to N deposition. Significant scientific advancements in recent years have included refinement of theoretical foundations of nutrient limitation, development and improvement of analytical technologies, and improved understanding of the role of N in regulating or influencing the cycling of other elements, especially C (see Section 3.3.3).

The key steps in the N cycle that are outlined in Figure 3-28. Processess within this cycle include N fixation, assimilation, mineralization (conversion of organic N to simple inorganic forms), nitrification (conversion of reduced inorganic N to oxidized inorganic N), and denitrification (the reduction of NO_3^- to NO, N_2O, and N_2 gas by microbes under anaerobic conditions). These steps generally require biologically mediated transformations. Key organisms involved in transforming N from one form to another include plants and microbes.
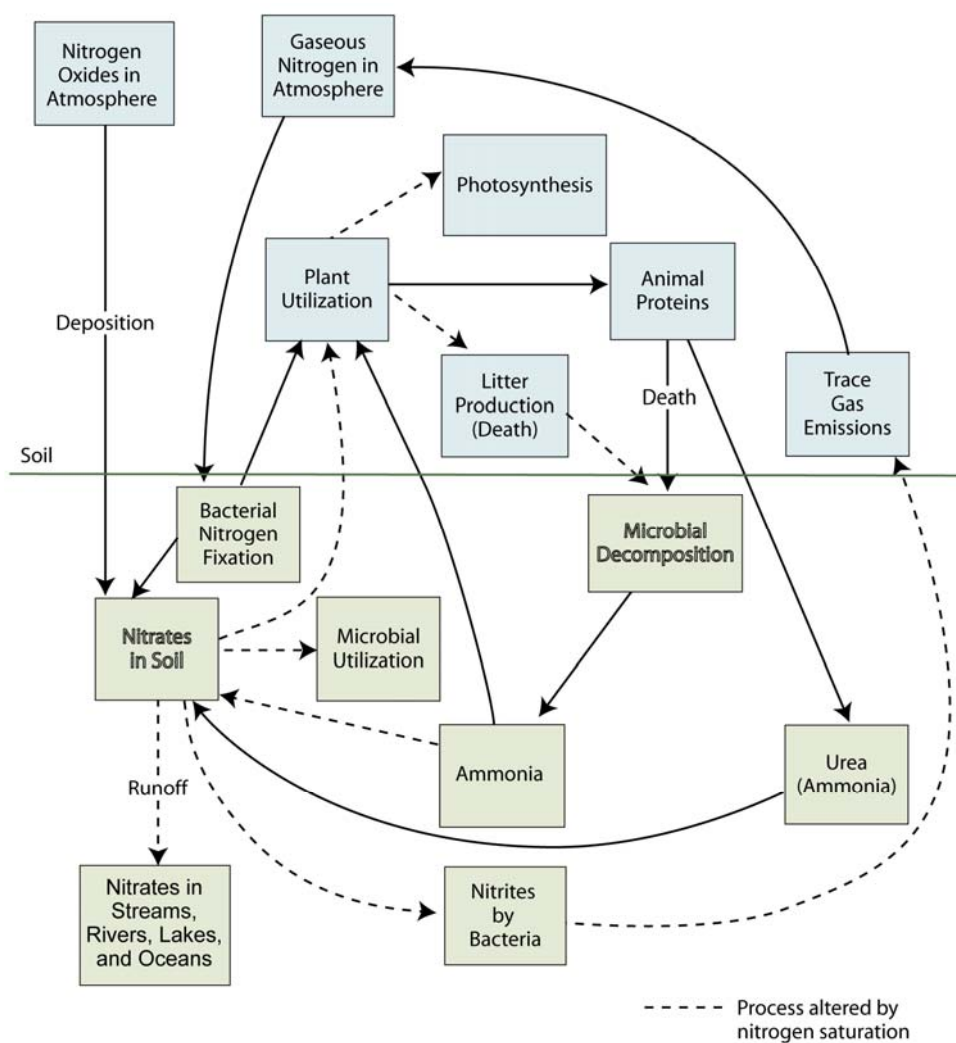
Figure 3-28.   N cycle (dotted lines indicated processes altered by N saturation).

In addition to direct effects on the ecosystem where it is deposited, N can be exported from the system and cause environmental effects in adjacent ecosystem. The two principal mechanisms for N export or loss from ecosystems are leaching and denitrification. Leaching removes N from terrestrial or transitional ecosystems, but adds it to aquatic ecosystems. Thus, an export from one ecosystem becomes an import to another. Denitrification removes N from terrestrial, transitional, and aquatic ecosystems and adds it to the atmosphere (Davidson et al., 2000; Seitzinger et al., 2006). Although denitrification provides a pathway for removing excess N from ecosystems, incidental production of NO and N_2O during denitrification is of concern due to the roles of NO as a precursor in the $p(O_3)$, and N_2O as a potent greenhouse gas (see Section 3.3.4 for N deposition effects on biogenic N_2O flux). Here leaching and denitrification are discussed in addition to other fundamentals of N cycling in terrestrial, transitional, and aquatic ecosystems.

3.3.2.1. Terrestrial Ecosystems

N-deposition affects terrestrial ecosystems throughout large areas of the U.S. N-availability to plants in soil is largely controlled by the process of N mineralization, or the microbial conversion from organic N to simple amino acids and then to inorganic forms such as NH_4^+ and NO_3^- (Schimel and Bennett, 2004). The two-step, aerobic, microbial process of autotrophic nitrification converts NH_4^+ to NO_3^-. Nitrification is an acidifying process, releasing 2 mol hydrogen ion (H^+) per mol NH_4^+ converted to NO_3^- (Reuss and Johnson, 1986; see Section 3.2 and Annex B for the effects of acidifying deposition). As the N cycle becomes enriched through cumulative N addition, N becomes more abundant, competition among organisms for N decreases, net nitrification rates often increase, and NO_3^- can leach from the ecosystem (Aber et al., 1989 and 2003).

Numerous experimental ^{15}N-addition studies have been conducted as a way of understanding how N cycles through terrestrial ecosystems. These studies have shown that trees typically take up only a small fraction of added ^{15}N; the vast preponderance is retained in the soil (Nadelhoffer et al., 1999a; Providoli et al., 2005; Templer et al., 2005; Tietema et al., 1998). This pattern persists even a decade after ^{15}N application (Nadelhoffer et al., 2004), but these experiments have been criticized for applying ^{15}N directly to the soil surface, thereby precluding direct canopy uptake of N from wet or dry deposition (Sievering, 1999; Sievering et al., 2000). Canopy ^{15}N experiments are now underway, but have not yet been published. Comparisons of rates of N deposition in throughfall and in total deposition suggest that forest canopies can take up an average of 16% of total atmospheric N input (Lovett, 1992), but this interception can be considerably higher (up to 90%) in some N-limited forests with large epiphyte loads (e.g., Klopatek et al., 2006). It remains unclear how much of the N from deposition that is retained in vegetation is then used in photosynthetic enzymes (e.g., Bauer et al., 2004).

N in forest ecosystems is stored primarily in the soil, and soil N often exceeds 85% of the total ecosystem N (Bormann et al., 1977; Cole and Rapp, 1981). Most soil N is contained in organic matter, typically bound in humic material or organo-mineral complexes that are resistant to microbial degradation. This N is not directly available for biological uptake by plants or microbes or for leaching loss into ground water or surface water.

Only what is termed the mineralizable, or labile, pool of N in the soil is considered to be biologically active (Aber et al., 1989). Bioavailable N often controls photosynthesis and net primary productivity (NPP) (e.g., Field and Mooney, 1986). Plants obtain N from the soil by absorbing NH_4^+, NO_3^-, or simple organic N compounds through their roots, or N is taken up by symbiotic organisms (e.g., fungi, bacteria, cyanobacteria) in plant roots (cf. Lilleskov et al., 2001; Schimel and Bennett, 2004). Plant roots, nitrifying bacteria, and microbial decomposers within the soil utilize, and compete for, this available soil N pool. Plant uptake of N can be energetically costly, as NO_3^- must be reduced to NH_4^+, and NH_4^+ fixed into amino acids before N can be used in plant processes. Some species reduce NO_3^- in their leaves, taking advantage of excess energy from photosynthesis, whereas other species are restricted to the more energy expensive approach of reducing NO_3^- in their roots.

N Saturation

The term N-saturation refers to the condition whereby the input of N to the ecosystem exceeds the requirements of terrestrial biota, and consequently an elevated fraction of the incoming N leaches from soils to surface waters. The original description of N saturation by Aber et al. (1989) described four stages. It was revised by Stoddard (1994) and Aber et al. (1998) (Figure 3-29). In Stage 0, N inputs are low and there are strong N limitations on growth. Stage 1 is characterized by high N retention and a fertilization effect of added N on tree growth. Stage 2 includes the induction of nitrification and some NO_3^- leaching, though growth may still be high. In Stage 3 tree growth declines, nitrification and NO_3^- loss continue to increase, but N mineralization rates begin to decline. While not all terrestrial ecosystems move through the stages of N saturation at the same rate or in response to the same N loading, several experimental N addition studies and a survey of 161 spruce-fir stands along a N deposition gradient support the concept of N saturation progressing from the onset of increase in net nitrification and NO_3^- leaching loss to the eventual decline in tree growth and increase in tree mortality (Aber et al., 1998).
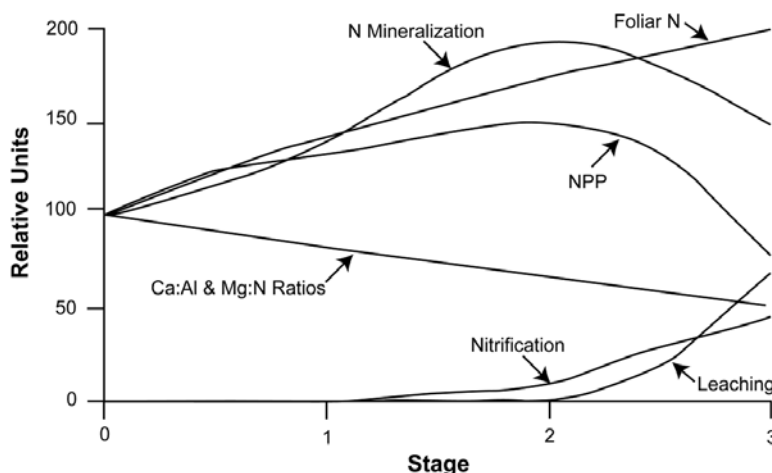
Figure 3-29. **Schematic illustration of the response of temperate forest ecosystems to long-term, chronic N additions. Changes from initial hypotheses of Aber et al. (1989) include the reduction in N mineralization in stage 3 and the addition of foliar Ca:Al and Mg:N ratios.**

Decades of atmospheric deposition of N have increased the availability of NO_3^- and NH_4^+ in some terrestrial ecosystems to levels where excess N availability results in net nitrification and associated NO_3^- leaching in drainage water. Severe symptoms of N saturation have been observed in the northern hardwood watersheds at Fernow Experimental Forest near Parsons, West Virginia (Peterjohn et al., 1996); in high-elevation, nonaggrading spruce-fir ecosystems in the Appalachian Mountains (Cook et al., 1994); throughout the northeastern U.S. (Aber et al., 1989; 1998); and lower-elevation eastern forests (Edwards and Helvey, 1991; Peterjohn et al., 1996; Adams et al., 1997, 2000).

Mixed conifer forests and chaparral watersheds with high smog exposure in the Los Angeles Air Basin also are N-saturated and exhibit the highest stream water NO_3^- concentrations documented within wildlands in North America (Bytnerowicz and Fenn, 1996; Fenn et al., 1998). In general, it is believed that deciduous forest stands in the eastern U.S. have not progressed toward N-saturation as rapidly or as far as coniferous stands. Deciduous forests may have a greater capacity for N retention than coniferous forests. In addition, deciduous forests tend to be located at lower elevation and receive lower atmospheric

inputs of N. Many deciduous forests have higher rates of N uptake and greater N requirement than coniferous forests (Aber et al., 1998).

NO_3^- Leaching

Nitrate leaching is the process of nitrate moving from one ecosystem compartment to another. The nitrate may first leach from terrestrial ecosystems to soil drainage waters where it then increases surface water NO_3^- concentrations and may be exported downstream. Because the pathway of NO_3^- leaching crosses over multiple ecosystem types is discussed in both the terrestrial, wetland and aquatic sections of the ISA. Two of the primary indicators of N enrichment in forested watersheds are the leaching of NO_3^- in soil drainage waters and the export of NO_3^- in stream water, especially during the growing season (Stoddard, 1994). The concentration of NO_3^- in surface water provides an indication of the extent to which N deposited atmospherically or otherwise leaches from the terrestrial ecosystem.

In most upland forested areas in the U.S., most N received in atmospheric deposition is retained in soil (Nadelhoffer et al., 1999a). Several different data compilations indicate that 80% to 100% of N deposition is retained or denitrified within terrestrial ecosystems that receive less than about 10 N/ha/yr (Aber et al., 2003; Dise and Wright, 1995; Kristensen et al., 2004; MacDonald et al., 2002; Sullivan, 2000a). In general, because much of the atmospherically deposited N is retained within the terrestrial ecosystem or denitrified during export, a relatively small fraction of this N reaches downstream estuaries (Alexander et al., 2002; Castro et al., 2001; Seitzinger et al., 2002; van Breemen et al., 2002).

Despite retention of most atmospheric N deposition within the terrestrial environment, N-related adverse effects on aquatic life do occur (Driscoll et al., 2003d). For example, although 70% to 88% of atmospheric N deposition was retained in the Catskill Mountains watersheds in upstate New York, fish populations could not be sustained because high NO_3^- concentrations in stream water during high flows caused the concentrations of inorganic Al to reach toxic levels (Lawrence et al., 1999; see Section 3.2).
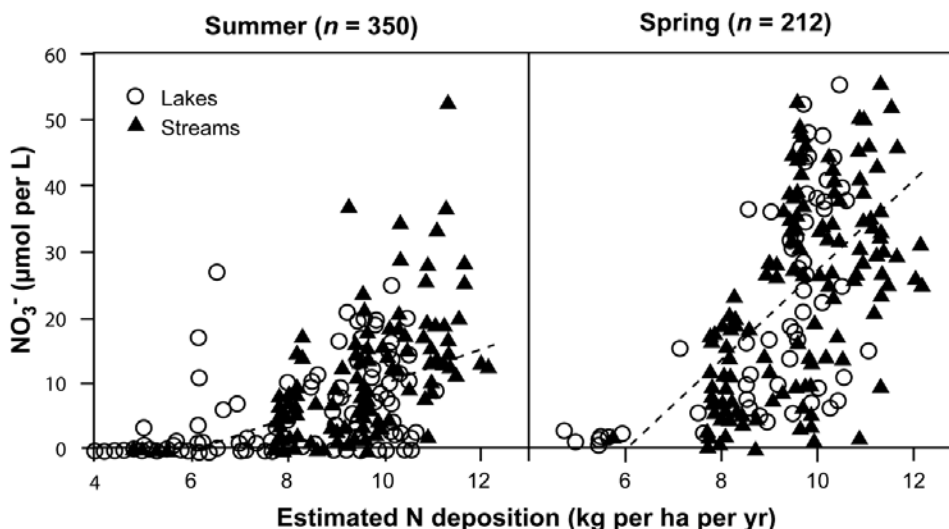
Figure 3-30. Surface water NO_3^- concentrations as a function of N deposition at the base of each watershed in summer and spring. N deposition to the whole watershed may be 2 to 6 kg N/ha/yr greater than at the base.

In the northeastern U.S., an analysis by Aber et al. (2003) of data collected during the mid- to late 1990s from lakes and streams suggested that nearly all N deposition is retained or denitrified in northeastern watersheds that receive less than about 8 to 10 kg N/ha/yr. An analysis of N deposition to forestland in the northeastern U.S. based on Ollinger et al. (1993) suggested that approximately 36% of the forests in the region received 8 kg N/ha/yr or more and may therefore be susceptible to elevated NO_3^- leaching (Driscoll et al., 2003d). Aber et al. (2003) further found that surface water NO_3^- concentrations exceeded 1 μeq/L in watersheds receiving about 9 to 13 kg N/ha/yr of atmospheric N deposition (Figure 3-30). The lakes and streams found to have high NO_3^- concentration were those receiving N deposition above this range, but responses were variable among those receiving high N deposition. Above this range, mean NO_3^- export increased linearly with increasing deposition at a rate of 0.85 kg NO_3^- kg N/ha/yr for every 1 kg N/ha/yr increase in deposition, although there was considerable variability in N retention among watersheds at higher rates of deposition (Figure 3-31) (Aber et al., 2003).
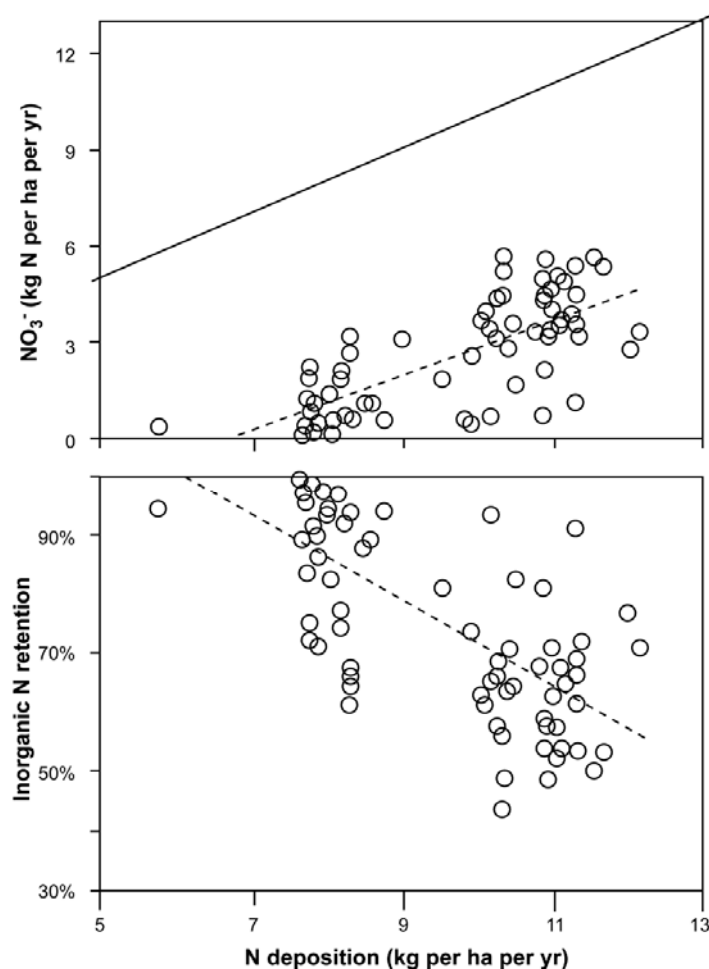
Figure 3-31. **a) N export in stream water as a function of N deposition at the base of sampled watersheds. N export is represented by the equation $NB_{exp} = 0.85\ N_{dep} - 5.8$; $r^2 = 0.56$; $p < 0.001$. (b) Watershed N retention decreases as N deposition at the base of the watersheds increases (N retention = -0.07 N deposition + 1.44; $r^2 = 0.50$).**

In the West, a study of mixed conifer forests of the Sierra Nevada and San Bernardino mountains reported that the deposition load that causes the onset of NO_3^- leaching is 17 kg N/ha/yr. Several studies in the Rocky Mountains indicate that the onset of NO_3^- leaching in alpine catchments occurs at approximately 10 kg N/ha/yr (Baron et al., 1994; Williams and Tonnesen 2000).

In other studies, the isotopic signature of ^{18}O in streamwater NO_3^- indicates that only a small percentage of the incoming NO_3^- from atmospheric deposition leached directly to drainage waters (e.g., (Spoelstra et al., 2001; Burns and Kendall, 2002; Pardo et al., 2004). The rest of the NO_3^- that leached from the terrestrial ecosystem was cycled by biota in soils or streams before being exported. That cycled N may have originated in atmospheric deposition, but its origin was not identified.

In general, field experiments have shown that NO_3^- leaching can be induced by chronic addition of N (Kahl et al., 1993, 1999; Norton et al., 1999; Edwards et al., 2002a; Peterjohn et al., 1996) (See Table 3-11). Several N-exclusion studies in Europe demonstrated that decreases in N deposition produced immediate reductions in NO_3^- leaching from forest stands (Gundersen et al., 1998; Quist et al., 1999). At a regional scale, the leaching transport of N from terrestrial to freshwater systems has important implications beyond its impact on upland lakes and streams, because N exports can ultimately also contribute to the eutrophication of coastal ecosystems (Howarth et al., 1996; Driscoll et al., 2003d).

Denitrification

The role of denitrification in terrestrial ecosystems is important to understand the fraction of the atmospheric deposition that is returned to the atmosphere and therefore does not have direct effects on terrestrial and aquatic ecosystems. Denitrification has been difficult to measure directly in most ecosystems, due to the difficulty of measuring small changes in N_2 and to the great degree of spatial and temporal heterogeneity inherent in the denitrification process (Davidson and Seitzinger, 2006). Additional information on measurement techniques is available in Annex C.

Denitrification is accomplished by facultative anaerobic denitrifying bacteria, and occurs only under anaerobic conditions in the presence of sufficient NO_3^- and organic C. Hence, most terrestrial denitrification occurs in "hotspots," that is, in sporadically wet places or times or in anaerobic soil microsites (McClain et al., 2003; Seitzinger et al., 2006). The high organic matter content of terrestrial soils provides an ample supply of C. Therefore, the factors that typically limit the rate of denitrification in terrestrial ecosystems are the NO_3^- supply and the occurrence of anaerobic conditions (See Annex C for additional studies and Section 3.3.4 for an analysis of N deposition effects on N_2O flux from terrestrial and wetland ecosystems).

Using a simple model of the fate of global N inputs to terrestrial ecosystems, Seitzinger et al. (2006) estimated that denitrification in terrestrial soils removed 46% (124 Tg/yr) of global N inputs from all sources (N deposition, fertilizer, and N fixation). Half of this denitrification (66 Tg/yr) was estimated to have occurred in agricultural systems. However, this model assumed that all N entering terrestrial systems was leached as NO_3^- if it was not taken up by plants. Hence, the model overestimated the potential for denitrification by the extent to which N accumulated in soils or ground water (Seitzinger et al., 2006).

Foliar N Concentration

The concentration of N in plant foliage, especially in forest trees, can provide an indicator of nutrient enrichment (McNeil et al., 2007) (Table 3-11). This indicator may be especially relevant because there is a potential to acquire regional-scale data on foliar N through remote sensing techniques. This allows rapid assessment of N status across large land areas. The N content in tissue of some plant species varies in proportion to N inputs (Baddeley et al., 1994; Hyvarinen and Crittenden, 1998; Pitcairn et al., 2003). Similarly, species typical of nutrient-poor environments tend to accumulate the amino acid arginine in plant tissue (Van Dijk and Roelofs, 1988). Therefore arginine concentration varies in proportion to N inputs. Foliar N and foliar arginine concentrations both provide good indices of N deposition effects.

There are reported interactions between N content and insects. Increased N content has been shown to increase palatability to defoliating insects and therefore increasing the extent of defoliation (Nordin et al., 1998; Forkner and Hunter, 2000).

Soil Carbon-to-Nitrogen Ratio

The N and C cycles are tightly coupled in forest soils. For example, NO_3^- leaching has been correlated with forest floor C:N. Nitrification and NO_3^- leaching rates are generally low on sites having soil C:N ratios above about 22 to 25 (Lovett et al., 2002; Ross et al., 2004). The C:N ratio of the forest floor can be changed by N deposition over time, although it is difficult to detect a change over time against the background of spatial heterogeneity (Galloway et al., 2003). The forest floor C:N ratio has been used as an indicator of ecosystem N status in mature coniferous forests (Table 3-11).

Table 3-11.   Summary of biogeochemical indicators of N deposition to terrestrial ecosystems.

Region/Country	Endpoint	Observations	Forest Type/ Species	Reference
White Mountains New Hampshire	Soil C:N Ratio Nitrification	Observation: field relationships between soil C:N ratio, canopy lignin:N ratio, and high spectral resolution remote sensing data was used to predict spatial patterns in C:N. Remote-sensed data were obtained from NASA's Airborne Visible and Infrared Imaging Spectrometer (AVIRIS) instrument. Preliminary regional estimates of soil C:N ratio suggested that 63% of the land area in the region had C:N below 22, which was suggested as a critical threshold for the onset of nitrification. Below C:N = 22, increasing, but variable, rates of nitrification were found.	Broadleaf and mixed conifer/ sugar maple (*Acer saccharum*), red maple (*Acer rubrum*), American beech (*Fagus grandifolia*), yellow birch (*Betula alleghaniensis*), paper birch (*Betula papyrifera*), red spruce (*Picea rubens*), balsam fir (*Abies balsamea*), eastern hemlock (*Tsuga canadensis*)	Ollinger et al. (2002)
Europe	Soil C:N Ratio NO_3^- Leaching	Observation and Modeling: data from 160 sites across Europe was used to determine that NO_3^- leaching when soil C:N ratio is above 30. NO_3^- leaching occurs with foliar N <13 mg N/g. The responses of soil solution nitrate concentration to changes in N input are more pronounced in broadleaf than in coniferous forests, because in European forests broadleaf species grow on the more fertile soils.	Broadleaf and mixed conifer/ three broadleaf species (*Quercus robur, Quercus petraea, Fagus sylvatica*) and six conifer species (*Picea abies, Picea sitchensis, Abies alba, Pinus sylvestris, Pinus nigra, Pseudotsuga menziesii*)	Kristensen et al. (2004)
Northeast U.S.	Soil C:N Ratio Nitrification surface water $[NO_3^-]$ foliar [N ion]	Observation: In a compilation of soil C:N and nitrification data from 250 plots across an N deposition gradient of 3.3 – 12.7 kg N/ha/yr showed a statistically significant but weak correlations between both soil C:N and nitrification to annual N deposition rate. Across plots, nitrification increased sharply as C:N ratio (by mass) decreased below about 22. Significant foliar chemistry alterations only were attributable to effects of climate and elevation. Strong relationship between surface water $[NO_3^-]$ and flux across N deposition gradient.	Hardwood and conifer forests; Red Spruce (*Picea rubens*), Sugar maple (*Acer saccharum*)	Aber et al. (2003)

Region/Country	Endpoint	Observations	Forest Type/ Species	Reference
Continental Divide, Colorado	Soil C:N Foliar C:N Mineralization Soil %N Foliar N:Mg Foliar N:P	Deposition Gradient: Comparison of Englemann spruce forest stands on the east (3 to 5 kg N/ha/yr) and west (1 to 2 kg N/ha/yr) slopes of the Continental Divide in Colorado. The east slope receives higher levels of N deposition due to proximal agricultural and urban areas. East slope sites showed (1) lower soil organic horizon C:N ratio, (2) lower foliar C:N ratio, (3) higher potential net mineralization, and (4) higher percent N, N:Mg ratio, and N:P ratio in foliage. These results suggested that even moderate levels of N deposition input can cause measurable changes in spruce forest biogeochemistry.	Englemann spruce (*Picea englemannii*) dominated mesic spruce-fir forests; *Vaccinium* spp. Understory, subalpine fir (*Abies lasiocarpa*) and lodgepole pine (*PInus contorta*)	Rueth and Baron (2002)
Adirondacks, New York	Foliar [N]	Deposition Gradient: Eight of nine major canopy tree species had increased foliar N in response to a gradient of roughly 4 to 8 kg N/ha/yr for wet deposition (total N deposition gradient of 5 to 10 N ha/yr). Species specific differences were strongly related to two functional traits that arise from within-leaf allocations of N resources: leaf mass per area and shade	Broadleaf and mixed conifer/ paper birch (*Betula papyrifera*), yellow birch (*Betula alleghaniensis*), red maple (*Acer rubrum*), sugar maple (*Acer saccharum*), American beech (*Fagus grandifolia*), white pine (*Pinus strobus*), eastern hemlock (*Tsuga canadensis*), balsam fir (*Abies balsamea*), red spruce (*Picea rubens*)	McNeil et al. (2007)
Scotland	Foliar [N] & [arginine]	Deposition Gradient: Total tissue N and arginine concentrations were closely correlated with both atmospheric NH_3 concentration and estimated N deposition (r^2 >l.97 and >0.78, respectively), and this affected species composition in a gradient of nitrophilous plant species closer to the N source replacing the more N sensitive species	Mixed woodland; plantation of *Pinus sylvestris; Fagus sylvatica*; various mosses, ferns, forbs	Pitcairn et al. (2003)
Vermont	Nitrification Basal area growth Mineralization Foliar %N	Field Addition: Additions of 25 kg N/ha/yr to spruce plots (ambient bulk deposition 5.4 kg N/ha/yr), in which net nitrification did not occur before treatment, triggered net nitrification in the second year of treatment, whereas nitrification was not triggered until the third year in plots receiving 19.8 kg N/ha/yr. Positive correlation between forest floor % N, nitrification potential and foliar %N increased with N addition	High elevation spruce-fir stand; Red spruce (*Picea rubens*), maple (*Acer spp.*) and birch (*Betula spp.*)	McNulty et al. (1996)
Colorado	Mineralization Nitrification Foliar [N] Organic Soil [N] and C:N	Field Addition: Additions of 25 kg N/ha/yr to plots in Loch Vale watershed (ambient bulk deposition ~3.2–5.5 kg N/ha/yr) doubled N mineralization rates and stimulated nitrification, while the addition of the same amount to plots receiving ambient bulk deposition of ~1.7 kg N/ha/yr in Fraser Experimental Forest elicited no microbial response but significantly increased foliar and organic soil horizon N, and decrease soil C:N.	Old-growth spruce-fir; Engelmann spruce (*Picea engelmanni*) Subalpine fir (*Abies lasiocarpa*) Lodgepole pine (*Pinus contorta*) *Vaccinium spp.*	Rueth et al. (2003)

Region/Country	Endpoint	Observations	Forest Type/ Species	Reference
Harvard Forest, MA	Soil [NO$_3^-$] Soil [NH$_4^+$]	Field Addition: Elevated concentrations of NO$_3^-$ plus NH$_4^+$ in soil water observed after 1 year of 150 kg N/ha/yr doses, and after 5 years of 50 kg N/ha/yr doses. In plots that received additions of 150 kg N/ha/yr, elevated concentrations were detected on the seventh year. In plots receiving 50 kg N/ha/yr, elevated soil concentrations were not observed after 15 years of treatment.	*Red pine plantation and mixed hardwood/ Pinus resinosa*	Magill et al. (2004)
Bear Brook Watershed, ME	NO$_3^-$ Leaching	Field Addition: Ammonium sulfate ([NH$_4$]$_2$SO$_4$) fertilization of a forested watershed resulted in long-term increases in NO$_3^-$ concentration in stream water and high annual export of N. The annual retention of N decreased from 96 % to 81%, with a cumulative retention of 82% of N inputs, mostly in soil. The export of N from the reference watershed has declined from 178 to 23 kg N/ha/yr during the treatment period.	Mixed hard and soft wood	Kahl et al., (1999); Norton et al. (1999)
Tunk Mountain Watershed, ME	NO$_3^-$ Leaching	Observation: Changes in watershed processing of nitrogen may influence acid-base status of surface waters. The very low concentrations of NH4+ and NO$_3^-$ in lake waters in Maine (Kahl et al., 1991) suggest that changes in N-status have not played a major role in changes in ANC. However, N loss to surface waters is well documented in Adirondack surface waters (Driscoll et al., 1991), coincident with the decline in ANC. The Wild River data also showed increased NO$_3^-$ concentrations during 1964-83. Different responses in soil reactions among sites could account for the different response of ANC to changing deposition patterns.	Mixed hard and soft wood	(Kahl et al., 1993)
Fernow Experimental Forest, WV	NO$_3^-$ Leaching Ca Leaching	Observation: The percentage of conductivity attributable to NO increased similar to concentration. In contrast, the percentage of conductivity attributable to Ca^{2+} decreased slightly overtime. The Ca^{2+} is believed to be pairing with the NO as the NO is leaching through the soil. While nitrification in mature stands can be strongly inhibited, limited nitrification, especially in forest gaps, and high anthropogenic inputs of NO$_3^-$ probably were primary sources of leached NO$_3^-$ Preferential adsorption of SO$_4^{2-}$, rather than NO$_3^-$, on soil colloids is given as an explanation for the lack of retention of NO$_3^-$ in the soil system and subsequent leaching to the stream.	Mixed hardwoods/ principally northern red oak (*Quercus rubra* L.), American beech, red maple (*A. rubrum* L.), sugar maple, sweet birch (*B. lenta* L.), and black cherry (*Prunus serotina*)	Edwards and Helvey (1991)
Fernow Experimental Forest, WV	NO$_3^-$ leaching	Observation: N saturation observed. Progressive increases in streamwater NO$_3^-$ and Ca concentrations were measured at the Fernow Experimental Forest in the 1970s and 1980s. This watershed has received higher N deposition (average throughfall input of 22 kg N/ha/yr of N in the 1980s) than is typical for low-elevation areas of the eastern U.S., however (Eagar et al., 1996), and this may help to explain the observed N saturation.	Mixed hardwoods	Peterjohn (1996)

Region/Country	Endpoint	Observations	Forest Type/ Species	Reference
Fernow Experimental Forest, WV	NO_3^- leaching	Field Addition: Annual experimental additions of 40 kg S/ha/yr and 35 kg N/ha/yr as ammonium sulfate fertilizer were applied to a 34 ha watershed with a 25-year-old stand of central Appalachian hardwoods. An adjacent watershed served as the control. After 5 years of treatment (total additions of 275 kg S/ha and 220 kg N/ha), stream water NO_3^-, Ca^{2+}, Mg^{2+} concentrations and export increased. Soil solution concentrations provide evidence that the treatment watershed is nitrogen-saturated, which was unexpected for such a young stand.	Mixed hardwoods	Adams et al. (1997; 2000)
Fernow Experimental Forest, WV	NO_3^- Leaching	Field Addition: Three times per year N was added as $(NH_4)_2SO_4^{2-}$ to watersheds. In the spring and autumn 7.1 and 8.1 kg N/ha/yr were added, and in the summer 21.3 and 24 kg N/ha/yr were added. Anion adsorption on WS3 apparently delayed increases in SO_4^{2-} leaching, but resulted in enhanced early leaching losses of Cl and NO_3^-. Leaching of Ca and Mg was strongly tied to NO_3^- and SO_4^{2-} leaching. F-factors for WS3 baseflow and peakflow indicated that the catch ment was insensitive to acid neutralizing capacity reductions both before and during treatment, although NO_3^- played a large role in reducing the treatment period F-factor.	Mixed hardwoods	Edwards et al. (2002b)
Greater Los Angeles area, CA	N Saturation	Observation: plant communities exposed to air pollution received sufficiently high levels of atmospheric N deposition to be N saturated. Symptoms of N saturation were evident in mixed conifer or chaparral sites receiving atmospheric deposition of 20 to 25 kg N/ha/yr or higher. In the more highly polluted study site (1) accumulation of NO_3^- in foliage of plants (2) accumulation of NO_3^- in soil (3) NO and N_2O emissions higher (4) higher N mineralization (5) low foliar and soil C:N, high foliar N:P.	Chaparral and mixed conifer forest; Ponderosa pine (*Pinus ponderosa*), Jeffrey pine (*P. jeffreyi*), white fir (*Abies concolor*), California black oak (*Quercus kelloggii*), iincense cedar (*Calocedrus decurrens*), sugar pine (*Pinus lambertiana*), bracken fern (*Pteridium aquilinum* var. pubescens Underw.)	Fenn et al. (1996)
Sierra Nevada and San Bernardino, CA	NO_3^- Leaching	Critical load for increased NO_3^- leaching calculated as 17 kg N/ha/yr and the empirical critical load for adverse effects on lichen communities is 3.1 kg N/ha/yr. Much of this study area is far above such levels of N deposition.	Mixed conifer forests; Ponderosa pine *(Pinus ponderosa)* Jeffrey pine *(P. jeffreyi.);* white fir *(Abies concolor);-* California black oak *(Quercus kelloggii),* incense cedar *(Calocedrus decurrens,* the lichen *Letharia vulpina*	Fenn et al. (2008)
San Bernardino Mountains, CA	N Saturation	Deposition Gradient: over the range of 12.1 to 31.7 kg N/ha/yr, the site nearest to urban area (Los Angeles) received much more N deposition, as well as other pollutants (i.e. S deposition), and received much more fog, coinciding with much more wet deposition of N in that site. Ecosystem was N saturated, as evidenced by high streamwater NO_3^- concentration, 151 and 65 µeq/L at upper and lower ends, respectively, of Devil Canyon West Fork	Mixed conifer forest; Ponderosa pine (*Pinus ponderosa*); Jeffrey pine (*P. jeffreyi*); white fir (*Abies concolor*); California black oak (*Quercus kelloggii*); incense cedar (*Calocedrus decurrens*)	Fenn et al. (2000)

Region/Country	Endpoint	Observations	Forest Type/ Species	Reference
San Bernardino Mountains, CA	DIN Export	Deposition Gradient: over the range of 11to 40kg N/ha/yr , dissolved inorganic N (DIN) export was scale dependent, with highest export occurring in watersheds of ~150/ha. Differences attributed to temporal asynchrony between N availability and biological demand	Mixed forest- chaparral, hardwood, coniferous; White alder (*Alnus rhombifolia*); California Bay Laurel (*Umbellularia californica*); Scrub oak (*Quercus dumosa*); Coast live oak (*Quercus agrifolia*)	Meixner and Fenn (2004)
Rocky Mountain Alpine Catchments	N Retention	Results from several studies suggest that the capacity of Rocky Mountain alpine catchments to sequester N is exceeded at input levels of about 10 kg N/ha/yr	Rocky Mountain alpine	Baron et al. (1994); Williams and Tonnessen (2000)

Disturbance and stand age effects on N retention

The varying degree of N assimilation, leaching and microbial transformation often reflect differences in N status among treatment sites. These variations have most often been attributed to disturbance history, dating back a century or more (Goodale and Aber, 2001). Sites which have undergone disturbances that cause loss of soil N, such as logging, fire, and agriculture, tend to be most effective at retaining atmospheric and experimental inputs of N. Fire causes substantial N losses from ecosystems (see Table 3-12). Timber harvest contributes to nutrient removal from the ecosystem via biomass export and acceleration of leaching losses (Bormann et al., 1968; Mann et al., 1988). In particular, logging contributes to loss of N and Ca^{2+} from the soil (Tritton et al., 1987; Latty et al., 2004). N retention capability often decreases with stand age, which suggests that older forests are more susceptible than younger forests to becoming N-saturated (Hedin et al., 1995). Aber et al. (1998) surmised that land use history may be more important than cumulative atmospheric deposition of N in determining the N status of a forest ecosystem. See Annex C for a more detailed discussion of how disturbance affects N cycling.

Table 3-12.   Effects of fire on nutrient concentrations in forests in Nevada and California.

Region/Country	Endpoint	Observations	Grassland Type/ Species	Reference
Lake Tahoe Basin, Nevada	Nutrient concentration in runoff	Field Measurement: Compared runoff from fixed plots within wildfire-burned and unburned areas in both summer and winter seasons. Wildfire increased the frequency and magnitude of elevated nutrient in discharge runoff for all 3 parameters studied: NO_3^- N, ammonium nitrogen, phosphate P. The mobilization of nutrients was increased due to wildfire, but the lack of O horizon material (surface organic layer of mineral soils) after burning may ultimately reduce discharge concentrations over time	Jeffery pine, white fir, sugar pine, Sierra chinquapin, currant, and snow brush, bitterbrush Soils: Cagwin series	Miller (2006)

Region/Country	Endpoint	Observations	Grassland Type/ Species	Reference
Lake Tahoe, Nevada	Leaching, N concentrations in forest floor and soil	Field Measurement: Fire and post-fire erosion caused large and statistically significant losses of C, N, P, S, Ca, and Mg from the forest floor; Before the burn, there were no significant differences in leaching, but during the first winter after the fire, soil solution concentrations of NH_4^+, NO_3^-, ortho-P, and (especially) SO_4^{2-} were elevated in the burned area, and resin lysimeters showed significant increases in the leaching of NH_4^+ and mineral N. The leaching losses of mineral N were much smaller than the losses from the forest floor and A11 horizons. The major short-term effects of wildfire were on leaching, whereas the major long-term effect was the loss of N from the forest floor and soil during the fire.	Sierra Nevada mixed conifer forest: Jeffrey pine (*Pinus jeffreyi*), white fir (*Abies concolor*), sugar pine (*Pinus lambertiana*) and incense-cedar (*Calocedrus decurrens*). Understory vegetation: green leaf manzanita (*Arctostaphylos patula*), snowbrush (*Ceanothus velutinus*). Soils: Cagwin series: coarse, loamy sand	Murphy et al. (2006)
Sierra Nevada, California	Forest floor and nutrient content, soil chemical properties, and soil leaching	Field Experiment: investigated the effect of forest thinning treatments and prescribed burning on C, N, ortho-P, and SO_4^{2-} in the forest floor organic layer and surface soil mineral horizons. The study included a prescribed fire and three timber harvest treatments: whole-tree thinning (WT) cut-to-length thinning (CTL), and no harvest (CONT). There were no statistically significant effects of burning on soil C, N, C:N, Bray-extractable P, exchangeable Ca^{2+}, K^+, or Mg^{2+}. Burning had no significant effect on soil solution pH, ortho-P, SO_4^{2-}, NO_3^-, or NH_4^+ as measured by ceramic cup lysimeters and no effect on the cumulative leaching of ortho-P, NO_3^-, or NH_4^+ as measured by resin lysimeters. Prescribed fire had little impact on total and soluble nutrients in the upper mineral soil layer. Loss of N capital from the forest floor appears to be the major effect of prescribed burning.	Jeffery pine (*Pinus jeffreyi*) forest	Murphy et al. (2006)
Sierra Nevada, California	Nutrient budget of C, N, Ca, P, K, S, Mg	Field Measurement/Modeling: effects of fire, post-fire salvage logging, and revegetation on nutrient budgets were estimated for a site that burned in a wildfire in 1981. 2 decades after the fire, the shrub ecosystem contained less C and more N than the adjacent forest ecosystem. C was exported in biomass during salvage logging and will not be recovered until forest vegetation occupies the site again. Most N was lost via volatilization during the fire rather than in post-fire salvage logging (assuming that foliage and O horizons were combusted). Comparison of the pre-fire and present day N showed the lost N was rapidly replenished in O horizons and mineral soils, probably due to N-fixation by snowbush. No differences in ecosystem P, K, or S contents or in soil extractable P or S between the shrub and forested plots. K^+, Ca^{2+}, and Mg^{2+} were greater in shrub than in adjacent forested soils. The large increase in Ca resulted from either the release of Ca from non-exchangeable forms in the soil or the rapid uptake and recycling of Ca by post-fire vegetation.	110–130 year old Jeffery pine (*Pinus jeffreyi*)	Johnson et al. (2005)

Region/Country	Endpoint	Observations	Grassland Type/ Species	Reference
Little Valley, Nevada	C and N loss	Field Measurement/ Modeling: On an ecosystem level, the fire consumed approximately equal percentages of C and N (12 and 9%, respectively), but a greater proportion of aboveground N (71%) than C (21%). Salvage logging was the major factor of C lost, and C lost will not be replenished until forest vegetation is reestablished. N_2 fixation by *Ceanothus velutinus* in the post-fire shrub vegetation appears to have more than made up for N lost by gasification in the fire over the first 16 year, and may result in long-term increases in C stocks once forest vegetation takes over the site. N loss from the fire equaled >1,000 years of atmospheric N deposition and >10,000 years of N leaching at current rates. Calculations of C and N losses from theoretical wildfires in the IFS sites show similar patterns to those in Little Valley. Calculated losses of N in most of the IFS sites would equal many centuries of leaching. Conceptual models of biogeochemical cycling in forests need to include episodic events such as fire.	Jeffery pine (*Pinus jeffreyi*) Mesic forests in the Integrated Forest Study (IFS).	Johnson et al. (2004)
N. Lake Tahoe, Nevada; Truckee, California (Tahoe National Forest); Glenbrook, Nevada (Lake Tahoe Basin)	C and N loss	Field measurement: The quantities of C and N volatilized from the forest floor by prescription fire in the Sierra Nevada were measured at three sites: Marlene, Sawtooth and Spooner. C losses calculated by the weight method were 6.12, 7.39, and 17.8 mg C/ha at the Sawtooth, Marlene, and Spooner sites. N losses calculated by the weight method were 56.2, 60.8, and 362 kg N/ha, at the Sawtooth, Marlene, and Spooner sites, respectively. N volatilization during prescribed fire is the dominant mechanism of N loss from these systems.	Marlene: Jeffery pine, white fir, snowbrush, squawcarpet, greenleaf manzanita, pinemat manzanita, Soils: Cagwin series Sawtooth: Jeffery and Ponderosa pine, Soils: Kyburz series Spooner: mixed confer, red fir, white fir, snowbrush and manzanita, Soils: Tahoma series	Caldwell et al. (2002)

3.3.2.2. Wetland Ecosystems

N dynamics in wetland ecosystems vary in time, with type of wetland and with environmental factors, especially water availability (Howarth et al., 1996). A wetland can act as a source, sink, or transformer of atmospherically deposited N (Devito et al., 1989) and these functions can vary with season and with hydrological conditions. Vegetation type, physiography, local hydrology, and climate all play significant roles in determining source and sink N dynamics in wetlands (Devito et al., 1989; Koerselman et al., 1993; Arheimer and Wittgren, 1994; Mitchell et al., 1996).

N Fixation and Mineralization

N fixation and mineralization are two mechanisms by which N becomes available for plants. It is documented that ecosystems may derive substantial amounts of new N inputs via N_2-fixation (Hurd et al., 2001). N mineralization has been shown to increase with N addition, and this can cause an increase in wetland N export to adjacent surface water (Groffman, 1994). Drought has been shown to inhibit mineralization and nitrification in soils leading to a decrease in NO_3^- concentration (Foster et al., 1992). However, drying may stimulate mineralization upon re-wetting (Kieft et al., 1987). A laboratory study

showed that within 24 h of re-wetting, extractable NO_3^- concentration in dried peat increased approximately 7-fold as compared to continuously moist peat (Watmough et al., 2004).

NO_3^- Leaching

Leaching losses from wetlands are rarely considered separately from leaching losses from upland terrestrial environments and the wet environments that occur in upland catchments. That is, when leaching losses from terrestrial ecosystems are quantified based on stream exports, estimated leaching losses implicitly include the net loss of NO_3^- from both terrestrial ecosystems and adjacent wetlands. Leaching losses of NO_3^- in water derived directly from wetlands are often small because of NO_3^- removal by denitrification. However, hydrologic flowpaths that deliver water to streams by bypassing wetland soils can deliver substantial quantities of NO_3^--rich water from terrestrial uplands.

Denitrification

Transitional ecosystems can remove significant quantities of NO_3^- from water because they represent a convergence of conditions of NO_3^-, O_2, and C that are requisite for denitrification. Denitrification is frequently optimized when NO_3^- from more oxic upland areas passes through wet, often C-rich and anoxic wetlands. In some cases NO_3^- concentration was found to be a better predictor of denitrification rates than soil moisture (Groffman, 1994), and there is evidence that in some cases denitrification is limited by C and NO_3^- supply in wetlands (Ashby et al., 1998).

Denitrification has been studied in riparian zone ecosystems (Lowrance, 1992; Pinay et al., 1993; Watts and Seizinger, 2001; Hefting et al., 2003) and seems to be related to C availability. Generally, riparian soils that are both rich in organic matter and anaerobic have high denitrification potential. Where riparian soils are aerobic, however, nitrification, rather than denitrification, can be the dominant process (Stevens et al., 1997).

Table 3-13.   Summary of N cycling studies for wetlands.

Region/Country	Endpoint	Observations	Wetland Type / Species	Reference
Canada	Soil [N]	Deposition Gradient: N deposition ranged from 2.7 to 8.1 kg N/ha/yr across 23 ombrotrophic peatlands. Soil [N] ($g/m^2/yr$) increased linearly with deposition (y[wet deposition] =3.50(soil N) +0.64; r^2=0.29, p<0.001)	*Peatland*	Moore et al. (2004)
Adirondack Mountains, New York	N sources used by vegetation	Isotopic tracer: The study estimated N_2 fixation by speckled alder in five wetlands by the ^{15}N natural abundance method and by acetylene reduction using a flow-through system. The study of alder-dominated wetlands showed that alder derived >85% of leaf N from N-fixation at an estimated rate of 43 kg N/ha/yr. Conclusion: speckled alder in wetlands of northern New York State relies heavily on N_2 fixation to meet N demands, and symbiotic N_2 fixation in speckled alders adds substantial amounts of N to alder-dominated wetlands in the Adirondack Mountains. These additions may be important for watershed N budgets, where alder-dominated wetlands occupy a large proportion of watershed area	*Alnus incana*	Hurd et al. (2001)
Rhode Island	Denitrification	Observation: the highest rates of denitrification (4 to 135 kg N/ha/yr) were observed in very poorly drained soils on nutrient-rich parent material, with lower rates (1.2 to 5.3 kg N/ha/yr) in soils that were better-drained or less nutrient-rich.		Groffman (1994)

Region/Country	Endpoint	Observations	Wetland Type / Species	Reference
Catskill Mountain, New York	Denitrification	Field Addition: Higher rates of denitrification per unit area associated with soils with higher organic matter content and water-filled pore spaces. Instantaneous NO_3^- concentration did not correlate with denitrification rate, suggesting that the rates of NO_3^- supply through microbial production or hydrologic transport were more important than in situ NO_3^- concentration. Denitrification was most stimulated by amendments with glucose alone or glucose plus NO_3^-, suggesting limitation by labile C and NO_3^- supply.		Ashby et al. (1998)
Adirondack Mountains, New York, Archer Creek Watershed	Denitrification	Ecological Gradient: Changes in stream N were measured in one riparian wetland and one beaver meadow: Strong effects of peatlands on local N concentrations, but little effect of peatlands on adjacent stream chemistry, since peatland ground water contributed little to streamflow.	Peatlands	McHale et al. (2004)
Smith Creek, Michigan	Denitrification	Field Additions/Measurement: Over a two-year period >1400 individual samples of subsurface waters were analyzed. Both spatial patterns of water chemistry and additions of labile C to demonstrate that the supply of degradable C from shallow flowpaths limited rates of NO_3^- removal via denitrification in near-stream zones. Thus, the immediate near-stream region may be especially important for determining the landscape-level function of many riparian wetlands.	Riparian wetlands	Hedin et al. (1998)

N deposition may stimulate biogenic emissions if the N supply is limiting the rate of denitrification in wetland soils (Hayden and Ross, 2005). Previous studies suggest that elevated N inputs to wetlands will often increase the rate of denitrification (Dierberg and Brezonik, 1983; Broderick et al., 1988; Cooper, 1990). This process increases the emission of nitrous oxide, a greenhouse gas, to the atmosphere (see Section 3.3.4).

In a review of the effects of riparian zones on NO_3^- removal from ground water, Hill (1996) concluded that there are large losses of NO_3^- to denitrification within riparian zones. However, there are important limitations to the generalization that riparian wetlands prevent the leaching of NO_3^- to streams. Not all water entering streams passes directly through adjacent riparian zones, and denitrification in deep subsurface flowpaths is often limited by the supply of labile C. In addition, not all streamwater passes through riparian zones, and large amounts of water may follow flowpaths beneath organic-rich riparian zones, allowing significant transport of NO_3^- to streams (McHale et al., 2004). The supply of degradable C from shallow flowpaths has been shown to limit rates of NO_3^- removal via denitrification in near-stream zones (Hedin et al., 1998).

In summary, wetland soils can be hotspots of NO_3^- removal by denitrification in anoxic sites rich in NO_3^- and labile C, but denitrification rates can be limited by suboptimal conditions of any single biogeochemical factor, and deep water flowpaths can bypass wetland denitrification altogether (see Table 3-13).

3.3.2.3. Freshwater Aquatic Ecosystems

As previously noted in Section 3.3.2.1., a large fraction of atmospheric N deposition is retained in most terrestrial ecosystems. Nevertheless, the fraction that does leach to streams can make a substantial contribution to total N inputs of downstream rivers and estuaries, especially in the eastern U.S. (Driscoll et al., 2003d).

NO₃⁻ Leaching

After NO_3^- leaches from terrestrial ecosystems it arrives in adjacent aquatic systems and may then be transported downstream. The following discussion is intended to build on the information introduced in Section 3.3.2.1 by addressing elevated NO_3^- concentration in surface water; and NO_3^- leaching downstream. The concentration of NO_3^- in surface water can serve as a chemical indicator of N input in excess of ecosystem requirements, and is relevance to acidification and eutrophication effects on surface water.

The relationship between wet deposition of N and streamwater output of NO_3^- was evaluated by Driscoll et al. (1989) for sites in North America (mostly eastern areas), and augmented by Stoddard (1994). The data showed a pattern of N leaching at wet inputs greater than approximately 5.6 kg N/ha/yr, which probably corresponds with a total N deposition input of about 8 to 10 kg N/ha/yr. In the Northeast, a survey of 230 lakes and streams documented NO_3^- concentrations ranging from less than 2 up to 42 μeq/L, with the highest median values occurring in the Adirondacks (Aber et al., 2003) (Figure 3-32).
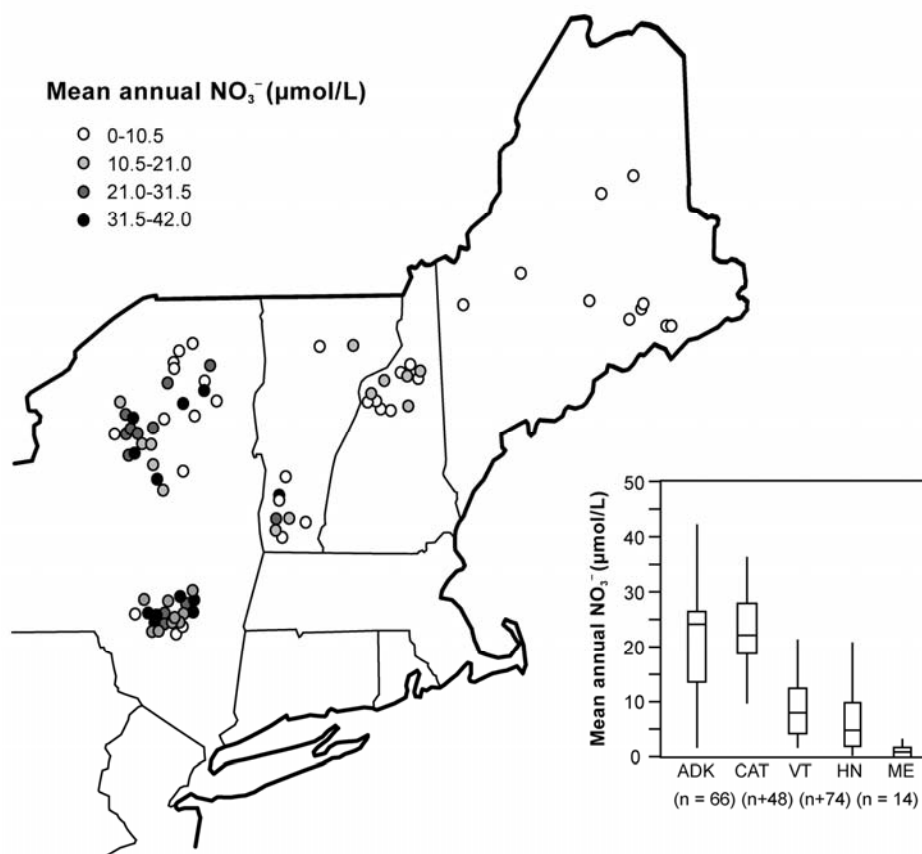
Figure 3-32. **Mean annual NO₃⁻ concentrations in 230 lakes and streams across the northeastern U.S. Inset indicates the median, quartile, and 90% range of mean annual NO₃⁻ in the Adirondacks (ADK), the Catskills (CAT), Vermont (VT), New Hampshire (NH), and Maine (ME).**

In the western U.S., NO_3^- concentrations of freshwater ecosystems have been shown to increase with proximity to urban areas. Results from the Western Lake Survey (WLS) conducted by the U.S. EPA

(Eilers et al., 1987), document increased N concentrations in high elevation lakes adjacent to and downwind of urban centers (Fenn et al., 2003a), such as those found in the Sierra Nevada and Colorado Front Range (see Figure 3-33). For example, NO_3^- concentrations in streamwater during the growing season in the Sierra Nevada were reported to range from 4 to 19 µeq/L (Fenn et al., 2003b). Concentrations above 10 µeq/L are generally considered high.

An interesting example from the Colorado Front Range indicates that lakes on the eastern and western slopes can experience significantly different levels of NO_3^-. A survey of 44 lakes east and west of the Continental Divide indicated that lakes on the western side of the Continental Divide averaged 6.6 µeq/L of NO_3^-, whereas lakes on the eastern side of the divide averaged 10.5 µeq/L of NO_3^- concentration. NO_3^- concentrations above 15 µeq/L have commonly been measured in lakes on the eastern slope of the Front Range, suggesting some degree of N saturation (Baron, 1992), and extreme values as high as 40 µeq/L have also been reported (Campbell et al., 2000). Williams et al. (1996a) concluded that N-saturation is occurring throughout high-elevation catchments of the Colorado Front Range. Many lakes in the Colorado Front Range have chronic NO_3^- concentrations greater than 10 µeq/L and concentrations during snowmelt are frequently much higher, due at least in part to leaching from tundra, exposed bedrock, and talus areas.

In the Unita Mountains of Utah and the Bighorn Mountains of central Wyoming, 19% of the lakes included within the Western Lakes Survey had NO_3^- concentrations greater than 10 µeq/L. This pattern suggests that N deposition in these areas may have exceeded the capability of these lakes to assimilate N. It is unknown if these concentrations of NO_3^- represent effects from anthropogenic sources or if this constituted a natural condition associated with inhibited NO_3^- assimilation in cold alpine environments.
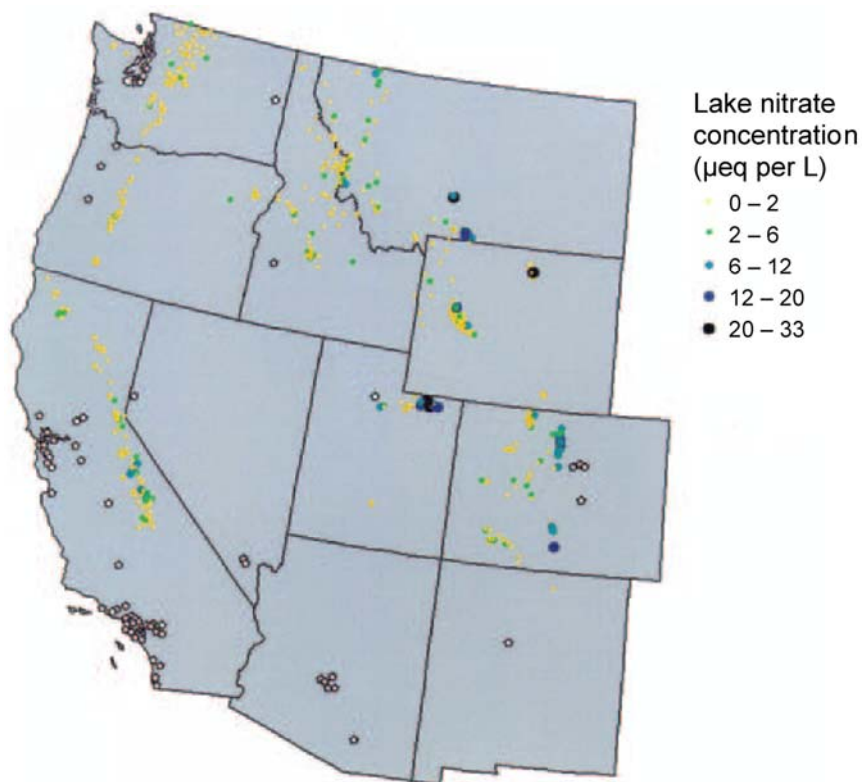
Source: Fenn (2003a). Reprinted with permission.

Figure 3-33. NO_3^- concentrations in high-elevation lakes in western North America. Circles represent cities with a population greater than 100,000.

Dissolved Inorganic Nitrogen

Dissolved inorganic nitrogen (DIN) concentrations in surface waters have been directly linked to wet deposition. Bergstrom and Jansson (2006) evaluated the relationship between wet-deposition and DIN concentration in 4296 lakes across Canada, Europe and the U.S. They calculated a significant correlation showing that DIN concentration increased with increasing N wet-deposition (log (y)= $1.34\log(x) - 1.55$, $r^2 = 0.70$, p <0.001).

Denitrification

Denitrification in freshwater aquatic ecosystems has been studied in small streams most intensively, though some work has been done at larger scales. N is cycled rapidly within streams, especially small streams with large relative areas for contact with benthic surfaces and hyporheic zones. For example, Peterson et al. (2001) found that ^{15}N-NH_4^+ added to streams of various sizes was taken up most rapidly in the smallest streams, and that these headwater streams exported less than 50% of their added NH_4^+. Nevertheless, the long-term fate of this removed or transformed and recycled N is more difficult to assess. Mulholland et al. (2004) found that addition of ^{15}N-NO_3^- to a headwater stream at Walker Branch, TN, indicated a mean uptake length of 35 m under ambient conditions. The uptake length extended three-fold (i.e., reduced uptake) under a modest fertilization treatment, which employed NO_3^- addition of approximately 500 µg N/L. Direct measurements of denitrification of added ^{15}N indicated that denitrification accounted for 16% of the NO_3^- loss under the ambient treatment, and only 1% of NO_3^- uptake under the fertilized treatment. Nearly all of the denitrification occurred as reduction to N_2 gas rather than to N_2O.

Hyporheic losses of NO_3^- to denitrification may be largely controlled by supplies of labile dissolved organic carbon (DOC). Bernhardt and Likens (2002) found that adding 6 mg/L of DOC as acetate to a small stream at Hubbard Brook, NH, reduced stream NO_3^- concentrations from ~5 to <1 µmol/L. In experimental mesocosms designed to mimic hyporheic flowpaths of a small river in the Catskill Mountains, NY, Sobczak et al. (2003) found that adding just 0.5 to 1.0 mg/L DOC from leaf litter resulted in the net consumption of nearly all of the 40 µmol/L NO_3^- in solution. Acetylene block measurements indicated that most NO_3^- loss was due to microbial assimilation rather than denitrification, consistent with the isotopic tracer results of Mulholland et al. (2004).

At large spatial scales, water residence time is the variable most frequently identified as a controller of N loss from aquatic ecosystems examined. Examples include lakes of various sizes (Howarth et al., 1996) and large river basins spanning the northeastern U.S. (Seitzinger et al., 2002). Compiling N loss data sets from a wide range of aquatic ecosystems, Seitzinger et al. (2006) found that water residence time alone explained 56% of the variance in rates of N loss across lakes, rivers, estuaries, and continental shelves, from fast-flowing river reaches (residence time of hour) with 0% to 15% N loss to century-scale turnover lakes that eventually incur 80% to 100% N loss.

N Transport Downstream: Urbanization and Determination of N Sources

The transport of N via rivers and streams represents an important source of N to downstream ecosystems. The transport and loss of N is determined by the net balance of delivery of N by direct atmospheric deposition and from upland terrestrial and associated transitional ecosystem sources, minus the uptake and gaseous loss of that N during transport. Alexander et al. (2002) showed ~70% of the N in headwater streams is from N deposition and the net transport of N from headwater streams is between 40–65% of the total N flux to lower order streams. Numerous studies have illustrated correlations between water quality or ecological conditions and various measures of the extent of urbanization, such as human population density or percent impervious surface (Hachmoller et al., 1991; Charbonneau and Kondolf, 1993; Johnson et al., 1997; Thorne et al., 2000; Alberti et al., 2007); see additional discussion of urbanization in Annex C). In many higher order streams and estuaries, atmospheric N combines with fertilizer N in agricultural areas and with N from wastewater treatment facilities in urban areas, and the

role of atmospheric deposition in residential and urban ecosystems is rarely addressed (see Section 3.3.2.4 for additional discussion of inputs to estuaries).

Table 3-14.   Summary of studies on the effects of N deposition on freshwater aquatic ecosystems.

Region/ Country	Endpoint	Observations	Ecosystem Type / Species	Reference
Eastern U.S.	$[NO_3^-]$ leaching	Observation: NO_3^- leaching observed at 5.6 kg N/ha/yr wet-deposition, which is equal to 8-10 kg N/ha/yr total N deposition.	streams	Driscoll et al. (1989); Stoddard (1994)
Western U.S.	surface water $[NO_3^-]$	Observation: surface water $[NO_3^-]$ is elevated downwind of urban areas in the West.	lakes	Fenn et al. (2003b)
Colorado Front Range, U.S.	surface water $[NO_3^-]$	Deposition gradient: higher levels of deposition on the eastern slope caused elevated lake water $[NO_3^-]$	lake	Baron (1992)
New England	N sources in rivers and streams	Modeling: Application of the statistical model SPARROW (SPAtially Referenced Regression On Watershed attributes) showed that first-order headwaters contributed 65%, 55%, and 40% of the N flux to 2nd, 4th, and higher-ordered catchments, respectively. Atmospheric deposition accounted for almost 70% of the total simulated N load to these headwater streams.	Rivers	Alexander et al. (2002; 2007)
Neuse Estuary, NC	water [N] N sources	Observation: Trends in N and P concentrations from 1998 to 2002 could be explained mainly by a combination of climate, management policies, and urban/agricultural development. Nutrient loading reductions did occur in response to imposed management practices in the watershed, but they were affected by increases in human and livestock population in the watershed. Thus, goals for estuarine and coastal nutrient loading reduction must consider the influence of within-watershed development	Watershed/ estuary	Burkholder et al. (2006)
Chesapeake Bay system	Watershed N sources	Modeling: The Choptank tributary of the Chesapeake Bay had become eutrophic over the last 50-100 years. Systematic monitoring of nutrient inputs began in 1970, and there have been 2- to 5-fold increases in nitrogen (N) and P inputs during 1970–2004 due to sewage discharges, fertilizer applications, atmospheric deposition, and changes in land use. Hydrochemical modeling and land-use yield coefficients suggest that current input rates are 4-20 times higher for N and P than under forested conditions existing 350 year ago. The Choptank watershed (1756 km^2) is dominated by agricultural land use (62%), with only 5% urban development. O_2 concentration in bottom waters of the Patuxent estuary is consistently below 3 mg/L in summer; O_2 levels have been steadily decreasing in the Choptank estuary over the past two decades and now approach 3 mg/L in wet years	Watershed/ estuary	Fisher et al. (1998; 2006)
Chesapeake Bay system	Watershed N sources	Modeling: The Patuxent watershed (2260 km^2) is dominated by forest (64%), with significant urban land use coverage (16%) and less intensive agricultural development (20%). Sewage is a major cause of nutrient enrichment. The low N: P of sewage inputs to the Patuxent results in an N-limited, P-saturated system, whereas the Choptank is primarily limited by N, but with P limitation of phytoplankton during spring river flows. Reduced eutrophication in dry years suggests that both estuaries will respond to significant decreases in nutrients	Watershed/estuary	Fisher et al. (1998; 2006)

In lowland areas, other terrestrial sources of N, such as fertilizer, livestock waste, septic effluent, and wastewater treatment plant outflow, often become much more important than in upland areas. In lowland areas, it is difficult to determine the percent of atmospheric N that leaches to drainage water because there are other ill-defined sources of N to drainage waters. In Table 3-14 studies are summarized that evaluate how atmospheric deposition of N to the estuary surfaces and to the terrestrial watershed interact with the other anthropogenic sources of N to make up the total anthropogenic N load to the system.

3.3.2.4. Estuarine and Coastal Marine Ecosystems

Estuaries and coastal marine environments tend to be N-limited, and many currently receive high levels of N input from human activities (Howarth et al., 1996; Vitousek and Howarth, 1991). The nature and extent of the impacts on estuarine and coastal environments is related, in part, to the export of N from upland systems to coastal environments, as discussed in previous sections. Denitrification is the primary mechanism of N output from the estuary and back to the atmosphere (See Annex C). Important environmental effects of NCAM include increased algal blooms, depletion of dissolved O_2 in bottom waters, and reduction in fisheries and sea grass habitats (Boynton et al., 1995; Howarth et al., 1996; Paerl, 1995, 1997; Valiela and Costa, 1988; Valiela et al., 1990). The general process of estuarine eutrophication is depicted in Figure 3-34.
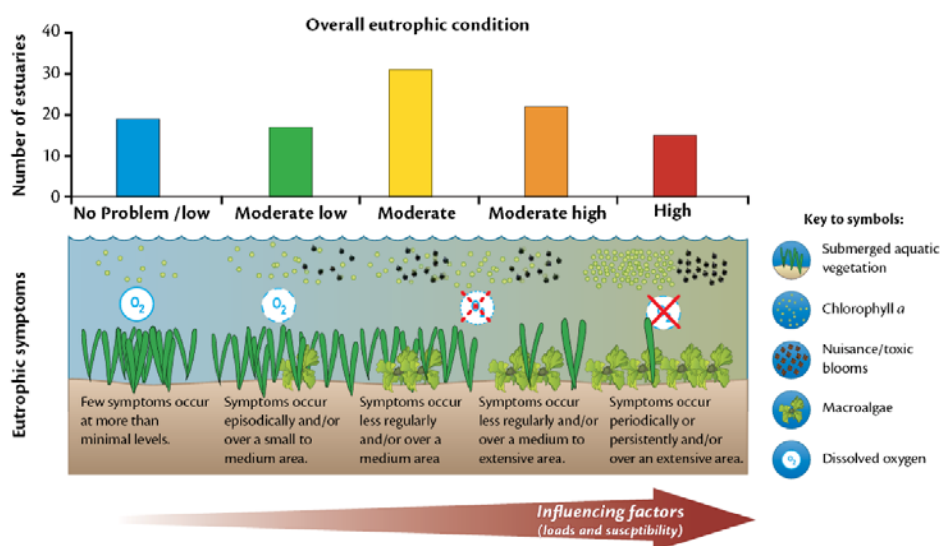
Figure 3-34. **A conceptualization of the relationship between overall eutrophic conditions, associated eutrophic symptoms, and influencing factors (N loads and susceptibility). Overall eutrophic condition was assessed for estuaries throughout the U.S.**

There is broad scientific consensus that N-driven eutrophication of shallow estuaries in the U.S. has increased over the past several decades and that environmental degradation of coastal ecosystems is now a widespread occurrence (Paerl et al., 2001b). For example, the frequency of phytoplankton blooms and the extent and severity of hypoxia have increased in the Chesapeake Bay (Officer et al., 1984) Pamlico estuary in North Carolina (Paerl et al., 1998), and along the continental shelf adjacent to the Mississippi and Atchafalaya River discharges to the Gulf of Mexico (Eadie et al., 1994). A recent national

assessment of eutrophic conditions in estuaries found that 65% of the assessed systems had moderate to high overall eutrophic conditions (Bricker et al., 2007). Estuaries with high overall eutrophic conditions were generally those that received the greatest N loads from all sources, including atmospheric and land-based sources (Bricker et al., 2007). The relative importance of the various N sources varies from estuary to estuary. Atmospheric sources are proportionately more important to estuaries that exhibit large surface area relative to watershed drainage area, and in those estuaries that drain watersheds dominated by natural ecosystems rather than agricultural or urban lands (Boyer et al., 2002).

Assessing the contribution of atmospheric N deposition to total N loading

The importance of atmospheric deposition as a cause of estuary eutrophication is determined by the relative contribution of atmospheric versus non-atmospheric sources of N input. Anthropogenic sources of N to estuarine and coastal ecosystems include atmospheric deposition, wastewater discharge, agricultural runoff, and urban runoff. Valigura et al. (2000) estimated that direct atmospheric deposition to the estuary surface generally constitutes at least 20% of the total N load for estuaries that occupy more than 20% of their watershed. The U.S. EPA (2000b) estimated that between 10% and 40% of the total N input to estuaries in the U.S. is typically derived from atmospheric deposition (http://www.epa.gov/ttn/oarpg/t3/reports/head_2kf.pdf).

Estimates of the relative contribution of each major source have been developed by using the Watershed Assessment Tool for Evaluating Reduction Scenarios for Nitrogen (WATERS-N) model (Castro and Driscoll, 2002). Driscoll et al. (2003a) estimated annual net anthropogenic N inputs to eight large watersheds in the Northeast for the year 1997 (see Figure 3-35). Input values of total atmospheric plus non-atmospheric anthropogenic N ranged from 14 kg N/ha/yr in the watershed of Casco Bay in Maine to 68 kg N/ha/yr in the watershed of Massachusetts Bay (Driscoll et al., 2003a). In all eight watersheds, net import of N in food for humans (input into estuaries as wastewater) was the largest anthropogenic input. Atmospheric deposition was estimated to be the second largest anthropogenic N input, ranging from 5 to 10 kg N/ha/yr, or 11% to 36% of the total inputs, with four watersheds ranging from 34% to 36% (Driscoll et al., 2003a) (Table 3-34). These results are broadly consistent with estimates by Boyer et al. (2002), who used a similar N budgeting approach for 16 large northeastern U.S. river basins and reported that N deposition contributes approximately 31% of the total N load to large river basins, although this fraction varies regionally (Boyer et al., 2002). Boyer et al. (2002) considered only the portions of each basin above USGS gauging stations, which often occurred above large population centers. Hence, the Driscoll et al. (2003a) budgets included regions with greater human food consumption than those considered by (Boyer et al., 2002).

Castro and Driscoll (2002) studied 10 estuaries along the U.S. east coast and found total atmospheric N inputs (watershed runoff plus direct deposition to the surface of estuary) accounted for 15-42% of the total N inputs. Simulated reductions of atmospheric N deposition by 25% and 50% of current deposition rates reduced the contribution made by atmospheric N deposition to the total N loads by 1–6% and 2–11%, respectively. Overall, results from the simulated reductions suggested that considerable reductions (>25%) in atmospheric N deposition were needed to significantly reduce the contribution made by atmospheric N deposition to the total N loads. In a later study, Driscoll et al. (2003a) estimated that the implementation of aggressive controls on both mobile N emissions sources and electric utilities would produce an estimated reduction in estuarine loading in Casco Bay, ME of 13% (Driscoll et al., 2003a).
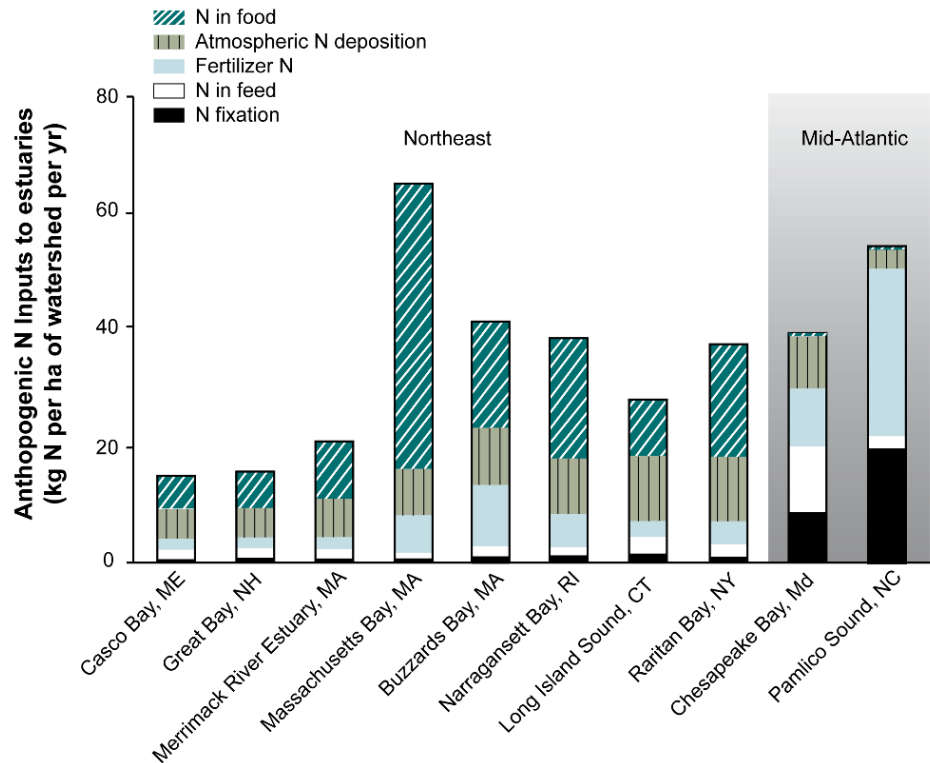
Figure 3-35. Estimated anthropogenic N inputs to the estuaries of the northeastern U.S., in kg N/ha/yr.

Source: Driscoll (2003a)

One of the challenges in determining the contribution of atmospheric N deposition to estuaries is estimating the inputs from upstream river basins. Smith et al. (1997) applied the SPAtially Referenced Regressions on Watershed Attributes (SPARROW) model to streamwater chemistry data from the National Stream Quality Accounting Network to evaluate NO_3^- leaching in large river basins. Leaching losses of N in large river systems provide important sources of N to estuaries and coastal marine waters. Smith et al. (1997) concluded that much of the U.S. probably exports less than 5 kg N/ha/yr, but that N export in watersheds of the northeastern U.S. is probably higher. For the watersheds that export more than 10 kg N/ha/yr, Smith et al. (1997) concluded that fertilizer was the largest source of N (48%), followed by atmospheric deposition (18%). In this analysis, fertilizer used for human food production was considered to be the ultimate source of N contributed to waterways through waste water treatment plants. If the analysis of N sources to estuarine water is restricted to only nonpoint sources of N, atmospheric deposition is often considered to be the largest individual source (Howarth, 2007; Howarth et al., 1996; Jaworski et al., 1997; NRC, 2000; Smith et al., 1997).

Overall, these estimates of the relative importance of atmospheric deposition, compared to non-atmospheric sources of N, typically involve many assumptions regarding dry deposition, riverine fluxes, and the relationship between human populations and wastewater inputs. Thus, such estimates entail considerable uncertainty. It is clear, however, that the relative contribution of atmospheric deposition to total N loading varies with the atmospheric N deposition level, land use, watershed and estuary areas, and hydrological and morphological estuarine characteristics. It is also clear that atmospheric deposition is generally an important contributor to the overall N load that stimulates eutrophication of estuaries in the eastern U.S. (Boyer et al., 2002; Driscoll et al., 2003c; Paerl et al., 2001b). See Annex C and Section 2.X for an additional discussion of estuarine N budgets.

3.3.2.5. Summary of N Effects on Biogeochemical Cycling of N and Associated Chemical Indicators

Terrestrial Ecosystems

The evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemical cycling of N in terrestrial ecosystems. This is supported by numerous observational, deposition gradient and field addition experiments. The main source of new N to non-managed terrestrial ecosystems is atmospheric deposition. N deposition disrupts the nutrient balance of ecosystem. The chemical indicators that are typically measured are summarized in Table 3-11 and include NO_3^- leaching, C:N ratio, N mineralization, nitrification, denitrification, foliar N and soil water NO_3^-, and NH_4^+. Values for these indicators that represent a threshold for the onset of a related biogeochemical or biological effect are also summarized. Note that N saturation does not need to occur to cause adverse effects on terrestrial ecosystems. However, in some regions N saturation is a plausible mechanism of net nitrification and associated NO_3^- leaching in drainage water. Leaching of NO_3^- from forest soils to stream water can acidify downstream waters and deplete soils of nutrient base cations, especially Ca and Mg (see Section 3.2).

In northeastern watersheds, Aber et al. (2003) suggested that nearly all N deposition is retained or denitrified in areas that receive less than about 8 to 10 kg N/ha/yr. Aber et al. (2003) further found that surface water NO_3^- concentrations exceeded 1 µeq/L in watersheds receiving about 9 to 13 kg N/ha/yr of atmospheric N deposition (Figure 3.30). The lakes and streams found to have high NO_3^- concentration were those receiving N deposition above this range, but responses were variable among those receiving high N deposition. Above this range, mean NO_3^- export increased linearly with increasing deposition at a rate of 0.85 kg NO_3^- kg N/ha/yr for every 1 kg N/ha/yr increase in deposition, although there was considerable variability in N retention among watersheds at higher rates of deposition (Aber et al., 2003).

In the West, a study of mixed conifer forests of the Sierra Nevada and San Bernardino mountains in California reported that the deposition load that causes the onset of NO_3^- leaching is 17 kg N/ha/yr. Several studies in the Rocky Mountains indicate that the onset of NO_3^- leaching in alpine catchments occurs at approximately 10 kg N/ha/yr (Baron et al., 1994; Williams and Tonnesen 2000).

Wetlands

The evidence is sufficient to infer a casual relationship between N deposition and the alteration of biogeochemical cycling of N in wetlands. N deposition contributes to total N load in wetlands that may also receive N from terrestrial run-off. The chemical indicators that are typically measured include NO_3^- leaching, N mineralization, and denitrification. N dynamics in wetland ecosystems are variable in time and with type of wetland and environmental factors, especially water availability (Howarth et al., 1996). A wetland can act as a source, sink, or transformer of atmospherically deposited N (Devito et al., 1989) and these functions can vary with season and with hydrological conditions. Vegetation type, physiography, local hydrology, and climate all play significant roles in determining source/sink N dynamics in wetlands (Arheimer and Wittgren, 1994; Devito et al., 1989; Koerselman et al., 1993; Mitchell et al., 1996).

N mineralization has been shown to increase with N addition, and this can cause an increase in wetland N export to adjacent surface water (Groffman, 1994). In general, leaching losses of NO_3^- in water derived directly from wetlands are often small because of NO_3^- removal by denitrification. Previous studies suggest that elevated N inputs to wetlands will often increase the rate of denitrification (Dierberg and Brezonik, 1983; Broderick et al., 1988; Cooper, 1990). This process limits the available N supply to soils and drainage waters; but increases the biogenic emission of greenhouse gasses to the atmosphere (see Section 3.3.4). Denitrification appears to be negligible in wetland environments that are typically nutrient (including N) poor, such as some bogs and fens (Morris, 1991).

Freshwater aquatic

The evidence is sufficient to infer a casual relationship between N deposition and the alteration of biogeochemical cycling of N in freshwater ecosystems. N deposition is the main source of N to headwater streams, lower order streams and high elevation lakes. The predominant chemical indicators are NO_3^- concentration in surface waters and DIN. Elevated surface water NO_3^- concentrations indicate N saturation of the terrestrial ecosystem and occur in both the eastern and western U.S. In the East, 8-10 kg N/ha/yr can cause increase NO_3^- concentrations (Driscoll et al., 1989; Stoddard 1994). In the West, elevated NO_3^- concentrations have been observed down wind of urban centers (Fenn et al., 2003a) and on slopes of the Colorado Front Range that are effected by elevated deposition from urban and agricultural sources (Baron et al., 1992)

Estuaries and coastal marine

The evidence is sufficient to infer a casual relationship between N deposition and the biogeochemical cycling of N in estuaries and coastal marine waters. The contribution of atmospheric N deposition to total N load is calculated for some estuaries and can be greater than 40%. Atmospheric deposition N is not the sole source of N loading to estuaries and it is unknown if atmospheric deposition alone is sufficient to cause eutrophication. In general, estuaries tend to be N-limited, and many currently receive high levels of N input from human activities to cause eutrophication (Vitousek and Howarth, 1991; Howarth et al., 1996, Elser et al., 2007). The most widespread chemical indicators of eutrophication are submerged aquatic vegetation, Chl *a*, algal blooms, macroalgae and dissolved O_2.

3.3.3. N Deposition Effects on Productivity and C Budgets

The addition of N from an exogenous source will alter the productivity of N-limited ecosystems. In a meta-analysis including terrestrial, freshwater and marine ecosystems, Elsner et al. (2007) found there were similar patterns of N and P limitation among ecosystem types. This finding is in contrast with the existing paradigm that N-limitation dominates in terrestrial ecosystems and P-limitation dominates in freshwater ecosystems. Marine ecosystems tend to be N-limited; however P-limitation can play an important role. It is important to distinguish between effects on primary productivity and effects on C sequestration. N addition to a given ecosystem may increase primary productivity; however this often does not translate into greater C sequestration because C lost from the ecosystem by respiration may offset the C gained by production. These topics are discussed for a range of ecosystem types in the following section.

3.3.3.1. Terrestrial Ecosystems

The following section discusses the mechanisms by which atmospheric N deposition alters C cycling in terrestrial ecosystems (see Figure 3-36). Although predicted values of atmospheric $[CO_2]$ in the future may alter the interaction between N and terrestrial C cycling (Hyvönen et al., 2007; Norby, 1998; Schindler and Bayley, 1993) this topic is beyond the scope this review. Available studies include N deposition gradients, N addition studies, modeling and time-trend analyses. Few studies have isolated the effect of chronic N deposition on plant growth and ecosystem C balances. In those that have, it is difficult to disentangle the effects of climate, disease and land use from N deposition effects. There are numerous field studies of N addition; however there are some difficulties in interpreting the results regarding chronic N deposition effects on ecosystems. Some studies add N in a large pulse at one time, a technique that does not simulate chronic N loads of smaller amounts that are characteristic of atmospheric deposition. Ecosystem growth response to a pulse of 100 kg N/ha at one time may not be same as 10 kg

N/ha/yr for 10 years, although the net load is the same. Additionally, there are few long-term addition studies therefore limiting the evaluation of changes in ecosystem response over decadal time scales.

Carbon accumulation in terrestrial ecosystems occurs above and below ground. C cycling is a complex process that can be quantified into ecosystem C budgets on the basis of net ecosystem productivity (NEP), defined as gross primary productivity (GPP) after subtracting the ecosystem respiration (vegetative + heterotrophic respiration). Factors that may increase terrestrial CO_2 sinks on a regional scale are increased NPP, and decreased respiration of CO_2 from leaf or soil processes. These two mechanisms may be altered by atmospheric deposition of N, tropospheric ozone exposure, increased CO_2 concentrations, land-use change and factors associated with climate warming (Beedlow et al., 2004; Caspersen et al., 2000; Melillo et al., 2002; Myneni et al., 1997; Ollinger et al., 2002; Nowak et al., 2004; Schimel et al., 2001). This adds to the uncertainty regarding the sources and sinks in the terrestrial biosphere (Houghton, 2003). It should be noted that it is not known whether present terrestrial C sequestration can be sustained, in view of limits of forest re-growth, nutrient availability and uncertainty about changes in the frequency of disturbances such as fire (Schimel et al., 2001; Scholes and Noble, 2001).
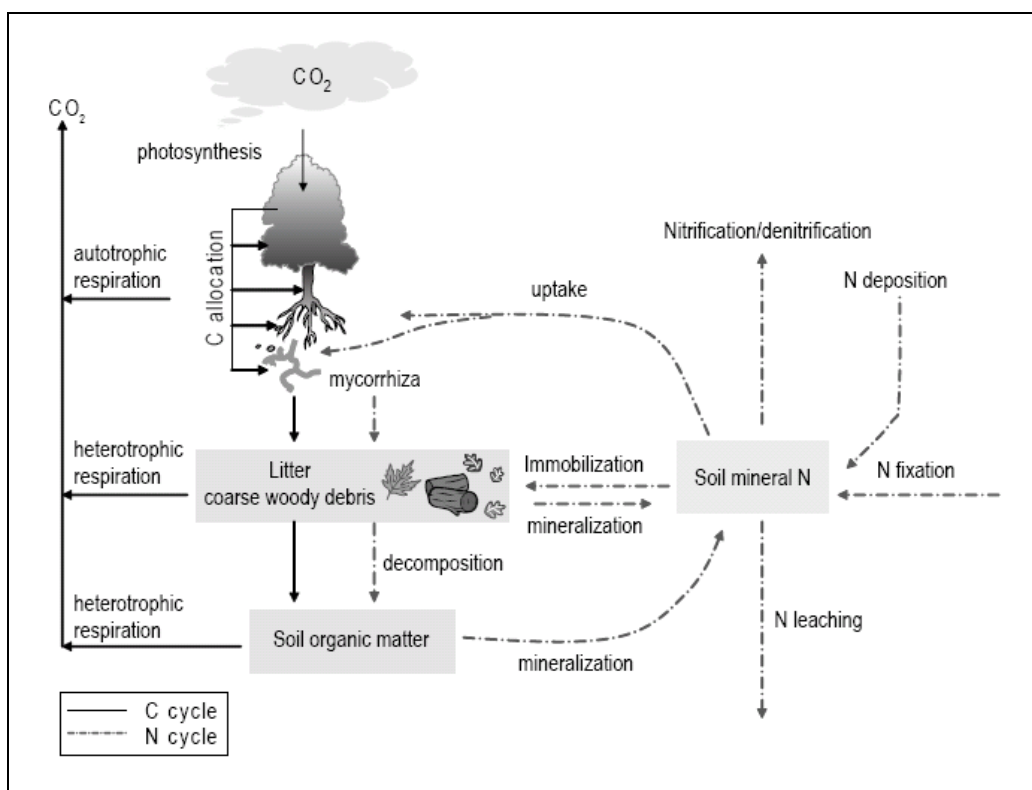
Figure 3-36.   Interactions between the C and N cycles.

Forests

C Allocation Interactions with Stressors

Addition of N is believed to decrease resistance to drought stress. This occurs because plants balance their resources to maximize above-ground processes, such as light and C capture, with below-ground processes, such as capture of water and other nutrients, including N (Sterner and Elser, 2002). N

addition often causes trees to allocate less photosynthate to roots than shoots (Minnich et al., 1995). Because shoot growth is more enhanced than root growth, the water supply from the roots can become insufficient during periods of drought to support water loss via transpiration (Fangmeier et al., 1994a; Krupa, 2003). Smaller root systems also cause greater susceptibility to wind-throw. For example, in Switzerland, the amount of trees uprooting during a strong storm event was significantly correlated with base saturation and N concentration in the leaves (positively) in beech trees (Braun et al., 2003). Across Europe, soil acidification and soil N content since the 1980s have accentuated the storm sensitivity due to changes in root architecture, including more superficial roots and loss of root ramification (Braun et al., 2003; Godbold et al., 1988; Puhe, 2003; Nilsson et al., 2004).

Deposition of N is also believed to reduce frost hardiness of plants (Dueck et al., 1990), which may play a role in red spruce die back (see Section 3.2). This is likely because the addition of N prolongs the growth phase of the plants during autumn and delays winter hardiness. This can cause detrimental effects if the first frost occurs early in the autumn period (Cape et al., 1991). Plant shoots also appear to be more susceptible to pathogenic fungal infection under high N status or changed nutrient balance such as an increase in the ratio of N to K^+ (Ylimartimo, 1991; Krupa, 2003). As opposed to shoot diseases, addition of N has been found to reduce mycorrhizal fungus colonization of roots (see more detailed discussion in Section 3.3.5.1).

Above-Ground Processes

Nitrogen availability often limits rates of net primary production in temperate terrestrial ecosystems (Vitousek and Howarth, 1991; LeBauer and Treseder, 2008); therefore there is an implicit link between the C and N cycles (Figure 3-36). Over 50% of N taken up by plants is used for photosynthetic enzymes. Rates of photosynthesis and net primary productivity (NPP) typically correlate with metrics of N availability such as leaf N content and net N mineralization rate (Field and Mooney, 1986; Reich et al., 1997a, 1997b; Smith et al., 2002). A meta-analysis of 126 N addition experiments evaluated N limitation of NPP in terrestrial ecosystems by evaluating above-ground plant growth in fertilized to control plots (LeBauer and Treseder, 2008). The results showed that most ecosystems are N limited with an average 29% growth response to N. The response ratio was significant within temperate forests, tropical forests, temperate grasslands, tropical grasslands, wetlands, and tundra, but not deserts (LeBauer and Treseder, 2008).

There is substantial evidence that N additions to trees cause increased leaf-level photosynthetic rates. However, the potential for N deposition to increase above-ground C biomass is limited for reasons related to the biogeochemical cycling of N (see more detailed discussion in Section 3.3.2.1). Briefly, C:N stoichiometry of the forest ecosystem compartments determines the C response to N deposition. Only a small portion of added N is taken up by vegetation, thus only a small portion of N contributes to C capture by trees (Nadelhoffer et al., 1999). A recent study reported that tree biomass (e.g., foliage, woody tissue, and fine roots) accumulated 7 to 16% of N additions (Nadelhoffer et al., 2004). N may be immobilized in the soil, leached out before biological assimilation, or, upon the addition of N, some other factor may become limiting to growth (e.g., water or other nutrients). Even though only a portion of N deposition is incorporated into vegetation, the general result of additional N is an increase in leaves, wood, and root biomass (Nilsson and Wiklund, 1995). The biological endpoints typically measured to evaluated plant growth in listed in Table 3-15.

Table 3-15.   Summary of N effects on forest carbon cycling.

Region/Country	Endpoint	Observations	Forest type/species	Reference
Europe	Growth (biomass)	Modeling: Large regions of forests were used as empirical data from which to build a model that forest biomass is accumulating, largely in response to increases in forest area and improved management, but other possible mechanisms of growth enhancement (including N) cannot be ruled out	Forests from Austria, Finland, Sweden, France, Germany, and Switzerland	Kauppi et al. (1992); Spiecker et al. (1996)
Norway	Growth (tree ring incre-ments)	Deposition gradient: A comprehensive analyses of regional forest growth trends analyzed tree increment cores from more than 31,000 plots. In this study, growth increased during the 1960s and 1970s and then declined in the 1990s, especially in southern regions exposed to the highest rates of N deposition (Figure 3-37)	Boreal forest (*Picea abies* and *Pinxus sylvestris*)	Nellemann and Thomsen (2001)
Sweden	Growth (stem volume)	Field Addition: chronic fertilization at 30 kg N/ha/yr continued to stimulate stemwood production even after 30 years, whereas a higher application (90 kg N/ha/yr) decreased stem volume growth, and an intermediate application (60 kg N/ha/yr) had little positive or negative effect relative to the control plots	Boreal forest, Scots pine forest	Högberg et al. (2006)
Bear Brook, ME, U.S.	Growth (basal area)	Field Addition: basal area increment of sugar maple was enhanced 13 to 104% by addition of 25 kg N/ha/yr as ($[NH_4]_2SO_4$), whereas red spruce was not significantly affected.	Sugar maple and red spruce	Elvir et al. (2003)
Fernow Experimental Forest, WV, U.S.	Growth	Field Addition: The application of 35 kg N/ha/yr as $(NH_4)_2SO_4$ enhanced growth of Black cherry (*Prunus serotina*) and yellow poplar (*Liriodendron tulipifera*) during the first 7 years, but led to reduced growth of these species relative to control trees in years 9 through 12, with no change in red maple (*Acer rubrum*) or sweet birch (*Betula lenta*)	Black cherry, yellow poplar, red maple, sweet birch	DeWalle et al. (2006)
Harvard Forest, MA, U.S.	Mortality	Field Addition: chronic N addition levels of 50 and 150 kg N/ha/yr for 15 years caused a 31% and 54% decrease, respectively, in red pine growth. As red pine has died, striped maple (*Acer pensylvanicum*), black cherry, and black birch (*Betula lenta*) have increased their contributions to annual litterfall production.	Red pine, striped maple, black cherry, black birch	Magill et al. (2004)
Northeastern U.S.	Live basal area	Field Addition: In a high-elevation red spruce-balsam fir (*Abies balsamea*) forest in the, N fertilization over 14 years led to a decrease in live basal area (LBA) with increasing N additions. In control plots, LBA increased by 9% over the course of the study, while LBA decreased by 18% and 40% in plots treated, respectively, with 15.7 kg N/ha/yr and 31.4 kg N/ha/yr.	Red spruce-balsam fir	McNulty et al. (2005)
Harvard Forest, MA, U.S.	Growth mortality root production	Field Addition: Control, low and high N additions of NH_4NO_3 (0, 50 and 150 kg N/ha/yr) were made over 15 years (1988-2003) to a pine plantation and mixed hardwood stand. Ambient deposition was calculated to be 8 kg N/ha/yr. N addition stimulated productivity, although the drought in 1995 induced significant mortality in small red maple trees. Fine root biomass was slightly, but not significantly, lower in highly fertilized stands relative to controls in both red pine and oak/maple ecosystems. Stem mortality of *Pinius resinosa* increased with N addition	Plantation: *Pinus resinosa* Hardwood stand: *Quercus velutina, Q. rubra, Betula lenta, Acer rubrum, Fagus grandiflora, Prunus serotina*	Magill et al. (2004)

Region/Country	Endpoint	Observations	Forest type/ species	Reference
Harvard Forest, MA	Growth Photosynthesis Needle age	Field Addition: Ambient deposition to the site was 8 kg N/ha/yr. N was applied as a concentrated solution of NH_4NO_3 divided into 6 equal monthly doses (May to Sept) totaling 50 (low N) and 150(high N) 8 kg N/ha from 1989-1999. Elevated nitrogen additions caused decreased photosynthesis and decreased needle age	Red pine (*Pinus resinosa*)	Bauer et al. (2004)
Ysselsteyn, The Netherlands	Growth Root production	Field Addition and deposition exclusion: improvements in wood accumulation rate, root production, and mycorrhizal associations occurred when a "clean roof" was installed at the site receiving the highest rate of N deposition (>40 kg N/ha/yr). Decreased production of fine roots may predispose N-fertilized plants to be more sensitive to intermittent drought, as well as to nutrient depletion exacerbated by acid deposition.	Coniferous- *Picea abies*, *Picea sitchesis*, *Pseudotsuga menziesii*, *Pinus sylvestris*	Emmett et al. (1998) Boxman et al. (1998b)
Southern CA, U.S.	N- saturation-reduced soil base satura-tion, and lack of a growth response	Observational: Areas of chaparral and mixed conifer forests that receive very high levels of dry N deposition in southern California have experienced significant environmental change over the past several decades	Chaparral and mixed conifer	Fenn et al., (1996, 2003a)
California	Growth (productivity) and mortality	Observational: high inputs of N_r appear to exhibit decreases in productivity and increases in mortality (Fenn et al., 1998).	Conifer forests	Fenn et al. (1998)
California	Litter accumulation, above-ground woody biomass, fire susceptibility	Field Addition: N fertilization has been shown to cause increased litter accumulation and C storage in above-ground woody biomass, which in turn may lead to increased susceptibility to more severe fires.	Ponderosa pine	Fenn et al. (2003a)
California	Growth	Increased N deposition caused increased growth for Jeffrey (*Pinus jeffreyi*) and Ponderosa pine (*Pinus ponderosa*) stands,	Mixed conifers	Takemoto et al. (2001)
North Carolina and Virginia	Growth (basal area), foliar chemistry, nitrification and mineralization	Deposition Gradient: Results from a study of 46 forest plots on six sites in North Carolina and Virginia dominated by American beech, sugar maple, and yellow birch suggested that N deposition is associated with changes in basal area, foliar chemistry, and nitrification and mineralization rates. Growth rates for the three tree species were similar at the lowest rates of N deposition, and then diverged as N deposition increased, with growth of yellow birch and American beech decreasing at the high N deposition loads. These differential growth rates have the potential to affect forest structure and biodiversity	American beech, sugar maple, and yellow birch	Boggs et al. (2005)
Fernow Experimental Forest, WV, U.S.	Stem growth Foliar N dynamics	Field Addition: sites fertilized annually with 35 kg N/ha (7.1 in the spring and 21.2 in the fall) of $(NH_4)_2SO_4$ over 11 years (1989-2000). Responses among three species differed for foliar [N] either showing no change or a decrease in the fertilized plots. For all three species N/P ratio initially increased with a subsequent decrease. Over a two year increment (1999-2001) stem diameter growth was 37% lower for all three species in the fertilized plots.	*Acer rubrum* *Liriodendron tulipifera* *Prunus serotina*	May et al. (2005)
California, Sequoia National Park	Growth	Field Addition: Aspen (*Populus tremuloides*) have been reported to show positive growth effects from fertilization at N deposition rates as low as 10 kg N/ha/yr	Aspen	Bytnerowicz et al. (2002)

Region/Country	Endpoint	Observations	Forest type/ species	Reference
Michigan	ANPP and surface soil organic matter	Field Addition: Chronic N fertilization (30 kg N/ha/yr applied as NaNO$_3$) for ten years (1994 to 2004) caused significant increases in ANPP for 3 out of the 10 years. There was a significant effect of year, however no consistent increase or decrease through time. After ten years of addition woody biomass and surface soil organic matter (0–10 cm) were both significantly greater for the treatment than control.	*Acer saccharum* (sugar maple)	Pregitzer et al. (2008)
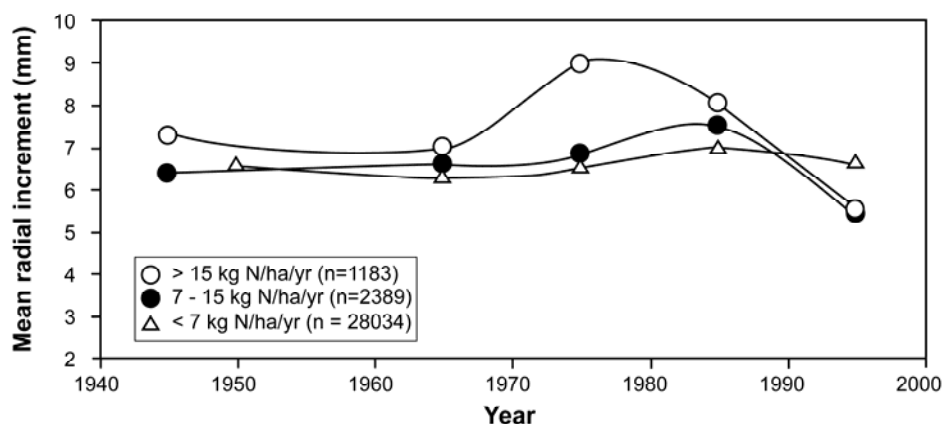
Figure 3-37. **Mean 5-year radial increment from 31,606 core samples from *Picea abies* during the period 1945 to 1996 for three atmospheric N deposition zones (high, medium, and low wet N-deposition in 1990), respectively. Note that the decline in radial increment after 1975 corresponds with the peak in exceedances for critical loads for the same areas. The increase and subsequent decline from 1965–1996 is significant (p <0.01) using Kruskal-Wallis analysis with Dunn's tests. S.E.s are all below 5% or 1–3.5 mm increment.**

Experimental N additions to forest ecosystems have elicited positive growth responses in some, but certainly not all, organisms (Emmett, 1999; Elvir et al., 2003; DeWalle et al., 2006; Högberg et al., 2006). Forest growth enhancement, can potentially exacerbate other nutrient deficiencies, such as Ca, Mg, or K. Multiple long-term experiments have demonstrated transient growth increases followed by increased mortality, especially at higher rates of fertilization (Elvir et al., 2003; Högberg et al., 2006; Magill et al., 2004; McNulty et al., 2005). An additional line of evidence comes from the experimental N removal studies: removal of N and S from throughfall increased tree growth in Europe (Beier et al., 1995; Boxman et al., 1998).

Decreased growth and increased mortality have more commonly been observed in high-elevation coniferous stands than in lower elevation hardwood forests, and these differences have been partially attributed to higher inputs of N at higher elevation and to response characteristics of coniferous, as opposed to deciduous, trees (Aber et al., 1998). Conifer forests that receive high inputs of N appear to exhibit decreases in productivity and increases in mortality (Fenn et al., 1998). For example, fertilization experiments at Mount Ascutney, VT suggested that N saturation may lead to the replacement of slow-

growing spruce-fir forest stands by fast-growing deciduous forests that cycle N more rapidly (McNulty et al., 1996; 2005).

Below-Ground Processes

Soils contain the largest near-surface reservoir of terrestrial C. More than 50% of C captured annually by plants may be allocated below ground (Kubiske and Godbold, 2001). Therefore, understanding the factors that control soil C storage and turnover is essential for understanding the C cycle and sequestration. Although there remains considerable uncertainty in the potential response of soil C to increases in N_r additions (Neff et al., 2002), a meta-analysis by Johnson and Curtis (2001) suggested that N fertilization caused an 18% increase in soil carbon content.

There is also evidence of a relationship between N deposition and root production. Nadelhoffer (2000) stated that N deposition functions to decrease forest fine-root biomass but to stimulate fine-root turnover and production. However, very high levels of N (>100 kg N/ha/yr) decreased root life span of *Pinus ponderosa* (Johnson et al., 2000).

Litter fall is usually the dominant source of soil organic C and a substantial source of organic N. Decomposition of litter fall is often facilitated by heterotrophic bacteria and mycorrhizae. The quantity of litter has been shown to increase with elevated N deposition (Schulze et al., 2000), with the result of increased microbial metabolism in soil. It is also well demonstrated that increased N availability reduces the ratio of C:N in leaf tissue. In turn, lower C:N in leaf litter has been shown to cause faster initial rates of decomposition (Melillo et al., 1982), however higher N litter can actually decompose more slowly in the long-term (Berg, 2000). N bound by leaf organic matter is released over a shorter period of time under higher decomposition rates, this leads to lower N retention by the soil (De Vries et al., 2006). A 10 year experiment that investigated decomposition in 21 sites from 7 biomes found net N release from leaf litter is predominantly driven by the initial N concentration and mass remaining regardless of climate, edaphic conditions, or biota (Parton et al., 2007). A recent meta-analysis by Knorr et al. (2005) indicated that, as expected, litter decomposition was stimulated by additional N deposition, however only at sites with low ambient N deposition rates (<5 kg N/ha/yr). Additional N deposition reduced decomposition at sites with moderate levels of N deposition (5 to 10 kg N/ha/yr).

Soil respiration is the dominant means by which plant-assimilated C is returned to the atmosphere as CO_2. Changes in the magnitude of soil CO_2 efflux due to changes in environmental conditions will likely influence the global atmospheric CO_2 budget (Schlesinger and Andrews, 2000). Overall, the effects of N addition on soil respiration are mixed; reductions at high levels of N (Lu et al., 1998; Bowden et al., 2004), no effect (Vose et al., 1995), and increases (Griffin et al., 1997; Mikan et al., 2000) all have been observed. At the Harvard Forest LTER Site Chronic Nitrogen Amendment Study, N additions increased soil respiration for hardwood stand, but not for pine stand during the first year of fertilization. However, continued N additions over a decade caused a 40% decrease in soil respiration for both stands and that was attributed mostly to a decrease in microbial respiration (Bowden et al., 2004).

Long-Term N Addition

There are few long-term experiments (10+ years) on N addition effects on the C cycle. Pregitzer et al. (2008) found that 30 kg N/ha/yr applied as $NaNO_3$ for ten years caused significant increases in ANPP for 3 out of the 10 years. There was a statistically significant effect of year, however no consistent increase or decrease through time. After ten years of addition, woody biomass and surface soil organic matter (0–10 cm) were both significantly greater for the treatment than control. May et al. (2005) found that 35 kg N/ha/yr applied as $(NH_4)_2SO_4$ over 11 years (1989-2000) caused different foliar [N] among three species either showing no change or a decrease in the fertilized versus control plots. For all three species N/P ratio initially increased with a subsequent decrease. Over a two year increment (1999-2001) stem diameter growth was 37% lower for all three species in the fertilized plots. At Harvard forest average atmospheric deposition of nitrogen was 8 kg N/ha/yr. N was applied as a concentrated solution of

NH_4NO_3 for treatments that totaled 50 kg N/ha/yr (low N) and 150 kg N/ha/yr (high N) from 1989-1999. Bauer et al. (2004) found that the nitrogen additions caused decreased photosynthesis and decreased needle age. At the same site Magill et al. (2004) found that fine root biomass was slightly, but not significantly, lower in highly fertilized stands relative to controls in both red pine and oak/maple ecosystems. Stem mortality of *Pinius resinosa* increased with N addition.

Regional Trends in NEP and NEE

An analysis of >100 young and mature forest stands from around the world indicated that annual values of CO_2 exchange varied from approximately −100 to 250 g $C/m^2/yr$ for boreal forests and 250 to 700 g $C/m^2/yr$ for temperate forests (Malhi et al., 1999). Net ecosystem exchange (NEE), defined as the difference between NPP and heterotrophic respiration, was positive when the forest was a sink that took up CO_2. Townsend et al. (1996) and Holland et al. (1997) modeled the impact of NO_Y and NH_X deposition on ecosystem C budgets by combining estimates of emissions with three dimensional transport models. They used spatially explicit estimates of N inputs and climate data as drivers for a process-based biogeochemical model to simulate ecosystem C dynamics globally. Their simulations predicted that CO_2-C uptake due to NO_Y deposition on land surfaces ranged from 0.3 to 1.4 Pg C uptake/yr (Townsend et al., 1996; Holland et al., 1997). The model allowed for variations in the degree of ecosystem N retention. The highest C uptake was calculated when trees were assumed to uptake 80% of N inputs, which is a likely overestimation because field studies suggested trees only took up a small portion (7–16%) of N deposition (Nadelhoffer et al., 1999).

Satellite observations of canopy greenness over the last 20 years across North America suggest enhancement of NEP in some regions, corresponding to observed changes in climate and forest management. Few such changes were observed in the northeastern U.S., where rates of N deposition are relatively high (Hicke et al., 2002). In another study, evaluation of tree growth rates in five states (Minnesota, Michigan, Virginia, North Carolina, and Florida) found little evidence for growth enhancement due to any factor examined, including N deposition, CO_2 fertilization, or climate change (Caspersen et al., 2000). Potential effects of N deposition on boreal forests of North America are of concern in part due to the large size of this terrestrial biome. Climate warming and N deposition may increase NPP and C sequestration in the boreal forest, but may also stimulate decomposition of soil organic matter, potentially leading to a net loss of C from the ecosystem (Kirschbaum, 1994; Mäkipää et al., 1999).

A recent European study suggested that N deposition increased forest growth (Magnani et al., 2007). Magnani et al. (2007) reported a strong correlation between estimated average long-term NEP and estimated 1990 N wet-deposition (Holland et al., 2005) for 20 forest stands mostly in western Europe and the conterminous U.S. The authors reported that when confounding effects of disturbance were factored out, carbon sequestration was found to be increased by moderate N deposition (estimated up to 9.8 kg N/ha/yr). However, this study did not evaluate forest stands that receive higher levels of N deposition that may be showing negative symptoms of N saturation. Several responses to this study have been critical of the methods and conclusions have been published (De Schrijver et al., 2008; De Vries et al., 2008; Sutton et al., 2008b). For example, Sutton et al. (2008b) re-analyzed the data from Magnani et al. (2007) and concluded the NEP response to N response reported by Magnani et al. (2008) was implausibly high (725 kg C/kg wet-deposited N). Magnani (2008) responded by calculating NEP sensitivity to total N deposition of approximately 175–225 kg C/kg N deposition and noted that one of the main effects of increased N availability is an increased allocation to woody tissues (with a high C:N ratio of up to 500:1). After considering the uncertainties in wet and dry N deposition and climate variability, Sutton et al. (2008b) reported the estimated NEP response to N deposition was 68 kg C/ deposited N. Sutton et al. (2008b) concluded that N deposition remains an important driver of NEP, but did not find support that the NEP was overwhelmingly driven by N deposition.

The U.S. EPA conducted a meta-analysis of 17 observations from 9 studies in U.S. forests to examine the effect of N fertilization on forest ecosystem C content (EC). Here EC was defined as the sum

of C content of vegetation, forest floor and soil (Johnson et al., 2006). To avoid possible confounded variability caused by site conditions, this meta-analysis only included studies of which control and treatment sites experienced the same climatic, soil and vegetation conditions. Studies on N nutrient effects along a deposition gradient, such as Magnani et al. (2007), were not included. The U.S. EPA meta-analysis revealed that while there was a great deal of variation in response, overall N addition increased EC by 6% for U.S. forest ecosystems (see Figure 3-38). Different from Magnani et al. (2007), this study did not find any correlation between the amount of N addition and the response magnitudes of EC.

It is uncertain if short term C accumulation may lead to long term C sequestration. N fertilization could reduce the capacity of ecosystem to sequester decay resistant soil C. Giardina et al. (2004) found that although N fertilization significantly increased plant production, the C flux moving to mineral soil was reduced by 22% in a humid tropical forest in Hawaii. Mycorrhizal biomass comprises a substantial carbon pool – represent up to 15% of soil organic matter in some ecosystems (Vogt et al., 1982). A meta-analysis by Treseder (2004) suggested that mycorrhizal abundance decreased 15% under N fertilization.
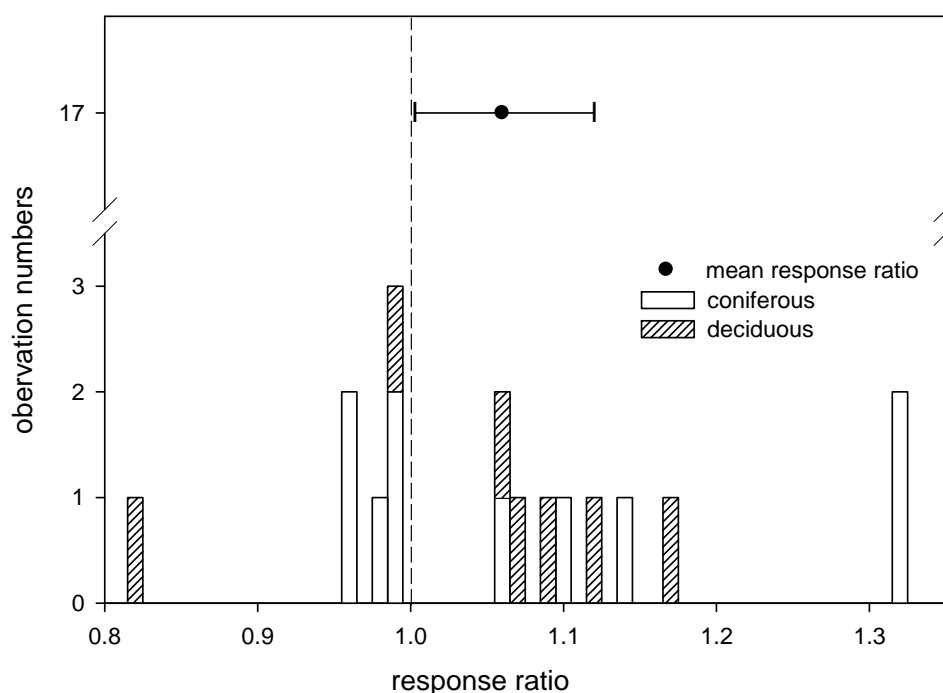
Figure 3-38. Effects of N addition on forest ecosystem C content. The bars show the distribution of the number of studies categorized by vegetation type. The dot with error bars shows the overall mean response ratio with 95% CI.

Arctic Tundra

Arctic tundra is adapted to cold temperature, short growing season, high soil moisture, and periodically low soil O_2 level. In general, arctic tundra plants respond to reduced N availability by changing the allocation of biomass to favor root growth (Bloom et al., 1985) or changing the efficiency with which N is used or stored (Chapin, 1980).

Mack et al. (2004) examined C and N pools in a long-term fertilization experiment at the arctic Long-Term Ecological Research site near Toolik Lake, AK. Fertilized plots in moist acidic tundra received 10 g N and 5 g N/m^2/yr from 1981 to 2000. This is approximately 5 to 8 times the annual soil N uptake requirement for above-ground production in the ecosystem. Two decades of fertilization shifted

community composition from graminoid tundra dominated by the tussock-forming sedge, *Eriophorum vaginatum*, to shrub tundra dominated by *Betula nana* (Shaver et al., 2001). Consequently, this greatly increased above-ground NPP, but had a larger effect on decomposition than on plant production, resulting in a net loss of almost 2,000 g C/m^2 from this ecosystem over 20 year (p <0.04). Carbon storage increased above ground because of the accumulation of woody shrub biomass and litter, but this was offset by a larger decrease of C in below-ground pools due to a pronounced decrease in the C contained in deep organic (>5 cm depth) and upper mineral soil layers. This study clearly showed that increased nutrient availability enhanced decomposition of below-ground C pools in deep soil layers more than it increased primary production, leading to a substantial net loss of C from this ecosystem.

The key process responsible for the C loss was identified as increased deep soil C decomposition in response to increased nutrient availability. The authors noted that increasing temperatures may amplify these effects and further stimulate C losses from high-latitude systems. The amount of N released due to a 3 to 7 ºC increase in mean annual temperature (MAT) is likely to range in magnitude from 7 to 9.4 g N/m^2/yr, respectively (Mack et al., 2004). This will cause species shifts in the vegetation community from tussock to increased shrub abundance and lead to decreased ecosystem C storage. Finally, the decreased soil moisture and increased depth of thaw that accompany temperature rise are predicted to have a positive effect on decomposition (Shaver et al., 2001), releasing more CO_2.

Grasslands

Below-Ground Factors

An investigation by Neff et al. (2002) of long-term effects (10+ years) of N deposition (10 kg N/ha/yr) in a dry meadow ecosystem indicated that N additions significantly accelerated decomposition of soil C fractions with decadal turnover times while further stabilizing soil C compounds in mineral-associated fractions with multi-decadal to century lifetimes. Despite these changes in the dynamics of different soil pools, no significant changes in bulk soil C were observed, highlighting a limitation of the single-pool approach for investigating soil C responses to changing environmental conditions (Neff et al., 2002). The authors noted that it remains to be seen if the effects that were caused by relatively high, decadal-term fertilizer additions are similar to those which would arise from lower, longer-term additions of N to natural ecosystems from atmospheric deposition.

Interactions with Fire

Several lines of evidence suggest that N deposition may be contributing to greater fuel loads and thus altering the fire cycle in a variety of ecosystem types (Fenn et al., 2003a). Invasive grasses, which can be favored by high N deposition, promote a rapid fire cycle in many locations (D'Antonio and Vitousek, 1992). The increased productivity of flammable understory grasses increases the spread of fire and has been hypothesized as one mechanism for the recent conversion of coastal sage scrub (CSS) to grassland in California (Minnich and Dezzani, 1998).

High grass biomass has also been associated with increased fire frequency in the Mohave Desert (Brooks, 1999; Brooks and Esque, 2002; Brooks et al., 2004). This effect is most pronounced at higher elevation, probably because the increased precipitation at higher elevation contributes to greater grass productivity. Increased N supply at lower elevation in arid lands can only increase productivity to the point at which moisture limitation prevents additional growth. Fire was relatively rare in the Mojave Desert until the past two decades, but now fire occurs frequently in areas that have experienced invasion of exotic grasses (Brooks, 1999).

Wetlands

Above-Ground Processes

The 1993 NO_X AQCD showed that N applications, ranging from 7 to 3120 kg N/ha/yr, stimulated standing biomass production by 6–413% (U.S. EPA 1993a). However, the magnitude of the changes in primary production depended on soil N availability and limitation of other nutrients. The degree of N limitation to growth is varied among wetlands across the U.S. (Bedford et al., 1999).

The genus *Sphagnum* dominates ombrotrophic bogs and some nutrient poor fens in the Northern U.S. and Canada. These mosses efficiently capture atmospheric deposition with retention rates between 50–90%, much of the variation due to the depth of the water table (Bedford et al., 1999). Studies conducted on 4 species of Sphagnum in Maine (2 to 4 kg N/ha/yr ambient deposition) and New York (10 to 13 kg N/ha/yr ambient deposition) document that higher N deposition resulted in higher tissue N concentrations and greater NPP (Aldous, 2002), but lower bulk density (Aldous, 2002). A study of *Sphagnum fuscum* in six Canadian peatlands showed a weak, although significant, negative correlation between NPP and N deposition when deposition levels were greater than 3 kg N/ha/yr (y = 150 – 3.4(x); r^2=0.01, p = 0.04) (Vitt et al., 2003). A study of 23 ombrotrophic peatlands in Canada with deposition levels ranging from 2.7 to 8.1 kg N/ha/yr showed peat accumulation increases linearly with N deposition (y = 2.84(x) +0.67, r^2 = 0.32, p <0.001), however in recent years this rate has begun to slow indicating limited capacity for N to stimulate accumulation (Moore et al., 2004).

Primary production of plant species from intertidal wetlands typically increases with N addition, however most studies apply fertilizer treatments that are several orders of magnitude larger than atmospheric deposition (Mendelssohn, 1979; Wigand et al., 2003; Tyler et al., 2007; Darby and Turner, 2008). N loads brought by tidal water and ground water (565–668 kg N/ha/yr) are much larger than N depositing directly to the surface of coastal marshes, which suggested that direct N deposition may have limited impacts on this ecosystem (Morris, 1991). On the other hand, indirect atmospheric deposition that is N deposited to the watershed and transported via surface or ground water, could be the major sources of the total N load to coastal marshes. For example, model calculation suggested that the contribution from the atmosphere (36 million kg N/yr) was about 21–30% of the total N loading (170 million kg N/yr) in Chesapeake Bay waters (U.S. EPA, 2000b). Therefore 30% of the N delivered to wetlands via estuarine tides would originate from atmospheric deposition. Future studies are needed to determine the role of indirect atmospheric N deposition on the nutrient budget of intertidal wetlands.

Below-Ground Processes

Bragazza et al. (2006) investigated the decomposition rates of recently formed litter peat samples collected in nine European countries under a natural gradient of atmospheric N deposition from 2 to 20 kg N/ha/yr. They found enhanced decomposition rates for material accumulated under higher atmospheric N supplies resulted in higher CO_2 emissions and dissolved organic carbon release. The increased N availability favored microbial decomposition by removing N constraints on microbial metabolism and through a chemical amelioration of litter peat quality with a positive feedback on microbial enzymatic activity. In a follow-up study, Bragazza and Freeman (2007) evaluated whether there was a relationship between N deposition and a decay-inhibiting polyphenol in the *Sphagnum* tissue. They found that as N deposition level increased the polyphenol concentration decreased. This observation implies the lower concentration of decay-inhibiting polyphenols would lead to accelerated peat decomposition. Although some uncertainty remains about whether Sphagnum will continue to dominate litter peat, these findings indicated that even without such changes, increased N deposition poses a serious risk to the valuable peatland C sinks.

Reduced vs. Oxidized N

The form of added N may regulate wetland response to N deposition. Experimental applications of NO_3^- appear to have been less effective at stimulating wetland plant productivity than applications of NH_4^+ (U.S. EPA, 1993a). This may reflect higher rates of denitrification in response to the added NO_3^-, suggesting the importance of competition between plants and microbes for bioavailable N. Plants appear to compete more successfully for NH_4^+ and microbes to compete more successfully for NO_3^-. An important caveat expressed by U.S. EPA (1993a), however, was that the results of relatively short-term N fertilization experiments are not necessarily good predictors of long-term wetland community responses to increased N inputs.

NEE of Grassland, Tundra and Wetlands

In the meta-analysis of 16 observations from 9 publications on the relationship between N addition and C sequestration of non-forest ecosystems, N addition had no significant effect on NEE of non-forest ecosystems (Figure 3-39). N limitation to NPP is globally distributed and therefore plant productivity is normally enhanced by N addition. A meta-analysis by Lebauer and Treseder (2008) indicated that N fertilization increased aboveground NPP (ANPP) in all non-forest ecosystems except for desert. However, N addition also has been observed to stimulate ecosystem C loss. For example, N fertilization stimulated soil organic carbon decomposition in arctic tundra. Increasing N deposition led to higher C loss in temperate peatlands (See Section 3.3.3.1). In an agricultural experiment site, Khan et al. (2007) observed that 40 to 50 years N fertilization resulted in a net decline in soil C despite massive residue C incorporation. This meta-analysis indicated that N addition had no significant impact on C sequestration in non forest ecosystems, which may be due to C gain via NPP was exceeded by C loss via heterotrophic respiration.
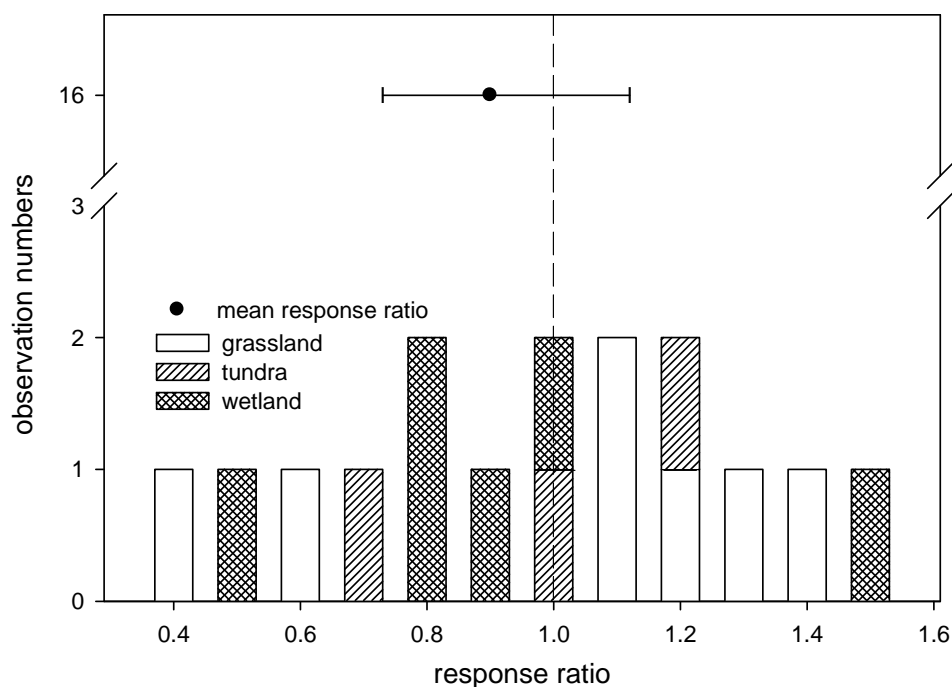
Figure 3-39. **Effects of N addition on NEE of non-forest ecosystems. The bars show the distribution of the number of studies categorized by vegetation type. The dot with error bars shows the overall mean response ratio with 95% CI.**

3.3.3.2. Freshwater Aquatic

The biogeochemical cycles of N, P and C are linked in freshwater ecosystems (Figure 3-40), therefore N additions alter the balance of all three cycles. In N-limited aquatic systems, atmospheric inputs of N increase productivity and alter biological communities, especially phytoplankton. N deposition effects on productivity are discussed in this Section. The results of numerous publications addressing the experimental additions of N are tabulated in Annex C. Evidence that altered productivity leads to altered community structure is discussed in Section 3.3.5.

Generally, the dose-response data for aquatic organisms such as those cited below are expressed in concentration units, as mg/L or µmol/L of N, for example. Such concentration data cannot be directly related to ecosystem exposure (i.e. deposition), which is generally expressed in such units as kg N/ha. This is because N deposition can result in widely varying concentrations of N compounds (especially NO_3^-) in water. For convenience, a concentration of 1 mg/L of N (as, for example, in the case of NO_3^--N or NH_4^+-N) is equal to 71.4 µmol/L or 71.4 µeq/L of NO_3^- or NH_4^+.
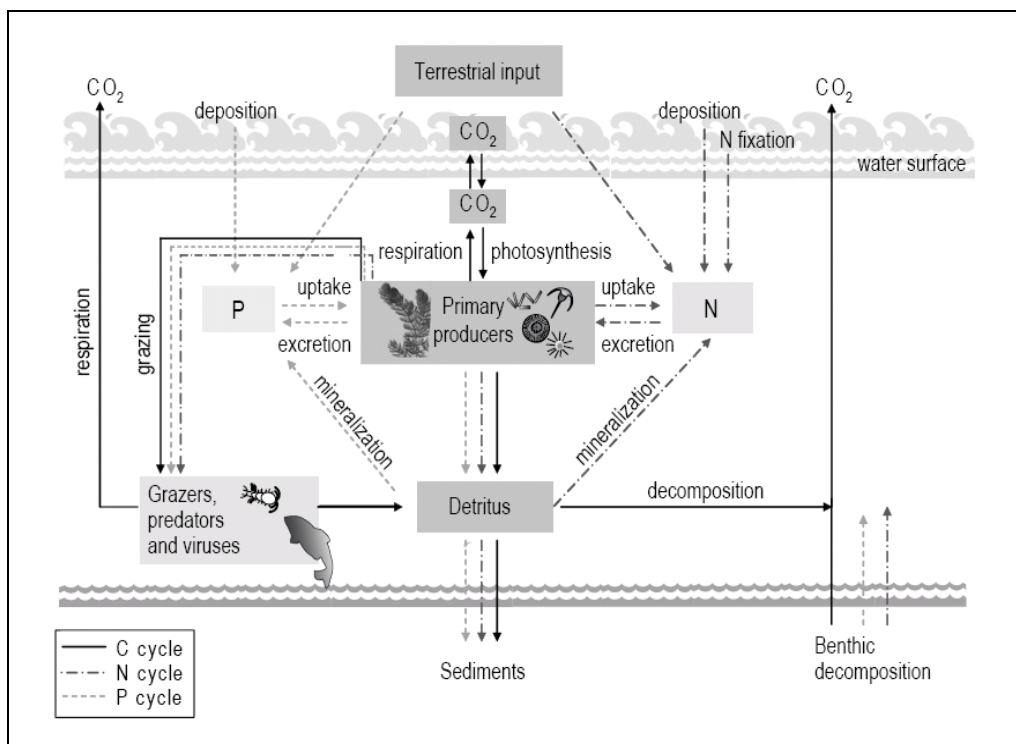
Figure 3-40.   N cycle in freshwater ecosystem.

N-Limitation

A freshwater lake or stream must be N-limited to be sensitive to N-mediated eutrophication. There are many examples of fresh waters that are N-limited or N and P co-limited (e.g., Elser et al., 1990; Fenn et al., 2003a; Tank and Dodds, 2003; Bergström et al., 2005; Baron, 2006; Bergström and Jansson, 2006). In a meta-analysis that included 653 datasets, Elser et al. (2008) found that N-limitation occurred as frequently as P-limitation in freshwater ecosystems. Recently, a comprehensive study of available data from the northern hemisphere surveys of lake along gradients of N deposition show increased inorganic N concentration and productivity to be correlated with atmospheric N deposition (Bergström and Jansson,

2006). The results are unequivocal evidence of N limitation in lakes with low ambient inputs of N, and increased N concentrations in lakes receiving N solely from atmospheric N deposition (Bergström and Jansson, 2006). These authors suggested that most lakes in the northern hemisphere may have originally been N-limited, and that atmospheric N deposition has changed the balance of N and P in lakes so that P-limitation is generally observed today. If this is correct, the role of atmospheric N deposition as an influence on aquatic primary production may have been underestimated throughout the entire history of limnology.

Recent research (e.g., Wolfe et al., 2001, 2003, 2006; Lafrancois et al., 2003; Das et al., 2005; Saros et al., 2005) has provided additional evidence indicating that N deposition has played an important role in influencing the productivity of oligotrophic, high-elevation lakes in the western U.S. and Canada, and the Canadian arctic. There is evidence suggesting historical N-limitation of some lakes based on paleolimnological studies conducted in mountainous regions of the western U.S. that have been the recipient of elevated levels of N, but not S, deposition over background values (see Section 3.3.4). Interactions between N and P loading are discussed in Annex C.

Productivity investigations have included gradient studies in which the relationship between lake N concentration and primary productivity (reported as Chl a, NPP, or an index such as the lake chemistry ratio of dissolved inorganic N [DIN] to total P, DIN:TP) was surveyed and correlated with atmospheric N deposition. Productivity studies have also included lake and stream bioassays in which N was added to waters in field or laboratory to measure the response. The most common, and easiest to document, indicators of change in algal productivity are measures of the concentration of Chl a and water clarity. However, clarity is also strongly influenced by erosional inputs of fine sediment to the lake or stream system. Chl a concentration is generally more directly tied to algal productivity than is water clarity.

Phytoplankton Biomass

Studies have shown an increase in lake phytoplankton biomass with increasing N deposition in several regions, including the Snowy Range in Wyoming (Lafrancois et al., 2003), the Sierra Nevada Mountains in California (Sickman et al., 2003), and across Europe (Bergström and Jansson, 2006). Gradient studies of undisturbed northern temperate, mountain, or boreal lakes that receive low levels of atmospheric N deposition found strong relationships between N-limitation and productivity where N deposition was low, and P and N+P limitations where N deposition was higher (Fenn et al., 2003a; Bergström et al., 2005; Bergström and Jansson, 2006).

Bergström and Jansson (2006) concluded the eutrophication caused by inorganic N deposition indicates that phytoplankton biomass in a majority of lakes in the northern hemisphere is limited by N in their natural state. Chemical data from 3,907 lakes and phytoplankton biomass data from 225 lakes from Swedish monitoring programs showed a clear north-south gradient of increasing lake concentrations and algal productivity related to the pattern of increasing N deposition input (Bergström et al., 2005). The lowest productivity was found at sites where wet N deposition was about 1.3 kg N/ha/yr; increasing productivity occurred at greater than 2.2 kg N/ha/yr (Bergström et al., 2005). Although these lakes are all in Sweden, the study size and the strong correlation between productivity and atmospheric N deposition makes the results likely relevant to North American audiences.

Experiments conducted with mesocosms in lakes where NO_3^- was below the detection level found a strong response in phytoplankton biomass with additions of N (bringing concentrations to ~1.0 mg N/L) and even stronger responses to additions of N plus P, but not P alone (Lafrancois et al., 2004). The reverse was found in Colorado Front Range lakes with ambient NO_3^- concentrations of ~1.0 mg/L: productivity increased with additions of N plus P or P only, but not NO_3^- alone (Lafrancois et al., 2004).

A meta-analysis of enrichment bioassays in 62 freshwater lakes of North America, including many of the studies described above, found algal growth enhancement from N amendments to be common in slightly less than half the studies (Elser et al., 1990). There was a mean increase in phytoplankton biomass of 79% in response to N enrichment (average of 46.3 µeq/L N) (Elser et al., 1990). This meta-analysis was recently repeated with a much large data set and similar results (Elser et al., 2007). Freshwater

enrichment bioassay studies from 990 separate studies worldwide were gleaned from the literature. The natural log (ln)-transformed response ratio (RR$_X$), a frequently used effect metric in ecological meta-analysis, was equal at about 0.3 for N and P experiments with stream benthos (periphyton) bioassays, and approximately equal at about 0.2 for lake phytoplankton. There was a stronger response to P than N in lake benthos studies, but the RR$_X$ for N was still about 0.3, showing that many sites increased productivity when fertilized with N alone (Elser et al., 2007). Additional studies are discussed in Table 3-16.

Table 3-16.   Summary of additional evidence of N effects on productivity of freshwater ecosystems.

Region	Endpoint	Observation	Ecosystem Type	Reference
Lake Tahoe, CA	Primary productivity Water clarity	Long-term (28 years) measurements showed that primary productivity has doubled, while water clarity has declined, mostly as a result of atmospheric N deposition	Lake	Goldman (1988); Jassby (1994)
Alaska	Primary production Fungal biomass Decomposition rates Benthic macroinvertebrate	N amendment experiments with 6.4 µM N to elicited responses throughout the ecosystem, including enhanced primary production, enhanced fungal biomass and elevated leaf litter decomposition rates, and a fourfold to sevenfold greater benthic macroinvertebrate abundance	Small arctic streams	Benstead et al. (2005)
Rocky Mountain Lakes, Colorado	Growth	In situ mesocosm: incubations the growth of the diatom A. *formosa* has been stimulated with N amendments during from 6.4 to 1616 µM N	Diatoms	McKnight et al., (1990)
Yellowstone National Park, Wyoming	Growth	In situ incubations in large lakes: stimulated F. *crotonensi*. This publication did not reveal how much N was added to the incubations	Lakes	Interlandi and Kilham, (1998)
Central Rocky Mountains of North America	Growth	The N requirements for A. *formosa* and F. *crotonensis* were determined to be 0.041 µM and 0.006 µM, respectively, and higher concentrations stimulated growth	Alpine lakes	Michel et al. (2006)

Chlorophyll *a*

The most widely used index of biological change in response to nutrient addition is measurement of Chl *a* concentration in water. Surveys and fertilization experiments show increased inorganic N concentration and aquatic ecosystem productivity (as indicated by Chl *a* concentration) to be strongly related. For example, a series of in situ meso- and microcosm N amendment experiments more than 30 years ago showed increases in lake algal productivity. Lake 226S in Ontario's Experimental Lake Area (ELA) showed doubling of average epilimnetic Chl *a* over five years of fertilization. However, because the response to P fertilization was much greater, the effects of N received less attention (Schindler, 1980). Other ELD lakes that had relatively low N to P concentration ratios experienced 3 to 10 times greater increases in Chl *a* than Lake 226S (Schindler, 1980).

Similar experiments at Castle Lake, California, the Snowy Range of southern Wyoming, and Alaskan arctic foothill lakes yielded measurable increases in Chl *a*, primary productivity and algal

detritus with N amendments (Axler and Reuter, 1996; Levine and Whalen, 2001; Nydick et al., 2003; Lafrancois et al., 2004; Nydick et al., 2004b).

Periphyton Biomass

N effects have been observed in periphyton, which grows on rocks or sediment in lakes and streams where there is sufficient light for photosynthesis. No studies have reported resource requirements for periphyton, although several papers described stimulated growth with N amendments from ecosystems throughout the U.S. (Annex C), including streams in Alaska, Arizona, Iowa, Texas, Minnesota, Missouri, and lakes in California, Colorado, and Massachusetts. Growth stimulation occurred with N additions ranging from 8 to 50 µM/L, or with exposure to 0.5 M N concentrations on agar substrate (Bushong and Bachmann, 1989; Allen and Hershey, 1996; Wold and Hershey, 1999; Smith and Lee, 2006). Additional lake bioassay experiments that enriched the water column down into the sediments found enhancement of periphyton growth on bioassay container walls in experiments in California, Wyoming, and Massachusetts (Axler and Reuter, 1996; Nydick et al., 2004a; Smith and Lee, 2006). Strong N limitation of benthic algae has also been inferred in streams of Arizona (Grimm and Fisher, 1986), California (Hill and Knight, 1988), Missouri (Lohman et al., 1991), and Montana (Lohman and Priscu, 1992; Smith and Nicholas, 1999).

Trophic Status Indices

Nutritional responses of aquatic ecosystems to atmospheric N deposition are heavily dependent on surface water P concentrations. Thus, chemical ratios of N to P can be very useful in evaluating eutrophication potential. A series of papers, described below, has been published exploring nutrient limitations and offering indices that describe the trophic state of freshwaters. Valuable insights have been gained from several indices, including total N to total P (TN:TP), dissolved inorganic N to total P (DIN:TP), dissolved inorganic N to total dissolved P (DIN:TDP), dissolved inorganic N to soluble reactive P (DIN:SRP), and dissolved inorganic N to the ratio of Chl a to total P (DIN:[Chl a:TP]). While there are publications that compare the effectiveness of some of these indices, it appears that different indices are useful for different purposes; we make no attempt to favor one over another.

Algal growth was reported to be limited at DIN:TP values between 5 and 20 (Schindler, 1980; Grimm and Fisher, 1986; Morris and Lewis, 1988; Downing and McCauley, 1992; Bergström and Jansson, 2006). When DIN:TP ratios are greater than reference values, growth stimulation, N and P colimitation, or P limitation commonly occurs (Sickman et al., 2003). In a Swedish lake survey, N-limitation occurred in lakes where the DIN:TP ratio was less than 7 (concentrations <33 µM N/L). Co-limitation of both N and P were found in lakes with DIN:TP ratio between 8 and 10, and P-limitation at DIN:TP values greater than 10. This corresponds roughly to N concentrations of 45 to 80 µM N/L for co-limited lakes, and concentrations >80 µM N/L for P-limited lakes (Bergström et al., 2005). Other thresholds for N-limitation were reported in the literature to occur at DIN:SRP ratios <4 (Lohman and Priscu, 1992) and <10 (Wold and Hershey, 1999).

Bergström et al. (2005) reported a new index, (DIN:[Chl a:TP]) to indicate the eutrophication of lakes from N deposition. The choice of DIN/[Chl a:TP] was based on whole lake experiments in Sweden (Jansson et al., 2001) and permits the assessment of a possible eutrophication effect of N deposition independent of differences in P input between lakes in different regions. These researchers found that the mean Chl a:TP ratios increased more than three times from low N to high N deposition areas, indicating that N deposition contributed to eutrophication.

3.3.3.3. Estuarine and Marine

In coastal marine ecosystems, the nutrients most commonly associated with phytoplankton growth are N, P, and Si (see Annex C for interactions between hydrology and nutrient cycling). Interactions

among the supplies of these nutrients can affect phytoplankton species composition in ways that might effect ecosystem function (Paerl et al., 2001a; Riegman, 1992). The relative proportions of these nutrients are important determinants of primary production, food web structure, and energy flow through the ecosystem (Dortch and Whitledge, 1992; Justic et al., 1995a; Justic et al., 1995b; Turner et al., 1998). There is a strong scientific consensus that N is the principal cause of coastal eutrophication in the U.S. (NRC, 2000) On average, human activity has likely contributed to a sixfold increase in the N flux to the coastal waters of the U.S., and N now represents the most significant coastal pollution problem (Howarth et al., 2002b; Howarth and Marino, 2006). Atmospheric deposition is responsible for a portion of the N input (Howarth et al., 2002a).

Ecological effects of accelerated estuarine eutrophication and climatic perturbations such as droughts, floods, and hurricanes are often observed most closely at the level of the primary producers. Phytoplankton can be divided into functional groups that reflect ecological change, for example: chlorophytes, cryptophytes, cyanobacteria, diatoms, and dinoflagellates (Pinckney et al., 2001).

The relative abundances of these groups can be determined using photopigment indicators which can be easily measured in the laboratory (Paerl et al., 2003). Changes in phytoplankton community composition, which may affect food web interactions, can have important effects on nutrient cycling. For example, if the growth of phytoplankton species that are more readily grazed by zooplankton (i.e., diatoms) is favored, trophic transfer will occur in the water column from diatoms to fish and nutrient export will take place as fish move to the ocean. However, if the phytoplankton that are favored by nutrient addition and disturbance are not readily grazed (i.e., cyanobacteria and dinoflagellates), trophic transfer will be poor. In that case, more unconsumed algal biomass will settle to the bottom where it can contribute to O_2 consumption and associated hypoxia (Paerl et al., 2003).

To evaluate the impacts of eutrophication, five biological indicators were used in the recent national assessment of estuary trophic condition: Chl *a*, macroalgae, dissolved O_2, nuisance/toxic algal blooms, and submerged aquatic vegetation (SAV) (Bricker et al., 2007) (Figure 3-41). Each of these indicators is discussed below and/or within the biodiversity section of this document (see Section 3.3.5.4).

N-Limitation

Estuaries and coastal waters tend to be N-limited and are therefore inherently sensitive to increased N loading (D'Elia et al., 1986; Howarth and Marino, 2006). There is a scientific consensus that N-driven eutrophication of shallow estuaries has increased over the past several decades and that environmental degradation of coastal ecosystems is now a widespread occurrence (Paerl et al., 2001a).

For example, the frequency of phytoplankton blooms and the extent and severity of hypoxia have increased in the Chesapeake Bay (Officer et al., 1984) and Pamlico estuaries in North Carolina (Paerl et al., 1998) and along the continental shelf adjacent to the Mississippi and Atchafalaya rivers discharges to the Gulf of Mexico (Eadie et al., 1994). It is partly because many estuaries and near-coastal marine waters are degraded by N enrichment that they are highly sensitive to potential adverse impacts from N addition from atmospheric deposition.

N enrichment of marine and estuarine waters can alter the ratios among nutrients and affect overall nutrient limitation. The sensitivity of estuarine and coastal marine waters to eutrophication from atmospheric N deposition depends on the supply of, and relative availability of, N and P. At upstream freshwater locations in Chesapeake Bay, P is often the limiting nutrient (Larson and Moore, 1985). At the transition between fresh water and salt water, N and P may be co-limiting, whereas the saltwater environments of the outer bay are usually N-limited (Fisher et al., 1998; Rudek et al., 1991). Nutrient limitation varies in space and over time, in response to changes in discharge and temperature that interact with estuarine morphology and hydrology (Paerl et al., 2006).

Primary symptoms		Description
	Chlorophyll *a* (Phytoplankton)	A measure used to indicate the amount of microscopic algae (phytoplankton) growing in a water body. High concentrations can lead to low dissolved oxygen levels as a result of decomposition.
	Macroalgal blooms	Large algae commonly referred to as "seaweed." Blooms can cause losses of submerged aquatic vegetation by blocking sunlight. Additionally, blooms may smother immobile shellfish, corals, or other habitat. The unsightly nature of some blooms may impact tourism due to the declining value of swimming, fishing, and boating.
Secondary symptoms		**Description**
	Dissolved oxygen	Low dissolved oxygen is a eutrophic symptom because it occurs as a result of decomposing organic matter (from dense algal blooms), which sinks to the bottom and uses oxygen during decay. Low dissolved oxygen can cause fish kills, habitat loss, and degraded aesthetic values, resulting in the loss of tourism and recreational water use.
	Submerged aquatic vegetation	Loss of submerged aquatic vegetation (SAV) occurs when dense algal blooms caused by excess nutrient additions (and absence of grazers) decrease water clarity and light penetration. Turbidity caused by other factors (e.g., wave energy, color) similarly affects SAV. The loss of SAV can have negative effects on an estuary's functionality and may impact some fisheries due to loss of a critical nursery habitat.
	Nuisance/toxic blooms	Thought to be caused by a change in the natural mixture of nutrients that occurs when nutrient inputs increase over a long period of time. These blooms may release toxins that kill fish and shellfish. Human health problems may also occur due to the consumption of contaminated shellfish or from inhalation of airborne toxins. Many nuisance/toxic blooms occur naturally, some are advected into estuaries from the ocean; the role of nutrient enrichment is unclear.

Source: Bricker et al. (2007))

Figure 3-41.   Description of the eutrophic symptoms included in the national estuary condition assessment.

The data for 92 worldwide coastal marine sites analyzed by Smith (2006), for which measurements of both total N and total P were available, illustrated that about half of the sites had total nitrogen (TN):total phosphorus (TP) above the Redfield ratio, which is commonly used to evaluate nutrient limitation in freshwater (TN:TP = 16). As was emphasized in earlier work on nutrient limitation in fresh waters by Redfield (1958) and Reiners (1986), elemental stoichiometry is a fundamental property of life that probably stems from the shared phylogenetic histories of marine and freshwater autotrophs (Smith, 2006; Sterner and Elser, 2002).

In general, the scientific community is at an early stage in development of an understanding of the effects of anthropogenic activities on the stoichiometry of nutrient loading to estuaries and marine waters (Dodds, 2006; Turner, 2002). Changes in nutrient stoichiometry in estuarine and marine ecosystems could alter algal assemblages and cascade to higher trophic levels (Frost et al., 2002).
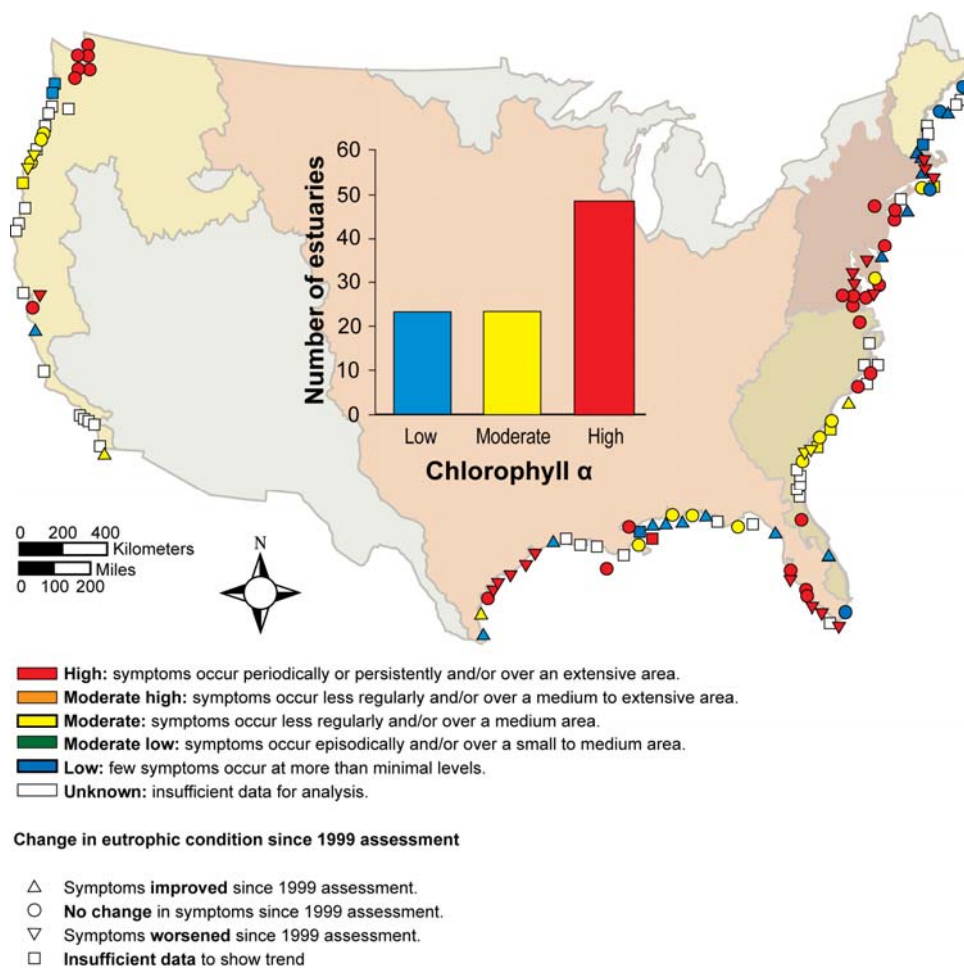
Figure 3-42. A high Chl *a* rating was observed in a large number of the nation's estuaries. White squares indicate that data were not available for a particular estuary.

Chlorophyll a

Chl *a* concentration in estuarine or marine water is an indicator of total phytoplankton biomass. It can signal an early stage of water quality degradation related to nutrient loading. High concentration of Chl *a* suggests that algal biomass is sufficiently high that it might contribute to low dissolved O_2 concentration due to increased decomposition of dead algae. In the national estuary condition assessment, high Chl *a* concentration was the most widespread documented symptom of eutrophication (Bricker et al., 2007) (see Figure 3-42). Half of the estuaries for which there were available data exhibited high Chl *a* concentration (Bricker et al., 2007).

San Francisco Bay, California is an example of an estuary that has experienced considerable increases in Chl *a* concentrations in recent years. Phytoplankton biomass in much of the bay has increased by more than 5% per year from 1993 to 2004. During this time, modeled primary production has doubled and nutrient loading is identified as one of eight possible causes (Cloern et al., 2006).

Macroalgal Abundance

Macroalgae are generally referred to collectively as seaweed. Macroalgal blooms can contribute to loss of important SAV by blocking the penetration of sunlight into the water column. Although

macroalgal data for estuaries in the U.S. were generally sparse, the national estuary condition assessment reported that conditions were moderate or high for 33 of the estuaries evaluated (Bricker et al., 2007).

Dissolved O_2

The decomposition of organic matter associated with increased algal abundance consumes dissolved O_2 and can reduce dissolved O_2 concentrations in eutrophic waters to levels that cannot support aquatic life. Decreased dissolved O_2 can lead to development of hypoxic or anoxic zones that are inhospitable to fish and other life forms. Perhaps the most important environmental effect of N input to coastal waters is the development of hypoxia. The largest zone of hypoxic coastal water in the U.S. has been documented in the northern Gulf of Mexico on the Louisiana-Texas continental shelf. During midsummer, this hypoxic zone has regularly been larger than 16,000 km^2 (Rabalais, 1998). The timing, duration, and spatial extent of hypoxia in this case are related mostly to the nutrient flux from the Mississippi River (Justic et al., 1993, 1997; Lohrenz et al., 1997; Paerl et al., 2001a; Rabalais et al., 1996).
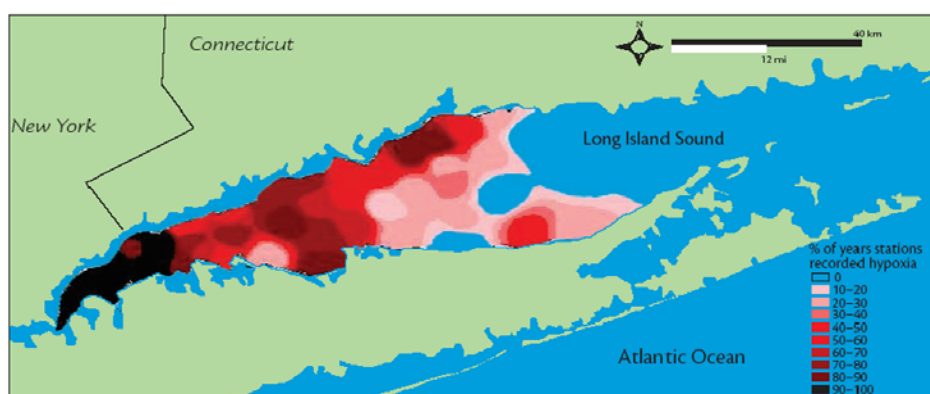
Source: Bricker et al. (2007))

Figure 3-43.   Frequency of hypoxia in Long Island Sound, 1994 to 2002.

Although impacts on dissolved O_2 can be quite severe in the areas where they are manifested, the national assessment reports that the severity of dissolved O_2 impacts related to eutrophication are relatively limited in many of the systems assessed (Bricker et al., 2007). In the shallow estuary of Long Island Sound, the existence of extended periods of low dissolved O_2 is a notable problem, and atmospheric deposition is considered to comprise a significant fraction of the total N loading. Dissolved O_2 levels below 3 mg/L are common, and levels below 2 mg/L also occur. During some years, portions of the Long Island Sound bottom waters become anoxic (<1 mg/L; see Figure 3-43).

Nuisance/Toxic Algal Blooms

Nuisance or toxic algal blooms reflect the proliferation of a toxic or nuisance algal species that negatively affects natural resources or humans. Such blooms can release toxins that kill fish and shellfish and pose a risk to human health. Unlike the other indicators of estuarine eutrophication, the role of nutrients in stimulating toxic algal blooms is less clear. Of the 81 estuary systems for which data were available, 26 exhibited a moderate or high symptom expression for nuisance or toxic algae (Bricker et al., 2007).

3.3.3.4. Summary of Nitrogen Effects on Carbon Cycling

The evidence is sufficient to infer a casual relationship between N deposition and alteration to the biogeochemical cycling of C in terrestrial, wetland, freshwater and marine ecosystems. N deposition causes alteration to the C cycle in forest ecosystems. Experimental N addition studies show a range of responses in terms of mortality and productivity. In general, moderate to high additions of N lead to either no significant change in growth rates or transient growth increases followed by increased mortality, especially at higher rates of fertilization (See Table 3-15). Although there remains considerable uncertainty in the potential response of soil C to increases in Nr additions (Neff et al., 2002), a meta-analysis by Johnson and Curtis (2001) suggested that N fertilization caused an 18% increase in soil carbon content. The effects of N addition on soil respiration are mixed; reductions at high levels of N (Lu et al., 1998), no effect (Vose et al., 1995) and increases (Griffin et al., 1997; Mikan et al., 2000) all have been observed.

Region trends in NEP have been documented through models based on observational gradient studies. Magnani et al. (2007) recently reported a strong correlation between estimated average long-term NEP (NEP_{av}) and estimated 1990 wet N deposition (up to 9.8 kg N/ha/yr) for 20 forest stands mostly in Western Europe and the conterminous U.S. Sutton et al. (2008b) critiqued the methods of Magnani et al. (2007). After considering the uncertainties in N deposition and climate variability, Sutton et al. (2008b) reported the estimated NEP response to N deposition was 68 kg C/wet-deposited N. Sutton et al. (2008b) agreed with Magnani et al. (2007) that N deposition remains an important driver of NEP_{av}, but did not support the NEP_{av} was overwhelmingly driven by N deposition. The ISA staff conducted a meta-analysis to examine the effect of N fertilization on forest ecosystem C content, defined as the sum of C content of vegetation, forest floor and soil (Johnson et al., 2006) and found that N addition increased ecosystem C by 6%. In summary, it remains unclear to what extent N deposition at current levels could potentially increase C sequestration in forest ecosystems in the U.S.

N addition causes alterations to the C cycle in Tundra. Mack et al. (2004) examined C and N pools in a long-term fertilization experiment at the arctic Long-Term Ecological Research site near Toolik Lake, AK. This study showed that increased nutrient availability enhanced decomposition of below-ground C pools in deep soil layers more than it increased primary production, leading to a substantial net loss of C from this ecosystem.

N deposition causes alteration to the C cycle in freshwater wetlands. In *Sphagnum*-dominated ombrotrophic bogs, higher N deposition resulted in higher tissue N concentrations and greater NPP (Aldous, 2002), but lower bulk density (Aldous, 2002). A study of 23 ombrotrophic peatlands in Canada with deposition levels ranging from 2.7 to 8.1 kg N/ha/yr showed peat accumulation increases linearly with N deposition (y = 2.84(x) + 0.67, r^2 = 0.32, p <0.001), however in recent years this rate has begun to slow indicating limited capacity for N to stimulate accumulation (Moore et al., 2004). Soil respiration has been studied in European countries under a natural gradient of atmospheric N deposition from 2 to 20 kg N/ha/yr. They found enhanced decomposition rates for material accumulated under higher atmospheric N supplies resulted in higher CO_2 emissions from soil. Primary production of plant species from intertidal wetlands typically increases with N addition, however most studies apply fertilizer treatments that are several orders of magnitude larger than atmospheric deposition (Darby and Turner, 2008; Mendelssohn, 1979; Tyler et al., 2007; Wigand et al., 2003).

N deposition causes alteration to the C cycle in freshwater aquatic ecosystems. The productivity of many freshwater ecosystems is currently limited by the availability of N (Elser et al., 2007). European and North American lakes may have been N-limited before human-caused disturbance, and remote lakes may have remained N-limited until slight increases in atmospheric N deposition brought about an increase in phytoplankton and periphyton biomass and induced P limitation. Numerous studies investigated the relationship between lake N concentration and primary productivity (reported as Chl *a*, NPP, or an index such as the lake chemistry ratio of dissolved inorganic N [DIN] to total P, DIN:TP) and atmospheric N deposition. N addition experiments of lake and stream bioassays in which N was added to waters in field or laboratory to measure the response. Gradient studies of undisturbed northern temperate, mountain, or

boreal lakes that receive low levels of atmospheric N deposition found strong relationships between N-limitation and productivity where N deposition was low, and P and N+P limitations where N deposition was higher (Bergström et al., 2005; Bergström and Jansson, 2006; Fenn et al., 2003a).

N deposition causes alteration to the C cycle in near coastal marine ecosystems. As previously mentioned, N deposition is not the sole source of N loading to estuaries and its contribution varies across the U.S. Estuaries and coastal waters tend to be N-limited and are therefore sensitive to increased atmospheric N loading (Elser et al., 2007; D'Elia et al., 1986; Howarth and Marino, 2006). This is at least partly because denitrification by microbes found in estuarine and marine sediments releases much of the added N inputs back into the atmosphere (Vitousek et al., 1997). However, other limiting factors occur in some locations and during some seasons. Levels of N limitations are affected by seasonal patterns. N-limited conditions are likely to be found during the peak of annual productivity in the summer.

Numerous studies evaluate the relationship between N loading, eutrophication and ecological endpoints including Chl-a, macroalgal abundance, dissolved O_2, nuisance/toxic and algal blooms In the national estuary condition assessment, high Chl a concentration was the most widespread documented symptom of eutrophication (Bricker et al., 2007) (see Figure 3-42).

3.3.4. Biogenic Trace Gases: Nitrous Oxide, Methane, Nitric Oxide and VOCs

Methane (CH_4) and nitrous oxide (N_2O) are greenhouse gases (GHGs) contributing to global warming. Although atmospheric concentrations of CH_4 (1774 ppb) and N_2O (319 ppb) are much lower than CO_2 (379 ppm), their global warming potential is 23 and 296 times that of CO_2, respectively. Human activities have dramatically increased atmospheric concentration of CH_4 by 48% and N_2O by 18% since pre-industrial times (IPCC 2007). The continuing increase of those GHGs concentrations have been shown to threaten human and ecosystem health. Anthropogenic N deposition to natural ecosystem is a primary component of global change. Additional N input not only changes the global N cycle, but also has profound effects on biogeochemical processes associated with GHGs emission (Vitousek et al., 1997; Dalal et al., 2003; Bodelier and Laanbroek 2004). In the following section, the effects of N addition on CH_4 and N_2O emissions were reviewed and quantitatively synthesized by meta-analysis. Further details on this meta-analysis including study site, ecosystem type, N addition level, chemical form of N, experimental conditions, relationship between N addition and CH_4 flux, are in included Annex C.

3.3.4.1. Methane

Atmospheric CH_4 originates mainly (70–80%) from biogenic sources (Le Mer and Roger, 2001). Methane is produced in anaerobic environment by methanogenic bacteria during decomposition of organic matter. Once produced in soil, CH_4 can then be released to the atmosphere or oxidized by methanotrophic bacteria in the aerobic zone (Le Mer and Roger, 2001). Methane production and oxidation processes occur simultaneously in most ecosystems. Wetland soils are generally CH_4 sources, accounting for about 20% of global CH_4 emission (see Annex C for a more detailed discussion of methane in wetlands). Non-flooded upland soils are the most important biological sink for CH_4, consuming about 6% of the atmospheric CH_4 (Le Mer and Roger, 2001). Numerous studies have demonstrated that N is an important regulatory factor for both CH_4 production and oxidation (Bodelier and Laanbroek, 2004).

The U.S. EPA conducted a meta-analysis, including 61 observations from 27 publications, to evaluate the relationship between N addition and CH_4 flux. Details on those publications, including study site, ecosystem type, N addition level, chemical form of N, experimental condition, are given in Annex C. The impact of N addition on CH_4 source and sink strength were estimated by CH_4 emission and CH_4

uptake respectively. The result suggested that N addition significantly increased CH_4 emission by 115% for grasslands and wetlands (Figure 3-44). This response ratio did not differ among vegetation type, N addition level, chemical form of N and experiment condition.
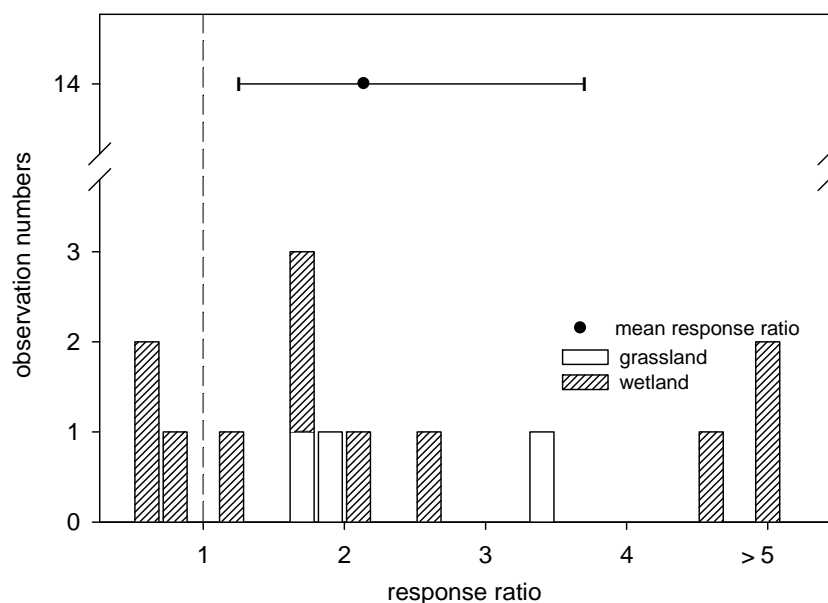
Figure 3-44. Effects of N addition on biogenic CH_4 emission. The bars show the distribution of the number of studies categorized by ecosystem type. The dot with error bars shows the overall mean response ratio with 95% CI.

Overall, N addition significantly reduced CH_4 uptake by 38% (Figure 3-45). Ecosystem type, N form and experiment condition influenced the degree of CH_4 uptake response to N addition (Figure 3-46). Methane uptake was reduced for all ecosystems, but this inhibition was significant only for coniferous and deciduous forest, with a reduction of 28% and 45%, respectively (Figure 3-46).

All forms of N fertilizer except urea were shown to reduce CH_4 uptake (Figure 3-46). Several possible mechanisms have been proposed to explain the inhibition in CH_4 oxidation by N addition. Besides the oxidation of CH_4, methane monooxygenase (MMO) can convert NH_4^+ to NO_3^-, and NH_4^+ therefore usually inhibits CH_4 oxidation by competing for MMO (Bodelier and Laanbroek, 2004). Methanotrophic bacteria are sensitive to osmotic stress induced by salts. Inhibition of CH_4 uptake by nitrogenous salts (e.g., KNO_3, NH_4Cl, and NH_4NO_3) and non-nitrogenous salts (e.g., K_2SO_4, KCl and NaCl) has been observed in field and laboratory studies (Bodelier and Laanbroek, 2004; King and Schnell, 1998). Other mechanisms, such as toxicity of nitrite (NO_2^-) produced by nitrification or denitrification processes, may also involve in the inhibition of CH_4 oxidation (Schnell and King, 1994).
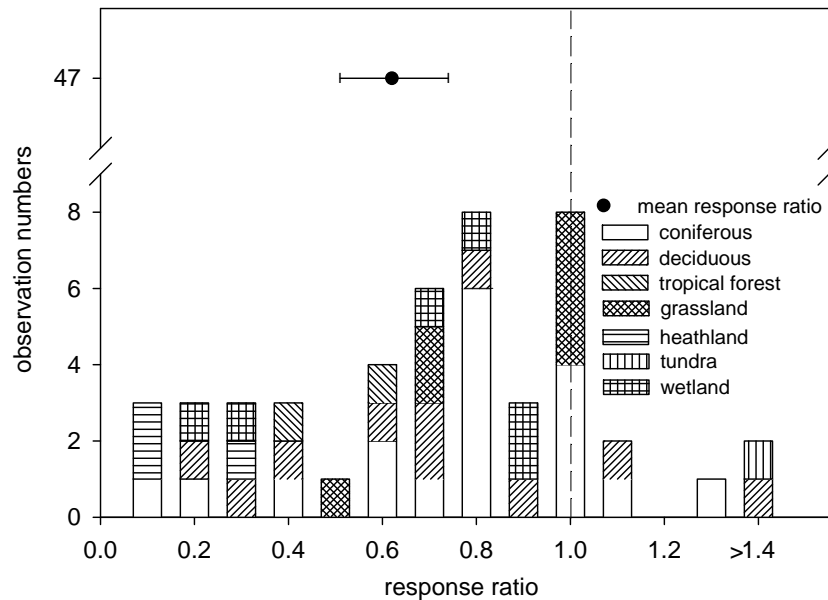
Figure 3-45. Effects of N addition on biological CH$_4$ uptake. The bars show the distribution of the number of studies categorized by ecosystem type. The dot with error bars shows the overall mean response ratio with 95% CI.

The mean response ratio of CH$_4$ uptake from laboratory incubation studies was significantly lower than that from field studies (Figure 3-46). This difference could be due to that the spatially and chemically heterogeneous field conditions resulted in large experimental errors (Crill et al., 1994; Gulledge and Schimel, 2000; Weitz et al., 1999). Also laboratory microcosms were characterized by a closed and incomplete N cycle, where N loss by leaching was very small and no plant competed for N with soil microbes. Therefore, N addition may result in stronger impacts on microbial processes under laboratory condition than under field condition

Several laboratory incubation studies found that CH$_4$ uptake rates decreased with increasing N input (Schnell and King 1994; King and Schnell 1998). This meta-analysis did not find significant correlation between the amount of N addition and the response ratio of CH$_4$ production/consumption (Figure 3-46). The lack of dose response relationship is probably because CH$_4$ production is influenced by multiple interactions of soil N content, soil moisture, pH and temperature (Le Mer and Roger, 2001), and varies greatly over small spatial and temporal scales (IPCC, 2001).
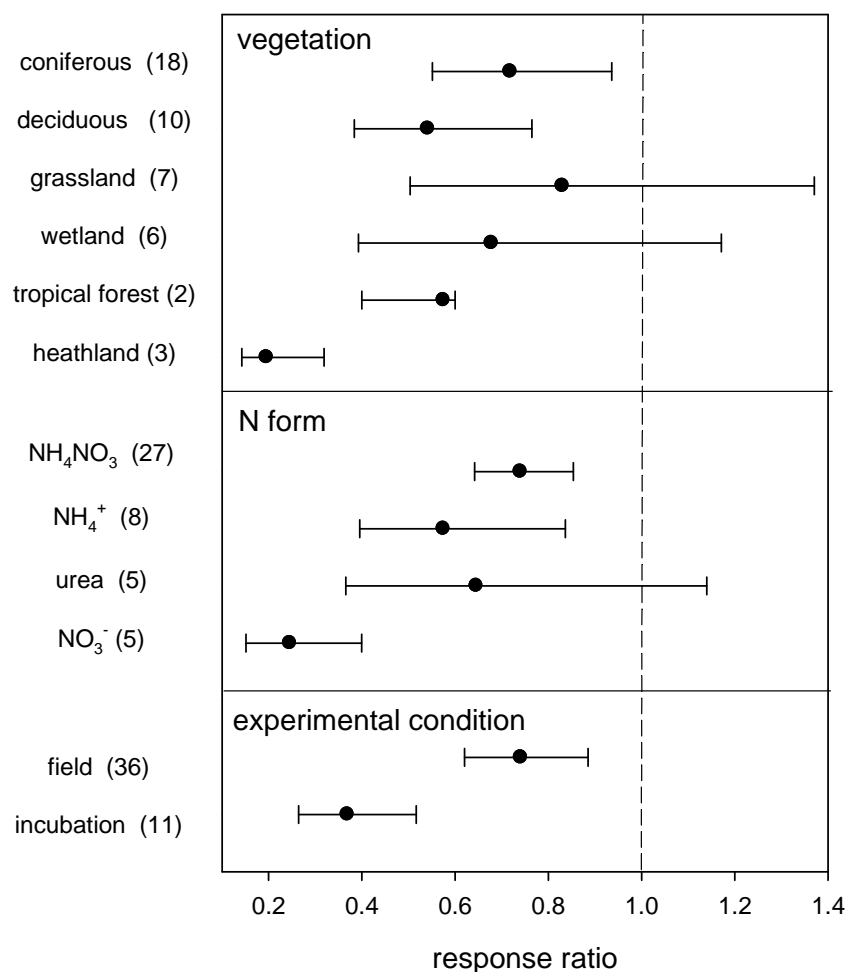
Figure 3-46.   Effects of N addition on biological CH₄ uptake. The data are expressed as the mean response ratio with 95% confident intervals. The numbers of studies included are indicated in parentheses.

3.3.4.2. Nitrous Oxide

Biogenic sources are the dominating contributors (>90%) to atmospheric N_2O. Terrestrial soil is the largest source of atmospheric N_2O, accounting for 60% of global emissions (IPCC, 2001). Nitrous oxide production in soil is mainly governed by microbial nitrification and denitrification (Dalal et al., 2003). The contribution of each process to the total N_2O production varies with environmental conditions. Denitrifying bacteria reduce NO_3^- or NO_2^- into N_2O or N_2 under anaerobic condition. In submerged soils such as wetland soil, denitrification should be the dominant contributing process to N_2O emission (Conrad, 1996). Increasing NO_3^- input generally increases denitrification rate under suitable condition of temperature and organic C supply. High soil NO_3^- concentrations also inhibit N_2O reduction to N_2 and result in high N_2O/N_2 ratio (Dalal et al., 2003). Under aerobic environment, autotrophic nitrifying bacteria obtain energy by reducing NH_4^+. Nitrous oxide is an intermediate product of the oxidation of NH_4^+ to NO_2^- or decomposition of NO_2^-. The increase in N_2O emission following NH_4^+ addition has been observed in many lab and field experiments (Aerts and Toet, 1997; Aerts and de Caluwe, 1999; Keller et al., 2005).

The U.S. EPA conducted a meta-analysis on the effects of N addition on N_2O emissions from non-agricultural ecosystems, including 99 observations from 30 publications. N addition normally increased N_2O emissions, but some studies also observed N_2O emission was decreased by N addition (Ambus and Robertson, 2006; Ambus et al., 2006; Borken et al., 2002; Curtis et al., 2006; Skiba et al., 1999). Although some natural ecosystems can be an N_2O sink (Chapuis-Lardy et al., 2007), very limited publications assessed the impact of N addition on N_2O uptake. Thus, only changes in N_2O production were estimated in this meta-analysis. Overall, the results of the meta-analysis indicated that N addition increased N_2O emission by 215% (Figure 3-47). The response of N_2O emissions was influenced by ecosystem type, the form and the amount of the N addition (Figure 3-48).
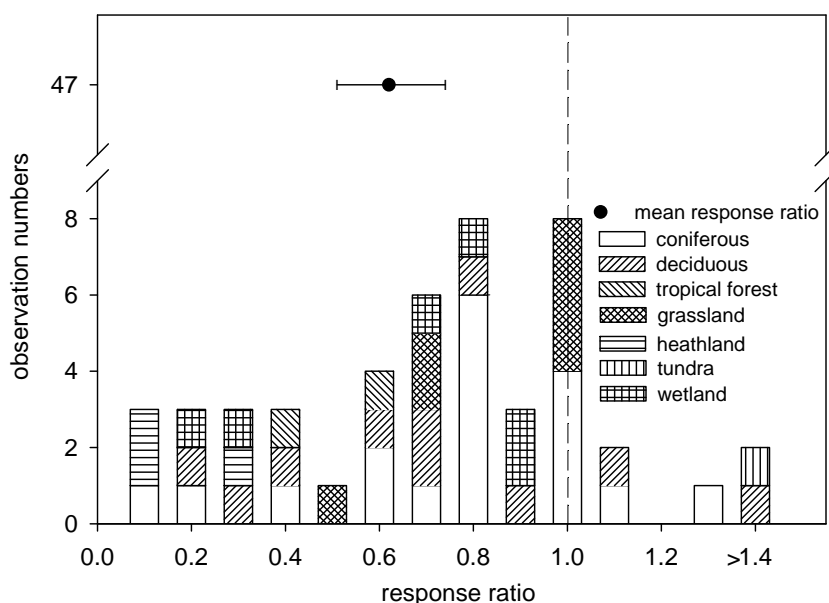
Figure 3-47. Effects of N addition on biogenic N_2O emission. The bars show the distribution of the number of studies categorized by vegetation type. The dot with error bars shows the overall mean response ratio with 95% CI.

Compared to other ecosystems, tropical forest emitted more N_2O under N enrichment condition (+735%) (Figure 3-48). This greater response may be because tropical forests are often P limited rather than N limited (IPCC, 2001). Hall and Matson (1999) measured N_2O emissions after adding N fertilizer in two tropical rainforests in Hawaii. They found that N_2O emissions from P-limited sites was 54 times greater in the short term N addition experiment and 8 times greater in the chronic N addition experiment compared to that from N-limited sites. The P-limited soil had higher inorganic N concentration than the N-limited soil (Hall and Matson, 1999) which increased N availability to the nitrifying and denitrifying bacteria. However, climatic conditions, especially temperature and precipitation, can also be important factors driving N_2O emissions from tropical forest ecosystem.

NO_3 caused a higher stimulation (+494%) o N_2O emissions than NH_4^+ did (+95%) (Figure 3-48), which was consistent with the previous field studies (Keller et al., 1988; Russow et al., 2008; Wolf and Russow, 2000). By adding ^{15}N labeled NO_3^- and NH_4^+ to soil, Russow et al. (2008) found that N_2O was mainly emitted by denitrification and the contribution of denitrification to the total N_2O production increased from 54% in soil with normal SOM content to 76% in soil with high SOM.

The Intergovernmental Panel on Climate Change (IPCC) issued a guideline for national GHGs inventories of biogenic N_2O (IPCC, 2000). In this guideline, the default N_2O emission factor is 1.25% for

N fertilizer applied to agricultural fields (i.e., 1.25% of the amount of N applied to a field will be emitted to the atmosphere as N_2O). Several studies have questioned the validity of this emission factor. Some studies suggested a much lower emission factor, such as 0.25% for rice paddy field (Yan et al., 2003) and 0.02% for semi-arid regions (Barton et al., 2008), while others found the amount of N_2O emission was not clearly related to the amount of N addition (Akiyama et al., 2005; Barnard et al., 2005; FAO/IFA, 2001). The U.S. EPA compiled ambient N_2O emission data from 36 studies and did not find any correlation between N_2O emission and the level of N deposition (Figure 3-49). In this meta-analysis, although the mean response ratio increased with the amount of N addition, the differences among the three levels (<75, 75–150 and >150 kg N/ha/yr) were not significant (Figure 3-48). The weak correlation is probably due to that the effect of N addition on N_2O emission is affected by many other biotic and abiotic factors such as fertilizer type, vegetation, temperature, soil drainage etc. (Dalal et al., 2003).
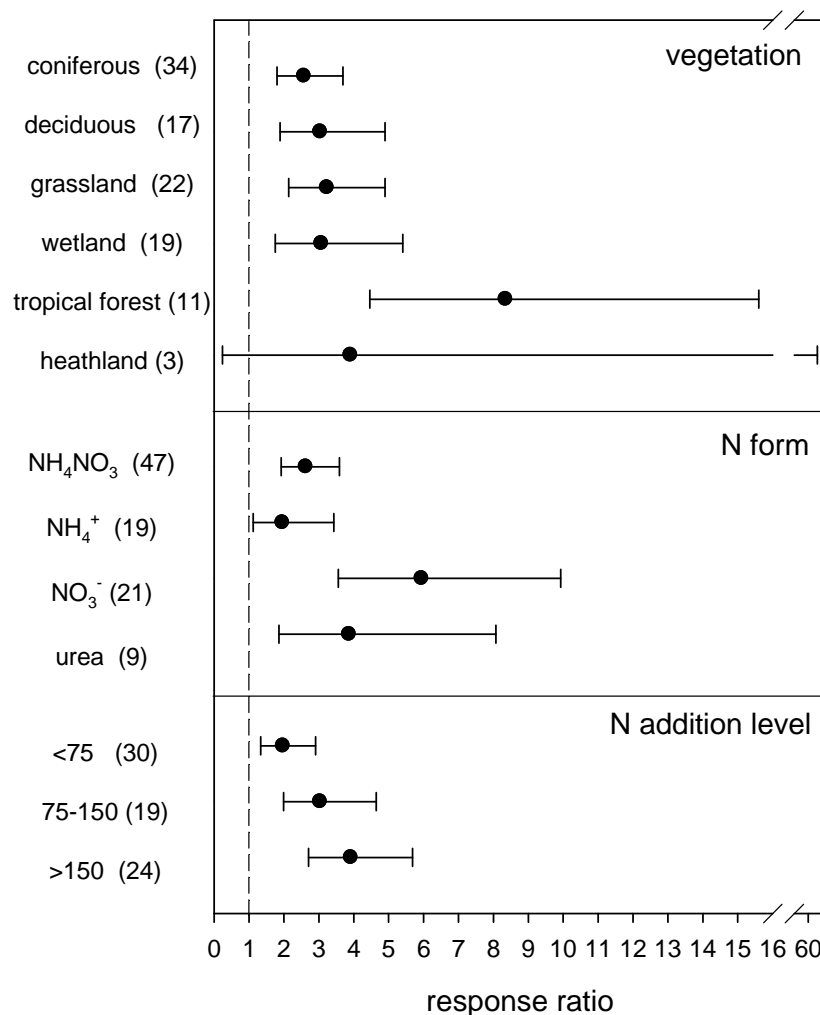
Figure 3-48. Effects of N addition on biogenic N_2O emission. The data are expressed as the mean response ratio with 95% confident intervals. The numbers of studies included are indicated in parentheses.
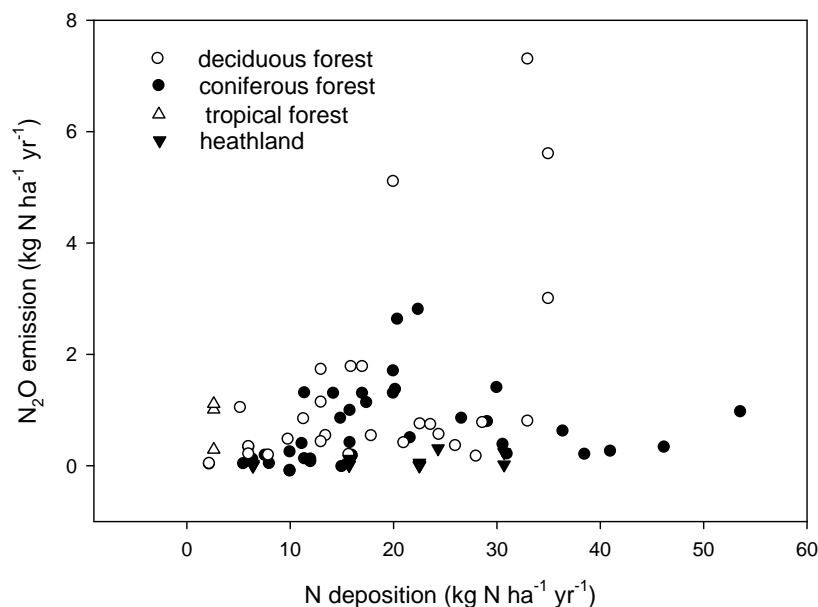
Figure 3-49. **The relationship between N₂O emission and N deposition. The data were compiled from 36 independent studies.**

3.3.4.3. Nitric Oxide and VOCs

N saturation caused by chronic N input often leads to increased soil NO emission (Hall and Matson 1999; Venterea et al., 2003; Venterea et al., 2004; Kitzler et al., 2006). Although nitrification and denitrification both contribute to NO production, many studies have found that NO flux increased in a manner that was consistent with nitrification rate increases, suggesting that NO emission is more triggered by nitrification activity rather than by denitrification activity (Wolf and Russow 2000; Venterea et al., 2004).

Monthly NO monitoring at Harvard Forest showed that NO emission increased at coniferous plots treated with 50 and 150 kg N/ha/yr and hardwood plots treated with 150 kg N/ha/yr (Venterea et al., 2003). NO emission accounted for 3.0-3.7% of N inputs to the high N plots and 8.3% of inputs to the coniferous low N plots. At two paired watersheds subjected to elevated N input, 35.5 kg N/ha/yr at Fernow Experimental Forest in Western Virginia and 25.2 kg N/ha/yr at the Bear Brook Watershed in Maine, NO emissions at the N amended watersheds (0.61-6.8 µg NO-N /m^2/h) were higher than the reference watersheds (0.21-1.4 µg NO-N /m^2/h). Mean NO fluxes at both watersheds were positively correlated with mean soil NO_3^- concentrations (Venterea et al., 2004). Similarly, (Pilegaard et al., 2006) found that NO emission from 7 coniferous forests in Europe were highly correlated with the rates of N-deposition (NO flux (µg N/m^2/h) = 25.52 ×N deposition (g N/m^2/yr) -13.93; r^2=0.82).

The response of NO production rates to N deposition may vary significantly between vegetation types and climatic regimes. The measurements of 15 forest sites across Europe showed that coniferous forest emitted more NO (31.0±15.6 µg NO-N/m^2/h) than deciduous forest (4.1±1.9µg NO-N/m^2/h), although the average N deposition to coniferous forests (16 ± 5 kg N/ha/yr) was similar to deciduous forests (15±2 kg N/ha/yr) (Pilegaard et al., 2006). Several studies, such as ButterbachBahl et al. (1997) and Venterea et al. (2003), also found that NO emissions from coniferous forest were generally higher than from deciduous forest. This difference is probably due to that the characteristics of coniferous forest floor, such as low soil moisture and low pH, favour nitrification and thus NO emission (Pilegaard et al., 2006).

In addition to vegetation type, climate and soil nutrient conditions also influence NO flux under N enrichment. Natural forests in tropic region are generally considered P limited, contrasting with N-limited temperate forests (Vitousek et al., 1997). After adding N (50 kg N/ha/yr) to three tropical rainforests (N limited, NP-limited and P limited) in Hawaii, Hall and Matson (2003) found that all N addition plots emitting more NO than control plots and responses of NO production to N addition increased in the order of: P limited sites >NP-limited sites >N limited sites. Hall and Matson (2003) work suggested that P-limited and N-limited ecosystems responded differently to N deposition. Rather than retaining N in ecosystems, anthropogenic N addition may immediately increase N trace gas loss if N availability exceeds biological demand.

3.3.4.4. Volatile Organic Compounds (VOCs)

Volatile organic compounds (VOCs) comprise a wide range of chemical compounds including hydrocarbons, halocarbons and oxygenates. Methane is one of the most important VOCs and the effect of N addition on CH_4 emission was discussed in Section 3.3.4.1. The available information for non-methane VOCs emissions is much sparser than that for CH_4, with only a few studies measuring isoprene emissions under N enrichment. Isoprene is the primary non-methane hydrocarbon emitted from temperate deciduous forest and tropical forest (Funk et al., 2006). Both pot and field studies found that there was a strong positive correlation between isoprene emission rates and leaf N concentrations (Litvak et al., 1996; Funk et al., 2006). N addition could significantly increase plant isoprene emissions by increasing leaf N concentrations (Harley et al., 1994; Litvak et al., 1996).

3.3.4.5. Summary of N Effects on Biogenic Trace Gases

Integrating 160 observations across 57 independent studies, this meta-analysis suggested that N addition tended to increase CH_4 emission, reduce CH_4 uptake and increase N_2O emission. Overall, N deposition may result in higher CH_4 and N_2O concentrations in atmosphere and exacerbate global warming, but these responses can also be influenced by many environmental factors, such as vegetation type, N form, and climate.

The evidence is sufficient to infer a casual relationship between N deposition and the alteration of biogeochemical flux of CH_4 in terrestrial and wetland ecosystems. N addition ranging from 10 to 560 kg N/ha/yr reduced CH_4 uptake by 38% across all ecosystems (Figure 3-45), but this inhibition was significant only for coniferous and deciduous forest, with a reduction of 28% and 45%, respectively (Figure 3-46). Wetlands are generally net sources of CH_4, but some wetlands can be net sinks depending on environmental conditions such as drainage and vegetation (Crill et al., 1994; Saarnio et al., 2003). The meta-analysis indicated that N addition, ranging from 30 to 240 kg N/ha/yr, increased CH_4 production by 115% from the source wetlands (Figure 3-44), but had no significant effect on CH_4 uptake of the sink wetlands (Figure 3-46).

The evidence is sufficient to infer a casual relationship between N deposition and the alteration of biogeochemical flux of N_2O in terrestrial and wetland ecosystems. Overall, the results of the meta-analysis discussed in Section 3.3.4 indicated that N addition ranging from 10 to 560 kg N/ha/yr. increased N_2O emission by 215% in terrestrial ecosystems (Figure 3-47). The response of N_2O emission to N for coniferous forest, deciduous forest and grasslands was significant (Figure 3-48). In the meta-analysis of 19 observations from studies that evaluated the effects of N additions ranging from 15.4 to 300 N kg N/ha/yr was shown to increase the production of N_2O by 207% in wetlands (Figure 3-48).

3.3.5. Species Composition, Species Richness and Biodiversity

A common response to environmental stress is the tendency for the more sensitive species to decrease in abundance, or to be eliminated, while the more tolerant species increase in abundance (Woodwell, 1970). Species composition and species richness, as well as impacts on rare or threatened species, indicate changes to biodiversity. The ecological consequences of changing species composition, richness and/or biodiversity can be profound. Selective removal of certain species can result in an impairment of ecosystem function, change in community structure and food web dynamics, and decrease in species richness and diversity. Such changes in species composition can occur in response to N addition to terrestrial, aquatic, and transitional ecosystems.

Weiss et al. (2006) presented an overview of potential biodiversity loss from N enrichment. A survey by Stohlgren et al. (1999) of variables that contribute to species richness and invisibility of sites found negative relationships between soil N, and species richness and numbers of nonnative plant species. The implication of this work is that N fertilization alters competitive interactions that may cause native species to be lost, with subsequent decrease in species richness.

Alteration of plant productivity and growth by N deposition (see Section 3.3.3) causes a cascading effect on the competitive interactions among species. Atmospheric deposition of N is expected to benefit those species that are best able to take advantage of the increased nutrient availability. Other species may experience decreased growth, reproduction and population size, because they are out-competed by species that are more successful under conditions of enhanced N availability. Numerous studies evaluate ecosystem response to levels of N addition that far exceed the range of N deposition levels in the U.S. This assessment focuses on the information most relevant to the review of the NAAQS, therefore research conducted at N loading levels that greatly exceed current conditions (>150 kg N/ha/yr) are excluded from the discussion.

3.3.5.1. Terrestrial Ecosystem Biodiversity

Atmospheric inputs of N can alleviate deficiencies and increase growth of some plants at the expense of others. Thus, N deposition can alter competitive relationships among terrestrial plant species and therefore alter species composition and diversity (Ellenberg, 1987; Kenk and Fischer, 1988; U.S. EPA, 1993a). Wholesale shifts in species composition are easier to detect in short-lived ecosystems such as annual grasslands, in the forest understory, or mycorrhizal associations than for long-lived forest trees where changes are evident on a decadal, or longer, time scale. Note species shifts and ecosystem changes can occur even if the ecosystem does not exhibit signs of N saturation.

Forests

Trees

There is very little information on the effect of N deposition on the biodiversity of overstory trees in the U.S. However, the altered growth rates caused by N enrichment have the potential to affect forest structure and biodiversity. The life span of many trees is 100 years or more, therefore observation of how growth rates effect biodiversity within established forests are difficult to observe on a decadal time scale.

N deposition has been observed to cause tree invasion into grasslands, also called forest encroachment. A study of the northern edge of the Great Plains (southern Canada), showed that increasing N deposition over a range of 8 to 22 kg N/ha/yr to aspen-dominated forest and boreal forest caused an increase forest expansion into the grasslands (Kochy and Wilson, 2001). The following mechanisms have been document to facilitate forest encroachment. Due to their height, trees and shrubs can intercept more airborne particulate N than grasses and they should therefore benefit most from N deposition (Kellman and Carty, 1986; Binkley, 1995). Fertilization also increases the water-use efficiency of woody invaders

(Bert et al., 1997) and this may enable them colonize temperate grasslands on dry, coarsely textured soils. Accelerated N cycling following deposition (Berendse, 1994; Carreiro et al., 2000; Högbom and Högberg, 1991) decreases competition for N and increases competition for light (Wilson and Tillman, 1991), and may give further advantage to tall or fast growing trees (Aerts et al., 1999). Overall, therefore, increased deposition rates may result in a self-maintaining positive feedback that allows trees to establish in grasslands (Wilson et al., 1998).

Understory Herbaceous Plants and Shrubs

Studies in Europe have generally been based on natural gradients, whereas findings in the U.S. have mostly been based on experimental N addition. The effects of increasing N deposition on herbaceous plants were reviewed by (Gilliam et al., 2006b). Reported effects include species shifts towards nitrophilous and more acid-tolerant plant species along a deposition gradient from 6 to 20 kg N/ha/yr in Swedish oak forests; a decline in abundance and cover of ericaceous shrubs along a deposition gradient from <3 to >12 kg N/ha/yr in the boreal forest in Sweden; and a decline in herbaceous cover under hardwoods following 3 years of N additions applied as $(NH_4)_2SO_4$ at rates ranging from 14 to 28 kg N/ha/yr. The decline in herbaceous cover in the latter study was attributed to increased shading by ferns, and the effect was more pronounced at sites that experienced lower ambient atmospheric N inputs.

Van Breemen and Van Dijk (1988) noted that over the previous several decades of N deposition the composition of plants in forest herb layers in The Netherlands had shifted toward species commonly found in N-rich areas. Brunet et al. (1998) and Falkengren-Grerup (1998) reported the effects of excessive N deposition on mixed-oak forest vegetation along a depositional gradient. Results of this study suggest that N deposition had affected non-woody vegetation directly by increased N availability and, indirectly, by accelerating soil acidity. Time series studies indicated that 20 of the 30 non-woody plant species that were associated most closely with high N deposition had increased in abundance in those areas in Europe that received high N deposition.

Mixed results have been reported in other studies. Research at Fernow Experimental Forest, West Virginia, indicated that application of 35 kg N/ha/yr applied as $(NH_4)_2SO_4$ for 6 years had no significant impact on the herbaceous layer in an Appalachian hardwood forest (Gilliam et al., 2006a). Fernow has been the recipient of high levels of N deposition for decades, raising the possibility that the herbaceous layer responded long ago to changes in N availability.

Mycorrhizal and Microbial Diversity

Mycorrhizal and microbial biodiversity can also be affected by N enrichment. Relationships among plant roots, mycorrhizal fungi, and microbes are critical for N cycling and for the growth and health of plants. Mycorrhizal fungal diversity has been shown to be associated with above-ground plant biodiversity and ecosystem productivity (Wall and Moore, 1999) and to be adversely affected by increased N availability (Egerton-Warburton and Allen, 2000). The loss of mycorrhizal function has been hypothesized as a key process contributing to reduced N uptake by vegetation and increased NO_3^- mobility from soil into drainage water under conditions of high N supply (U.S. EPA, 2004).

Progressive decline in ectomycorrhizal fungal species richness in Alaskan coniferous forest (white spruce [*Picea glauca*] dominant) occurred along a local N deposition gradient, from 1 to 20 kg N/ha/yr, downwind from an industrial complex (Lilleskov et al., 2002). Ectomycorrhizal fungal communities are important in tree nutrition, and ectomycorrhizal fungal trees tend to be dominant in N-limited forest ecosystems.

N fertilization at rates of 54 and 170 kg N/ha/yr (as NH_4NO_3) led to a decline in ectomycorrhizal fungal diversity and species composition in an oak savanna at Cedar Creek Natural History Area in Minnesota (Avis et al., 2003). In the reference plots, five species collectively accounted for more than 40% cover versus four plant species in the lower N addition plots. In the higher N addition plots, a single plant species accounted for more than 40% cover.

Compton et al. (2004) investigated the effects of 11 years of experimental N addition on forest soil microbial ecology. Experimental N addition decreased the C content of microbial biomass in the O horizon of both experimental forest stands, based on chloroform fumigation-extraction. In addition, the use of N-containing substrates by microbes appeared to be reduced by N addition in the pine stand, but not in the hardwood stand. In addition, the use of N-containing substrates by microbes appeared to be reduced by N addition in the pine stand, but not in the hardwood stand. The mechanisms responsible for such changes are not clear (Arnebrandt et al., 1990; Compton et al., 2004). It is possible that added N has both direct (nutrient) and indirect (soil chemistry, organic matter quality, and quantity) effects on microbial ecology. Effects can be manifested on mycorrhizal fruiting body abundance, hyphal networks, and community composition (Frey et al., 2004; Lilleskov et al., 2002).

Grasslands

Reduced biodiversity in response to N deposition is reported for grasslands in the U.S. and Europe. Clark and Tilman (2008) recently evaluated the effects of chronic N deposition over 23 years in Minnesota prairie-like successional grasslands and in a native savanna grassland, each originally dominated by a species-rich mixture of native C_4 grasses and forbs (Cedar Creek Long Term Ecological Research Site, Minnesota). Experimental N addition ranged from 10 to 95 kg N/ha/yr above ambient atmospheric N deposition (6 kg N/ha/yr). The N addition rate reduced plant species numbers by 17% relative to controls receiving ambient N deposition. Moreover, species numbers were reduced more per unit of added N at lower addition rates and relative species number was reduced at all addition levels. This suggests that chronic but low-level N deposition may decrease diversity below the lowest addition levels tested (the critical load was calculated as 5.3 kg N/ha/yr with an inverse prediction interval of 1.3–9.8 kg N/ha/yr). A second experiment showed that a decade after cessation of N addition, relative plant species number, although not species abundances, had recovered, demonstrating that some effects of N addition are reversible.

Change in species composition in response to N deposition has been observed regardless of soil type in European grasslands. Such effects have been found in calcareous, neutral, and acidic environments, species-rich heaths, and montane-subalpine grasslands (Bobbink et al., 1992b; 1998; Bobbink, 1998; Stevens et al., 2004). A transect of 68 acid grasslands across Great Britain, covering the lower range of ambient annual N deposition (5 to 35 kg N/ha/yr), indicates that long-term, chronic N deposition significantly reduced plant species richness. Species richness declined as a linear function of the rate of inorganic N deposition, with a reduction of one species per 4–m^2 quadrant for every 2.5 kg N/ha/yr of chronic N deposition.

Grasslands are well known to respond to increased N availability through changes in growth rates of both native and exotic species. Under high N supply, exotic grasses often out-compete other species, and cause changes in plant community composition (Lowe et al., 2002). A summary of studies, which have shown altered plant community composition, or growth rates of plant species that have implications for community composition is in Table 3-17. Increased availability of N to grasses can also affect herbivores that feed on grasses by altering food quality, quantity, and phenology, and perhaps by changing the relationships between herbivores and their predators (Throop and Lerdau, 2004).

Table 3-17.   Summary of N effects on grassland biodiversity.

Region/Country	Endpoint	Observations	Grassland Type/ Species	Reference
San Francisco Bay Area, CA	Bay Checkerspot Populations	**Observation:** Serpentinitic soils sustain native grasses that support populations of the endangered Bay Checkerspot butterfly. Several lines of evidence indicate that dry N deposition is responsible for grass invasion and subsequent decline of the butterfly population. However, this relationship is uncertain.	Serpentine Grasslands Bay Checkerspot Butterfly (*Euphydryas Editha Bayensis*)	Weiss (1999)
Colorado	Growth	**Greenhouse experiment**: they tested the response of grassland species to increased N availability (0, 10, 40, 70, or 100 kg N/ha/yr) over 75 days. All of the grass species exhibited increased growth with increased N availability. Native species did not consistently grow better at low N levels than the exotic species. Two of the exotic grasses exhibited the greatest increase in growth, while another of the exotics exhibited the smallest increase in growth.	Two North American Native Species (Blue Grama And Western Wheatgrass) and Four Exotic Species (Cheatgrass, Leafy Spurge, Canada Thistle, and Russian Knapweed)	Lowe et al. (2002)
Plant Research Laboratory, University of Illinois at Chicago	Growth and Tissue Quality	**Field Addition**: N additions in (0.1, 1, 3 mmol N addition for 80 days), caused species-specific growth and plant tissue quality changes. C_3 grasses (*Elymus virginicus L., E. Canadensis L.*) showed a greater positive growth response to N additions than C_4 grasses (*Andropogon geradii Vitmanm, Schizachyrium scoparium Michx.*) and forbs (*Solidago nemoralis Ait., S. rigida L.*). Species with smaller initial biomass exhibited the greatest increase in biomass, with a sevenfold to eightfold increase in *S. nemoralis* and *E. canadensis* and only a threefold increase in *S. rigida*.	Tallgrass Prairie	Lane and BassiriRad (2002)
Jasper Ridge Biological Preserve in California	Species Richness and Diversity	**Field Addition**: 70 kg N/ha/yr over three years led to decreased to a decline in total species richness, species diversity decreased by 5% and all three N-fixing forbs disappeared.	Nine Annual Species: *Avena Barbata, Bromus Hordeaceus, Lolium Multiflorum, Avena Fatua, Bromus Diandrus, Anagallis Arvensis, Geranium Dissectum Erodium Botrys, Vicia Sativa,* and one Biennial Species, *Crepis Vesicaria*	Zavaleta et al. (2003)
Lund University, Lund, Southern Sweden	Growth	**Greenhouse experiment**: Sand-solution experiments studying how growth was effected by N concentrations of 50, 250 and 1250 µM in a simulated acid forest soil solution, similar to naturally occurring soil solutions is Southern Sweden. 46% of grasses displayed a significantly greater biomass at 250 than at 50 µM N as compared with only 7% for the herbs. Some species attained their highest biomass at 1250 µM N and others at 50 µM N. Grasses grew better than herbs in response to experimental addition of N. At the highest experimental N deposition rates, growth was limited for most species by the supply of nutrients other than N.	15 Herb and 13 Grass Species	Falkengren-Grerup (1998)

Region/Country	Endpoint	Observations	Grassland Type/ Species	Reference
Minnesota, Cedar Creek Natural History Area	Species Composition	**Field Addition**: N enrichment over a 12 year period on 162 plots using a N addition gradient from 0 to 30 g $N/m^2/yr$. Plots initially dominated by native warm-season grasses shifted to low-diversity mixes of species dominated by cool-season grasses at all but the lowest rates of N addition. Grasslands with high N retention and C storage rates were the most vulnerable to loss of species and major shifts in N cycling in response to experimental N enrichment.	Three N-Limited Minnesota Grasslands with Varying Successional Age, Species Composition, and Total Soil C	Wedin and Tilman (1996)
San Francisco Bay Area, CA	Species Composition	**Observational**: N deposition levels of 10 to 15 kg N/ha/yr, exotic nitrophilous grasses have been reported to have displaced native grass species, likely due to greater N availability from deposition and from the cessation of grazing, which previously exported N out of the system	Grasslands	Fenn et al. (2003a)
Jasper Ridge Biological Preserve in California	Npp	**Field Addition**: 70 kg N/ha/yr applied as $(CaNO_3)_2$ increased NPP by 30%	Grasslands	Shaw et al. (2003)
Jasper Ridge Biological Preserve in California	Herbivory, Leaf Tissue N And Growth Rates	**Field Addition**: 70 kg N/ha/yr applied as $(CaNO_3)_2$ caused altered herbivory by gastropod which differed by species ($\downarrow$, $\uparrow$ and no change), 5 out of 6 species had increased leaf tissue, 5 out of 6 species had increased growth rates	Grasslands	Cleland et al. (2006)
Michigan old field	Biomass	**Field Addition**: 120 kg N/ha/yr applied as NH_4NO_3 pellets had a significant positive growth effect on annual dicot biomass but no significant growth effect on annual grass biomass.	Grasslands	Huberty et al. (1998)
Brookhaven Nat. Lab., Long Island, New York and the Sciences Greenhouse Facility, SUNY, Stony Brook, NY	Vegetative and Seed Biomass and Decreased Root: Shoot Ratios	**Field Additions and Greenhouse experiment:** N addition to common ragweed (*Ambrosia artemisifolia*) led to increased vegetative and seed biomass and decreased root: shoot ratios. N deposition may indirectly affect biomass production and allocation through affecting insect herbivory. The particularly strong influence of both herbivory and N deposition on *A. artemisifolia* reproduction suggests potential population and community-level consequences.	*Ambrosia Artemisiifolia* (Common Ragweed) and two of its Insect Herbivores; a Leaf Beetle, *Ophraella Communa Lesage* (*Coleoptera: Chrysomelidae*), and an Aphid, *Uroleucon Tuataiae Olive* (*Hemiptera: Aphididae*)	Throop (2005)

Not all studies have shown an effect of N addition on species richness or diversity. In old agricultural fields in Michigan, increased N deposition changed neither the successional timing nor the gain or loss of species numbers (Huberty et al., 1998). A lack of response in species richness may have been due to application of mid-growing season fertilization in the experimental design. Huberty and colleagues (1998) suggested that N additions may change the dominance structure instead of the species composition, of these successional old-field communities. Other studies in Michigan on successional grasslands showed no response to N application of 10 kg $N/m^2/yr$, equivalent to about 2.5 times current deposition rates (Ambus and Robertson, 2006).

Arid and Semi-Arid Land Ecosystems

Some arid and semi-arid ecosystems in the southwestern U.S. are considered sensitive to N enrichment effects and receive high levels of atmospheric N deposition. However, water is generally more

limiting than N in these systems. Nevertheless, enhanced N may play a role in the observed invasion of some exotic plant species and associated changes in ecosystem function, especially where water supply is adequate.

In semi-arid ecosystems, results from several N fertilization experiments showed increased biomass of nonnative plant species over native species; decreased soil moisture under some conditions; and increased fire risk where dense mats of grasses replaced shrub cover (See Table 3-18).

Much of the arid land data are from the coastal sage scrub (CSS) communities of southern California, down-wind of the Los Angeles Basin, where dry N deposition is very high. The CSS community in California has been declining in land area and in shrub density over about the past 60 years and is being replaced in many areas by Mediterranean annual grasses (Padgett and Allen, 1999; Padgett et al., 1999). N deposition is considered a possible cause or contributor to this ecosystem alteration. More than 30 kg N/ha/yr of atmospheric N is deposited to portions of the Los Angeles Air Basin (Bytnerowicz and Fenn, 1996). The CSS community is of particular interest because about 200 sensitive plant species and several federally listed threatened or endangered animal species are found in the area.

Native shrub and forb seedlings in the CSS community are unable to compete with dense stands of exotic grasses, and thus are gradually replaced by the grasses, especially following disturbances such as fire (Cione et al., 2002; Eliason and Allen, 1997; Yoshida and Allen, 2001). Biodiversity impacts have also been documented for microbial communities in coastal sage scrub ecosystems. It has been hypothesized that the decline in coastal sage shrub species could be linked to the decline of the arbuscular mycorrhizal community (Egerton-Warburton and Allen, 2000).

Table 3-18.   Summary of N effects on arid and semi-arid ecosystems.

Region/Country	Endpoint	Observations	Ecosystem Type/ species	Reference
Southeast Idaho	Species composition and cover	**Field Addition:** 6 or 12 kg N/ha/yr applied as NH_4NO_3 for 6 years (in addition to ambient inputs of 1.3 to 1.4 kg N/ha/yr) resulted in a decrease in soil moisture caused by shifts in plants species composition and cover. However, there were no effects on perennial grass cover in response to experimental N additions	Sagebrush (*Artemisia tridentata*) steppe eco-system	Inouye (2006)
Southern California	Plant community	**Observation:** Dry N deposition is above 30 kg N/ha/yr in some places. Native shrub and forb seedlings in this plant community are unable to compete with dense stands of exotic grasses, and thus are gradually replaced by the grasses, especially following disturbances such as fire	Coastal sage scrub	Eliason and Allen, (1997); Yoshida and Allen (2001); Cione et al. (2002)
Southern California	Plant community	**Greenhouse and deposition gradient experiments**: N deposition is considered a possible cause or contributor to declining shrub density over about the past 60 years and is being replaced in many areas by Mediterranean annual grasses	Coastal sage scrub	Allen et al. (1998); Padgett and Allen (1999); Padgett et al. (1999)

Region/Country	Endpoint	Observations	Ecosystem Type/ species	Reference
Southern California	Response of native and nonnative plants.	**Greenhouse Experiment:** N (as 5.4 g/L NH_4Cl or 10g/L KNO_3) was added to obtain soil N concentrations of 2, 20, 40, and 80 µg/g. The grasses demonstrated a 1.5– to 2.5– fold growth increase when soil N levels increased from 20 to 40 µg/g. To achieve a comparable growth increase, shrubs required higher soil N levels (between 20 and 80 µg/g). These lab experiments agree with observations in the field, where exotic grasses, especially once established, have replaced native shrubs under elevated N deposition.	Coastal sage scrub	Padgett and Allen (1999)
Southern California	Plant root-to-shoot growth ratios	**Greenhouse Experiment:** Changes in plant root-to-shoot growth ratios were observed in the plant community, which is composed largely of the drought-resistant deciduous shrubs *Artemisia californica*, *Encelia farinosa,* and *Eriogonum fasciculatum*.	Coastal sage scrub	Padgett and Allen (1999); Padgett et al. (1999)
Southern California	Response of native and nonnative plants.	**Observation:** More than 30 kg N/ha/yr of atmospheric N is deposited to this ecosystem in portions of the Los Angeles Air Basin). Decreases in the diversity of native plants paralleled increases in exotic grass biomass.	Coastal sage scrub	Bytnerowicz and Fenn (1996)
Colorado Plateau	Response of native and nonnative plants.	**Field Addition:** For 2 years, plots were treated with 0, 10, 20, or 40 kg N/ha/yr as a KNO_3 solution. Galleta (*Hilaria jamesii*) and Indian ricegrass (*Oryzopis hymenoides*) showed no increase in leaf photosynthesis or tiller size, but ricegrass showed a 50% increase in tiller density in the second year at the 20 and 40 kg N/ha/yr application levels. For both species, the increased N application hastened the onset of water stress. Unexpectedly, a non-native species, Russian thistle (*Salsola iberica*) showed a rapid growth response to the highest fertilization rate in the first summer, when rainfall was above average. The authors suggested that the timing and amount of N deposition could facilitate noxious weed invasion and thus change community composition.	Arid grassland	Schwinning et al. (2005)
Joshua Tree National Park, California	Response of native and nonnative plants.	**Deposition Gradient:** 18 locations, chosen to cover the dominant vegetation types (Creosote Bush Scrub, Joshua Tree Woodland, Pinyon Juniper Woodland), were sampled for atmospheric concentrations of NO, NO_2, NH_3, and soil [N]. The relationship between reactive atmospheric N concentrations and soil N were consistent in most sites. Observations along the N gradient did not reveal a clear relationship between non-native grass cover and soil N concentration up to 20 µg/g.	Arid grassland	Allen et al. (2007)
Joshua Tree National Park, California	Response of native and nonnative plants.	**Field Addition:** Was applied at levels of 5 and 30 kg N/ha/yr at four sites over a 2 year period. Low-elevation sites were dominated by creosote bush scrub and higher-elevation sites by pinyon-juniper woodland. Non-native grass biomass increased significantly at three of four treatment sites that received 30 kg N/ha/yr, but not at the sites that received 5 kg N/ha/yr. A soil N concentration of 23 µg/g was conservatively considered the low threshold for significant plant N response based on this fertilization study.	Arid grassland	Allen et al. (2007)

Region/Country	Endpoint	Observations	Ecosystem Type/ species	Reference
Western U.S.	Fire cycle	**Observation:** Vegetative changes stimulated by nutrient enrichment from N deposition may affect the frequency and severity of subsequent disturbance. Several lines of evidence suggest that N deposition may be contributing to greater fuel loads, thus altering the fire cycle in a variety of ecosystem types. Invasive grasses, which can be favored by high N deposition, promote a rapid fire cycle in many locations.	Arid grassland	Fenn et al. (2003a)
San Francisco Bay area	Response of native and nonnative plants	**Observation:** N deposition levels of 10 to 15 kg N/ha/yr, exotic nitrophilous grasses have displaced native grass species, likely due to greater N availability from deposition and from the cessation of grazing, which previousy exported N out of the system. Since this change in species composition, populations of the rare and threatened bay checkerspot butterfly (*Euphydryas editha bayensis*) have declined greatly. It has been hypothesized that the response of the butterfly has been due to the vegetative changes.	Grasslands dominated by exotic annuals such as wild oat (*Avena fatua*), brome (*Bromus mollis*), and ryegrass (*Lolium multiflorum*).	Fenn et al. (2003a)

Mycorrhizal and Microbial Diversity

It has been hypothesized that the decline in coastal sage shrub species in California could be linked to the decline of the arbuscular mycorrhizal community (Egerton-Warburton and Allen, 2000). The authors discerned a shift in arbuscular mycorrhizal community composition with decreased species richness and diversity along a deposition gradient (2 to 57 μg N/g as soil NO_3^-). These shifts in mycorrhizal fungal communities may facilitate replacement of native plant communities by Mediterranean annual grasslands. Larger-spored fungal species (*Scutellospora* and *Gigaspora*) have decreased in number due to a failure to sporulate, with a concomitant proliferation of small-spored species. This pattern suggests selective pressure favoring the smaller spored species of fungi (Egerton-Warburton and Allen, 2000), and that N enrichment of the soil might alter the arbuscular mycorrhizal species composition and diversity.

Desert Ecosystems

Some desert ecosystems in the southwestern U.S. are considered sensitive to N enrichment effects and receive high levels of atmospheric N deposition. However, water is generally more limiting than N in these systems. Nevertheless, N deposition can stimulate plant growth and cause the observed invasion of some exotic plant species and associated changes in ecosystem function, especially where water supply is adequate. Most evidence is from field additions of N, levels ranging from 10–100 kg N/ha/yr (Table 3-19).

Fertilization experiments in the Mojave Desert showed that increased levels of N deposition could favor the establishment of nonnative species where the non-natives are already prevalent (Brooks, 2003). There is also evidence that N deposition decreases the growth of desert legumes (Baez et al., 2007). A link between N deposition and decrease in legumes has been found across other North American sites (Suding et al., 2005). The effect on legumes may be attributable because legumes, which are N fixers, often compete better under low N supply.

There is evidence from the desert ecosystems that N accumulates during periods of drought, and that more N is immobilized during periods of high precipitation (Stursova et al., 2006). Thus, where water and N appear to be co-limiting factors, the observed pattern of higher rates of N deposition during months with higher precipitation may result in a stronger fertilization effect than if N deposition were independ-

ent of precipitation (Hooper and Johnson, 1999; Asner et al., 2001; Knapp and Smith, 2001; McLain and Martens, 2006).

Table 3-19.   Summary of N effects on desert ecosystems.

Region/Country	Endpoint	Observations	Grassland type/ species	Reference
Chihuahuan Desert	Growth response of native species	**Field Addition:** 20 kg N/ha/yr addition in one season showed blue gramma (*Bouteloua gracilis*) was favored over black gramma (*Bouteloua eriopoda*), the current dominant species	blue gramma and black gramma	Baez et al. (2007)
Jornada Basin, New Mexico	Growth response of native species	**Field Addition:** Black grama and another dominate species, creosote bush (*Larrea tridentate*) did not significantly increase biomass after experimental additions of 25 kg N/ha/yr, but did after additions of 100 kg N/ha/yr	black grama and creosote bush	Ettershank et al. (1978); Fisher et al., (1998)
Chihuahuan Desert,	Growth response of native species	**Field Addition:** Additions of 100 kg N/ha/yr over about a decade, resulted in percent soil N that was 15–61% higher, extractable NO_3- that was 25–175% higher, and extractable NH_4 that was 247–1721% higher compared to control plots (Stursova et al., 2006). The resultant biologic effects were a 30% increase in cover of warm season grasses and a 52% reduction in cover of legumes (Baez et al., 2007).	Grasses and legumes	Stursova et al., (2006); Baez et al. (2007)
Mojave Desert	Native vs. non-native	**Field Addition:** At application rates of 32 kg N/ha/yr over 2 years, both density and biomass of non-native plants increased (54% increased biomass), while native species biomass declined by about 39%. Plant responses were influenced by rainfall events rather than by average annual rainfall, with the annual plants thriving in a year when high rainfall events triggered germination.	Grasses	Brooks (2003)
Great Basin Desert, sites near Mono Lake, CA	Growth and seed viability	**Field Addition:** *Sarcobatus vermiculatus*, a desert shrub found demonstrated a twofold to threefold increase in stem growth, a 2.5 to 4 fold increase in viable seed production, and a 17% to 35% increase in leaf N with N additions. N was applied in March and November as NH_4NO_3, at a cumulative addition rate of 233.6 g N per plant.	*Sarcobatus vermiculatu*	Drenovsky and Richards (2005)
Mojave desert	Growth response	**Field Addition:** The shrub *Larrea tridentata* showed no increased growth response to N additions (at 10 and 40 kg N/ha/yr $CaNO_3$) but did respond to increased water	*Larrea tridentata*	Barker et al. (2006)
Mojave and Sonoran deserts.	Native vs. non-native	**Observation:** Invasive annuals showed a greater response to elevated N than native species, and have recently invaded. Though their invasion is correlated with greater N deposition, no causation has been established.		Fenn et al. (2003a)

Lichens

Lichens are frequently used as indicators of air pollution and atmospheric deposition levels (see Annexes A and C for an additional discussion). In addition to being good subjects for biomonitoring, they

constitute important components of the forest ecosystem by contributing to biodiversity, regulating nutrient and hydrological cycles, and providing habitat elements for wildlife (McCune and Geiser, 1997).

Little is known about the mechanisms that control growth and resource partitioning in lichens, which are complex symbiotic systems comprised of a fungus (mycobiont) and a green alga and/or cyanobacterium (photobionts) (Palmqvist, 2000; Sundberg et al., 2001). Organic compounds required for growth are produced via photobiont photosynthesis. Production is strongly coupled with N utilization. The non-photosynthetic fungus comprises much of the lichen biomass and requires N for protein synthesis, nucleic acids and fungal cell wall (chitin) synthesis (Palmqvist et al., 1998). Carbon and N uptake must be balanced for coordinated development of lichen thalli (Sundberg et al., 2001).

Lichens can be classified on the basis of their response to atmospheric pollution. Nitrophytic lichens occur in areas that receive high atmospheric N deposition; acidophytic lichens are prevalent in areas that receive low N input (Rouss 1999)(Gaio-Oliveira et al., 2005; van Herk, 2001). Lichens differ with respect to N requirements. Many lichens that have a cyanobacterial photobiont are N-fixing, whereas those with a green algal photobiont are dependent on atmospheric deposition for their N supply.

N-fixing lichen species are particularly affected by N deposition (Dahlman et al., 2002). Cyanobacteria have been shown to grow on either NO_3^- or NH_4^+ sources when administered at non-toxic concentrations. More rapid growth was observed with NH_4^+ fertilization as compared with NO_3^- fertilization (Rückert and Giani, 2004). Ammonium is more easily assimilated; both NO_3 and nitrite must first be reduced to NH_4^+ before assimilation (Rückert and Giani, 2004).

Lichens with a green algal photobiont are solely dependent on atmospheric deposition as a source of N. However, a buildup of N within the thallus can lead to toxicity. Lichens exhibit varying degrees of sensitivity to increasing N deposition, owing to diverse mechanisms of responding to high N supply by reducing N uptake or assimilating N into non-toxic forms such as arginine (Dahlman et al., 2003; Gaio-Oliveira et al., 2005).

Lichens that contain a cyanobacterial photobiont appear to be more sensitive to adverse effects from atmospheric N deposition than most other lichens (Hallingback and Kellner, 1992; Hallingbäck, 1991). In Sweden, the proportion of cyanobacterial lichens that has disappeared or is threatened is three times as large as the corresponding proportion of lichens having green algal photobionts (Hallingbäck, 1991). Low pH may be the most important effect of air pollution on *Peltigera aphthosa* in Sweden. Nevertheless, there is some indication that NH_4^+ in combination with SO_4^{2-} is more detrimental than low pH per se (Hallingback and Kellner, 1992). The decline of lichens containing cyanobacteria in parts of northern Europe has been associated with N deposition in the range of 5 to 10 kg N/ha/yr (Bobbink et al., 1998). In fact, epiphytic cyanobacteria-containing lichens may be among the most sensitive species in humid forested ecosystems to atmospheric N deposition (Bobbink et al., 1998; Hallingbaeck, 1991).

Epiphytic macro lichens (those that grow attached to trees or other plants) exhibit different sensitivities to atmospheric pollutants, with some species being adversely impacted at air pollution levels that may not be considered high relative to other sensitive receptors. Particularly sensitive genera include A*lectoria, Bryoria, Ramalina, Lobaria, Pseudocyphellaria, Nephroma,* and *Usnea* (Blett et al., 2003; McCune and Geiser, 1997).

Community composition of epiphytic lichens in the U.S. can be altered by relatively small increases in N deposition (Fenn, 2003a). Most epiphytic lichens meet their nutritional requirements from atmospheric deposition and can store N in excess of their nutritional needs (van Herk, 1999). Early work in the San Bernardino Mountains, CA indicated that lichen cover was inversely related to estimated oxidant doses (Sigal and Nash, 1983). In recent analysis it has been determined that up to 50% of lichen species that occurred in the region in the early 1900s have disappeared, with a disproportionate number of locally extinct species being epiphytic cyanolichens (Fenn et al., 2003a; Nash and Sigal, 1999). The calculated critical load for lichen communities in mixed conifer forests in California is 3.1 kg N/ha/yr (Fenn et al., 2008).

The Pacific Northwest retains widespread populations of pollution-sensitive lichens (Fenn, 2003a). However, in urban areas, intensive agricultural zones, and downwind of major urban and industrial centers in the Pacific Northwest, there are few air pollution-sensitive lichen species, such as epiphytic

cyanolichens, and high N concentrations have been measured in lichen tissue (Fenn, 2003a). With N enrichment, especially around urban and agricultural areas, there is a shift towards weedy, nitrophilous lichen species (Fenn, 2003a). Replacement of sensitive lichens by nitrophilous species has undesirable ecological consequences. In late-successional, naturally N-limited forests of the Coast Range and western Cascade Mountains, for example, epiphytic cyanolichens make important contributions to mineral cycling and soil fertility (Antoine, 2001, 2004; Pike, 1978; Sollins et al., 1980), and together with other large, pollution-sensitive macrolichens, are an integral part of the food web for mammals, insects, and birds (McCune and Geiser, 1997). Sensitive lichen species appear to be negatively affected by N inputs as low as 3 to 8 kg N/ha/yr (Fenn, 2003a). (A summary of additional experiments on lichens is given in Table 3-20.)

Table 3-20.   Summary of N effects on lichens.

Region/ Country	Endpoint	Observations	Ecosystem Type / Species	Reference
Netherlands	Species richness	**Deposition Gradient:** Van Dobben, et al. (2001) recorded epiphytic lichen presence, tree bark chemical composition, and atmospheric concentrations of SO_2, NO_2 and NH_3 at 123 sites along depositional gradients. Relationships between atmospheric and bark chemistry and the composition of the lichen vegetation were evaluated (ter Braak and Wiertz, 1994). Results showed nearly all lichen species investigated were negatively affected by exposures to SO_2 and NO_2, collectively decreasing lichen species richness. Of somewhat less importance were the ecological factors such as bark pH, host tree species and tree diameter.	Epiphytic lichens	Van Dobben, et al. (2001) ter Braak and Wiertz (1994)
Scotland and northern England	Community composition	**Deposition Gradient:** The authors suggested that the empirical critical load of N deposition for protection of community composition of lichens and bryophytes was in the range of 11 to 18 kg N/ha/yr	Atlantic oak woods	Mitchell et al. (2005)
Umea, Vasterbotten, Sweden	NH_4^+ vs. NO_3 uptake rate	**Isotopic Tracer:** In a study of ^{15}N uptake in 14 lichen associations (for simplicity, designated as "species"), found that NH_4^+ uptake was significantly greater, and to a higher extent passive, relative to amino acid or NO_3^- sources of N. Differences were also observed in NO_3^- uptake, depending on photobiont group; cyanobacterial lichens had a lower NO_3^- uptake rate than green algal lichens. Morphology and microhabitat were not found to be associated with N uptake	Cyanobacterial lichens and green algal lichens	Dahlman et al. (2004)
Sweden	NH_4^+ vs. NO_3 uptake	The assimilation and allocation of externally added N was investigated for two N-fixing tripartite (possessing both green algal and cyanobacterial phytobionts) lichen species, *Peltigera aphthosa* and *Nephroma articum*. N uptake ranged from 2 to 27 percent of the 5 kg N/ha/yr that was applied during the experiment over a 3 month period. Atmospheric deposition in this part of Sweden (~5 kg N/ha/yr was about one-fourth the total experi-mental N application rate. NH_4^+ was absorbed to a greater extent than was NO_3^-. In general, ^{15}N levels of NH_4^+ treated thalli were about four times higher than for NO_3^- treated thalli. To some extent, this may reflect the increased energy requirements of NO_3^- reduction as compared with NH_4^+ assimilation (Raven et al., 1992) and/or the adsorption of positively charged NH_4^+ on the negatively charged functional groups present on hyphal cell walls.	*Peltigera aphthosa* and *Nephroma articum*	Dahlman et al. (2002),
Sweden	NH_4^+ vs. NO_3 uptake	NH_4^+ to be the preferred N source for the green algal foliose lichen *Plathismatia glauca*, followed by glutamine and then NO_3^-. This species responded to increased N availability by increasing growth rate and C assimilation capacity through increased investment in the photobiont cells	*Plathismatia glauca*, a foliose lichen	Palmqvist and Dahlman (2006)

Region/ Country	Endpoint	Observations	Ecosystem Type / Species	Reference
Pampulha reservoir (Belo Horizonte, Brazil)	NH_4^+ vs. NO_3 growth	Cyanobacteria have been shown to grow on either NO_3^- or NH_4^+ sources when administered at non-toxic concentrations. More rapid growth was observed with NH_4^+ fertilization as compared with NO_3^- fertilization. Ammonium is more easily assimilated; both NO_3 and nitrite must first be reduced to NH_4^+ before assimilation	Cyanobacteria	von Rückert and Giani (2004)
Sweden	NH_4^+ in combination with SO_4^{2-}	Low pH may be the most important effect of air pollution on *Peltigera aphthosa* in Sweden. Nevertheless, there is some indication that NH_4^+ in combination with SO_4^{2-} is more detrimental than low pH per se (Hallingbäck and Kellner, 1992).	*Peltigera aphthosa*	Hallingbäck and Kellner (1992)
Santo Antonio, near Serra de Aire Candeeiros Natural Park, central Portugal	NH_4^+ uptake Physiological responses	Comparison of the physiological responses of two lichens to increased N supply. Uptake was quantified using ^{15}N labeled NH_4^+. Cholrophyll a and ergonsterol were used as indirect markers of algal and fugal activity, respectively. The acidophytic lichen *Evernia prunastri* showed greater N uptake from NH_4^+ than the nitrophytic lichen *Xanthoria parietina*. In the acidophytic lichen, but not the nitrophytic lichen, ergosterol concentrations decreased with increasing N uptake, and an increase in the NH_4^+ pool was also observed at the highest N doses (216 kg N/ha/yr, applied as nine applications over a 2-month period). These differences can partially explain the higher tolerance of *X. parietina* to high N deposition.	*Evernia prunastri* and *Xanthoria parietina*	Gaio-Oliveira et al. (2005)

Alpine

Herbaceous plants in alpine communities are considered very sensitive to changes in N deposition. A combination of short growing season, strong seasonal variation in moisture and temperature, shallow and poorly developed soils, steep terrain, sparse vegetation, and low rates of primary productivity generally limit the N uptake and retention capacity of herbaceous plant species in alpine ecosystems (Burns, 2004; Fisk et al., 1998). Alpine herbaceous plants are generally considered N-limited and changes in alpine plant productivity and species composition have been noted in response to increased N inputs (Bowman et al., 2006; Vitousek et al., 1997) (See Table 3-21).

Research on N enrichment effects on alpine and subalpine ecosystems in the Western U.S. has mainly been limited to studies at the Loch Vale Watershed in Rocky Mountain National Park and the Niwot Ridge LTER site, both located east of the Continental Divide in Colorado (see review by Burns, 2004). Changes in alpine plant species composition on Niwot Ridge have included increased cover of the plant species that tend to be most responsive to N fertilization in some of the long-term monitoring plots (Fenn, 2003a; Korb and Ranker, 2001). These changes are likely due to response to changes in N deposition. However, the influences of climatic change, particularly changes in precipitation (Williams et al., 1996b) and pocket gopher disturbance (Sherrod and Seastedt, 2001) could not be ruled out as contributors to vegetation change (Fenn, 2003a). Other environmental factors also affect the species make-up of alpine ecosystems, but long-term experimental fertilization plots demonstrate a clear response of alpine flora to N, including shifts toward graminoid plants that shade smaller flowering species, and accompanying changes in soil N cycling (Bowman et al., 2006).

Table 3-21.   Summary of N effects on alpine ecosystems.

Region/Country	Endpoint	Observations	Ecosystem Type / Species	Reference
Niwot Ridge, CO and Southern Wyoming	Community shift	**Field Addition:** 25 kg N/ha/yr added during summer caused a community shift towards greater dominance of hairgrass (*Deschampsia sp.*) in wet alpine meadows, but the increase in plant biomass (+67%) and plant N content (+107%) following N fertilization was higher in graminoid-dominated dry meadows than in forb-dominated wet meadows (+53% plant biomass, +64% standing N crop, respectively)	Wet and dry alpine meadow, alpine tundra, talus, alpine and subalpine forest—Englemann spruce, Bristlecone pine, surface waters, algae, amphibians	Bowman et al. (1995); Burns (2004)
Niwot Ridge, CO	Plant foliage productivity species richness.	**Field Addition:** Showed that 4 years of N addition to alpine vegetation at rates ranging between 100 and 200 kg N/ha/yr (depending on the year) caused marginal increases in alpine plant foliage productivity but reduced species richness.	Wet and dry alpine tundra-sedge *Kobresia myosuroides*. *Acomastylis rossii, Polygonum viviparurn Trifolium. A.rossii* and *Deschumnpsia caespitosa. D. caespitosa, Caltha leptosepala, Sibbaldia procurnbens* and *Trifolium parryi.*	Seastedt and Vaccaro (2001)
Niwot Ridge, CO	Species composition species diversity plant biomass tissue [N]	**Field Addition:** Additions of 20, 40, and 60 kg N/ha/yr (on top of ambient N deposition near 5 kg N/ha/yr) over an 8 year period to a dry alpine meadow led to a change in plant species composition, an increase in species diversity and plant biomass, and an increase in tissue N concentration at all treatment levels within 3 years of application. Much of the response was due to increased cover and total biomass of sedges (*Carex spp.*). There was a significant decrease in Kobresia biomass with increasing N input. Vegetation composition appeared to respond at lower N input levels than those that caused measurable changes in soil inorganic N content. Changes in an individual species (*Carex rupestris*) were estimated to occur at deposition levels near 4 kg N/ha/yr. Changes in the plant community, based on the first axis of a detrended correspondence analysis, were estimated to occur at deposition levels near 10 kg N/ha/yr. In contrast, increases in NO_3^- leaching, soil solution NO_3^- concentration, and net nitrification occurred at levels above 20 kg N/ha/yr. The authors concluded that changes in vegetation composition preceded detectable changes in soil indicators of ecosystem response to N deposition.	Dry alpine meadow	Bowman et al. (2006)

Mycorrhizae across ecosystems

Microbial biodiversity can also be affected by N enrichment. Interactions between atmospherically deposited N and terrestrial vegetation frequently occur in the rhizosphere. The rhizosphere includes the soil that surrounds and is influenced by plant roots (Wall and Moore, 1999). Relationships among plant roots, mycorrhizal fungi, and microbes are critical for N cycling and for the growth and health of plants. The plant provides shelter and C; the fungi and bacteria provide access to potentially limiting nutrients, particularly N and P.

A meta-analysis of the effect of N and P fertilization on mycorrhize observed a 15% decrease in mycorrhizal abundance due to N fertilization across 16 studies at 31 sites, covering a range of grassland, shrubland, temperate and boreal forest ecosystems (Treseder, 2004). Declines in mycorrhizal abundance were slightly higher at higher rates of N fertilization, but there was significant variation across all studies. The loss of mycorrhizal function has been hypothesized as a key process contributing to reduced N uptake by vegetation and increased NO_3^- mobility from soil into drainage water (U.S. EPA, 2004).

NO_3^- versus NH_4^+ deposition

Plants also exhibit different degrees of response to NO_3^- versus NH_4^+ deposition. In general, fast-growing annual species, including many agricultural crops, and fast growing pioneer trees such as birch (*Betula* spp.) prefer NO_3^- (Pearson and Stewart, 1993). Slow-growing perennial plant species generally prefer NH_4^+. There are also many plant species which readily utilize both NO_3^- and NH_4^+ (Krupa, 2003). These include members of the family Ericaceae (e.g., *Calluna, Erica, Vaccinium*), conifer trees, and climax species such as *Quercus* and *Fagus* (Krupa, 2003).

3.3.5.2. Transitional Ecosystems

Wetlands in the U.S. support over 4200 native plant species, of which 121 are federally threatened or endangered (http://plants.usda.gov/). Wetlands can be divided into three general categories based on hydrology. Hydrologic pathways are often the same pathways of N input; therefore they are useful for discussing the N sources and sensitivity to atmospheric N deposition. Nearly all new N comes from atmospheric deposition in ombrotrophic bogs because they only receive water inputs via precipitation and they develop where precipitation exceeds evapotranspiration and where there is some impediment to drainage of the surplus water (Mitsch and Gosselink, 1986). Fens, marshes and swamps are characterized by ground and surface water inputs that are often on the same order of magnitude as precipitation (Koerselman et al., 1989). Lastly, intertidal wetlands receive water from precipitation, ground/surface water and marine/estuarine sources.

The balance of competition among plant species in some sensitive wetland ecosystems can be altered by N addition, with resulting displacement of some species by others that can utilize the excess N more efficiently (U.S. EPA, 1993a). The sensitivity of wetlands is particularly important given that they contain a disproportionately high number of rare plant species that have evolved under N-limited condition (Moore et al., 1989) (See Annex C). In general these include the genus *Isoetes sp.,* of which three species are federally endangered; insectivorous plants like the endangered green pitcher *Sarracenia oreophila;* and the genus *Sphagnum*, of which there are 15 species are listed as endangered by eastern U.S. states. Roundleaf sundew (*Drosera rotundifolia*) is also susceptible to elevated atmospheric N deposition (Redbo-Torstensson, 1994). This plant is native to, and broadly distributed across, the U.S. and is federally listed as endangered in Illinois and Iowa, threatened in Tennessee, and vulnerable in New York (http://plants.usda.gov/).

Freshwater wetlands

Peatlands and bogs are among the most vulnerable transitional ecosystems to adverse nutrient-enrichment effects of N deposition (Krupa, 2003). The sensitivity of peatland *Sphagnum* species to

elevated atmospheric N deposition is well documented in Europe (Berendse et al., 2001; Tomassen et al., 2004). *Sphagnum squarrosum* and *S. fallax* have been observed to be negatively affected by experimentally elevated atmospheric N and S inputs in Europe (Kooijman and Bakker, 1994). The genus *Sphagnum* dominates ombrotrophic bogs and some nutrient poor fens in the northern U.S. and Canada. These mosses efficiently capture atmospheric deposition with retention rates between 50–90%, much of the variation due to the depth of the water table (Aldous, 2002). Studies conducted on 4 species of Sphagnum in Maine (2 to 4 kg N/ha/yr ambient deposition) and New York (10 to 13 kg N/ha/yr ambient deposition) document that higher N deposition resulted in higher tissue N concentrations and greater NPP, but lower bulk density (Aldous, 2002). A study of *Sphagnum fuscum* in six Canadian peatlands showed a weak, although significant, negative correlation between NPP and N deposition when deposition levels were greater than 3 kg N/ha/yr (y = 150 – 3.4x, p=0.04, r^2=0.01) (Vitt et al., 2003). A study of 23 ombrotrophic peatlands in Canada with deposition levels ranging from 2.7 to 8.1 kg N/ha/yr showed peat accumulation increases linearly with N deposition (y = 2.84(x) + 0.67, r^2 = 0.32, p <0.001), however in recent years this rate has begun to slow indicating limited capacity for N to stimulate accumulation (Moore et al., 2004).

The sensitivity of peatland *Sphagnum* species to elevated atmospheric N deposition is well documented in Europe (Berendse et al., 2001; Tomassen et al., 2004). *Sphagnum squarrosum* and *S. fallax* have been observed to be negatively affected by experimentally elevated atmospheric N and S inputs in Europe (Kooijman and Bakker, 1994). Roundleaf sundew (*Drosera rotundifolia*) is also susceptible to elevated atmospheric N deposition (Redbo-Torstensson, 1994).

Sarracenia purpurea is a long lived (30–50 years) northern pitcher plant and widely distributed in bogs, fens and swamps across Canada and the eastern U.S. (Ellison and Gotelli, 2002). *S. purpurea* has adapted to nutrient poor environments and very sensitive to increasing N input. In a study of *S. purpurea* in Vermont and Massachusetts, Ellison and Gotelli (2002) conducted a series of N enrichment experiments by augmenting N availability to leaves with 0, 0.1 and 1 mg N/L NH_4^+ solution for one growing season. Population growth rates, estimated by demographic survey, were positive for 0 and 0.1 mg N/L additions (equal to atmospheric deposition of 0–1.4 kg N/ha/yr)[1] and negative for 1 mg N/ L additions (equivalent to 10–14 kg N/ha/yr)[1] (Gotelli and Ellison, 2006). Based on the annual demographic rates, a non stationary matrix model forecasted that the extinction risk within the next 100 years increased substantially if N deposition rate increase (1–4.7%) from the rate of 4.5–6.8 kg N/ha/yr (Gotelli and Ellison, 2002).

Increasing N availability not only reduced population growth of *S. purpurea*, also dramatically altered plant morphology. *S. purpurea* produces carnivorous leaves (pitcher) and photosynthesis efficient leaves (phyllodia). N enrichment was shown to stimulate the photosynthesis rate and increase the production of phyllodia relative to pitcher (Ellison and Gotelli, 2002). The field N deposition simulation experiment (ranged from 0–35 kg N/ha/yr)[1] revealed a positive linear relationship between N deposition level and relative keel size (keel width/total width). This correlation was supported by the field surveys of 26 sites across Massachusetts and Vermont (Ellison and Gotelli, 2002), and 39 sites across Canada and eastern U.S. (Ellison and Gotelli, 2002). The relative kneel size of northern pitcher plant increased with increasing NH_4^+ concentration in soil water, and may be used as bioindicator (log $[NH_4^+]$ = -1.57 + 1.78x relative keel size).

In wet heathlands in Europe, changes in plant species composition have been attributed to elevated atmospheric N deposition (Roem and Berendse, 2000). Diverse plant communities have been replaced by monospecific stands Dutch wet heathlands (Aerts and Berendse, 1988; Houdijk et al., 1993). In other studies, wetland species such as *Calluna vulgaris* can successfully compete with grasses even at relatively

---

[1] N treatments were selected to represent annual N deposition measured at the nearest monitoring sites of National Atmospheric Deposition Program (NADP). The unit of N treatments reported in the publication was precipitation-weighted mean concentrations (mg N/ L), from which we calculated the level of deposition (kg N/ha/yr) using the equation: *Deposition= Precipitation-Weighted Mean Concentrations × Annual Precipitation*. More detailed information on nitrogen deposition is available on the NADP website: http://nadp.sws.uiuc.edu/sites/ntnmap.asp?

high rates of N deposition, as long as the vegetative canopies are closed (Aerts et al., 1990). However, N deposition causes nutrient imbalances, and increased plant shoot-to-root ratio, and therefore increases in the sensitivity of shrubs to drought stress, frost stress, and attack by insect pests (Heil and Diemont, 1983). These can result in gaps in the canopy of the shrub layer, which can then be readily invaded by grasses that are more efficient in using the additional N and therefore gain a competitive advantage (Krupa, 2003).

Riparian wetlands

Marler et al. (2001) evaluated the potential impacts of experimentally elevated stream water nutrient concentrations on three riparian wetland tree species: Fremont cottonwood (*Populus fremontii*), Goodding willow (*Salix gooddingii*), and exotic saltcedar (*Tamarix ramosissima*) in the riparian zone of the Salt River near Phoenix, AZ. The results from this 43−day experiment showed that growth of all three riparian plant species responded positively to increased nutrient supply (treatment 3 and 4) (Marler et al., 2001). The exotic and invasive salt cedar showed the greatest increases in biomass at high nutrient supply. Other studies have also found that exotic plant species often respond more rapidly than native vegetation to increased nutrient supply (Milberg et al., 1999; Paschke et al., 2000). This experiment was conducted to simulate impacts of wastewater effluent on riparian zones, and N additions were therefore very large nutrient supply to riparian systems via atmospheric N deposition in the U.S. is more typically in the range of treatments in this experiment that showed minimal response to N addition.

Table 3-22. Summarized responses of coastal marshes ecosystem to N fertilization. The table includes studies in which the lowest fertilization treatment is below 400 kg N/ha/yr, a value at the higher end of the range that includes direct and indirect N deposition.

Site	Species	Responses	N enrichment	Reference
Walden Creek (NC)	*Spartina alterniflora*	**Field Addition:** (1) increased the growth of short Spartina, but had no effect on tall Spartina; (3) biomass production of short Spartina increased linearly with N addition; and (3) ammonium showed higher growth stimulation on short Spartina than NO_3 does	0, 280, 560, 1120 kg N/ha/yr	Mendelssohn et al. (1979)
Narragansett Bay (RI)	*Spartina patens; Spartina alterniflora*	**Field Addition:** (1) decreased the density and extent of S patens; (2) decreased the extent of tall S. alterniflora increased with	N gradient from 9 to 3282 kg N/ha/yr	Wigand et al. (2003)
Great Sippewissett Marsh (MA)	*Spartina alterniflora*	**Field Addition:** increased live above ground biomass, leaf area coverage, evapotranspiration	396 kg N/ha/yr	Howes et al. (1986)

Intertidal wetlands

Wetland eutrophication could significantly damage the structure and function of coastal marshes. N enrichments were shown to facilitate the invasion of nonnative species (Tyler et al., 2007); shift the competition between native species (Mendelssohn, 1979; Wigand et al., 2003; Crain 2007); increase herbivore damage on plants (Bertness et al., 2008); stimulate evapotranspiration (Howes et al., 1986); change microbial community and pore water chemistry (Caffrey et al., 2007); and alter carbon allocation

between root and shoot (Darby and Turner, 2008). Most N fertilization experiments add levels of N orders of magnitude above that expected by atmospheric deposition. A summary of experiments that include addition levels below 400 kg N/ha/yr is given in Table 3-22.

3.3.5.3. Freshwater Aquatic Ecosystems

Paleolimnological studies

The paleolimnological method of taxonomic identification of fossil diatoms in lake sediments has been augmented in recent years with cell counts and pigment concentrations of Chl *a* and chlorophyll derivatives, rendering inferences about trophic state from proxies preserved in sediments more robust than before (Das et al., 2005). Paleolimnological studies of mountain lakes that have only been disturbed by atmospheric deposition and climate change have reported changes in diatom species assemblages, increases in cell numbers, and pigment-inferred increases in whole lake primary production. These inferred changes have been coincident with regional surrogates for increased N deposition. Such changes have included increases in human population, industrial animal production, and fossil fuel combustion emissions (Das et al., 2005; Saros et al., 2003; Wolfe et al., 2001a, 2003). In most, but not all, of these studies, the observed changes in ecology were inconsistent with changes in climate and more concordant with effects from increased atmospheric N deposition.

Available data suggest that the increases in total N deposition do not have to be large to elicit an ecological effect. For example, a hindcasting exercise determined that the change in Rocky Mountain National Park lake algae that occurred between 1850 and 1964 was associated with an increase in wet N deposition that was only about 1.5 kg N/ha (Baron, 2006). Similar changes inferred from lake sediment cores of the Beartooth Mountains of Wyoming also occurred at about 1.5 kg N/ha deposition (Saros et al., 2003). Pre-industrial inorganic N deposition is estimated to have been only 0.1 to 0.7 kg N/ha based on measurements from remote parts of the world (Galloway et al., 1995; Holland et al., 1999). In the western U.S., pre-industrial, or background, inorganic N deposition was estimated by (Holland et al., 1999) to range from 0.4 to 0.7 kg N/ha/yr.

Bioassay, mesocosm, and laboratory experiment

Bioassay, mesocosm, and laboratory experiments have been conducted on algae (both phytoplankton and periphyton), invertebrates, amphibians, and fish, to determine effects of N on sensitive aquatic organisms (see Annex C). Some freshwater algae are particularly sensitive to the effects of added nutrient N and experience shifts in community composition and biodiversity with increased N deposition. For example, two species of diatom, *Asterionella formosa* and *Fragilaria crotonensis*, now dominate the flora of at least several alpine and montane Rocky Mountain lakes and sharp increases have occurred in Lake Tahoe (Baron et al., 2000; Interlandi and Kilham, 1998; Saros et al., 2003, 2005; Wolfe et al., 2001 and 2003). The timing of this shift has varied, with changes beginning in the 1950s in the southern Rocky Mountains and in the 1970s or later in the central Rocky Mountains (Figure 3-50). These species are opportunistic algae that have been observed to respond rapidly to disturbance and slight nutrient enrichment in many parts of the world (See Annex C for additional discussion).

Further evidence for the relationship between N enrichment and algal changes has been provided by N addition studies that include in situ mesocosm studies (Lafrancois et al., 2004; McKnight et al., 1990; Saros et al., 2005) and in situ incubations in large lakes (Interlandi and Kilham, 1998). Differences in resource requirements allow some species to gain competitive advantage over others upon nutrient addition, causing changes in species composition (Lafrancois et al., 2004; Saros et al., 2005; Wolfe et al., 2003). A summary of these experiments is given in Table 3-23. This is in keeping with findings of Interlandi and Kilham (2001), who demonstrated that maximum species diversity was maintained when N levels were low (<3 µM) in lakes in the Yellowstone National Park region.

The implication of this research is that species diversity declines with increasing availability of N. In studies of lake sediment diatom remains, typical oligotrophic species such as *Aulacoseria perglabra*, *Cyclotella steligera*, and *Achnanthes spp.* declined coincident with the rise in dominance of *A. formosa* and *F. crotonensis* (Wolfe et al., 2001b, 2003).
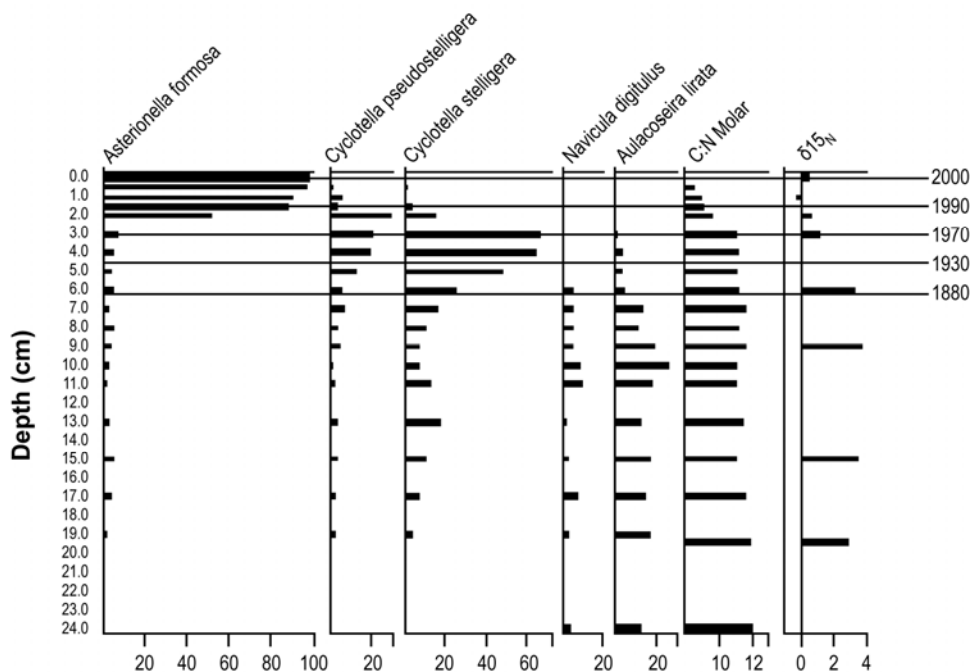
Figure 3-50.   Diatom assemblage sediment patterns in Emerald Lake, WY.

Community shifts in phytoplankton other than diatoms have also been observed under conditions of elevated N availability (Lafrancois et al., 2004). For example, a positive correlation between the proportion of the phytoplankton comprised of chrysophytes and the concentration of NO_3^- in lake water was found in a survey of 15 Snowy Range lakes (Lafrancois et al., 2003). Chlorophytes, like the two diatom species identified above, generally prefer high concentrations of N and are able to rapidly dominate the flora when N concentrations increase (Findlay et al., 1999). This occurs in both circumneutral and acidified waters (Findlay et al., 1999; Wilcox and Decosta, 1982).

In summary, survey data and fertilization experiments demonstrate that increase in algal productivity, as well as species changes and reductions in biodiversity, have occurred at sensitive high elevation lakes in the western U.S. in response to increased availability of N.

Table 3-23.   N effects on algal species composition and biodiversity

Region	Endpoint	Observation	Ecosystem Type	Reference
Snowy Range, Wyoming	Community shifts in phytoplankton	**Mesocosm Experiment**: correlation between the proportion of the phytoplankton comprised of chrysophytes and the concentration of NO_3^- in lake water was found in a survey of 15 lakes. Chrysophytes were favored in lakes having lower N and cyanophytes and chlorophytes favored in lakes having higher N	Lakes	Lafrancois et al. (2003)
Beartooth Mountains of Montana-Wyoming	Diatom community	**Paleo and Observation**: evaluation of resource requirements for dominant diatom species with paleolimnological reconstructions and contemporary surveys of the flora of seven lakes. Results reinforced the likelihood that recent increases in dominant diatom numbers have been the result of N enrichment rather than climatic change	Lakes	Saros et al. (2005)
Colorado Front Range	Community shifts in phytoplankton	**Paleo**: sediment cores showed increasing representation of mesotrophic diatoms in recent times, as compared with pre-development conditions	Lakes	Wolfe et al., (2001b)
Lake Tahoe, CA	Community shifts in phytoplankton	**Paleo**: there has been a sharp increase in the ratio of araphidinate pennate to centric diatoms since about 1950 (largely due increases in *Fragilaria crotenensis*), associated with increased N loading to the lake. Jassby et al. (1994) showed that atmospheric deposition supplies most of the N to Lake Tahoe.	Lakes	Goldman (1988)

3.3.5.4. Estuarine and Marine Ecosystems

In coastal ecosystems, eutrophication can cause changes in marine biodiversity and species composition. Phytoplankton production and community composition in estuarine and marine environments also respond to differences in the form of atmospheric N input. Major algal functional groups, including diatoms, dinoflagellates, cyanobacteria, and chlorophytes, may show different responses to changing mixtures of added N (Paerl et al., 2002).

Phytoplankton

In addition to causing increased phytoplankton biomass, as indicated by Chl *a* measurements (see Section 3.3.3.2), excess N can contribute to changes in phytoplankton species composition. High loadings of N and P can also increase the potential for Si limitation, with associated changes in diatoms. Such changes to the phytoplankton community can also affect higher trophic levels. For example, Officer and Ryther (1980) and Turner et al. (1998) suggested that a shift in the Si-to-N atomic ratio to less than 1 would alter the marine food web. Specifically, the diatom-to-zooplankton-to-higher tropic level ratios would decrease, whereas flagellated algae (including those that often contribute to hypoxia) would increase (Paerl et al., 2001a).

Changes in phytoplankton species abundances and diversity have been further documented through in situ bioassay experiments such as the results reported by Paerl et al. (2003) for the Neuse River Estuary in North Carolina. Effects were species-specific and varied dramatically depending on whether, and in what form, N was added. The findings illustrate the potential impacts of N additions on phytoplankton community structure (see Figure 3-51).

Changing phytoplankton community composition has numerous potential ecological ramifications, including modifications to the ecosystem food web and nutrient dynamics. For example, if the nutrient mix favors species that are not readily grazed (e.g., cyanobacteria , dinoflagellates), trophic transfer will be poor and relatively large amounts of unconsumed algal biomass will settle to the bottom, which could stimulate decomposition, O_2 consumption, and the potential for hypoxia (Paerl et al., 2003).

Reduced vs. Oxidized N

The form of N input to coastal aquatic ecosystems has an important influence on its effects. Atmospheric deposition of reduced N has increased relative to oxidized N in the eastern U.S., and this trend is expected to continue in the future under existing emissions controls. Such patterns can influence marine eutrophication responses. Some studies suggest that large diatoms tend to dominate coastal waters when NO_3^- is supplied (Paerl et al., 2001a; Stolte et al., 1994), whereas smaller diatom species have a greater preference for NH_4^+ uptake. Thus, ongoing trends of decreasing NO_3^- deposition and increasing NH_4^+ deposition might lead to changes in species distributions and size distributions of phytoplankton, with cascading effects on trophic structure and biogeochemical cycling (Paerl et al., 2001a).

Not all studies have found variation in algal response with the form of N applied. For example, Richardson et al. (2001) examined the effects of different forms of N application (NO_3^-, NH_4^+, urea) on the structure and function of estuarine phytoplankton communities in mesocosm experiments in the Neuse River Estuary, NC. Even though NH_4^+ is more readily taken up by phytoplankton in this estuary than is NO_3^- (Twomey et al., 2005), the results of the Richardson et al. (2001) study suggested that phytoplankton community structure was determined more by the hydrodynamics of the system than by the form of N available for growth.

Twomey et al. (2005) measured Neuse River Estuary phytoplankton uptake rates of NH_4^+, NO_3^-, and urea. Ammonium was the dominant form of N taken up, contributing about half of the total N uptake throughout the estuary. Uptake varied spatially; in particular NO_3^- uptake declined from 33% of the total uptake in the upper estuary to 11% and 16%, respectively in the middle and lower estuary. Urea uptake contributed least to the total in the upper estuary (16%) but comprised 45 and 37% of the total N uptake in the middle and lower estuary. Therefore, N budgets based only on inorganic forms may seriously underestimate the total phytoplankton uptake (Twomey et al., 2005).

Submerged Aquatic Vegetation (SAV)

SAV provides important nursery grounds to many estuarine fish. There are few data documenting the long-term response of SAV in coastal ecosystems to N loading. The national assessment (Bricker et al., 2007) suggested that only a small fraction of the estuary systems evaluated reported high severity of SAV loss. Most of those that did report moderate or high loss were located in the Mid-Atlantic region. However, where SAV loss is a problem, the results can be severe, and there is evidence suggesting a correlation with increases in N loading. For example, at Waquoit Bay, Massachusetts, Valiela et al. (1990) reported a strong negative relationship between modeled N loading and measured eelgrass area based on measurements of eelgrass coverage from 1951 to 1992.
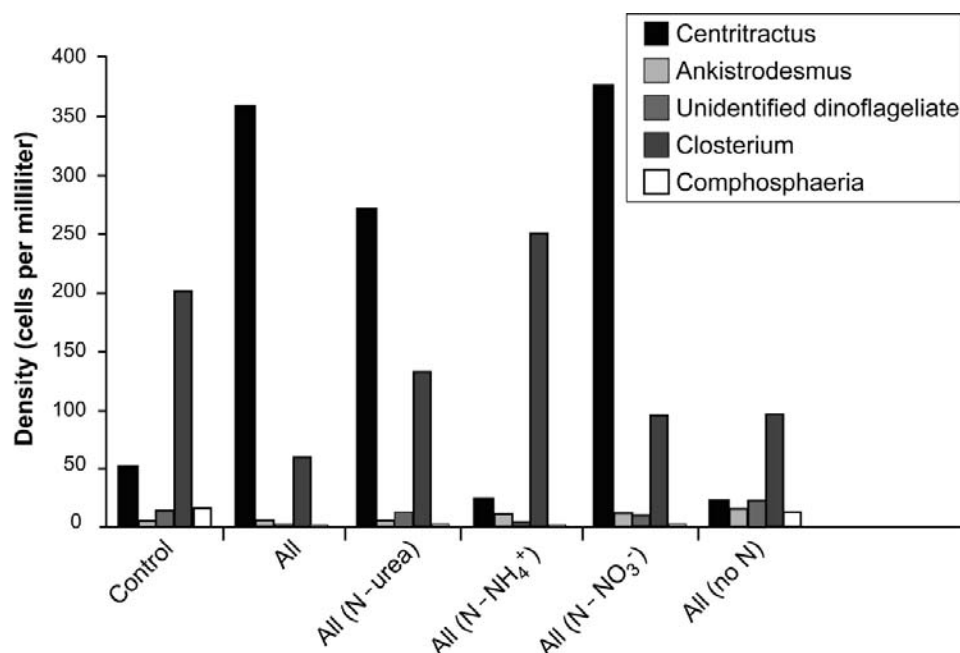
Figure 3-51. **Microscopic counts of phytoplankton species composition in the Neuse River Estuary, NC following 36-h in situ bioassays to manipulate available forms of N. Treatments included a control (unamended estuarine water sample), all nutrients (N, P, vitamins, trace metals, and Si), all with urea as the N form, all with ammonium (NH_4^+) as the N form, all with NO_3^- as the N form, and all with no N. Bars represent the mean density of cells present (three replicate counts for each treatment).**

3.3.5.5. Summary of N Effects on Species Composition, Species Richness and Biodiversity

Terrestrial

The evidence is sufficient to infer a causal relationship between N deposition and the alteration of species richness, species composition and biodiversity in terrestrial ecosystems. The ecological effects of N deposition were described for a variety of taxa and ecosystem types including: forests, grasslands, arid and semi-arid, deserts, lichens, alpine, and mycorrhizae. Among the most sensitive terrestrial taxa are lichens. Empirical evidence indicates that lichens in the U.S. are adversely affected by deposition levels as low as 3/ha/yr. Among the most sensitive ecosystems are Alpine ecosystems; alteration of plant cover of an individual species (*Carex rupestris*) in Alpine communities were estimated to occur at deposition levels near 4 kg N/ha/yr and modeling indicates that deposition levels near 10 kg N/ha/yr alter plant community assemblages.

Wetland

The evidence is sufficient to infer a causal relationship between N_r deposition and the alteration of species richness, species composition and biodiversity in wetland ecosystems. The effect of N deposition on wetland ecosystems depends on the fraction of rainfall in its total water budget. The sensitivity to N deposition was suggested as bogs >fens >intertidal wetlands (Morris, 1991).

Excess N deposition can cause shifts in wetland community composition by altering competitive relationships among species, which potentially leads to effects such as decreasing biodiversity, increasing non-native species establishment and increasing the risk of extinction for sensitive and rare species. Wetlands contain a high number of rare plant species (Bedford and Godwin, 2003; Moore et al., 1989; U.S. EPA,1993a). High levels of atmospheric N deposition increase the risk of decline and extinction of these species that are adapted to low N conditions. In general these include the genus *Isoetes sp.*, of which three species are federally endangered; insectivorous plants like the endangered green pitcher *Sarracenia oreophila*; and the genus Sphagnum, of which there are 15 species are listed as endangered by eastern U.S. states. Roundleaf sundew (*Drosera rotundifolia*) is also susceptible to elevated atmospheric N deposition (Redbo-Torstensson, 1994). This plant is native to, and broadly distributed across, the U.S. and is federally listed as endangered in Illinois and Iowa, threatened in Tennessee, and vulnerable in New York (http://plants.usda.gov/). In the U.S., *Sarracenia purpurea* can be used as a biological indicator of local N deposition in some locations (Ellison and Gotelli, 2002).

Freshwater Aquatic

The evidence is sufficient to infer a causal relationship between Nr deposition and the alteration of species richness, species composition and biodiversity in freshwater aquatic ecosystems. Evidence from multiple lines of research and experimental approaches support this observation, including paleolimnological reconstructions, bioassays, mesocosm and laboratory experiments. Increased N deposition can cause a shift in community composition and reduce algal biodiversity. Elevated N deposition results in changes in algal species composition, especially in sensitive oligotrophic lakes.

In the West, a hindcasting exercise determined that the change in Rocky Mountain National Park lake algae that occurred between 1850 and 1964 was associated with an increase in wet N deposition that was only about 1.5 kg N/ha (Baron, 2006). Similar changes inferred from lake sediment cores of the Beartooth Mountains of Wyoming also occurred at about 1.5 kg N/ha deposition (Saros et al., 2003).

Some freshwater algae are particularly sensitive to added nutrient N and experience shifts in community composition and biodiversity with increased N deposition. For example, two species of diatom (a group of algae), *Asterionella formosa* and *Fragilaria crotonensis*, now dominate the flora of at least several alpine and montane Rocky Mountain lakes. Sharp increases have occurred in Lake Tahoe (Baron et al., 2000; Interlandi and Kilham, 1998; Saros et al., 2003; Saros et al., 2005; Wolfe et al., 2001b; Wolfe et al., 2003). The timing of this shift has varied, with changes beginning in the 1950s in the southern Rocky Mountains and in the 1970s or later in the central Rocky Mountains. These species are opportunistic algae that have been observed to respond rapidly to disturbance and slight nutrient enrichment in many parts of the world.

Estuarine Aquatic

The evidence is sufficient to infer a causal relationship between N deposition and the alteration of species richness, species composition and biodiversity in estuarine ecosystems. Increased N deposition can cause shifts in community composition, reduced hypolimnetic DO, reduced biodiversity, and mortality of submerged aquatic vegetation. The form of deposited N can significantly affect phytoplankton community composition in estuarine and marine environments. Small diatoms are more efficient in using NO_3^- than NH_4^+. Increasing NH_4^+ deposition relative to NO_3^- in the eastern U.S. favors small diatoms at the expense of large diatoms. This alters the foundation of the food web. Submerged aquatic vegetation is important to the quality of estuarine ecosystem habitats because it provides habitat for a variety of aquatic organisms, absorbs excess nutrients, and traps sediments. Nutrient enrichment is the major driving factor contributing to declines in submerged aquatic vegetation coverage. The Mid-Atlantic region is the most heavily impacted area in terms of moderate or high loss of submerged aquatic vegetation due to eutrophication. Indicators to assess the eutrophic condition of estuarine and coastal waters are given in Figure 3-34.

3.3.6. N Deposition Effects on NO$_3^-$ Toxicity

NO$_3^-$ in freshwater at extremely high concentrations can have direct adverse effects on many life stages of fish, as well as on invertebrates and amphibians. These effects occur at levels that are typically more than 30 times higher than those that would commonly be attributable to atmospheric deposition, and therefore NO$_3^-$ concentration has not been defined as a primary biological indicator. These effects are described in Annex C.

3.3.7. Critical Loads and Other Quantified Relationships between Deposition Levels and Ecological Effects

This section highlights a variety of sensitive chemical and biological receptors that have been used in developing critical loads for nutrient effects of N deposition on natural ecosystems. Sensitive receptors for effects of excess nutrient N deposition on surface water could include water chemistry, productivity, and the response of important taxa. Key sensitive receptors for assessing effects on soil include soil chemistry and soil solution chemistry. Sensitive receptors for flora include macro-lichens and vascular plant species that are adapted to nutrient-poor environments. In some cases, the chemical receptors may be easier to characterize, although they likely also reflect important biological changes that may be more difficult to document. Background information on critical loads is presented in Annex C. Empirical models of critical loads for nutrient-N have been in use in Europe for some time (UNECE, 2004). Efforts have begun to develop empirical relationships in the U.S.

3.3.7.1. Empirical Critical Loads for Europe

Within the United Nations Economic Commission for Europe (UNECE) Long Range Transboundary Air Pollution (LRTAP) convention, empirical procedures have been developed to set critical loads for atmospheric N deposition to protect against effects caused by nutrient enrichment. Empirical critical loads of N deposition for natural and semi-natural terrestrial and wetland ecosystems were first presented in a background document for the 1992 LRTAP workshop on critical loads held at Lökeberg, Sweden (Bobbink et al., 1992b). A number of European expert workshops have taken place to reach agreement among specialists regarding the impacts of N deposition on various ecosystems and related critical loads (Achermann and Bobbink, 2003; Bobbink et al., 1992b; Bobbink et al., 1996; Hornung et al., 1995; Nilsson and Grennfelt, 1988).

Information from the period 1996–2002 on the effects of increased N deposition on the structure and function of natural and semi-natural ecosystems in Europe was evaluated in Bobbink et al. (2003). The updated N critical loads were discussed and approved by full consensus at the November 2002 expert meeting held under the LRTAP Convention in Berne, Switzerland, (Achermann and Bobbink, 2003). Values for areas with low N deposition were updated by a CLRTAP workshop on critical loads of N in low-deposition areas (Stockholm, Sweden, March 2007) and adopted by ICP M&M and WGE in 2007. The resulting values are given in Table 3-24.

Table 3-24   Biological indicators for the effects of elevated N deposition and related empirical critical loads for major ecosystem types (according to the eunis classification) occurring in Europe.

Ecosystem Type	Biological Effect Indicators	Empirical Critical Load (kg N/ha/yr)
GRASSLANDS AND TALL FORB HABITATS (E)		
Sub-Atlantic semi-dry calcareous grassland	Increased mineralization, nitrification and N leaching; increased tall grasses; decreased diversity	15–25
Non-Mediterranean dry acid and neutral closed grassland	Increase in nitrophilous graminoids, decline of typical species	10–20
Inland dune grasslands	Decrease in lichens, increase in biomass, accelerated succession	10–20
Low and medium elevation hay meadows	Increased tall grasses, decreased diversity	20–30
Mountain hay meadows	Increase in nitrophilous graminoids, changes in diversity	10–20
Moist and wet oligotrophic grasslands	Increase in tall graminoids, decreased diversity, decrease in bryophytes	10–25
Alpine and subalpine meadows	Increase in nitrophilous graminoids, changes in diversity	10–15
Moss and lichen dominated mountain summits	Effects on bryophytes and lichens	5–10
HEATHLAND HABITATS (F)		
Northern wet heaths	Decreased heather dominance, transition heather to grass, decline in lichens and mosses	10–20
Dry heaths	Transition from heather to grass, decline in lichens	10–20
Arctic, alpine, and subalpine scrub habitats	Decline in lichens, mosses, and evergreen shrubs	5–15
COASTAL HABITAT (B)		
Shifting coastal dunes	Increased biomass, increased N leaching	10–20
Coastal stable dune grasslands	Increase in tall grasses, decreased prostrate plants, increased N leaching	10–20
Coastal dune heaths	Increase in plant production, increased N leaching, accelerated succession	10–20
Moist to wet dune slacks	Increase in biomass and tall graminoids	10–25
MIRE, BOG, AND FEN HABITATS (D)		
Raised and blanket bogs	Changed species composition, N saturation of Spagnum	5–10
Poor fens	Increased sedges and vascular plant, negative effects on mosses	10–20
Rich fens	Increase in tall graminoids, decreased diversity, decrease of characteristic mosses	15–35
Mountain rich fens	Increase in vascular plants, decrease in bryophytes	15–25

Ecosystem Type	Biological Effect Indicators	Empirical Critical Load (kg N/ha/yr)
FOREST HABITATS (G)		
Mycorrhizae	Reduced sporocarp production, reduced below ground species composition	10–20
Ground vegetation	Changed species composition, increased nitrophilous species; increased susceptibility to parasites (insects, fungi, virus)	10–15
Lichens and algae	Increase in algae; decrease in lichens	10–15

Source: Achermann and Bobbink (2003). Reprinted with permission.

3.3.7.2. Empirical Critical Loads for U.S.

Efforts have begun to develop empirical relationships in the U.S., particularly for western ecosystems, however there is currently no published assessment for the U.S or the continent of North America. Table 4-4 summarizes publications of deposition levels and related ecological effects, presenting critical loads when reported in the original publication. Table 4-4 includes N levels at which effects are manifested in terrestrial and freshwater ecosystems that have been documented through N addition and deposition gradient studies. Several important studies from Europe published after the assessment by Bobbink et al. (2003) are included in addition to some publications from Asia. Dose-response relationships between N and ecological indicators are given in Table 3-25.

In terrestrial ecosystems, the reported effect levels range from 4 to 5 kg N/ha/yr for changes in the abundance of individual sensitive alpine plant species, to 20 kg N/ha/yr for community level changes in alpine plant communities. Clark and Tilman (2008) calculate the CL for the onset of reduced relative species number in grasslands to be 5.3 kg N/ha/yr with a 95% inverse prediction interval of 1.3–9.8 kg N/ha/yr. A critical load of 3.1 kg N/ha/yr is considered protective of lichen communities in the West (Fenn et al., 2008).

Differences in the levels at which increased nitrification and NO_3^- leaching have been observed in eastern and western watersheds. For example, Rueth (2002) observed increased rates of nitrification in old-growth forests in Colorado at approximately 5 kg N/ha/yr, whereas Aber et al. (2003) associated the onset of NO_3^- leaching in eastern forests with deposition levels of 7 to 10 kg N/ha/yr. The critical load for NO_3^- leaching in western chapparal ecosystems is 17 kg N/ha/yr (Fenn et al., 2008).

There is evidence that freshwater wetlands in the U.S. and Canada that are dominated by *Sphagnum* sp. are affected by N deposition. Most evidence documents N retention, peat accumulation and changes in NPP, and is not sufficient to quantify a critical load. The suggested critical load for protecting the population health of northern pitcher plant is 10–14 kg N/ha/yr (Gotelli and Ellison 2006). There are no publications suggesting critical loads for coastal wetland ecosystems.

Table 3-25.   Summary of dose-response curves for N deposition and ecological indicators.

Ecosystems	Deposition Range (kg N/ha/yr)	Effect	Indicator	Study Region	Response Curve	Reference
N DEPOSITION						
Forest	1–75	Nutrient enrichment	N leaching	65 forest sites across Europe	$Y = 0.48(X) - 2.17$ ($r^2 = 0.69$; $p < 0.001$) Y: N leaching (kg N/ha/yr) X: total inorganic N deposition (kg N/ha/yr)	Dise and Wright (1995); Lawrence (1995, 2007)
Forest	2–8 *wet deposition only	Acidification/ Nutrient enrichment	%N in the Oa horizon	12 red spruce stands across the northeastern U.S.	$Y = 0.097(X) + 1.03$ ($r^2 = 0.63$) Y: N content in the Oa horizon (%) X: wet inorganic N deposition (kg N/ha/yr)	Driscoll et al. (2001)
Forest	0–50 *throughfall N	Acidification/ Nutrient enrichment	Soil solution NO_3^-	104 European monitoring site	Conifers: $Y = 0.06e^{0.132(X)}$ ($r^2 = 0.59$, $p = 0.0001$) Deciduous: $Y = 0.018e^{0.266(X)}$ ($r^2 = 0.65$, $p = 0.0001$) Y: NO_3^- concentration in soil water (averages Jan 1996 to Jan. 1998) (mg N/L) X: throughfall N deposition (averages 1993–1997) (kg N/ha/yr)	Gundersen et al. (2006)
Forest	0–40 *throughfall N	Acidification/ Nutrient enrichment	Soil solution NO_3^-	104 European monitoring site	Conifers: $\log(Y) = 0.06(X) - 1.2$ ($r^2 = 0.59$, $p = 0.0001$) Broadleaves: $\log(Y) = 0.12(X) - 1.8$ ($r^2 = 0.65$, $p=0.0001$) Y: NO_3^- concentration in soil water (averages Dec 1995 to Feb. 1998) (mg N/L) X: Throughfall N deposition (averages 1993 – 1997) (kg N/ha/yr)	Kristensen et al. (2004)
Forest	0–25 *bulk precipitation N	Acidification/ Nutrient enrichment	Soil solution NO_3^-	104 European monitoring site	Conifers: $\log(Y) = 0.09(X) - 1.3$ ($r^2 = 0.32$, $p<0.0001$) Broadleaves: $\log(Y) = 0.09(X) - 1.18$ ($r^2 = 0.16$, $p=0.02$) Y: NO_3^- concentration in soil water (averages Dec 1995 to Feb. 1998) (mg N/L) X: Bulk precipitation N deposition (averages 1993 – 1997) (kg N/ha/yr)	Kristensen et al. (2006)

Ecosystems	Deposition Range (kg N/ha/yr)	Effect	Indicator	Study Region	Response Curve	Reference
Forest	Relation between throughfall and bulk precipitation N input			104 European monitoring site	Conifers: Y = 1.8(X) – 2.3 (r^2=0.65, p <0.0001) Broadleaves: Y=0.86(X) – 4.9 (r^2 = 0.32, p = 0.0008) Y: Throughfall N deposition (averages 1993–1997) (kg N/ha/yr) X: Bulk precipitation N deposition (averages 1993–1997) (kg N/ha/yr)	Kristensen et al. (2006)
Forest	0–40 *throughfall N	Acidification/ Nutrient enrichment	Foliage N	104 European monitoring site	Conifers: Y = 0.14(X) + 12.7 (r^2 = 0.40 , p <0.0001) Y: Foliage N concentration (mg/g) X: Throughfall N deposition (averages 1993–1997) (kg N/ha/yr)	Kristensen et al. (2006)
Forest	0–40 *throughfall N	Acidification/ Nutrient enrichment	C:N organic layer	104 European monitoring site	Conifers: Y = -0.21(X) + 31.5 (r^2 = 0.19 ; p = 0.0002) Broadleaves: Y = -0.48(X) + 32.3 (r^2 = 0.14; p = 0.036) Y: C:N organic layer X: Throughfall N deposition (averages 1993 – 1997) (kg N/ha/yr)	Kristensen et al. (2006)
Spruce forest	5 to 30 kg N/ha/yr	Nutrient enrichment N_2O flux	showed a significant and positive correlations between increasing N deposition and increasing N_2O flux	2 sites in Germany and Ireland	Y = 4.7 + 1.4(X) (r^2 = 0.38, p <0.001) Y = N_2O flux rates (µg N_2O N/m^2/h) X= NH_4^+ input by wet deposition (mmol/m^2)	Butterbach-Bahl et al. (1998)
Spruce forest	5 to 30 kg N/ha/yr	Nutrient enrichment NO flux	showed a significant and positive correlations between increasing N deposition and increasing NO flux	2 sites in Germany and Ireland	Y = 14.1 + 16.7(X) (r^2 = 0.67, p <0.001) Y= NO flux rates (µg NO–N/m^2/h) X= NH_4^+ input by wet deposition (mmol/m^2)	Butterbach-Bahl et al. (1998)
Spruce forest	5 to 30 kg N/ha/yr	Nutrient enrichment CH_4 oxidation rate	showed a significant and negative correlations between increasing N deposition and decreasing CH_4 oxidation rate	2 sites in Germany and Ireland	Y = -34.7 + 3.4(X) (r^2 = 0.33, p <0.001) Y= CH_4 oxidation rate (µg CH_4/m^2/h) X= NH_4^+ input by wet deposition (mmol/m^2)	Butterbach-Bahl et al. (1998)

Ecosystems	Deposition Range (kg N/ha/yr)	Effect	Indicator	Study Region	Response Curve	Reference
Grassland	5–35	Acidification/ Nutrient enrichment	Species richness	68 acid grasslands across UK	$Y = 23.3 - 0.408(X)$ (r^2=0.70; p <0.0001) Y: plant species richness X: total inorganic N deposition (kg N/ha/yr)	Stevens et al. (2004)
Lakes	1–16* *wet deposition only	Nutrient enrichment	water [DIN]	4296 lakes across USA, Canada and Europe	$\log(Y) = 1.34\log(X) - 1.55$ ($r^2 = 0.70$; p <0.001) Y: water DIN (µg/L) X: wet deposition (kg N/km^2/yr)	Bergstrom and Jansson (2006)
Lakes	1–16* *wet deposition only	Nutrient enrichment	Chl a: Tot-P	515 lakes across USA, Canada and Europe	$\log(Y) = 1.03\ln(X) - 1.43$ ($r^2 = 0.52$; p <0.001) Y: Chl a : Tot-P X: wet deposition (kg N/ km^2/yr)	Bergstrom and Jansson (2006)
Surface water	3.1 to 17.6 * * net anthropogenic nitrogen inputs (NANI)	Nutrient enrichment	Riverine exports of anthropogenic N	16 watersheds from Maine to Virginia	$Y = (0.00087(Q) - 0.096)$ NANI - 101 Y: Riverine N flux (kg N /km^2/yr) Q: riverine discharge NANI: Net anthropogenic N inputs (N/km^2/yr)	Howarth and Marino (2006)
Surface water	4–12	Acidification/ Nutrient enrichment	Surface water [NO$_3$$^-$]	220 lakes and streams across the northeastern U.S.	Summer: $Y = 2.5(X) - 14.4$ ($r^2 = 0.30$, p <0.001) Spring: $Y = 6.7(X) - 40.7$ ($r^2 = 0.38$, p <0.001) Y: NO$_3$$^-$ concentration in water (µmol/L) X: N deposition (kg N/ha/yr)	Aber et al. (2003)
Stream water	5–13	Acidification/ Nutrient enrichment	N export	83 lakes and streams across the northeastern U.S.	$Y = 0.85(X) - 5.8$ ($r^2 = 0.56$, p = 0.01) Y: NO$_3$$^-$ export (kg N/ha/yr) X: N deposition (kg N/ha/yr)	Aber et al. (2003)
Stream water	5–13	Acidification/ Nutrient enrichment	Inorganic N retention	83 lakes and streams across the northeastern U.S.	$Y = -0.07(X) + 1.44$ ($r^2 = 0.50$, p = 0.01) Y: inorganic N retentions (kg N/ha/yr) X: N deposition (kg N/ha/yr)	Aber et al. (2003)
Estuary	8–24* *N loads from atmospheric deposition, human waster water and fertilization application	Nutrient enrichment	Eelgrass area (ha)	Waquoit Bay	$Y = -1.9(X) + 50.7$ ($r^2 = 0.89$) Y: Eelgrass area (ha) X: modeled N load (kg N/ha/yr)	Driscoll et al. (2003)

Ecosystems	Deposition Range (kg N/ha/yr)	Effect	Indicator	Study Region	Response Curve	Reference
Peatland	0–160	Acidification/ Nutrient enrichment	NPP of *Sphagnum fuscum*	8 bogs in North America and Europe	$Y = 831e^{-0.185(X)} - 48$ ($r^2 = 0.73$, p <0.01) Y: difference between NPP of *S. fuscum* under augmented N and control treatment (g/m^2/yr); X: N deposition (kg N/ha/yr)	Vitt et al. (2003)
Peatland	2–20	Nutrient enrichment	Decomposition of litter collected from the field and incubated and constant temperature	12 bogs from 9 European countries	$Y = 0.98 + 0.21\ln(X)$ ($r^2 = 0.75$, p <0.01) four days incubation $Y = 0.49 + 0.11\ln(X)$ ($r^2 = 0.73$, p <0.01) 10 days incubation Y: CO^2 emission (mg/g/h) X: N deposition (g/m^2/yr)	Bragazza et al. (2006)
Peatland	2–20	Nutrient enrichment	Decomposition of litter collected from the field and incubated and constant temperature	12 bogs from 9 European countries	$Y = 4.3 + 2.4\ln(X)$ ($r^2 = 0.61$, p = 0.01) Y: DOC concentration (mg/g) X : N deposition (g/m^2/yr)	Bragazza et al. (2006)
Peatland	2.7 to 8.1 kg N/ha/yr	Nutrient enrichment	Showed N accumulation increases linearly with N deposition	23 ombrotrophic peatlands in Canada	$Y = 3.50(X) + 0.64$ ($r^2 = 0.29$, p <0.001) Y: N accumulation in soil (g/m^2/yr) X : N wet deposition (g/m^2/yr)	Moore et al. (2004)

3.3.8. Characterization of Sensitivity and Vulnerability

3.3.8.1. Extent and Distribution of Sensitive and Vulnerable Ecosystems

In general, ecosystems that are most responsive to nutrient enrichment from atmospheric N deposition are those that receive high levels of N loading, are N-limited, or contain species that have evolved in nutrient-poor environments. Species that are adapted to low N supply will often be more readily outcompeted by species that have higher N demand when the availability of N is increased (Aerts, 1990; Krupa, 2003; Tilman and Wedin, 1991). As a consequence, some native species can be eliminated by N deposition (Ellenberg, 1985; Falkengren-Grerup, 1986, 1989; Roelofs, 1986; Stevens et al., 2004). Note the terms "low" and "high" are relative to the amount of bioavailable N in the ecosystem and the level of deposition.

The following discussion of sensitive ecosystems is organized into three ecosystem categories: terrestrial, transitional, and aquatic. Case studies are intended to highlight ecosystems and/or regions where there are many publications documenting the effects of N deposition, thus they can provide sufficient data for quantitative risk assessment.
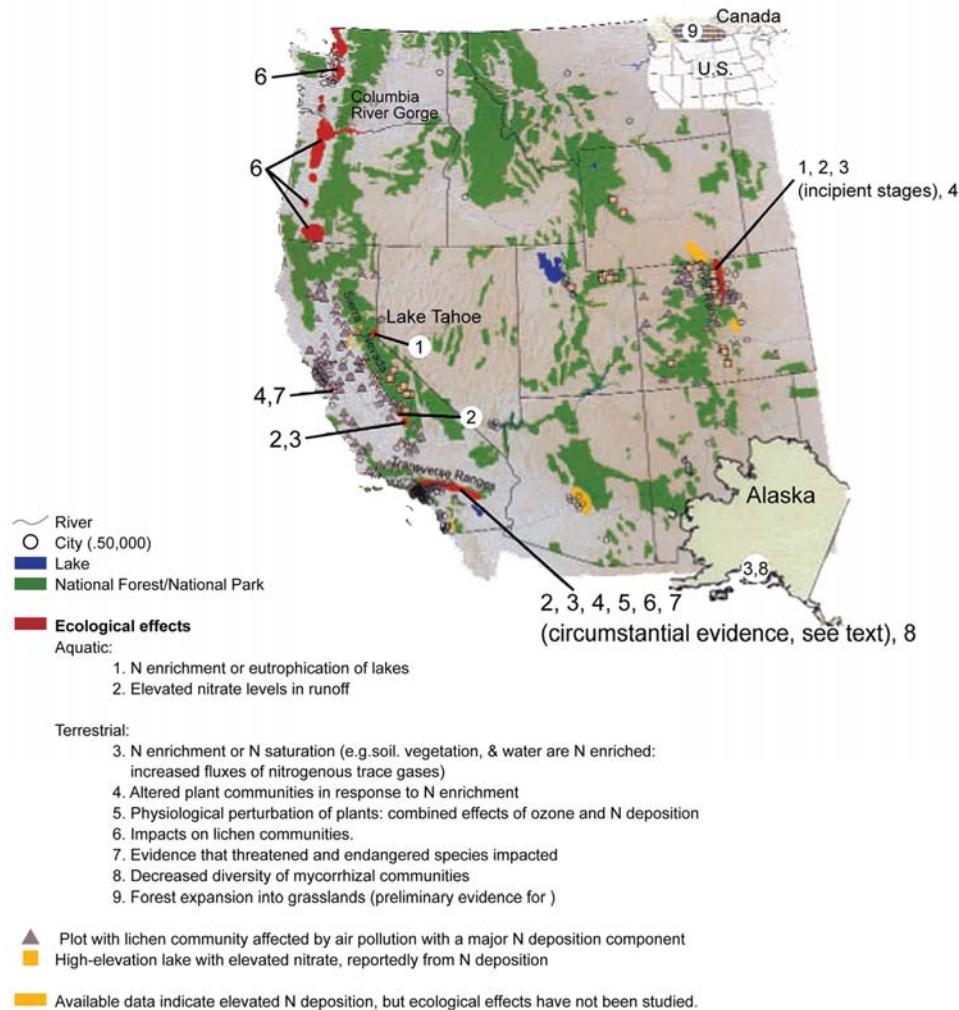
Figure 3-52. Map of the western U.S. showing the primary geographic areas where N deposition effects have been reported. Eutrophication effects are more widespread and of greater importance than acidification effects in western North America. Areas where effects of air pollution on lichen communities have been reported in CA are represented by pink triangles. The plots in north central CO where lichen community changes were observed are exposed to emissions of both N and sulfur (S) from two large power plants in Craig, CO and Haydens, CO (Peterson et al., 2001). The areas shown in red in OR and WA (lichen communities affected by N deposition) are kriged data (Geiser and Neitlich, 2007). Only lakes at an elevation greater than 1000 m and with a NO_3 concentration of more than 5 μeq/L (measured in fall surveys or on an annual volume-weighted basis) are shown in thisfgure. Other high-elevation lakes in the West also had elevated NO_3 concentrations, but were F excluded because N sources other than N deposition may have contributed to the elevated concentrations of NO_3.

Terrestrial

Most terrestrial ecosystems are N-limited, therefore they are sensitive to perturbation caused by N additions (LeBauer and Treseder, 2008). Little is known about the full extent and distribution of the terrestrial ecosystems in the U.S. that are most sensitive to adverse impacts caused by nutrient enrichment

from atmospheric N deposition. Effects are most likely to occur where areas of relatively high atmospheric N deposition intersect with N-limited plant communities. The factors that govern the vulnerability of terrestrial ecosystems to nutrient enrichment from N deposition include the degree of N-limitation, rates and form of N deposition, elevation, species composition, length of growing season, and soil N retention capacity.

Regions and ecosystems in the western U.S. where N enrichment effects have been documented in terrestrial ecosystems are shown on Figure 3-52 (Fenn, 2003a). The alpine ecosystems of the Colorado Front Range (see case study), chaparral watersheds of the Sierra Nevada, lichen and vascular plant communities in the San Bernardino Mountains (see case study) and the Pacific Northwest, and the southern California coastal sage scrub community are among the most sensitive terrestrial ecosystems.

In the eastern U.S., the degree of N saturation of the terrestrial ecosystem is often assessed in terms of the degree of NO_3^- leaching from watershed soils into ground water or surface water. Stoddard (1994) estimated the number of surface waters at different stages of saturation across several regions in the eastern U.S. Of the 85 northeastern watersheds examined, 40% were in N-saturation Stage 0, 52% in Stage 1, and 8% in Stage 2 (stages are defined in Section 3.3.2.1). Of the northeastern sites for which adequate data were available for assessment, those in Stage 1 or 2 were most prevalent in the Adirondack and Catskill Mountains. Effects on individual plant species have not been well studied in the U.S. More is known about the sensitivity of particular plant communities. Based largely on results obtained in more extensive studies conducted in Europe, it is expected that the more sensitive terrestrial ecosystems include hardwood forests, alpine meadows, arid and semi-arid lands, and grassland ecosystems.
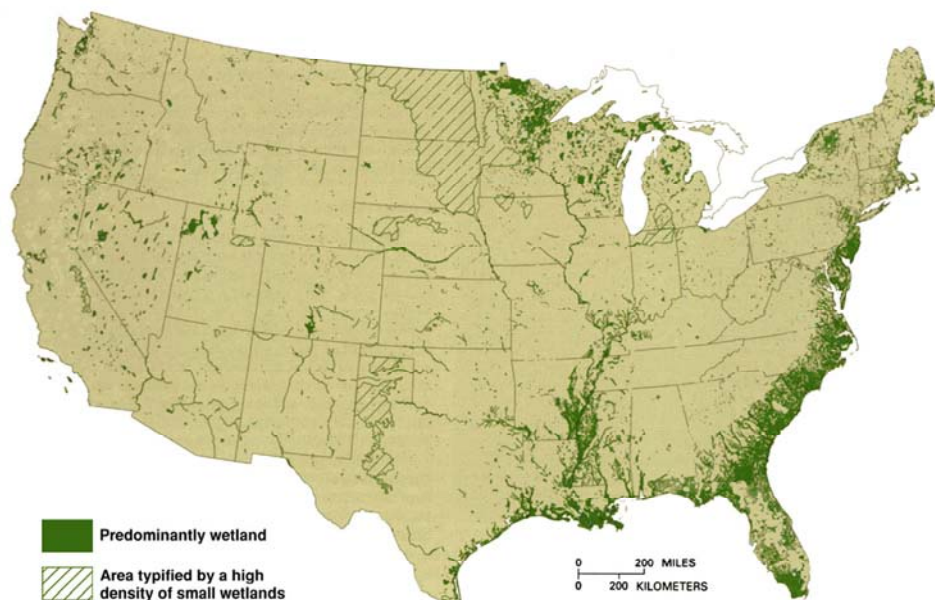
Source: Data were obtained from the National Land Cover Data (NLCD) (2001) (http://www.mrlc.gov/)

Figure 3-53.   Location of wetlands in CONUS.

Transitional

About 107.7 million acres of wetlands are widely distributed in the conterminous U.S., 95 percent of which are freshwater wetlands and 5 percent are estuarine or marine wetlands (U.S. FWS 2005) (Figure 3-53). At one end of the spectrum, ombrotrophic bogs are very sensitive to N deposition because they receive exogenous nutrients exclusively from precipitation, and the species in them are adapted to

low levels of N (Bridgham et al., 1995, 1996; Shaver and Melillo 1984). Intertidal wetlands are at the other end of the spectrum; in these ecosystems marine/estuarine water sources generally exceed atmospheric inputs by one or two orders of magnitude (Morris, 1991). Data are not available with which to evaluate the extent to which wetlands in the U.S. have been affected by nutrient enrichment from N deposition. Wetlands are widely distributed, including some areas that receive moderate to high levels of N deposition.

Peat-forming bog ecosystems are among the most sensitive transitional ecosystems to the effects of N deposition. In the conterminous U.S., peat-forming bogs are most common in areas that were glaciated, especially in portions of the Northeast and Upper Midwest (U.S. EPA, 1993a). In Alaska, these ecosystems are common in poorly drained locations throughout the state.

Nutrient concentrations in wetland waters associated with the Great Lakes suggest that coastal Great Lakes wetlands are N-limited. Hill et al. (2006) found that more wetlands were N- than P-limited at each of the five Laurentian Great Lakes. This result is consistent with the apparent N-limitation of most North American marsh lands (Bedford et al., 1999). Nutrient loading to lakeshore wetlands is a concern throughout the lower lakes (Lakes Erie, Ontario, and the southern part of Lake Michigan) and in some localized areas of the upper lakes (Hill et al., 2006). Both agricultural and atmospheric sources of nutrients contribute to this stress.

Coastal marsh ecosystems, unlike bog ecosystems, often receive large N inputs in tidal water, groundwater, and surface runoff. Atmospheric inputs to these systems are important because any N addition has the potential to contribute to eutrophication of coastal marshes and nearby marine and estuarine ecosystems (Galloway et al., 2003; Paerl, 2002). At many locations, especially along the Atlantic and Gulf coasts, atmospheric N inputs probably contribute to eutrophication problems in coastal marshes either by direct deposition to the wetland or from marine water inputs of N that originated from atmospheric deposition.

Freshwater Aquatic

Aquatic systems in which N has been observed to influence ecological processes either receive extremely high inputs (e.g., Dumont et al., 2005), or have very low initial N concentrations, and respond rapidly to additional inputs (Baron et al., 2000; Bergström and Jansson, 2006). Eutrophication effects on freshwater ecosystems from atmospheric deposition of N are of great concern in lakes and streams that have very low productivity and nutrient levels and that are located in remote areas. In more productive freshwaters, nutrient enrichment from N deposition usually does not stimulate productivity or community changes because P is more commonly the limiting nutrient. Also, in many places with even minor levels of human disturbance, nutrient enrichment with both N and P from non-atmospheric sources is common. Thus, eutrophication effects from N deposition are most likely to be manifested in undisturbed, low-nutrient surface waters such as those found in the higher elevation areas of the western U.S. The most severe eutrophication from N deposition effects is expected downwind of major urban and agricultural centers.

High concentrations of lake or streamwater NO_3^-, indicative of ecosystem saturation, have been found at a variety of locations throughout the U.S., including the San Bernardino and San Gabriel Mountains within the Los Angeles Air Basin (Fenn et al., 1996), the Front Range of Colorado (Baron et al., 1994; Williams et al., 1996b), the Allegheny Mountains of West Virginia (Gilliam et al., 1996), the Catskill Mountains of New York (Murdoch and Stoddard, 1992; Stoddard, 1994), the Adirondack Mountains of NY (Wigington et al., 1996), and the Great Smoky Mountains in TN (Cook et al., 1994). All of these regions, except CO, received more than about 10 kg N/ha/yr atmospheric deposition of N throughout the 1980s and 1990s. In contrast, the Front Range of Colorado receives up to about 5 kg N/ha/yr of total (wet plus dry) deposition (Sullivan et al., 2005), less than half of the total N deposition received at many of these other locations.

Table 3-26.   Changes in aquatic ecosystems associated with elevated N loadings in the Western U.S.

Ecological or Environmental Impact	Location	Level of Uncertainty	Possibility of Broader Occurrence (at other sites)	Reference
EFFECTS IN AQUATIC SYSTEMS				
Elevated NO_3^- in runoff; most severe in southern California and in chaparral catchments in the southwestern Sierra Nevada	Transverse ranges of southern California; low-elevation catchments in the Sierra Nevada; high-elevation catchments in the Colorado Front Range	Well-documented response	It is unclear how widespread this phenomenon is outside the ecosystems listed, because there is littler information from low-elevation systems in the Sierra Nevada and elsewhere.	Williams et al. (1996a); Fenn and Poth (1999); Fenn et al. (2003a)
N enrichment and shifts in diatom communities in alpine lakes	Colorado Front Range; Lake Tahoe (California/Nevada border)	Documented for two lakes east of the Continental Divide and Lake Tahoe	These effects seem likely in other N-enriched lakes but have not been investigated.	Baron et al. (2000); Wolfe et al. (2001b); Goldman (1988).
Reduced lake water clarity and increased algal growth	Lake Tahoe (California/Nevada border); high-elevation lakes throughout central and southern Sierra Nevada	Well-documented response; N and P deposition believed to be important factors	Lake Tahoe is an unusual case because of its renowned lake clarity; extent of occurrence elsewhere in northern Sierra Nevada is unknown.	Jassby et al. (1994); Sickman et al. (2003).
Increased NO_3^- concentrations in high-elevation lakes	Several regions, mainly downwind of urban centers	Fairly well established from lake surveys, but more data needed for improved definition of frequency and severity	Evidence suggests that urban plumes and agricultural emissions affect lake NO_3^- levels. There is also evidence of impacts on low-elevation lakes.	Figure 2, Sickman et al. (2002)

High concentrations of NO_3^- in surface waters in the western U.S. are not widespread. NO_3^- concentrations during the fall sampling season were low in most western lakes sampled in the Western Lakes Survey. Only 24 sampled lakes were found to have NO_3^- concentrations greater than 10 µeq/L. Of those, 19 lakes were situated at high elevation, most above 3,000 m (Eilers et al., 1987). Other effects on aquatic ecosystems in the west are summarized in Table 3-26.

There is some evidence suggesting that reductions in atmospheric N deposition could decrease the extent of eutrophication in at least some of the Great Lakes. It has generally been believed that the Laurentian Great Lakes are P-limited (Downing and McCauley, 1992; Rose and Axler, 1998; Schelske, 1991). Water quality in the open waters of these lakes has been improving in recent years in response to controls on point sources of P (Nicholls et al., 2001). Work by Levine et al. (1997), however, suggested a more complicated pattern of response to nutrient addition for Lake Champlain. They added nutrients to in situ enclosures and measured indicators of P status, including alkaline phosphatase activity and

orthophosphate turnover time. Although P appeared to be the principal limiting nutrient during summer, N addition also resulted in algal growth stimulation. P sufficiency appeared to be as common as P deficiency. During spring, phytoplankton growth was not limited by P, N, or Si, but perhaps by light or temperature (Levine et al., 1997).

Estuarine and Coastal Aquatic

N is an essential nutrient for estuarine and marine fertility. However, excessive N contributions can cause habitat degradation, algal blooms, toxicity, hypoxia (reduced dissolved O_2), anoxia (absence of dissolved O_2), reduction of sea grass habitats, fish kills, and decrease in biodiversity (Boynton et al., 1995; Howarth et al., 1996; Paerl, 1995; 1997; Valiela and Costa, 1988; Valiela et al., 1990). Each of these potential impacts carries ecological and economic consequences. Ecosystem services provided by estuaries include fish and shellfish harvest, waste assimilation, and recreational activities (Costanza et al., 1997).
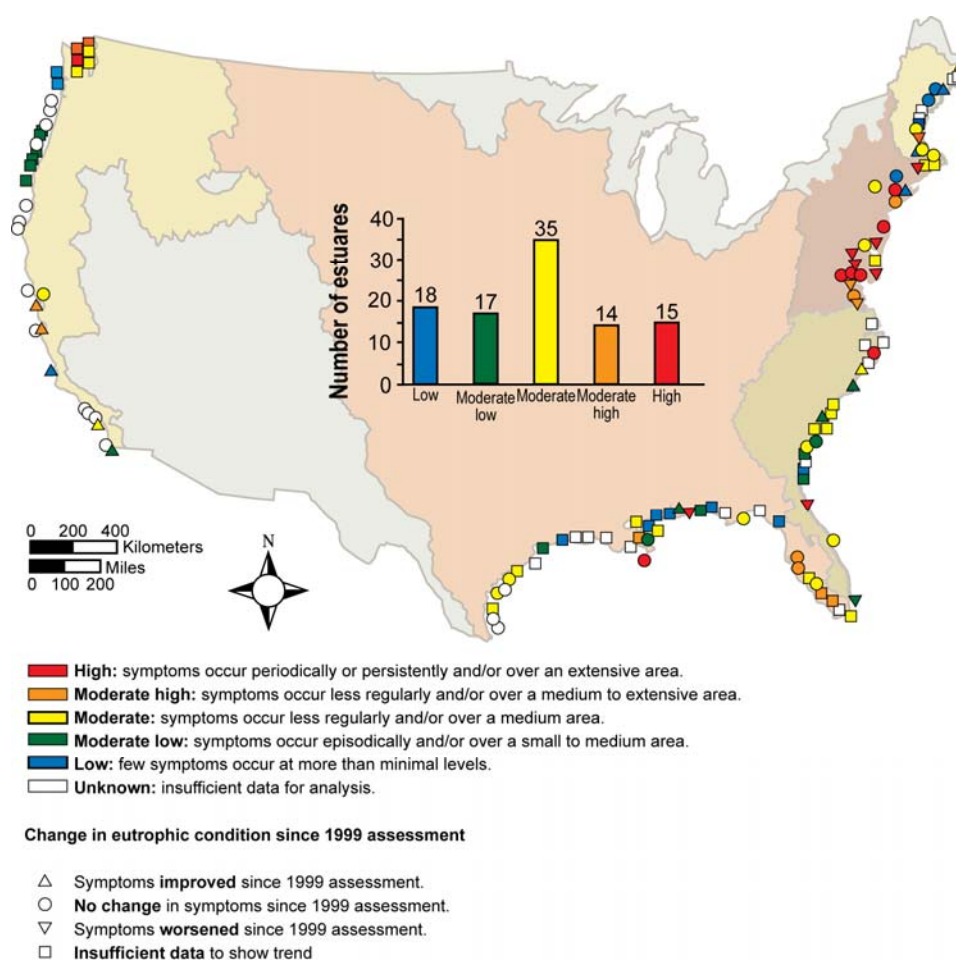
Source: Bricker et al. (2007)

Figure 3-54.   Overall eutrophication condition on a national scale.

Estuaries and coastal waters tend to be N-limited and are therefore inherently sensitive to increased atmospheric N loading (D'Elia et al., 1986; Howarth and Marino, 2006). The national estuary condition assessment conducted by Bricker et al. (2007) found that the most impacted estuaries occurred in the mid-Atlantic region and the estuaries with the lowest symptoms of eutrophication were in the North Atlantic. N over-enrichment is a major environmental problem for coastal regions of the U.S., especially in the eastern and Gulf Coast regions. Of 138 estuaries examined by Bricker et al. (1999), 44 were identified as showing symptoms of nutrient over-enrichment. Estuaries are among the most biologically productive ecosystems on Earth and provide critical habitat for an enormous diversity of life forms, especially fish. Of the 23 estuaries examined in the Northeast, 61% were classified as moderately to severely degraded (Bricker et al., 1999). Other regions had mixtures of low, moderate, and high degree of eutrophication (See Figure 3-54).

The estuaries with the greatest extent of eutrophication corresponded with conditions related to both the degree of N loading and the inherent sensitivity of the estuary, as influenced by morphology and water flushing dynamics (see Annex C for a discussion of estuarine sensitivity). The most eutrophic estuaries were generally those that had large watershed-to-estuarine surface area, high human population density, high rainfall and runoff, low dilution, and low flushing rates (Bricker et al., 2007).

Bricker et al. (2007) evaluated the future outlook of the nations estuaries based on population growth and future management plans. They predicted that trophic conditions would worsen in 48 estuaries, stay the same in 11, and improve in only 14 by the year 2020. Between 1999 and 2007, an equal number of estuary systems have improved their trophic status as have worsened. The assessed estuarine surface area with high to moderate/high eutrophic conditions have stayed roughly the same, from 72% in 1999 (Bricker et al., 1999), to 78% in the recent assessment (Bricker et al., 2007).

Studies linking changes in estuary nutrient status to atmospheric N deposition have been limited, though it is noted that many states are addressing atmospheric inputs as part of their development of Total Maximum Daily Load plans to address estuarine water quality impairments, including those associated with low dissolved O_2. In an effort to evaluate the contribution of atmospheric N deposition to the future reduction in N loading to estuaries, Castro and Driscoll (2002) reported model calculations that suggested that considerable reductions (more than 25%) in atmospheric N deposition will be needed to reduce the contribution made by atmospheric N deposition to the total N loads to their study estuaries in the northeastern U.S. A simulated reduction in atmospheric deposition of 25% of ambient deposition rates reduced the contribution made by atmospheric deposition to the total estuarine N loads by only 1% to 6% (Castro and Driscoll 2002). In a later study, Driscoll et al. (2003b) estimated that reduction of both mobile N emissions sources and electric utilities would produce an estimated reduction in estuarine N loading in Casco Bay, Maine of 13% (Driscoll et al., 2003c). Casco Bay receives the lowest atmospheric and non-atmospheric N loading per unit area of watershed (4 kg N/ha/yr) of the eight estuaries in the northeastern U.S. evaluated by (Driscoll et al., 2003a) (Figure 3-35).

3.3.8.2. Case Study: Alpine and Subalpine Communities of the Eastern Slope of the Rocky Mountains

Some alpine plant communities occur in areas that receive moderately elevated atmospheric N deposition; especially those proximal to urban areas (see Annex C for a map). Because alpine plant species are typically adapted to low nutrient availability, they often are sensitive to effects from N enrichment.

Research on N enrichment effects on alpine and subalpine ecosystems in the western U.S. has been limited mainly to studies at the Loch Vale Watershed in Rocky Mountain National Park and the Niwot Ridge Long-Term Ecosystem Research site; both located east of the Continental Divide in Colorado (see review by Burns 2004). Research has been conducted in this region on both the terrestrial and aquatic effects of nutrient enrichment.

Terrestrial Effects

Changes in biomass production and NO_3^- leaching are indicative of effects on the health and vigor of plants in alpine and subalpine ecosystems. Biomass production responses of alpine communities to increased N deposition are dependent on moisture regimes (Fisk et al., 1998) and are driven by shifts in species composition. In a fertilization experiment, the addition of 25 kg N/ha/yr during summer caused a community shift towards greater dominance of hairgrass (*Deschampsia sp.*) in wet alpine meadows. However, the increase in plant biomass (+67%) and plant N content (+107%) following N fertilization was higher in graminoid-dominated dry meadows than in forb-dominated wet meadows; +53% plant biomass, +64% standing N crop, respectively (Bowman et al., 1995; Burns, 2004).

Alteration of plant productivity and species richness has been observed in fertilization experiments. Seastedt and Vaccaro (2001) showed that four years of N addition to alpine vegetation at rates ranging between 100 and 200 kg N/ha (depending on the year) caused marginal increases in plant foliage productivity but reduced species richness. In a follow-up study at Niwot Ridge additions of 20, 40, and 60 kg N/ha/yr (on top of ambient N deposition near 5 kg N/ha/yr) over an 8 year period to a dry alpine meadow led to an increase in plant biomass, and an increase in tissue N concentration at all treatment levels within three years of application. Much of the response was due to increased cover and total biomass of sedges (*Carex spp.*). There was a significant decrease in *Kobresia myosuroides* with increasing N input.

High elevation alpine zones exhibit a relatively low capacity to sequester atmospheric deposition of N because of steep slopes, shallow soils, sparse vegetation, short growing season and other factors (Baron et al., 1994; Williams et al., 1996b). Results from several studies suggest that the capacity of Rocky Mountain alpine catchments to sequester N is exceeded at deposition levels less than 10 kg N/ha/yr (Baron et al., 1994; Williams and Tonnessen, 2000). The changes in plant species that occur in response to N deposition in the alpine zone can result in further increased leaching of NO_3^- from the soils, because the plant species favored by higher N supply are often associated with greater rates of N mineralization and nitrification than the preexisting species (Bowman et al., 1993; 2006; Steltzer and Bowman, 1998; Suding et al., 2005).

Effects of N deposition to alpine terrestrial ecosystems in this region include community-level changes in plants, lichens, and mycorrhizae. Alpine plant communities are sensitive to changes in species composition in response to added N (Bowman et al., 1995; Seastedt and Vaccaro, 2001). Plant species composition likely responds at lower N input levels than those that cause measurable changes in soil inorganic N content. For example, Bowman et al. (2006) conducted a N-addition experiment in the Colorado Front Range with 20, 40, or 60 kg N/ha/yr (see Figure 3-55). Experimental sites were monitored for 8 years along with a reference site that received about 5 kg N/ha/yr total ambient deposition. Changes in plant species composition associated with the treatments occurred within 3 years of the initiation of the experiment, and were significant at all levels of N addition.

Using changes of individual species abundance and ordination scores to evaluate critical load, the critical load for total N deposition was estimated for change in individual species to be 4 kg N/ha/yr and for overall community change to be 10 kg N/ha/yr (Bowman et al., 2006). In contrast, increases in NO_3^- leaching, soil solution inorganic NO_3^-, and net nitrification were detectable at levels above 20 kg N/ha/yr (Bowman et al., 2006). These results indicate that changes in plant species composition may be detectable at lower N deposition rates than the level at which the traditional soil indicators signal ecosystem responses to N deposition. This response suggests that changes in species composition are probably ongoing in alpine dry meadows of the Front Range of the Colorado Rocky Mountains at current atmospheric N deposition levels. This research also demonstrated that long-term experimental fertilization plots illustrate a clear response of alpine flora to N addition, including shifts toward graminoid plants that shade smaller flowering species, and accompanying changes in soil N cycling (Bowman et al., 2006).

Changes in alpine plant species composition have also been documented on Niwot Ridge, where increased cover of plant species that are most responsive to N fertilization has occurred in some of the long-term monitoring plots (Fenn et al., 2003a; Korb and Ranker, 2001). These changes have probably

developed in response to changes in N deposition. However, the influences of climatic change, particularly changes in precipitation (Williams et al., 1996b) and pocket gopher disturbance (Sherrod and Seastedt, 2001) could not be ruled out (Fenn et al., 2003a). The altered N cycling provided the potential for replacement of some native plant species by more competitive, faster growing native species (Baron et al., 2000; Bowman, 2000; Bowman and Steltzer, 1998).

Aquatic Effects

Rocky Mountain National Park has been the site of research addressing the effects of N deposition on algal species abundance in freshwater lakes. Wolfe et al. (2001) analyzed sediments from Sky Pond and Lake Louise, two small alpine lakes located at more than 3300 m elevation on the east slope of the Colorado Front Range in Rocky Mountain National Park. Before 1900, the diatom flora was typical of oligotrophic Rocky Mountain lakes, dominated by such species as *Aulacoseira distans*, *A. perglabra*, *Fragilaria pinnata*, *F. construens*, and various *Achnanthes* spp. The mesotrophic planktonic species *Astrionella formosa* and *Fragilaria crotonensis* were present in trace frequencies, but became common elements of the diatom flora during the 20th century. Between 1950 and 1970, *A. formosa* became the dominant taxa in both lakes. It is known from studies in other locations as an opportunistic alga that responds rapidly to disturbance and nutrient enrichment (Renberg et al., 1993; Anderson et al., 1995; Reavie and Smol, 2001). This shift in diatom species is apparently the result of environmental stimulation, rather than recent colonization, as evidenced by the presence of these mesotrophic taxa in the older sediment record.
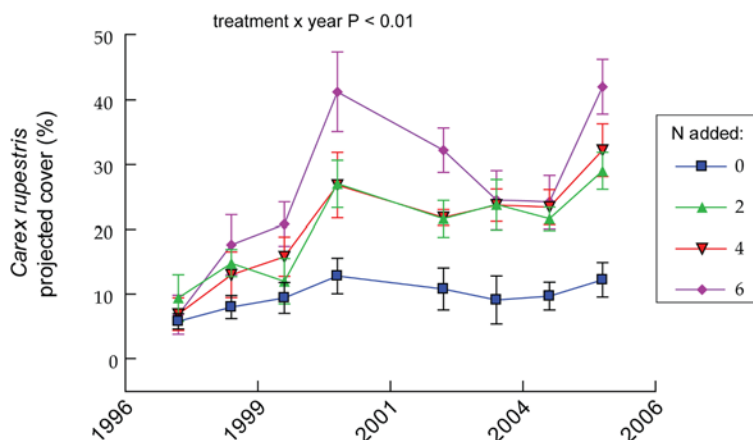
Source: Bowman et al. (2006))

Figure 3-55.   Changes in plant species composition associated with N addition treatments in an alpine dry meadow of the Colorado Front Range.   Within 3 years of the initiation of the experiment, statistically significant changes in the cover of Carex rupestris occurred at all treatment levels.

Additional corroborative evidence for the linkage between atmospheric N deposition and the observed diatom shifts in these alpine lakes is provided by the results of laboratory (Interlandi and Kilham, 1998) and in-lake (McKnight et al., 1990) N addition experiments. In both sets of experiments, growth of *A. formosa* and *F. crotonensis* was accelerated by experimental N addition. The post-1950 period of rapid shifts in diatom species composition in Sky Pond and Lake Louise corresponded with intensification of agricultural practices, animal husbandry, and population growth in adjacent regions to

the east of Rocky Mountain National Park (Wolfe et al., 2001). Nevertheless, N deposition at that time was estimated to be low, probably less than 2 kg N/ha/yr (Baron, 2006).

3.3.8.3. Case Study: Chesapeake Bay

Chesapeake Bay is the largest estuary in the U.S. and one of the most sensitive to N inputs (Bricker et al., 1999; Howarth, 2007). Eutrophication effects have been pronounced in Chesapeake Bay (Howarth, 2007) and it is perhaps the best known example in the U.S. of human activities leading to accelerated estuarine eutrophication and its associated negative effects. In the recent national assessment of eutrophic conditions in estuaries, the Chesapeake Bay stands out as a system with both physical features and N loading levels that make it particularly vulnerable to eutrophication (Bricker et al., 2007).

The role of atmospheric N deposition was not considered as a factor in estuary eutrophication in the U.S., and was ignored until Fisher and Oppenheimer (1991) suggested that it could constitute up to 40% of the total N inputs to the Chesapeake Bay. Recent studies have reported more conservative estimates (Boyer et al., 2002); however, Fisher and Oppenheimer (1991) drew attention to the potential for atmospheric deposition as an important contributor to the overall N budget of estuaries in the eastern U.S. N inputs to the Chesapeake Bay have increased substantially over the last 50 to 100 years. The increase is attributed to rapid acceleration of the use of chemical fertilizers in agriculture, the increasing human population density and associated wastewater discharge, and rising atmospheric N emissions within the airshed and consequent deposition within the Chesapeake Bay watershed. Atmospheric deposition of N is currently estimated to contribute about one-fourth of the total N loading to Chesapeake Bay (Boyer et al., 2002; Howarth, 2007)

Human activities have increased the susceptibility of the Chesapeake Bay to the effects of atmospheric N deposition. For example, the filling in of wetlands and deforestation for agricultural and urban development, have reduced the ability of natural ecosystem processes to remove or trap nutrients, thereby further accelerating nutrient delivery to the bay. In addition, diseases and over-harvesting led to a dramatic decline of the once highly abundant eastern oyster, seriously reducing the natural filtering of algae and other organic matter from the water column.

As a result of these changing conditions, eutrophic symptoms intensified in the Chesapeake Bay from the mid-1950s to the mid-1980s. The most apparent symptoms were high production of algae; increasingly turbid water; major declines in SAV abundance and species; and increasingly worsening anoxia and hypoxia (Boesch et al., 2001). The recent national estuary condition assessment (Bricker et al., 2007) reported that Chl a, dissolved O_2, nuisance/toxic algal blooms, and SAV rated "high" in Chesapeake Bay in terms of severity of effects associated with eutrophication. In addition, macroalgae and toxic algal bloom conditions have worsened since the previous national assessment in 1999 (Bricker et al., 1999, 2007).

Concentrations of Chl a in the surface mixed layer have increased tenfold in the seaward regions of the bay and one-and-one-half- to twofold elsewhere, paralleling estimates of increased loading of N and P to the bay since 1945 (Harding and Perry, 1997).

SAV began to decline as a result of nutrient enrichment during the mid-1960s, disappearing entirely from the Patuxent and lower Potomac Rivers. By 1980, many areas of the bay that once contained abundant SAV beds had none or only very small remnants left (Orth and Moore, 1984). Research indicated that the major driving factor in the decline of SAV was nutrient enrichment, which was causing excessive growth of algae in the water column and on SAV leaf blades (epiphytic algae). This algal growth decreased light availability to the submerged plants to the point that they could not survive (Kemp et al., 1983; Twilley et al., 1985).

There is an annual cycle of O_2 depletion in the Chesapeake Bay that begins as the water starts to warm in spring, and O_2 depletion accelerates during and following the spring freshet. The spring accumulation of algal biomass is more than sufficient to create conditions for O_2 depletion and summer anoxia (Malone, 1991, 1992). Hypoxia (very low dissolved O_2 concentration ~ <2mg/L) and anoxia

(absence of dissolved O_2) generally occur from May through September, with the most severe conditions observed in mid-summer. Seasonal hypoxia has been a feature of the Chesapeake Bay since deforestation during the colonial period (Cooper and Brush, 1991; Malone, 1991), but evidence suggests an increase in the extent of the problem in recent decades (Malone, 1991; Officer et al., 1984). Estuarine eutrophication is sometimes accompanied by increases in the populations of species of algae, often cyanobacteria that produce toxins. Such chemicals can affect people, fish, shellfish, and other organisms. Blooms of algae that produce toxins in Chesapeake Bay have become more extensive over approximately the past decade (Bricker et al., 2007).

In 1983, the U.S. EPA, District of Columbia, and states of Virginia, Maryland, and Pennsylvania signed the first Chesapeake Bay Agreement, which established the Chesapeake Bay Program—a voluntary government partnership that directs and manages bay cleanup efforts. Scientific findings from the program led to the signing of the second Chesapeake Bay Agreement in 1987, in which it was agreed to reduce by 40% the N and P entering the Chesapeake Bay by the year 2000. Point source reductions have been most successful, especially for P. Between 1985 and 1996, emissions from P point sources were reduced by 58% and N by 15%. Nonpoint source reductions have been slower, largely because nonpoint sources of nutrients are more difficult to control. Nonpoint source emissions of N and P have been reduced by only 7% and 9%, respectively (Boesch et al., 2001). Strategies to reduce nonpoint source nutrients include changes such as adoption of better agricultural practices, reduction of atmospheric N deposition, enhancement of wetlands and other nutrient sinks, and control of urban sprawl.

3.3.8.4. Case Study: San Bernardino

The San Bernardino Mountains lie east of the Los Angeles Air Basin in California. Pollutants generated in the greater LA metropolitan area are transported 60–100 km downwind and affect mid-elevation forests in the San Bernardino Mountains and the San Gorgonio Class I Wilderness area. The primary source of air pollution is fossil fuel combustion. Approximately half of the air pollution in the LA air basin is generated from mobile sources including trucks, trains, cars, ships, and buses (South Coast Air Quality Management District). On the western end of the San Bernardino Mountains, nearly half of the N deposition is in reduced forms (Fenn and Poth, 2004), most of which is believed to originate from dairy farms in the Chino/Norco area.

In the San Bernardino Mountains, a wide variety of N species (NO, NO_2, HNO_3, HNO_2, NO_3^-) are deposited to vegetation and soil surfaces, in gaseous, wet, and dry forms. Ammonium ($NH_4 +$) can also be transported moderate distances from feedlots for cattle and poultry (Bytnerowicz, 2002). Along a west to east gradient in the San Bernardino Mountains, throughfall N deposition goes from averaging 71 kg N/ha/yr at Camp Paivika (nearer to the pollutant sources), to 9 kg N/ha/yr at Barton Flats (farther from the sources), 45 km east of Camp Paivika (Breiner et al., 2007; Fenn et al., 2008). These throughfall measurements were made using ion exchange resin columns that measure total NO_3^- and NH_4^+ deposition from precipitation, plus fog or dry deposition that has been scavenged by the overstory pine canopy and then washed through the canopy (Fenn and Poth, 2004).

Several key ecological endpoints in the mixed conifer forests of the San Bernardino Mountains have been linked to anthropogenic N deposition. Because air pollution has been high since 1945 in the LA air basin (Lee et al., 2003), N deposition is in excess of plant and microbial demand (Fenn et al., 1996). The cardinal symptom of excess N is the export of high NO_3^- levels in streamwater (see 3.3.2.1), which is well demonstrated for areas with N deposition above 17 kg N/ha/yr in the San Bernardino and San Gabriel Mountains (Breiner et al., 2007; Fenn and Poth, 1999; Fenn et al., 2008; Michalski et al., 2004; Riggan et al., 1985, Fenn et al., 2008). Other indicators of excess N in the ecosystem include lowered litter C:N and elevated emissions of NO and N_2O from the soil (see 3.3.4.2), which have been observed at the more polluted sites in the San Bernardino Mountains. Lichen communities in the San Bernardino Mountains have also been dramatically changed by the disappearance of up to 50% of the species that occurred in the region in the early 1900s, due to N pollution (Fenn et al., 1996; Nash and Sigal 1999). A

disproportionate number of the locally extinct lichen species are cyanolichens. N deposition has also been tentatively linked to reduction in fine root biomass in Ponderosa pine (*Pinus ponderosa* C. Lawson) at three sites (Grulke et al., 1998; Fenn et al., 2008). However, ozone is also believed to contribute to decreased C allocation to fine roots (Grulke et al., 1998), and could be a confounding factor (see below). Recently, (Grulke et al., 1998) have used the linkages between N deposition and effects described above to calculate empirical and simulated (i.e. DayCent, Simple Mass Balance for N as a nutrient) critical loads for N deposition for California mixed conifer forests.

The effects of high N deposition in the forests of San Bernardino Mountains are compounded by the high ozone exposures that have occurred throughout the past 65 years. For example, from west to east, O_3 concentrations were high at Camp Paivika (80 ppb/h, averaged over 24 h, from April 15 through October 15, from 1993 through 1995(Grulke et al., 1998); moderately high (72 to 74 ppb/h) 5 km further east near Rim Forest; and moderate (62–64 ppb/h) 45 km east of Camp Paivika, at Barton Flats. Both O_3 exposure and N deposition reduce foliar retention (Grulke and Balduman, 1999) and alter tissue chemistry of both needles and litter (Poth and Fenn, 1998). In addition, confounding factors such as drought and fire suppression add to the complexity of ecosystem response (Arbaugh et al., 2003, Minnich et al., 1995; Takemoto et al., 2001) . Extensive crown injury measurements have also been made, linking ambient O_3 exposure data to chlorotic mottle and needle retention (Arbaugh et al., 1998). Ozone exposure and N deposition reduce carbon allocation to stems and roots (Grulke et al., 1998), further predisposing trees to drought stress, windthrow, root diseases, and insect infestation (Takemoto et al., 2001). Recently, Grulke et al. (2008) reported that various lines of phenomenological and experimental evidence indicate that N deposition and ozone pollution contribute to the susceptibility of forests to wildfire in the San Bernardino Mountains by increasing stress due to drought, weakening trees, and predisposing them to bark beetle infestation. Figure 3-56 shows the multiple factors contributing to susceptibility to wildfires in the San Bernardino Mountains.
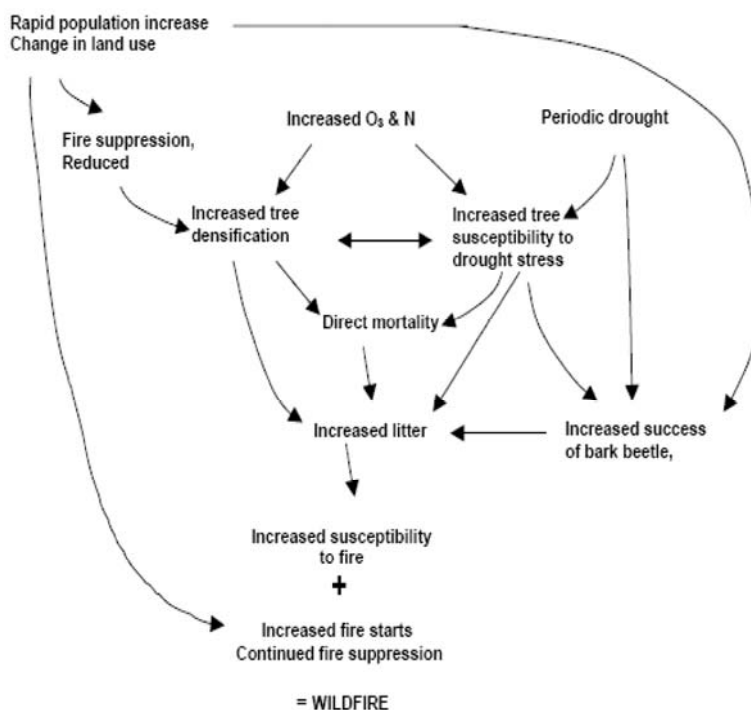
Figure 3-56. **Diagram of multiple factors contributing to forest susceptibility to wildfire.**

3.3.9. Ecosystem Services

Ecosystem services are the benefits people obtain from ecosystems (Millenium Ecosystem Assessment, 2005). This concept has gained recent interest and support because it recognizes that ecosystems are valuable to humans and important in ways that are not generally appreciated (Daily 1997). It also provides a context for assessing the collective effects of human actions on a broad range of the goods and services upon which humans rely.

There are no publications at this time that focus on the ecosystem services specifically affected by N deposition. Some valuation studies address the effects of N enrichment from multiple sources (see Annex F). The evidence reviewed in this ISA illustrates that N deposition affects ecosystem services in the following categories (defined by Hassan et al., 2005):

- Supporting: nutrient cycling, biodiversity

- Provisioning: forest yields, fishing yields in estuaries

- Regulating: water quality, air quality, climate regulation (interactions with greenhouse gases CO_2, N_2O, CH_4), fire frequency and intensity, disease resistance

- Cultural: swimming, boating, recreation, biodiversity

In general, both ecosystem structure and function play essential roles in providing goods and services (Table 3-27) (Daily, 1997). Ecosystem processes provide diverse benefits including absorption and breakdown of pollutants, cycling of nutrients, binding of soil, degradation of organic waste, maintenance of a balance of gases in the air, regulation of radiation balance and climate, and fixation of solar energy (Westman, 1977; Daily, 1997; World Resources Institute, 2000). These ecological benefits, in turn, provide economic benefits and values to society (Costanza et al., 1997; Pimentel et al., 1997). Goods such as food crops, timber, livestock, fish, and drinking water have market value. The values of ecosystem services such as flood-control, wildlife habitat, cycling of nutrients, and removal of air pollutants are more difficult to measure (Goulder and Kennedy, 1997).
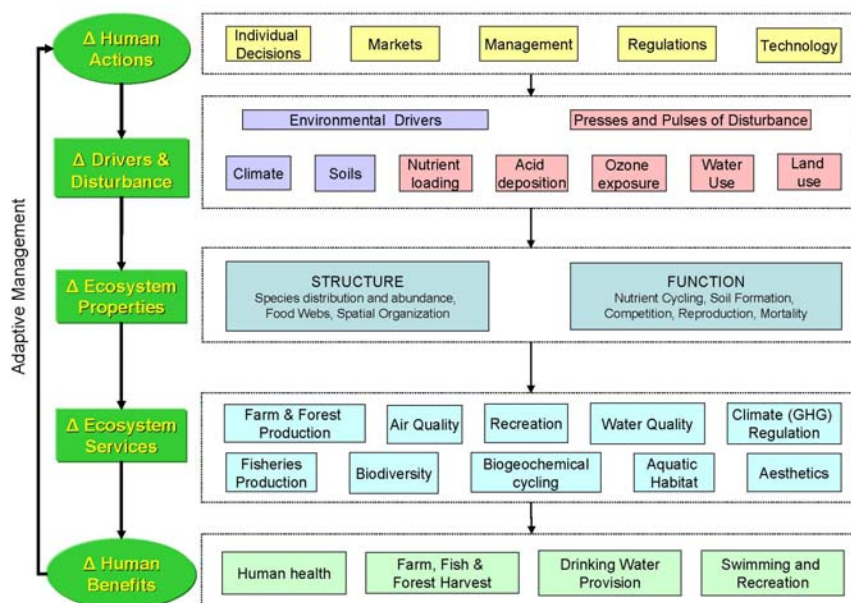
Figure 3-57. Diagram of relationships of human actions, N loading, and ecosystem services.

Particular concern has developed within the past decade regarding the consequences of decreasing biological diversity (Ayensu et al., 1999; Chapin et al., 1998; Hooper and Vitousek, 1997; Tilman, 2000; Wall, 1999). Human activities that decrease biodiversity also alter the complexity and stability of ecosystems, and change ecological processes. In response, ecosystem structure, composition and function can be affected (Pimm, 1984; Tilman and Downing, 1994; Tilman, 1996; Chapin et al., 1998; Levlin, 1998; Peterson et al., 1998; Daily and Ehrlich, 1999; Wall, 1999). Biodiversity is an important consideration at all levels of biological organization, including species, individuals, populations, and ecosystems. Human-induced changes in biotic diversity and alterations in the structure and functioning of ecosystems are the two most dramatic ecological trends of the past century (Vitousek et al., 1997b; U.S. EPA, 2004). The deposition of nutrient N from the atmosphere alters ecosystem structure and function by altering nutrient cycling and changing biodiversity.

How does N deposition impact ecosystem services? Figure 3-57 illustrates some of the relationships between human actions, N loading, and ecosystem services. Human actions that affect N loading influence the disturbances and physical drivers. These changes influence ecosystem structure and function, which in turn alter the production of ecosystem goods and services. In the bottom row, the impacts on human benefits or endpoints are shown. These endpoints are highlighted because they are most easily linked to valuation (Boyd and Banzhaf 2007). Changes in human benefits from ecosystems can then lead to policy changes, resulting in a feedback between these endpoints and human actions. Information supporting several of the benefits outlined in Figure 3-57 is developed. These relationships are futher discussed for some outcomes below, drawing upon the evidence presented in the preceeding sections.

Human Health. Increasing N deposition has a number of ecological effects that can be linked to human health. Harmful algal blooms in some areas are linked to increased N loading, and these can cause bans in swimming as they contain neurotoxins. In addition, links between acid deposition and mercury mobilization are important for human health in areas where fish, birds and shellfish are consumed.

Swimming and Recreation. Appropriate uses are identified by taking into consideration the use and value of the water body for public water supply, for protection of fish, shellfish, and wildlife, and for recreational, agricultural, industrial, and navigational purposes. Increases in N in estuaries can result in hypoxic zones and fish kills, with numerous negative impacts on commercial and recreation fishing and shellfish harvest. Harmful algal blooms (e.g., red tide) can be linked to increased N loading, and lead to swimming bans as they contain neurotoxins. Unpleasant odors and dead fish and wildlife can also reduce the value of areas for swimming, recreation and even impact property values.

Drinking Water. Forests, wetlands and streams all store and remove nitrogen at various timescales via plant and microbial uptake, biogeochemical stabilization, and denitrification. This N removal is a valuable ecosystem service, protecting water quality. In particular, the provision of clear, cool and clean water as a drinking water supply is an important service provided by forested watersheds, recognized by many states (e.g., Ashendorff et al., 1997). Air pollution can threaten the provision of this service, by directly increasing nitrogen loads, some of which will enter the drinking water supply, and also by affecting forest health, which could in turn decrease water quality and affect other forest ecosystem services. N inputs can impair the ability of terrestrial and aquatic ecosystems to retain and remove N (Aber et al., 1989, 1998; Mulholland et al., 2008; see Section 3.3.2), which can lead to degradation of water quality for many uses.

Forest Supporting and Provisioning Services. Nitrogen limits the primary production of most terrestrial ecosystems on earth (Vitousek and Howarth 1991; LeBauer and Treseder 2008; see Section 3.3.3). Food and timber harvests have increased tremendously via inputs of properly timed inputs of nitrogen fertilizers. However, nitrogen additions to agricultural and industrial forest lands typically far exceed (100 to >300 kg N/ha/yr) the atmospheric deposition of N, which therefore only makes a small contribution to total N loading. Managed ecosystems are not within the scope of this review. Increases in availability of this limiting nutrient via atmospheric deposition could increase forest production over large non-managed areas. Some studies suggest that chronic N additions via deposition can increase production in forests (Holland et al., 1997; Magnani et al., 2007), but other studies show little effect on wood

production (e.g., Nadelhoffer et al., 1999) (see Section 3.3.3.1). Leaching of nitrate can promote cation losses, which in some cases create nutrient imbalances, slower growth and lessened disease and freezing tolerances for forest trees, particularly in sensitive areas such as high elevation forests. The net effect of increased N on forests in the U.S. is a key unknown.

Table 3-27.   Primary Goods and Services Provided by Ecosystems

Ecosystem	Goods	Services
Coastal Ecosystems	Fish and shellfish Fish meat (animal feed) Seaweeds (for food and industrial use) Salt Genetic resources	Moderate storm impacts (mangroves, barrier islands) Provide habitat and breeding areas/hatcheries/nurseries for wildlife (marine and terrestrial) Maintain biodiversity Dilute and treat wastes Provide harbors and transportations routes Provide human and wildlife habitat Provide employment Contribute aesthetic beauty and provide recreations
Forest Ecosystems	Timber Fuel wood Drinking and irrigation water Fodder Non timber products (vines, bamboos, leaves, etc.) Food (honey, mushrooms, fruit, and other edible plants; game) Genetic resources	Remove air pollutants, emit O_2 Cycle nutrients Maintain array of watershed functions (infiltration, purification, flow control, soil stabilization) Maintain biodiversity Sequester atmospheric carbon Moderate weather extremes and impacts Generate soil Provide employment Provide human and wildlife habitat Contribute aesthetic beauty and provide recreation
Freshwater	Drinking and irrigation water Fish Hydroelectricity Genetic resources	Buffer water flow (control timing and volume) Dilute and carry away wastes Cycle nutrients Maintain biodiversity Provide aquatic habitat Provide transportation corridor Provide employment Contribute aesthetic beauty and provide recreation

Ecosystem	Goods	Services
Grassland Ecosystems	Livestock (food, game, hides, and fiber) Drinking and irrigation water Genetic resources	Maintain array of watershed functions (infiltration, purification, flow control, and soil stabilization) Cycle nutrients Remove air pollutants and emit O_2 Maintain biodiversity Generate soil Sequester atmospheric carbon Provide human and wildlife habitat Provide employment Contribute aesthetic beauty and provide recreations

Source: World Resources Institute (2000).

3.4. Other Welfare Effects

This section includes the non-acidification effects of sulfur and direct phytotoxic effects of gas-phase NO_X and SO_X on vegetation. Materials and structures damage caused by NO_X and SO_X are addressed in Annex E.

3.4.1. Non-Acidification Effects of Sulfur

As discussed in Section 3.2, a number of environmental effects are associated with S deposition, in particular soil and water acidification. However, S deposition also contributes to nutrient enrichment, toxicity, and has secondary effects on the cycling and bioavailability of Hg, a highly neurotoxic contaminant. High concentrations of SO_2 can harm vegetation by causing foliar injury, decreasing plant growth, and eliminating sensitive plant species, although atmospheric concentrations of SO_2 are seldom high enough to cause these effects on vegetation at ambient air pollution levels in the U.S. The biogeochemical cycling of S is closely linked with the cycling of other important elements, including C, N, P, Al, and Hg. Therefore, S deposition can influence the cycling of these elements in ways that influence nutrient availability or contaminant toxicity. In particular, current research suggests that S deposition influences the cycling of Hg in transitional and aquatic ecosystems by stimulating SO_4^{2-}-reducing bacteria, which are responsible for the bulk of Hg methylation, a key process that increases the bioavailability of Hg.

3.4.1.1. Biological Role of Sulfur

Effects on Plants

S is an essential plant nutrient. Low dosages of S serve as a fertilizer, particularly for plants growing in S-deficient soil (Hogan et al., 1998). A certain level of foliar SO_4^{2-} is necessary for adequate plant S nutrition (Johnson and Mitchell, 1998; Marschner, 1995), and S deficiency has been shown to occur at foliar SO_4^{2-} levels below 80 μg/g in *Pinus radiata* (Turner and Lambert, 1980). Nevertheless, the annual increment of S in vegetation is usually small compared to atmospheric deposition and leaching fluxes. Plants require similar levels of S and P, but S is generally available in much higher concentrations

in soil. Storage of S in vegetation is of minor significance in the retention or loss of S in most forests (Johnson and Mitchell, 1998; Mitchell et al., 1992a, 1992b).

Atmospheric deposition is an important component of the S cycle. This is true not only in polluted areas where atmospheric deposition is very high, but also in areas of low S deposition. Biochemical relationships between S and N are involved in plant protein synthesis and metabolism. S deficiency reduces NO_3 reductase and glutamine synthetase activity. N uptake in forests, therefore, could be loosely regulated by S availability, but SO_4^{2-} additions in excess of needs do not necessarily lead to injury (Hogan et al., 1998; Turner and Lambert, 1980). Current levels of S deposition throughout much of the U.S. exceed the capacity of most plant communities to immobilize the deposited S (Johnson, 1984; Lindberg, 1992). S excesses associated with acidic deposition have been found (Johnson et al., 1982a; Meiwes and Khanna, 1981; Shriner and Henderson, 1978).

S deficiency in forest soil is rare, but has been reported in remote areas that receive very low levels of atmospheric S deposition and that have inherently low S levels in soil (Kelly and Lambert, 1972; Schnug, 1997; Turner et al., 1977, 1991). In such cases, atmospheric S deposition might be taken up by vegetation, with little SO_4^{2-} leaching. Within areas of the U.S. influenced by acidic deposition, this is not expected to be a common phenomenon. To some extent, plant uptake of S is determined by the availability of N. This is because most S in plant tissue is in protein form, with a specific S:N ratio (Johnson et al., 1982a; Turner et al., 1977, 1991).

S plays a critical role in agriculture, and is an essential component of fertilizers (Ceccotti and Messick, 1997). It is particularly important for plants growing in S-deficient soil (Hogan et al., 1998). The most important source of S to vegetation is SO_4^{2-}, which is taken up from the soil by plant roots (Marschner, 1995). There are few field demonstrations of foliar SO_4^{2-} uptake (Krupa and Legge, 1986, 1998, 1999; U.S. EPA, 2004). Rather, SO_4^{2-} in throughfall is often enriched above levels in precipitation. The relative importance of the contribution of foliar leachate versus prior dry-deposited SO_4^{2-} particles to this enrichment is difficult to quantify (Cape et al., 1992). The major factor controlling the movement of S from the soil into vegetation is the rate of release through microbial decomposition of S from organic to inorganic forms (Marschner, 1995; May et al., 1972; U.S. EPA, 1982c, 1993b).

S deposition can also have direct effects on plants via nutrient enrichment pathways. Sulfur is an essential nutrient for protein synthesis in plants. Adequate S supply for sustaining plant health is 0.01% to 0.05% in soils (Nriagu, 1978). SO_4^{2-} is the dominant form of bioavailable S in soils. Plants can also utilize volatile S compounds such as SO_2 in the atmosphere to fulfill nutrient requirements (Rennenberg, 1984). This S is directly available for diffusive uptake through the leaf surface to support plant growth (Jager and Klein, 1980), and can also become bioavailable in the soil for plant root uptake (Moss, 1978). However, excess S inputs via atmospheric deposition can be toxic to plants and result in delayed flowering, reduced growth, and mortality (Rennenberg, 1984; Roelofs, 1991; Smith, 1981; Smolders and Roelofs, 1996). Plants that have exhibited reduced growth due to S toxicity have also been observed to have reduced molybdenum (Mo) uptake and increased copper (Cu), manganese (Mn), and zinc (Zn) uptake (Gupta and Mehla, 1980; Munro and Gupta, 1969). The threshold level of S toxicity is variable among species (Mudd and Kozlowski, 1975).

Koch et al. (1990) found that hypoxia and high levels of sulfide (>1 mM) limited wetland plant growth by inhibiting nutrient uptake. Sulfide toxicity to plants (e.g., *Carex* spp. *Juncus acutiflorus*, *Galium palustre, Gramineae*) has also been observed in wetland mesocosm experimentally enriched with SO_4^{2-} (Lamers et al., 1998). Biomass regrowth was significantly reduced for these species for both 2 and 4 mmol/L SO_4^{2-} treatments (Lamers et al., 1998). Van der Welle (2007) also showed that increased SO_4^{2-} loading had negative effects on aquatic macrophytes (*Stratiotes aloides* and *Elodea nuttallii*), via sulfide toxicity. Though *S. aloides* was native to the study region (The Netherlands) of Van der Welle (2007), it is considered a noxious invasive plant in the U.S. However, *E. nuttallii* is native to the U.S., widely distributed across 33 states, and is considered threatened in Kentucky and a species of concern in Tennessee (http://plants.usda.gov/). Negative impacts from elevated rates of atmospherically deposited SO_4^{2-} on this species could be of concern. It is important to note, however, that the SO_4^{2-} concentrations

reported in these studies were much higher than would generally be expected to occur in regions of the U.S. exposed to elevated atmospheric S deposition.

Fe concentrations can influence the level of sulfide toxicity in wetland sediments (Lamers et al., 2002; Smolders et al., 2001). Free sulfide produced through SO_4^{2-} reduction is able to bind with Fe, forming insoluble Fe sulfide (FeS). If sufficient Fe is present, this complexation can reduce or eliminate sulfide toxicity to plants by removing the free sulfide from solution. Van der Welle (2007) confirmed the role of Fe in buffering against sulfide toxicity to plants by observing no toxic effects when sufficient Fe was available to precipitate free sulfide.

However, the formation of FeS can disrupt, or compete with, Fe phosphate ($FePO_4$) complexation, resulting in P release and potential undesirable eutrophication effects on downstream receiving waters (Caraco et al., 1989; Smolders et al., 2003). Iron(III) hydroxides and iron(III) phosphates are reduced in anaerobic soils and highly insoluble FeS is formed, increasing phosphate (PO_4^{3-}) mobility and bioavailability in surface waters (Smolders et al., 2006). This process has been termed "internal eutrophication" since P is mobilized from within the system and is not contributed from an external source (Roelofs, 1991). Increased nutrient availability via SO_4^{2-}-induced P release from wetland sediments can result in changes in aquatic vegetation community composition. Rooted aquatic macrophytes can be out-competed by non-rooting floating species and filamentous algae (Smolders et al., 2003). If Fe is available in high enough concentrations, it can prevent P release from saturated soils with high S loading by providing adequate Fe to bind with sulfide without releasing P (Van der Welle, 2007).

The observation that NO_3^- addition decreases P release in wetland enclosures provides further indication that S-induced P release is related to redox conditions and microbial dynamics in the soil profile (Lucassen et al., 2004). Sufficiently high NO_3^- concentrations can prevent SO_4^{2-} reduction, and subsequent interruption of Fe-P binding, by maintaining redox status above that suitable for SO_4^{2-} reduction (Lucassen et al., 2004). In the absence of a sufficient supply of NO_3^- to act as a redox buffer, SO_4^{2-} will undergo reduction and potentially trigger the internal eutrophication mechanism described above (Lucassen et al., 2004). It is important to note that most research on the topic of internal eutrophication of has occurred in Dutch peatlands that have historically experienced much larger N loading than those in the U.S., making it difficult to extrapolate these findings to U.S. systems.

Effects on Methane-producing Microbes

Increased atmospheric S deposition and its impacts on microbial community structure can also affect CH_4 emissions from saturated soils. Early investigation into the effects of elevated pore water SO_4^{2-} concentrations on CH_4 emissions from wetland soils involved the application of a single large dose of SO_4^{2-} (Fowler et al., 1995). CH_4 production was observed to be suppressed (40% less than the control) three weeks after the addition of SO_4^{2-}. This was followed by a 4–week recovery period, after which CH_4 production had returned to pre-treatment levels. These results led to the hypothesis that large single addition of SO_4^{2-}, as applied by Fowler (1995), only stimulate SO_4^{2-}-reducing bacterial (SRB) activity for a short time. Fowler concluded that studies that more closely approximated long-term SO_4^{2-} loading, as with atmospheric S deposition, were necessary. Dise and Verry (2001) and Gauci et al. (2002) showed that smaller and more numerous SO_4^{2-} additions sustained CH_4 emission suppression in wetland soils. These studies more closely approximated SO_4^{2-} enrichment associated with acidic deposition. These results provided support to the hypothesis that continuous elevated SO_4^{2-} deposition, as encountered in areas affected by acidic deposition, contributes to sustained suppression of CH_4 emissions from wetland soils.

Gauci et al. (2004) considered both methods of SO_4^{2-} addition (a single large dose versus numerous small doses) in the same experiment. Rates of SO_4^{2-} addition ranged between 15 and 100 kg S/ha/yr to wetland soils previously exposed to 4 kg S/ha/yr of atmospheric S deposition. They observed that CH_4 emissions from these wetland soils were almost equally suppressed under each treatment, and that each treatment experienced the same CH_4 emission "recovery" as found in the single-dose Fowler et al. (1995) study. The two main conclusions from Gauci et al. (2004) were that 15 kg S/ha/yr is either at or above the rate of S deposition required to achieve maximum CH_4 emission suppression, and that a single large dose

of S has similar effects on CH_4 emission suppression as do numerous smaller doses. The authors observed that CH_4 emissions from treated soils recovered to levels that were observed from untreated soils during the period of plant senescence. This led to the hypothesis that SRB will out-compete CH_4 producing bacteria under conditions of elevated S deposition and during vigorous plant growth when available C substrate is limited, but that root exudates and root degradation during the period of plant senescence provides adequate substrate to sustain both methanogenic and SRB bacteria populations. Although the suppression of CH_4 emissions can fluctuate based upon plant growth cycles, elevated S deposition is considered to shift microbial community structure in favor of SRB over methanogenic bacteria, reducing annual CH_4 emissions from saturated soils (Granberg et al., 2001). However, climate change simulations suggest that increased soil temperature may override the suppressive effect that elevated S deposition has on CH_4 emissions (Gauci et al., 2004; Granberg et al., 2001).

3.4.1.2. Cycling and Storage of Sulfur

Terrestrial Ecosystems

Considerable effort was devoted in the 1980s to the computation of S budgets for watersheds and forest plots, with the objective of evaluating S retention and release. These budgets were subject to complications from fluxes that could not be measured directly, such as dry deposition and weathering, but they generally indicated net S retention at sites south of the line of glaciation — a result attributed to net adsorption of SO_4^{2-} (Cappellato et al., 1998; Rochelle and Church, 1987). During the 1990s, little or no decrease in SO_4^{2-} concentration occurred in streams in the Ridge and Blue Ridge physiographic provinces, despite regional decreases in atmospheric deposition of S (Webb et al., 2004), and no evidence of S addition from mine drainage. This lack of response in stream chemistry has been generally attributed to a shift in S equilibrium between the adsorbed and solution phases under conditions of decreased atmospheric inputs of SO_4^{2-}. This interpretation is supported by a decrease in concentrations of adsorbed SO_4^{2-} from 1982 to 1990 in a Piedmont soil in South Carolina that received decreasing levels of S deposition during this period (Markewitz et al., 1998). This same soil also experienced an increase in adsorbed SO_4^{2-} from 1962 to 1972 (Markewitz et al., 1998). The only published S budget more recent than 1992 for an unglaciated site in the U.S. (Castro and Morgan, 2000) also suggested a net release of SO_4^{2-}. This upland Maryland watershed released 1.6 times more SO_4^{2-} than measured in throughfall in 1996–97.

Numerous S budgets were compiled in the 1980s for glaciated sites, and results generally indicated that inputs approximately equaled outputs on an annual basis (Rochelle and Church, 1987). The observation of little or no S retention at glaciated sites was attributed to relatively low SO_4^{2-} adsorption capacity in soils. Balanced S budgets in glaciated regions implied that decreases in atmospheric deposition of S would lead directly to decreases in SO_4^{2-} leaching. The strong correlation between recent decreases in both atmospheric S deposition and SO_4^{2-} concentrations in surface waters is widely recognized to be a result of this direct linkage (Stoddard et al., 2003). Nevertheless, considerable evidence also indicates that S inputs in glaciated ecosystems do not behave conservatively, but instead are cycled in part through microbial and plant biomass (Alewell and Gehre, 1999; David et al., 1987; Likens et al., 2002). As a result, large quantities of S are stored in organic forms within the soil. David et al. (1987) found that annual S deposition (wet plus dry) at a site in the central Adirondack region of New York was about 1% of the organic S pool in the soil. Houle et al. (2001) estimated that annual S deposition at 11 sites in North America ranged from 1% to 13% of the organic S pool in soil.

The S cycle in forest ecosystems can be represented as a series of input, uptake, and output terms (Figure 3-58). Some of the fluxes illustrated in this schematic drawing can be measured in the field, including wet deposition, litterfall, and throughfall. Other fluxes must be calculated or estimated, which involves considerable uncertainty (Johnson and Mitchell, 1998). Perhaps the most important uncertainty concerns the amount of dry deposition, which can be substantial (Lindberg et al., 1990).
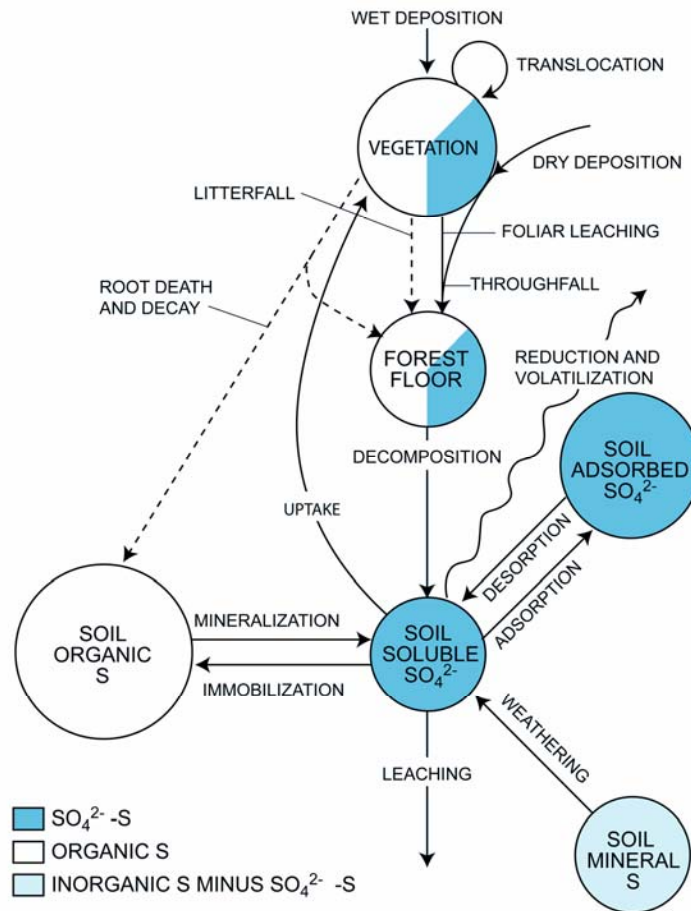
Figure 3-58. Representation of the S cycle in forest ecosystems.

Atmospheric deposition is an important part of the S cycle, including in areas that are not exposed to appreciable air pollution levels. In fact, although agricultural S and geologic S (especially associated with mining activities) can be locally important or dominant, atmospheric S inputs may constitute the major source of S input to many terrestrial ecosystems (Johnson and Mitchell, 1998; Probert and Asmosir, 1983).

Much of the organic S stored in soil is in C-bonded forms that are relatively unreactive, but can be oxidized by bacteria or mineralized to SO_4^{2-} under oxic conditions, which are typically found in moderately well drained to well drained soils (Johnson and Mitchell, 1998). Carbon-bonded S in forest soils can be found in a variety of organic S compounds, including amino acids, sulfolipids, and sulfonic acids. Carbon-bonded S can also be found in humic material in the form of aliphatic and aromatic structures (Likens et al., 2002). Furthermore, strong correlations have been shown between levels of atmospheric deposition of S and concentrations of S in soil (Driscoll et al., 2001b; Novák et al., 2005). Long-term increases in concentrations of total S in soils that are at least partially attributable to increases in organic S have also been documented (Knights et al., 2000; Lapenis et al., 2004), although the study of Houle et al. (2001) did not find a relation between these factors. A Swedish "clean roof" study also provides some insight into the role of organic S in possibly delaying chemical recovery from acidification due to S deposition (Mörth et al., 2005). After 9 years of application of pre-industrial levels of

S deposition, the amount of SO_4^{2-} in runoff still exceeded inputs by 30%. Most of the S in runoff was attributed to mineralization of organic S in the O horizon.

Thus, research on the effects of atmospheric S deposition on soils has indicated pronounced changes in soils from sustained SO_4^{2-} leaching, and accumulation of S through physical/chemical adsorption and biological assimilation. The recent evidence of net loss of S from soils at a number of sites is likely a response to decreased atmospheric inputs. The gradual loss of previously accumulated S contributes to continued SO_4^{2-} leaching. Uncertainties in estimates of ecosystem fluxes such as weathering and dry deposition, and complications in discerning the effects of desorption from mineralization make it difficult to predict when S outputs will no longer exceed inputs as levels of S deposition continue to decline. Research based on experimental reduction of S inputs suggests that this process will occur on a decadal time scale (Martinson et al., 2005; Mörth et al., 2005). The long-term role of C-bonded S adds further uncertainty because enhancement of S mineralization by a warming climate could also affect S retention and release (Driscoll et al., 2001b; Knights et al., 2000). This process can be microbially catalyzed, and bacteria are generally more active at higher temperature.

Transitional Ecosystems

Transitional ecosystems exert important controls on watershed S budgets, especially in watersheds that contain extensive wetland development. Sulfur storage in wetland soils provides an important buffering system that restricts chronic SO_4^{2-} leaching to surface waters. Input-output studies of bogs in Massachusetts (Hemond, 1980),Ontario (Urban and Bayley, 1986), and Minnesota (Urban and Eisenreich, 1988) suggested more than 50% retention of atmospheric S inputs. However, oxidation of S that was previously stored in wetland soils can provide an important episodic source of SO_4^{2-} to downstream surface waters. Thus, the presence of wetlands in a watershed can either temporarily increase or decrease the flux of SO_4^{2-} to surface waters, and these differences are largely determined by changes in hydrology and redox conditions in wetland soils. Overall, wetlands act as sinks for S because of microbial SO_4^{2-} reduction and sequestering of reduced S as sulfide minerals and organic S.

Changes in S flux that are controlled by processes in transitional ecosystems can have important effects on surface water chemistry. For example, reduction of SO_4^{2-} in sediments by assimilatory and dissimilatory processes is an important source of acid neutralizing capacity (ANC) to lakes having long hydraulic residence time, and a likely source also to beaver ponds and wetlands. In-lake ANC production is mostly due to S retention from microbial SO_4^{2-} reduction (Brezonik et al.; Schindler and Bayley, 1993; Turner et al., 1990b). It is unlikely, however, that the changes in S flux caused by wetlands and ponds in a watershed would be large enough to have any direct non-acidification effects on biota. More likely, the major non-acidification effects of wetland influence on S cycling relate to changes in Hg methylation in wetland soils. This is discussed in Section 3.4.1.4. Other changes can also occur, including enhanced release of N and P from wetland soils.

Some of the organic S in wetlands can be converted to reduced S gasses, including dimethylsulfide and hydrogen sulfide (under acidic conditions), and released to the atmosphere. Up to 30% of the atmospheric deposition of S in remote areas may be derived from release of reduced S gasses from wetlands (Nriagu et al., 1987). Thus, wetland processes can have important effects on local atmospheric S deposition and trace gas emissions.

Aquatic Ecosystems

In aquatic ecosystems that are sensitive to acidification from atmospheric S deposition, SO_4^{2-} is generally highly mobile within the ecosystem. Acid-sensitive streams tend to be relatively fast-flowing, high-gradient, low-order streams that exhibit high SO_4^{2-} mobility. Acid sensitive lakes tend to be relatively small, headwater lakes with short hydraulic residence times (weeks to months). In such streams and lakes, most of the SO_4^{2-} contributed by inflowing ground and surface waters is directly flushed through the ecosystem and emerges as outflow.

However, larger streams, streams that flow through series of ponds (i.e., beaver ponds) or lakes, and especially larger lakes, tend to have longer hydraulic residence, and provide opportunity for microbial S reduction in sediments. This S reduction can have important effects on the concentration of SO_4^{2-} in drainage water, and results in the generation of ANC. The importance of sediment reactions to the acid-base chemistry of surface water depends mainly on the flux rate of material across the sediment-water interface and the amount of time that water remains in contact with the sediment (Baker and Brezonik, 1988; Kelly et al., 1987; Turner et al., 1991). In some lakes having long water residence times, about half of the input SO_4^{2-} is retained in lake sediments (Baker and Brezonik, 1988; Kelly et al., 1987).

S is an essential nutrient for algae and planktonic bacteria. Nevertheless, S concentration in most lakes is well above the limiting concentration for algal productivity, and therefore biotic S uptake in the water column is not a quantitatively important part of the S cycle in acid-sensitive lakes (Turner et al., 1991).

3.4.1.3. Export of Sulfur

Terrestrial Ecosystems

In order for atmospherically deposited S to exert influence on drainage water, with the range of associated environmental effects that can occur, it must be exported as SO_4^{2-} from the soil. If the incoming S in atmospheric deposition is retained in the vegetation or soil compartments, it will not be available to affect soil water or surface water downstream within the watershed. In areas of S deposition, almost all deposited S moves into the soil and can then be exported from the terrestrial ecosystem or adsorbed on soil. In most parts of the U.S., most deposited S is exported in drainage water. In much of the southeastern U.S., however, S adsorption on soil substantially limits S export (See discussion in Annex B).

Transitional Ecosystems

When saturated, wetland soils act as sinks for incoming S via SO_4^{2-} reduction. Sulfide is produced through this process and sequestered in anoxic wetland sediments (Mitsch and Gosselink, 2000). However, it has been observed that wetlands can act as sources of SO_4^{2-} to downstream drainage waters during storm events that follow prolonged periods of drought (Dillon and LaZerte, 1992; Devito and Hill, 1999; Eimers and Dillon, 2002; Jeffries et al., 2002; Laudon et al., 2004; Mitchell et al., 2006). The mechanism has been described as follows. SO_4^{2-} is produced through oxidative processes in wetland sediments when they are exposed to atmospheric O_2 as the water table falls during periods of drought. This newly formed SO_4^{2-} is mobile, and therefore can be flushed from the wetland into streams or lakes when the water table rises as more typical hydrologic conditions resume. This flush of SO_4^{2-} can result in episodic acidification of downstream surface waters (Laudon et al., 2004) and potentially prolong the chemical recovery of surface water ANC as S deposition declines (Aherne et al., 2006).

Much of the supporting research on this topic has been performed within the boreal watersheds of Ontario, Canada (Dillon and LaZerte, 1992; Devito and Hill, 1997; Jeffries et al., 2002; Aherne et al., 2004; Laudon et al., 2004). A Sphagnum-conifer wetland within the Plastic Lake watershed in Ontario was determined to be a source of SO_4^{2-} to downstream drainage waters after extended periods of summertime drought (Dillon and LaZerte, 1992). Comparisons of stream water chemistry were made between the wetland inlet and the wetland outlet, which drains a watershed consisting entirely of upland soils. The results showed little difference between SO_4^{2-} concentrations in the wetland inlet and outlet during typical hydrologic conditions. However, SO_4^{2-} concentrations in the outlet increased by up to a factor of 5 during storm events that followed extended periods of drought. This occurred during 4 separate years.

Most the study watersheds in the Plastic Lake region of Ontario, Canada have consistently exported more SO_4^{2-} than was atmospherically deposited on an annual basis over an 18–year period (Eimers and

Dillon, 2002). This observation suggests either the existence of an internal watershed SO_4^{2-} source, or an underestimation of S deposition. It is possible that dry deposition is underestimated (Likens et al., 1990; Edwards et al., 1999), but a variety of potential watershed sources of additional S have also been proposed in areas that are sensitive to atmospheric S deposition, including:

- weathering of S-containing minerals (Baron et al., 1995)

- desorption of SO_4^{2-} previously adsorbed to soils when S deposition was higher (Driscoll et al., 1995; (Mitchell et al., 1996)

- mineralization of S previously incorporated into organic matter (Driscoll et al., 1998)

- drought-related oxidation and release of S stored in wetlands and riparian soils (Dillon and LaZerte, 1992; Dillon et al., 1997)

Underestimation of dry deposition was not considered to be a significant issue for the Canadian study watersheds (Eimers and Dillon, 2002). Furthermore, mineral weathering is not considered a significant source of SO_4^{2-} in that region, due to the low S content of the bedrock (Neary et al., 1987). Reoxidation and mobilization of S stored in wetland sediments was considered the most likely explanation for the observed higher SO_4^{2-} outputs for those watersheds that contain a significant proportion of wetland. Other mechanisms, including increased soil SO_4^{2-} desorption and/or increased S mineralization in response to decreased S deposition inputs, may explain the SO_4^{2-} input/output imbalance observed in watersheds containing little or no wetland area (Alewell and Gehre, 1999; Eimers and Dillon, 2002). Jeffries et al. (1995, 2002) determined that within the Turkey Lakes watershed in western Ontario wetland, reoxidation and SO_4^{2-} remobilization mechanism can delay lake acidification recovery by as much as 6 years.

Wetland S transformations have been incorporated into state-of-the-science modeling to better describe climate-induced acidification effects on lake water chemistry (Aherne et al., 2004, 2006). A wetland component to the MAGIC model was developed and tested for its ability to predict observed stream water SO_4^{2-} fluxes from the Plastic Lake watershed (Aherne et al., 2004). This model was then used to investigate acidification recovery under two different climate scenarios: an "average climate" scenario consisting of long-term (most recent 20 years) monthly precipitation and runoff;and a "variable climate" scenario that included sequential repetition of the measured monthly precipitation and runoff for the preceding 20 years. The average climate scenario did not include any significant drought periods, whereas the variable climate scenario included several periods of summer drought.

Model results under the average climate scenario suggested that chemical recovery of lake water would occur, with ANC reaching 40 µeq/L by 2020 and 50 µeq/L by 2080. However, the variable climate scenario projected that recovery would be greatly reduced. ANC recovery by 2080 was estimated to only reach 2.6 µeq/L. The authors acknowledged that reiterating the past 20 years of climate under the variable climate scenario was somewhat arbitrary. Nevertheless, results suggested that climate effects on the cycling of S can modify chemical recovery of lake water from acidification in watersheds that are wetland-influenced.

Aquatic Ecosystems

Export of S from surface waters is controlled primarily by retention in sediments through microbial SO_4^{2-} reduction. In-stream and in-lake biological demand for S is generally a very small component of the S input levels in areas affected by atmospheric S deposition. Sulfur reduction can be an important process regulating S export from aquatic ecosystems, mainly in waters that exhibit long hydraulic retention. Sulfur reduction in lake and pond sediments can also be closely associated with Hg methylation. Therefore, the dynamics of S storage and export can influence the bioavailability of Hg to fish, piscivorous wildlife, and humans who consume large quantities of fish.

3.4.1.4. Sulfur and Methylation of Mercury

Hg has long been established to be a potent neurological, reproductive, and developmental toxin that accumulates at progressively higher concentrations in higher trophic levels (biomagnification). The biogeochemical cycle of Hg is closely tied to that of S, and the presence of SO_4^{2-} in wetlands and lake sediments is essential for entry of Hg into the food web. Hg is taken up by living organisms and bioaccumulates in the MeHg form. For the protection of human health, the U.S. EPA set the fish tissue criterion for MeHg at 0.3 μg/g. This has resulted in 2,436 fish consumption advisories for Hg in 2004, 2,682 in 2005 and 3,080 in 2006. Forty-eight states, one territory, and two tribes have issued Hg advisories. Eighty percent of all fish consumption advisories have been issued, at least in part, because of Hg. Most of the new Hg advisories issued in 2005 and 2006 were in Wisconsin (293), Michigan (46), New York (36) and Minnesota (32). In 2005, American Samoa, Kansas, Oklahoma and Utah started issuing Hg advisories, and Iowa started in 2006. In 2006, a total of 14,177,175 lake acres and 882,963 river miles were under advisory for Hg. As of July 2007, 23 states have issued statewide advisories for Hg in freshwater lakes and/or rivers.

Examples of elevated tissue and blood Hg have also been reported in terrestrial animals, and a few of those studies included comparisons between aquatic and terrestrial species. In a survey of four species of turtles in and around a portion of river with a long-term history of industrial Hg pollution, Bergeron et al. (2007) observed that species differences in blood Hg level varied with the proportion of the species' diet that is aquatic. The species with the smallest aquatic component to its diet still had higher blood Hg at contaminated sites than at non-contaminated sites. However, its blood Hg level at contaminated sites was approximately 90% lower than the three other species. In non contaminated parts of the river, blood Hg level was very low for all species, even though it was lower in the most terrestrial one than in the others. A survey of songbirds on the same 24 km stretch of river (Cristol et al., 2008) found elevated Hg in the blood of terrestrial birds in proximity to the river, but not at reference sites away from the river, or upstream from the contaminated portion. In their survey of northeastern freshwater avian species, Evers et al. (2005) observed that among birds living in ecosystems with a large aquatic component, blood, egg, and tissue Hg levels were much lower in insectivorous species than in piscivorous ones. Rimmer et al. (2005) sampled blood and feather samples of insectivorous passerines in their summer and winter habitat in the northeastern U.S. and southeastern Canada, and Cuba, Haiti and the Dominican Republic. They found elevated MeHg in birds without clear connection to aquatic food webs. However, the putative role of S in Hg methylation in terrestrial ecosystems has not been explored.

SRB are the main agent of Hg methylation in transigional and aquatic environments, and changes in SO_4^{2-} deposition have been shown to result in commensurate changes in both Hg methylation, and Hg levels in fish.

Effects of Mercury in Aquatic Biota

Adverse effects of Hg, including behavioral, reproductive, neurochemical, and hormonal effects, have been demonstrated in piscivorous mammals and birds (Scheuhammer et al., 2007; U.S. EPA, 1996b), and MeHg has been shown to be the form in which Hg accumulates in tissue of fish and piscivorous species (Becker and Bigham, 1995; Bloom, 1992; Harris et al., 2003; Scheuhammer et al., 2007). Exposure of fish and wildlife to Hg occurs primarily through the diet. Top predatory, especially piscivorous, animals feeding on aquatic food chains are at greatest risk for Hg accumulation and toxicity (Scheuhammer et al., 2007). Wildlife living in inland lake habitats tends to accumulate higher tissue concentrations of Hg than those living in coastal habitats (Evers et al., 2005; Frederick et al., 2002) .

Available data suggest that numerous wild populations of fish, birds, and mammals experience MeHg exposures that are high enough to cause substantial reproductive, behavioral or health impairment. Reproduction is the component of response that appears to be most affected (Scheuhammer et al., 2007). In fish, exposure to MeHg can affect growth, reproductive ability, morphological characteristics, and feeding efficiency. Examples of studies documenting the effects of MeHg on fish include Friedmann et al.

(1996), who investigated the effects of low-level (0.137 µg Hg/g) and high-level (0.987 µg Hg/g) dietary Hg concentrations (as MeHg) on hatchery juvenile walleye (*Stizostedion vitreum*). These experimental Hg exposures were chosen to reflect dietary Hg concentrations commonly encountered in North American lakes and streams. Results showed impaired fish growth and impaired gonad development in males. Fjeld et al. (1998) exposed grayling (*Thymallus thymallus*) embryos to varying concentrations of MeHg (0.16, 0.8, 4.0, and 20 µg Hg/L) during their first 10 days of development. This exposure resulted in body tissue MeHg concentrations of 0.09, 0.27, 0.63, and 3.80 µg Hg/g respectively. Morphological deformities were observed in fish exposed to the highest level of MeHg. Samson and Shenker (2000) also observed morphological disturbance in zebrafish (*Danio rerio*) at embryonic MeHg exposure levels of 20 and 30 µg CH_3HgCl/L. Other fish such as mummichog (*Fundulus heteroclitus*) and rainbow trout (*Oncorhynchus mykiss*) have also been observed to suffer teratogenic effects such as cyclopia, tail flexures, cardiac malformations, jaw deformities, twinning, and axial coiling from embryonic MeHg exposure (Samson and Shenker, 2000). Fish survival and subsequent population status can be jeopardized as a result of exposure to MeHg. Fathead minnows (*Pimephales promelas*) showed impaired feeding efficiency after exposure to both 6.79 and 13.57 µg $HgCl_2$/L (Grippo and Heath, 2003). Reduced feeding efficiency and competitive ability was also observed in grayling exposed to 0.8 to 20 µg Hg/L as embryos (Fjeld et al., 1998).

Role of Sulfur in the Biogeochemical Cycle of Mercury

The global cycle of Hg has atmospheric, aquatic, edaphic, and biotic components. In the atmosphere, Hg is transported locally, regionally, and globally, depending on speciation. Both elemental and oxidized forms are found in soil and aquatic environments, but the oxidized form is more prevalent. MeHg is the form that is found in tissues (Figure 3-59). SRB are the main agent of Hg methylation in the environment. Although Hg methylation in watersheds has been shown to occur through other processes, their contribution to MeHg loads is negligible in comparison to that of SRB-mediated methylation. Addition of SO_4^{2-} has been demonstrated to stimulate Hg methylation by SRB in studies spanning scales from the culture of isolated bacteria, to the experimental amendment of entire lakes. Those studies have included addition of SO_4^{2-} at rates corresponding to observed deposition.
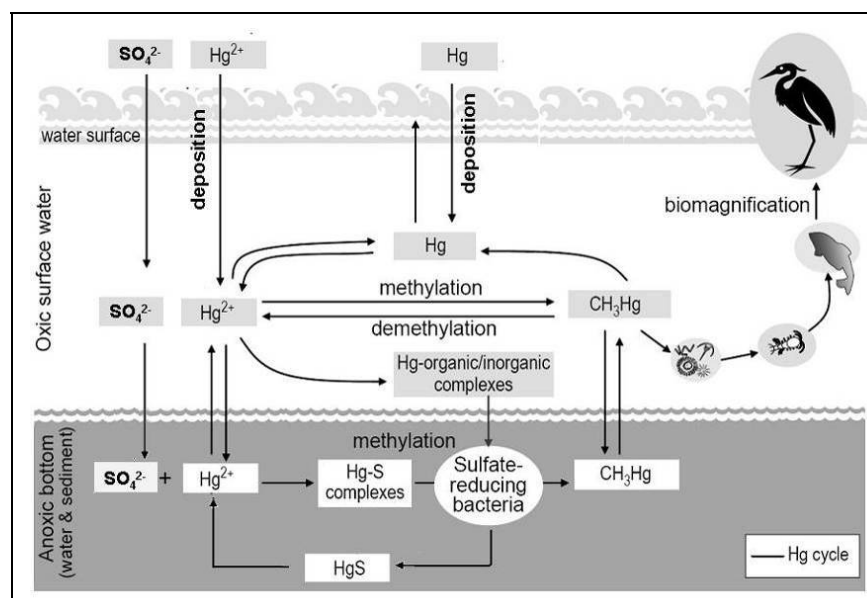
Figure 3-59.   Simplified cycle of mercury, showing the role of sulfur. Arrows are not proportional with actual rates.

SRB are commonly found in anoxic wetland and lake bottom sediments (Compeau and Bartha, 1985; Gilmour and Henry, 1991; 1992). Under increased SO_4^{2-} availability, their number and activity increase. The mechanisms for Hg methylation, as mediated by SRB, have been discussed by Choi et al. (1994), Ekstrom et al. (2003), and Ekstrom and Morel (2004). Abiotic mechanisms responsible for Hg methylation have been discussed by Weber (1993), Hintelmann and Evans (1997), and Siciliano et al. (2005). Studies demonstrating the response of SRB-mediated methylation to SO_4^{2-} in pure cultures include King et al. (2000), and Benoit et al. (2001). This response has also been established in samples of soil and sediments (Compeau and Bartha, 1985; Gilmour et al., 1992; Harmon et al., 2004), and in experimental manipulations in wetlands and lakes (Benoit et al., 2003; Branfireun et al., 1999; 2001; Frost et al., 1999; Harmon et al., 2004; Jeremiason et al., 2006; Watras et al., 2006; Wiener et al., 2006).

Evidence regarding the importance of SRB in MeHg production was provided by Compeau and Bartha (1985), and Gilmour et al. (1992), who showed that MeHg production was substantially reduced with addition of a known SRB inhibitor (Na_2MoO_4). This is also in agreement with observations of SRB-mediated Hg methylation in salt marsh sediments (Compeau and Bartha, 1985). The work of Gilmour et al. (1992) considered anoxic lake bottom sediments, rather than wetland sediments. However, anoxia is also common in freshwater wetland sediments, where SO_4^{2-} addition has also been observed to enhance Hg methylation (Branfireun et al., 1999; Harmon et al., 2004; Jeremiason et al., 2006). Accumulation of sulfidic forms of S in sediments, also resulting from SRB activity, has been shown to diminish the availability of S to SRBs, and thus net Hg methylation (Benoit et al., 1998; 1999a; 2001; Gilmour, 1998; King et al., 2001a).
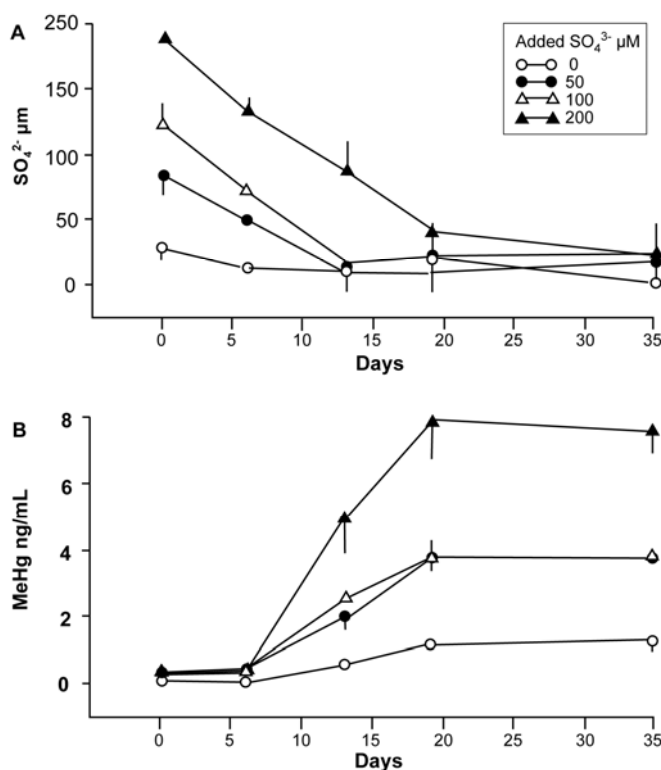
Source: Gilmour et al. (1992).

Figure 3-60. **(A) SO_4^{2-} and (B) MeHg concentrations as a function of time in sediment slurries made from Quabbin Reservoir littoral sediments. Each delta point represents the average value from three separate incubations and the associated standard error.**

Gilmour et al. (1992) investigated MeHg production within anoxic sediments of a reservoir located in central Massachusetts. Elevated MeHg production with SO_4^{2-} addition was measured in both experimental laboratory slurries (Gilmour et al., 1992) (Figure 3-60B) and intact sediment cores. The background SO_4^{2-} concentration in the experimental sediment slurries was 60 µeq/L. SO_4^{2-} additions of 0, 100, 200, and 400 µeq/L were applied to these samples in the presence of 50 mg/L of Hg as $HgCl_2$. The rate of production and the final concentration of MeHg increased in proportion to the initial SO_4^{2-} concentration. Furthermore, SO_4^{2-} concentrations decreased during the experiment (Gilmour et al., 1992), experiment (Figure 3-60A), suggesting that SO_4^{2-} reduction had occurred. MeHg production within isolated lake bottom sediment cores was also enhanced across a gradient of SO_4^{2-} addition (3 to 1040 µmol sodium SO_4^{2-} [Na_2SO_4]; Figure 3-61). Sediment MeHg production was most enhanced when SO_4^{2-} concentration was above about 60 µeq/L, with increased production from a pre-treatment background MeHg concentration of 0.26 ng/g to approximately 7.0 to 8.5 ng/g. These results suggest maximum MeHg production at SO_4^{2-} concentrations between about 200 and 400 µeq/L, although optimal conditions for methylation are likely to vary with other factors that influence SO_4^{2-} reduction. SO_4^{2-} concentrations in the range of these experiments (about 60 to 200 µeq/L) are often found in waters affected by S deposition in the U.S.

Interacting factors

Many studies have also shown an association between low lake water pH and high Hg concentrations in fish (Driscoll et al., 1994a; Grieb et al., 1990; Kamman et al., 2004; Suns and Hitchin, 1990). Hrabik and Watras (2002) found that decreases in fish Hg concentration in an experimentally de-acidified lake basin exceeded those in the reference lake basin by a factor of 2 over a 6–year period of experimental de-acidification. The association between low pH and high Hg accumulation in fish suggests a response of methylation to pH, but although SRB activity does respond to pH (Kelly et al., 2003), quantification of the interactive effects of pH with SO_4^{2-} in the environment has only been tentative.

Other interacting factors, mainly Fe, P, and dissolved organic matter, have been identified, but very incompletely quantified (Munthe, 2007; Watras and Morrison, 2008). Driscoll et al. (2007b) developed indicators of Hg sensitivity using two stratified, random-probability surveys of northeastern lakes combined with the survey data sets of Chen et al. (2005). This analysis showed that lakes with Hg levels above the U.S. EPA criterion of 0.3 µg/g in yellow perch had significantly higher DOC, and lower pH, ANC, and total P than lakes with fish Hg concentrations below 0.3 µg/g (Driscoll et al., 2007b). Based on the probability surveys, they calculated that about 20% of lakes in the region had total P concentrations above 30 µg/L and yellow perch Hg concentrations below 0.3 µg/g. In the remaining 80% of lakes, 75% had yellow perch Hg concentrations exceeding 0.3 µg/g when surface water DOC levels exceeded 4.0 mg C/L, a pH of less than 6.0, or an ANC of less than 100 µeq/L. Most Hg in the water column of freshwaters is bound to organic matter, either to DOC or to suspended particulate matter. Therefore, total Hg and MeHg concentrations are often positively correlated with DOC in lake waters (Driscoll et al., 1994a; Mierle and Ingram, 1991; U.S. EPA, 1996b). DOC, in turn, has an important influence on pH. Thus, several interrelated factors seem to affect Hg loading in tissue. For example, Driscoll (1995) found one or more yellow perch exceeding the 0.5 µg/g action level in 14 of 16 Adirondack study lakes despite wide ranges in pH (to above 7) and ANC (to above 200 µeq/L). Driscoll et al. (1994a) concluded that the most obvious factor regulating the concentration and availability of both total Hg and MeHg in Adirondack lakes is DOC. They found increased fish Hg concentrations with increasing DOC up to DOC concentrations of about 8 mg/L, followed by lower concentrations in the highly dystrophic Rock Pond (DOC = 26 mg/L). They hypothesized that DOC may bind with MeHg at very high DOC concentration, limiting the bioavailability of the Hg. In addition, calculations made by Driscoll et al. (1995) with the Hg Cycling Model suggested that increases in DOC result in increasing concentrations of Hg in biota, but decreases in the bioconcentration factor of Hg in fish tissue. Because the transport of Hg to Adirondack lakes appeared to be linked to DOC production from wetlands within the watersheds of the study lakes, Driscoll et al. (1995) concluded that DOC is important in regulating Hg concentrations in the lakes, and

ultimately the supply to fish. In a peatland experiment testing the effects of various sources of organic C, Mitchell et al. (2008) demonstrated that while SO_4^{2-} is required for methylation of Hg, the addition of some sources of C greatly enhanced the process. The combinations of C and SO_4^{2-} additions that enhanced methylation in the experiment corresponded to the combinations present in MeHg 'hot spots' within watersheds that include peatlands.
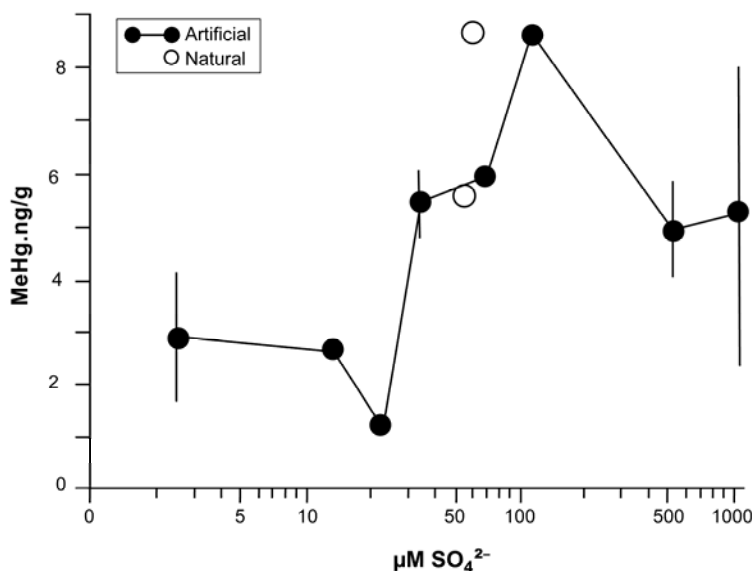
Figure 3-61. MeHg produced in sediment cores incubated two weeks under artificial lake water containing 3–1040 µM Na₂SO₄. Error bars represent standard error between two replicate cores. Data from cores incubated under natural water are shown individually. The average MeHg concentration in unamended Purgee sediments sampled in July was 0.26 ± 0.01 ng/g (n = 2).

Several researchers have suggested that the export of Hg from terrestrial watersheds to lakes may be controlled in large part by the nature of watershed soils and the transport of naturally occurring organic acids (Engstrom et al., 1994; Meili, 1991; Mierle, 1990; Mierle and Ingram, 1991). This suggestion is based partly on the fact that dissolved organic matter strongly binds with Hg, and partly on the observed positive correlation between Hg accumulation in lake sediments and the ratio of the watershed area to the lake area in relatively undisturbed watersheds ($r^2 = 0.91$; $r^2 = 0.91$) (Engstrom et al., 1994). Engstrom et al. (1994) concluded that Hg export from the terrestrial watershed to lake water may be explained by factors regulating the export of fulvic and humic matter and by watershed area. They based this conclusion on the close correlation between Hg concentration and humic matter in surface waters, the observation that peak concentrations of both Hg and dissolved organic matter tend to occur during periods of high runoff, and the experimental determination that Hg transport occurs primarily in upper soil horizons.

Ecosystems Characteristics Conducive to Methylation

S deposition is most likely to result in enhanced Hg methylation in regions that receive relatively high levels of atmospheric Hg and S deposition and that exhibit characteristics conducive to methylation. These include low ANC and low pH surface waters, with large upstream or adjoining wetlands (Chen et al., 2005; Scheuhammer and Blancher, 1994; Scheuhammer et al., 2007). Such sensitive ecosystems are prevalent in portions of the northeastern U.S. and southeastern Canada, but ecosystems with high Hg

methylation are present in other regions as well. Studies of Hg concentration in feathers, blood, and eggs of the common loon (*Gavia immer*) indicate decreasing concentrations from west to east in this region (Evers et al., 1998; 2003). This pattern is in general agreement with patterns of deposition of both Hg and S.

Wetland environments have been shown to be significant areas of MeHg production and sources of export to downstream receiving waters (St. Louis et al., 1994). Wetland MeHg production has been measured at rates 26 to 79 times higher than in upland areas of a Canadian boreal forest (wetland: 1.84 to 5.55 mg/ha/yr; upland: 0.07 mg/ha/yr) (St. Louis et al., 1994). Watersheds containing 14.0% to 16.3% wetland yielded 5 to 14 times more MeHg than upland catchments that lacked wetlands (St. Louis et al., 1994). In the same region, St. Louis et al. (1996) found that all watersheds were net sinks for total Hg, but that watersheds containing wetlands regularly exported MeHg (St. Louis et al., 1996). However, MeHg export from these watersheds was not directly proportional to percent wetland coverage, indicating that other variables are also involved in the major processes that regulate MeHg production and export. In particular, the level of atmospheric Hg deposition and the acid-base chemistry of drainage water may be important.

Branfireun et al. (1996) measured highest peat and pore water MeHg concentrations in wetland areas that exhibited characteristics of a poor fen environment (i.e., interaction with nutrient-poor ground water). St. Louis et al. (1996) observed that high water yield resulted in high MeHg export. Thus, the proportion of upland to wetland land area within a watershed was not the only control on MeHg export, but wetland type and annual water yield also played important roles (St. Louis et al., 1996).

As noted by Munthe (2007), multiple hydrological, chemical, and biological characteristics of watersheds determine the movement of Hg between compartments. With regards to MeHg, however, the chemical and biological characteristics of the lake compartment may be more critical: comparing two remote lakes, one a seepage lake, and the other a drainage lake. Watras and Morrison (2008) found that although wetland MeHg export was the dominant external source of MeHg to the drainage lake, in-lake methylation remained four- to seven-fold greater than loading from the wetland. Likewise, Harris et al. (2007) demonstrated, using traceable stable isotopes of Hg in a whole ecosystem experiment, that nearly all of the increase in fish MeHg came from Hg deposited to the lake surface, with less than 1% of Hg deposited to the watershed being exported to the lake, in any form.

Regardless, methylation of Hg occurs in anoxic sediments that contain a sufficient C source to support SO_4^{2-}-reducing bacterial activity along with an adequate supply of SO_4^{2-} for SRB-mediated SO_4^{2-} reduction. These conditions are found in lake and pond bottom sediments (Gilmour et al., 1992), freshwater wetland sediments (Branfireun et al., 1999; Harmon et al., 2004; Jeremiason et al., 2006), and salt mash sediments (Compeau and Bartha, 1985). Such wetland systems, expected to exhibit high levels of Hg methylation, can be found throughout the U.S.

In a 1998 preliminary national survey of 106 sites from 21 basins across the U.S., Krabbenhoft et al. (1999) examined the relations of total Hg and MeHg in water, sediment and fish, and concluded that wetland density was the single most important factor controlling MeHg production at the basin scale. Four study basins along the east coast of the U.S. had the greatest methylation efficiency, while nationwide, sub-basins characterized as mixed agriculture and forest cover types had the highest methylation efficiency. A recent study of biological Hg hotspots in the northeastern U.S. and southeastern Canada (Evers et al., 2007) analyzed more than 7,300 observations of Hg levels in seven species from three major taxonomic groups to quantify the spatial heterogeneity in tissue Hg concentrations. Using published effect thresholds for Hg tissue concentrations, they identified five known and nine possible biological Hg hotspots. They reported that two of the biological hotspots, located in the Adirondack Mountains of New York and south-central Nova Scotia, occur in areas with relatively low to moderate atmospheric Hg deposition and high landscape sensitivity, as determined by the abundant forest and wetland cover as well as the acidic surface water conditions (Evers et al., 2007). Using data collected by the Northeastern Ecosystem Research Cooperative (NERC) initiative (Evers and Clair, 2005) to examine the link between Hg deposition and biotic Hg, (Driscoll et al., 2007b) concluded that "forested regions with a prevalence of wetland and unproductive surface waters," which are common in the northeastern

U.S., "promote high concentrations of Hg in freshwater biota." In contrast, in a study of over 600 randomly selected streams and rivers throughout the western U.S., (Peterson et al., 2007) found little relationship between fish tissue Hg concentrations and surface water pH, SO_4^{2-}, or DOC. They attributed the lack of a relationship to the fact that low pH (<7) and high DOC systems were rare in the West. The major factors controlling fish tissue Hg concentrations in western streams and rivers were fish size and feeding group, not water chemistry. Likewise, a 1999 survey of high altitude western lakes with both low Hg and low MeHg (Krabbenhoft et al., 2002) identified high pH and elevated rates of photo-demethylation as the likely causes for low net methylation. Water clarity and high sunlight exposure were cited as sources of enhanced photo degradation of MeHg.

Sulfur Deposition and MeHg in Fish

As shown by Harris and Rudd (2007), the response of fish MeHg to changes in Hg deposition can occur on a time scale of less than a year. In their comprehensive synthesis of information on all elements of the connection between environmental Hg loading, and Hg in fish, Munthe (2007) concluded that several interacting factors are expected to affect the speed and magnitude of the changes in fish contamination that result from changes in Hg loading. As indicated previously, numerous studies have ascertained that SO_4^{2-} supply is a principal driver of MeHg production, and Hrabik and Watras (2002) showed that decreased deposition of both Hg and SO_4^{2-} are followed by MeHg decrease in fish. Drevnick et al. (2007), however, were able to establish an explicit linkage between S deposition and fish Hg, by verifying that even in the absence of change in Hg deposition, changes in S deposition alone result in commensurate changes in MeHg accumulation in fish.

3.4.1.5. Summary of S and Methylation of Mercury

The evidence is sufficient to infer a causal relationship between S deposition and increased methylation of Hg, in aquatic environments where the value of other factors is within adequate range for methylation. The main agent of Hg methylation is SO_4^{2-}-reducing-bacteria, and experimental evidence from laboratory to mesocosm scales has established that only inconsequential amounts of MeHg can be produced in the absence of SO_4^{2-}. These experimental results are highly coherent with one another, and with observational studies at larger scales. Changes in the amount of SO_4^{2-} present have been shown to be followed by commensurate changes in MeHg, and mechanistic links have been established between variation in SO_4^{2-} and variation in methylation of Hg.

Quantification of the relationship between SO_4^{2-} and methylation of Hg in natural settings has proved difficult because of the presence of multiple interacting factors in aquatic environments where SO_4^{2-} and Hg are present. The amount of MeHg produced has been shown to vary with O_2 content, temperature, pH, and supply of labile organic carbon. In some watersheds, such as high altitude lakes in the Western U.S., no effect of changes in SO_4^{2-} deposition have been recorded on methylation of Hg,. This is because one or several interacting factors were not present in the amounts required for methylation to occur at more than inconsequential rates. Watersheds with conditions known to be conducive to Hg methylation can be found in the northeastern U.S. and southeastern Canada, but significant biotic Hg accumulation has been observed in other regions that have not been studied as extensively, and where a different set of conditions may exist.

Mercury is a highly neurotoxic contaminant, and enters the food web in the methylated form. MeHg is then concentrated in higher trophic levels, including fish eaten by humans, with undesirable consequences for affected species, and for populations that consume large amounts of fish. Once MeHg is present, other variables influence how much of it accumulates in fish. Current evidence indicates that increased S deposition very likely results in MeHg accumulation in fish.

3.4.1.6. S Nutrient Enrichment Case Study: Interactive Effects of S and Hg in Little Rock Lake, WI

Little Rock Lake is an 18–ha precipitation-dominated seepage lake located in a forested and undisturbed catchment of north central Wisconsin. The extensive experimental work conducted at Little Rock Lake was described by Hrabik and Watras (2002). The research at Little Rock Lake provides considerable insight into the interactions of S and Hg in the lake, and also bioaccumulation of Hg in fish in freshwater ecosystems.

In 1984, the lake was divided into two basins by placing an impermeable curtain across a narrow lake section. One of the basins was experimentally acidified from pH 6.1 to 4.7 by mixing H_2SO_4 into the surface water over a period of 6 years (Watras and Frost, 1989). The other basin was left undisturbed to serve as a reference. Beginning in 1990, the treated basin was left to de-acidify naturally.

Hg accumulation in yellow perch showed significant declines in fish in both the experimental and reference basins between 1994 and 2000, commensurate with declines in atmospheric deposition of Hg. Fish Hg concentrations in the experimental basin were 57% higher in 1994 than in 2000, whereas concentrations were 36% higher in the reference basin (Hrabik and Watras, 2002). The authors determined that half of the decrease in fish Hg concentration was attributable to lakewater de-acidification and the other half was associated with regional declines in atmospheric Hg deposition. In the reference basin, which had higher pH and exhibited a lower rate of de-acidification, 15% of the decrease in fish Hg concentration was due to de-acidification (Hrabik and Watras, 2002).

These findings were consistent with the hypothesis that SO_4^{2-} and newly added Hg synergistically contribute to enhanced bioaccumulation of Hg in fish. In subsequent analyses, Watras et al. (2006) found that maximum MeHg concentrations in hypolimnetic waters were directly correlated with the SO_4^{2-} deficit (mean epilimnetic SO_4^{2-} concentration - minimum hypolimnetic SO_4^{2-} concentration) and they observed a correlation between MeHg and lakewater SO_4^{2-} concentrations. The tracking of external loads of Hg and S, and internal loads of Hg and MeHg suggested a tight biogeochemical connection among atmospheric deposition, SO_4^{2-} reduction, and Hg methylation. However, these relationships did not fully explain the observed large inter-annual variability in MeHg accumulation. The variability appeared to be influenced by OC, terrestrial runoff and temperature.

The results from the Little Rock Lake acidification experiment suggest that S deposition plays an important role in the accumulation and methylation of Hg in freshwater ecosystems, and that acid deposition and Hg deposition have a disproportionately larger effect together than either would have separately (Watras et al., 2006).

3.4.2. Direct Phytotoxic Effects of Gaseous N and S on Vegetation

This section is intended to provide a brief overview of the exposure and phytotoxic effects of gaseous N and S compounds on vegetation. This recognizes that the major focus of this review is the effect of acidifying deposition and N deposition on ecosystems. However, direct effects of gaseous N and S could augment the effects of deposition on vegetation and effects of gaseous N and S may occur in some areas.

The effects of gaseous pollutants such as SO_2, NO_2, NO, HNO_3 and O_3 on vegetation have been studied since the 1950s and 1960s. Methodologies have been developed to study these effects in the lab, greenhouse, and in the field. The methodologies to study gaseous pollutants effects on vegetation have been recently reviewed in the 2006 O_3 AQCD (U.S. EPA, 2006b). A thorough description of the methodologies used to expose vegetation to gaseous pollutants can be found in Section AX9.1 of the 2006 O_3 AQCD (U.S. EPA, 2006b) and Section 9.2 in the 1993 NO_2 AQCD (U.S. EPA, 1993a).

Uptake of gaseous pollutants in a vascular plant canopy is a complex process involving adsorption to surfaces (leaves, stems, and soil) and absorption into leaves. These pollutants penetrate into leaves

primarily in gaseous form through the stomata, although there is evidence for limited pathways via the cuticle. Pollutants must be transported from the bulk air to the leaf boundary layer to get to the stomata. Although the transport of pollutants through a boundary layer into the stomata region is known to be important, and even rate limiting in many cases of low wind velocity, its description has been defined from aeronautical concepts and usually relates to smooth surfaces that are not typical of leaf-surface morphology; however, it is nearly the only treatment available (Gates, 1968). Once through the boundary layer, the gas must enter the leaf through the stomata. The entry of gases into a leaf is dependent upon the physical and chemical processes of gas phase and surfaces as well as the stomatal aperture. The aperture of the stomata is controlled largely by the prevailing environmental conditions, such as humidity, temperature, and light intensity. When the stomata are closed, as occurs under dark or drought conditions, resistance to gas uptake is very high and the plant has a very low degree of susceptibility to injury (Figure 3-62). The stomatal control of uptake of gaseous pollutants is described in more detail in AX9.2 of the 2006 O_3 AQCD (U.S. EPA, 2006b) and Section 9.3.1.5 of the 1993 NO_X AQCD (U.S. EPA, 1993a). It should be noted that unlike higher plants, mosses and lichens do not have a protective cuticle barrier to gaseous pollutants, a major reason for their sensitivity to gaseous S and N.
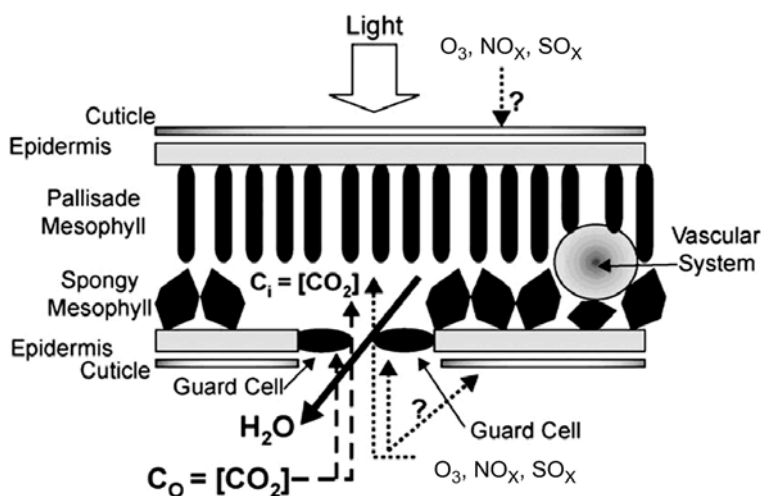
Figure 3-62.   **The microarchitecture of a dicot leaf. While details among species vary, the general overview remains the same. Light that drives photosynthesis generally falls upon the upper (adaxial leaf surface. CO₂, SOₓ, NOₓ, and O₃ gases generally enter through the stomata on the lower (abaxial) leaf surface, while water vapor exits through the stomata (transpiration).**

3.4.2.1. Direct Phytotoxic Effects of SO_2 on Vegetation

It has been known since the early 1900s that exposure of plants to SO_2 can cause damage and death (Wislicenus, 1914). The large sources of SO_2 were ore smelters. Sulfides in the ore were oxidized during smelting and resulted in large releases of SO_2. Emissions from large ore smelters in the U.S. and Canada resulted in large areas denuded of vegetation surrounding these facilities (Swain 1949; Thomas 1951). Much of the damage to the vegetation was due to acute effects of high concentrations of SO_2. However, as early as 1923 researchers recognized that SO_2 might reduce plant growth without acute symptoms of foliar injury (Stoklasa, 1923). In the 1950s through the early 1980s, there was much research on the effects of lower levels of SO_2 as well as the interaction with other pollutants such as O_3 and NO_2. Since

then, there has been much less research on the effects of SO_2 on vegetation, especially in the U.S., due to the decreasing ambient concentrations of SO_2. The effects of SO_2 on vegetation are summarized below.

Currently, SO_2 is the only criteria pollutant with a secondary NAAQS distinct from the primary standard. This standard is to protect acute foliar injury resulting from SO_2 exposure. The standard is a 3-h average of 0.50 ppm and was promulgated in 1970 to protect against acute foliar injury in vegetation. The last AQCD for ecological effects of SO_X was completed in 1982 and concluded that controlled experiments and field observations supported retaining this secondary standard (U.S. EPA, 1971, 1982b, 1982c).

Acute foliar injury usually happens with hours of exposure, involves a rapid absorption of a toxic dose and involves collapse or necrosis of plant tissues. Another type of visible injury is termed chronic injury and is usually a result of variable SO_2 exposures over the growing season. After entering the leaf, SO_2 is converted to sulfite and bisulfite, which may be oxidized to SO_4^{2-}. SO_4^{2-} is about 30 times less toxic than sulfite and bisulfite. The conversion of sulfite and bisulfite to SO_4^{2-} results in net H^+ production in the cells. Kropff (1991) proposed that the appearance of SO_2-induced leaf injury was likely due to a disturbance of intracellular pH regulation. Kropff (1991) pointed out several studies that the pH of homogenates only shifted towards greater acidity when plants were lethally damaged from long-term SO_2 exposures (Grill, 1971; Jager and Klein, 1977; Thomas et al., 1944). The appearance of foliar injury can vary significantly between species and growth conditions affecting stomatal conductance. Currently there is not regular monitoring for SO_2 foliar injury effects in the U.S.

Besides foliar injury, long-term lower SO_2 concentrations can result in reduced photosynthesis, growth, and yield of plants. These effects are cumulative over the season and are often not associated with visible foliar injury. As with foliar injury, the effects of foliar injury vary among species and growing environment. The 1982 SO_2 AQCD summarized the concentration-response information available at the time (U.S. EPA, 1982b). Effects on growth and yield of vegetation were associated with increased SO_2 exposure concentration and time of exposure. However, that document concluded that more definitive concentration-response studies were needed before useable exposure metrics could be identified. Because of falling ambient SO_2 concentrations and focus on O_3 vegetation effects research, few studies have emerged to better inform a metric and levels of concern for effects of SO_2 on growth and productivity of vegetation.

Since the 1982 SO_2 AQCD was published, several studies have investigated a number of different effects of SO_2 effects on plants. Most recent research has been performed in areas of Europe where ambient SO_2 concentrations are generally higher than in the U.S. A brief summary of some of the major studies are presented in Table 3-28.

SO_2 is considered to be the primary factor causing the death of lichens in many urban and industrial areas, with fruticose lichens being more susceptible to SO_2 than many foliose and crustose species (Hutchinson et al., 1996). Damage caused to lichens in response to SO_2 exposure includes reduced photosynthesis and respiration, damage to the algal component of the lichen, leakage of electrolytes, inhibition of N fixation, reduced K^+ absorption, and structural changes (Belnap et al., 1993; Farmer et al., 1992; Hutchinson et al., 1996). Significant reductions in lichen photosynthesis have been measured at concentrations as low as 91 ppb over 2–4 hours (Huebert, 1985; Sanz, 1992). Damage to the algal component of the thallus is evidenced by its discoloration. The entire thallus dies soon after algal cells are damaged (Hutchinson et al., 1996). At higher levels, SO_2 deactivates enzymes by chemical modification leading to reduced metabolic activity and loss of membrane integrity (Zeigler, 1975, Nieboer et al., 1976). It also binds to the central metal atoms of enzymes, adversely affecting membrane function and cell osmolality. In addition, SO_2 competitively inhibits carbonate (HCO_3) and phosphate (H_2PO_4) interactions with enzymes (Hutchinson et al., 1996). Low pH increases the toxicity of SO_2 action (Farmer et al., 1992). The toxic effects of atmospheric deposition of SO_2 are lessened when lichen are attached to a substrate, typically bark or rock, having high pH or superior buffering capacity (Richardson and Cameron, 2004). Van Herk (2001) evaluated relationships between bark pH and air pollution levels as two significant variables affecting epiphytic lichen composition, and concluded that bark pH was the primary factor regulating the distribution of acidophilic species in The Netherlands. In studies of unpolluted areas,

differences in bark chemistry also affect the presence and distribution of epiphytes (Farmer et al., 1992). Indirect effects on bark pH, caused by acidification and high SO_2 concentrations, also affect lichen distribution (Farmer et al., 1992).

3.4.2.2. Direct Phytotoxic Effects of NO, NO$_2$ and PAN

It is well known that in sufficient concentrations nitric oxide (NO) and NO_2 can have phytotoxic effects on plants through decreasing photosynthesis and inducing visible foliar injury (U.S. EPA, 1993a). The 1993 NO_X AQCD concluded that concentrations of NO_2 or NO in the atmosphere are rarely high enough to have phytotoxic effects on vegetation (U.S. EPA, 1993a). Since the 1993 NO_X AQCD, very little new research has been done on these phytotoxic effects to alter this conclusion. However, it is known that these gases alter the N cycle in some ecosystems, especially in the western U.S., and contributing N saturation (Bytnerowicz and Fenn, 1996; Fenn et al., 2003a). See Section 3.3 for a discussion of the nutrient effects of N.

In general, NO and NO_2 enters leaves through stomata (Saxe, 1986). However, it has also been shown that the leaf cuticle may be an important receptor for NO_2 and there is evidence of transport of NO and NO_2 across isolated cuticles (Lendzian and Kerstiens, 1988). Several studies have demonstrated that plant canopies can directly assimilate N in the form of NO_2, but canopy uptake of NO_2 is generally small relative to total plant uptake (Hanson et al., 1989, Nussbaum et al., 1993; Ammann et al., 1999; Segschneider et al., 1993; Vallano and Sparks, 2008; von Ballmoos et al., 1993). After entering the leaves, NO_2 dissolves in the extracellular water of the sub-stomatal cavity to form HNO_2 and HNO_3, which then dissociate to form nitrite, NO_3^-, and protons (Bytnerowicz et al., 1998b). Both cell and tonoplast membranes contain ATP-dependent H^+ pumps and the tonoplast pumps are strongly inhibited by NO_3^- (Bytnerowicz et al., 1998b). If extra protons are deposited in vacuoles of the plant cells during normal cellular regulation, then additional acidity will occur in combination with additional NO_3^-. This combination can cause disruptions in cellular control (Taylor and MacLean, 1970). NO_3^- and nitrite are metabolized to amino acids and proteins through a series of enzymatic reactions mainly involving NO_3^- and nitrite reductases (Amundson and MacLean, 1982). The effectiveness of plants to reduce NO_3^- and nitrite to amino acids and proteins determines the potential of the plant to detoxify NO and NO_2 (Wellburn, 1990). Reduction of NO_3^- takes place outside of the chloroplast while the reduction of nitrite is coupled with the light reactions of photosynthesis. Therefore, when leaves are exposed to NO and NO_2 in the dark, highly phytotoxic levels of nitrite accumulate and may lead to greater toxicity to NO and NO_2 at night (Amundson and MacLean, 1982). Exposure to NO produces both NO_3^- and nitrite in the leaves, but the rate of NO_3^- accumulation is much slower than nitrite. Thus, plants exposed to high NO could be at risk to elevated concentrations of nitrite (Wellburn, 1990). More detailed information on the cellular effects of NO and NO_2 can be found in the 1993 NO_X AQCD.

The functional relationship between ambient concentrations of NO or NO_2 and a specific plant response, such as foliar injury or growth, is complex. Factors such as inherent rates of stomatal conductance and detoxification mechanisms and external factors, including plant water status, light, temperature, humidity, and the particular pollutant exposure regime, all affect the amount of a pollutant needed to cause symptoms of foliar injury. Plant age and growing conditions, and experimental exposure techniques also vary widely among reports of experimental exposures of plants to NO_2. An analysis conducted in the 1993 NO_X AQCD of over 50 peer-reviewed reports on the effects of NO_2 on foliar injury indicated that plants are relatively resistant to NO_2, especially in comparison to foliar injury caused by exposure to O_3 (U.S. EPA, 1993a). With few exceptions, visible injury was not reported at concentrations below 0.20 ppm, and these occurred when the cumulative duration of exposures extended to 100 hours or longer. At 0.25 ppm, increased leaf abscission was reported on navel orange trees (*Citrus sinensis* L), but only after exposures in excess of 1000 hours (Thompson et al., 1970). Green bean plants used as bio-indicators of NO_2 injury in Israel developed foliar injury symptoms when ambient concentrations

exceeded 0.5 ppm (Donagi and Goren, 1979). Only when concentrations exceeded 1 ppm did injury occur on most plants in less than one day (U.S. EPA, 1993a).

Reductions in rates of photosynthesis have been recorded in experimental exposures of plants to both NO and NO_2, but usually at concentrations significantly higher than would normally be encountered in ambient air. For example, Sabaratnam et al. (1988) reported that soybean (*Glycine max*) exposed 7 hours/day for 5 days showed an increase in photosynthetic rates at a concentration of 0.2 ppm, but a reduction in net photosynthesis at a concentration of 0.5 ppm. Short-term exposures of soybean to 0.6 ppm NO_2 for 2 to 3 hours also had no effect on net photosynthesis (Carlson, 1983). Most plants appear to be more susceptible to NO than to NO_2, as shown by Saxe (1986), who exposed a variety of horticultural plants raised in greenhouses (species of *Hedera*, *Ficus*, *Hibiscus*, *Nephrolepis*, and *Dieffenbachia*) to both NO and NO_2. Saxe (1986) reported that reductions in net photosynthesis occurred at doses of NO that were 22 times less than that for NO_2. However, these reductions in net photosynthesis required concentrations as high as 1 ppm NO for 12 hours to elicit a response in these plants.

Hundreds of studies have been conducted on the effects of NO_2 on growth and yield of plants mostly performed in the 1970s and 1980s. These studies varied widely in plant species, growing conditions, exposure equipment, concentrations, durations, exposure regimes, and environmental conditions during exposures. No clear dose-response relationships for exposure to NO_2 and reductions in growth and/or yield of plants have emerged from these experiments. Readers are referred to the analysis of over 100 studies conducted in the 1993 NO_X AQCD. A few key studies are highlighted in this section. Several plant species appear to be susceptible to reductions in growth by relatively low concentrations of NO_2 (less than 0.2 ppm), particularly when exposed during low-light conditions. For example, nearly continuous exposure to 0.1 ppm NO_2 for eight weeks significantly reduced growth of Kentucky blue grass (*Poa pratensis* L) (Ashenden, 1979; Whitmore and Mansfield, 1983). Eight species of tree seedlings were exposed to 0.1 ppm NO_2 for six hours/day for 28 days, resulting in reduced shoot or root growth in two species, white ash (*Fraxinus americana* L.) and sweetgum (*Liquidambar styraciflua* L.), reduced height growth in two clones of loblolly pine (*Pinus taeda* L.), and no effects on the other species (Kress and Skelly, 1982). No effects of NO_2 at 0.1 ppm or lower were observed on numerous other species, including potato (*Solanum tuberosum* L.), black poplar (*Populus nigra* L.), radish (*Raphanus sativus* L.), soybean, or peas (*Pisum sativum* L.) (U.S. EPA, 1993a). No effects of NO_2 were observed on soybeans grown in field plots subjected to a series of 10 episodic exposures averaging 0.4 ppm for 2.5 or 3 hours (Irving et al., 1982). Numerous studies have reported negative effects on growth of a variety of plants exposed to 0.5 ppm NO_2 and above (U.S. EPA, 1993a), but these concentrations are unrealistically high relative to current ambient levels of NO_2.

The 1993 NO_X AQCD reviewed the extensive literature on the effects of NO_2 in combination with other gaseous air pollutants, particularly SO_2 and O_3, and concluded that combinations of pollutants can cause reductions in photosynthesis or foliar injury at concentrations lower than those associated with NO_2 acting alone. However, the plant responses occur at concentrations much higher than are found in ambient air (U.S. EPA, 1993a). In addition, the presence of NO_2 in combination studies did not produce symptoms different from those caused by the dominant pollutant, either SO_2 or O_3, so that a plant response produced by combinations of NO_2 with other air pollutants in the field would be difficult, if not impossible, to distinguish from those of the other single pollutants (U.S. EPA, 1993a).

Since the 1993 NO_X AQCD was completed, most new research on NO_2 exposure to vegetation has taken place in Europe and other areas outside the U.S. For example, foliar NO_3 reductase activity was increased in Norway spruce (*Picea abies*) trees growing near a highway with average exposures of about 0.027 ppm compared to trees growing 1300 meters away from the highway with NO_2 exposures less than 0.005 ppm (Ammann et al., 1995). This was consistent with other studies on Norway spruce in the field and laboratory (von Ballmoos et al., 1993; Thoene et al., 1991). Muller et al. (1996) found that the uptake rate of NO_3^- by roots of Norway spruce seedlings was decreased by the exposure to 0.1 ppm of NO_2 for 48 hours. Similarly, soybean plants grown in Australia had decreased NO_3 uptake by roots and reduced growth of plants exposed to 1.1 ppm of NO_2 for 7 days (Qiao and Murray, 1998). In a Swiss study, poplar cuttings exposed to 0.1 ppm for of NO_2 for approximately 12 weeks resulted in decreased stomatal

density and increased specific leaf weight, but did not result in other effects such as leaf injury or a change in growth (Gunthardt-Goerg et al., 1996). However, NO_2 enhanced negative effects of ozone, including leaf injury, on these poplars when the pollutants were applied in combination (Gunthardt-Goerg et al., 1996).

Peroxyacetyl nitrate (PAN) is a well-known photochemical oxidant, often co-occurring with O_3 during high photochemical episodes, which has been shown to cause injury to vegetation (See reviews by Cape, 2003, 1997; Kleindienst, 1994 Smidt, 1994; Temple and Taylor, 1983). Acute foliar injury symptoms resulting from exposure to PAN are generally characterized as a glazing, bronzing, or silvering of the underside of the leaf surface; some sensitive plant species include spinach, Swiss chard, lettuces, and tomatoes. Petunias have also been characterized as sensitive to PAN exposures and have been used as bioindicators of in areas of Japan (Nouchi et al., 1984). Controlled experiments have also shown significant negative effects on the net photosynthesis and growth of petunia (*Petunia hybrida* L.) and kidney bean (*Phaseolus vulgaris* L.) after exposure of 30 ppb of PAN for four hours on each of three alternate days (Izuta et al., 1993). As mentioned previously, it is known that oxides of N, including PAN, could be altering the N cycle in some ecosystems, especially in the western U.S., and contributing N saturation (Bytnerowicz and Fenn, 1996; Fenn et al., 2003a, see Section 3.3). However, PAN is a very small component of N deposition in most areas of the U.S. Although PAN continues to persist as an important component of photochemical pollutant episodes, there is little evidence in recent years suggesting that PAN poses a significant risk to vegetation in the U.S.

3.4.2.3. Direct Phytotoxic Effects of HNO_3

Relatively little is known about the direct effects of HNO_3 vapor on vegetation. It has been established that HNO_3 has a very high deposition velocity compared to other pollutants and may be an important source of N for plants (Hanson and Lindberg, 1991; Hanson and Garten, 1992; Vose and Swank, 1990). This deposition could contribute to N saturation of some ecosystems close to sources of photochemical smog (Fenn et al., 1998). For example, in mixed conifer forests of the Los Angeles basin mountain ranges HNO_3 has been estimated to provide 60% of all dry deposited N (Bytnerowicz et al., 1999).

Norby et al. (1989) reported that exposure of 75 ppb of HNO_3 for one day increased nitrate reductase activity in red spruce foliage. In another study, foliar nitrate reductase activity was also increased in California black oak (*Quercus kelloggi*), canyon live oak (*Quercus chrysolepis*) and Pondersosa pine (*Pinus ponderosa*) seedlings exposed to HNO_3 concentrations of 65 to 80 ppb for 24 hours (Krywult and Bytnerowicz, 1997). Because the induction of nitrate reductase activity is a step in a process leading to the formation of organic N compounds (amino acids), the nitrate from HNO_3 could function as an alternative source of N for vegetation (Calanni et al., 1999). However, in plants under stress, the reduction of nitrate to amino acids consumes energy needed for other metabolic processes.

At high ambient concentrations, HNO_3 can cause vegetation damage. Seedlings of Ponderosa pine and California black oak subjected to short-term exposures from 50–250 ppb of HNO_3 vapor for 12 hours showed deterioration of pine needle cuticle at 50 ppb in light (Bytnerowicz et al., 1998a). Oak leaves appeared to be more resistant to HNO_3 vapor, however, with 12-h exposures in the dark at 200 ppb producing damage to the epicuticular wax structure (Bytnerowicz et al., 1998a). The observed changes in wax chemistry caused by HNO_3 and accompanying injury to the leaf cuticle (Bytnerowicz et al., 1998a) may predispose plants to various environmental stresses such as drought, pathogens and other air pollutants. Because elevated concentrations of HNO_3 and ozone co-occur in photochemical smog (Solomon et al., 1988), synergistic interactions between the two pollutants are possible (Bytnerowicz et al., 1998b). However, it should be noted that the experiments described above were observed at relatively short-term exposures at above ambient concentrations of HNO_3. Long-term effects of lower air concentrations that more approximate ambient HNO_3 should be investigated.

It has been suspected that HNO_3 may have caused a dramatic decline in lichen species in the Los Angles basin (Nash and Sigal, 1999). The suggestion was strengthened by transplant of *Ramalina* lichen species from clean air habitats (Mount Palomar and San Nicolas Island) to analogous polluted habitats in the Los Angeles basin and repeatedly observing death of the lichens over a few weeks in the summer (Boonpragob and Nash, 1991). Associated with this death was massive accumulation of H^+ and NO_3^- by the lichen thalli (Boonpragob et al., 1989). Recently, Riddell et al. (2008) exposed the healthy *Ramalina menziesii* thalli to moderate (8–10 ppb) and high (10–14ppb) HNO_3 in month-long fumigations and reported a significant decline in chlorophyll content and carbon exchange capacity compared to thalli in control chambers. Thalli treated with HNO_3 showed visual signs of bleaching and by day 28 were clearly damaged and dead. The damage may have occurred through several mechanisms including acidification of pigments and cell membrane damage (Riddell et al., 2008). The authors concluded that *Ramalina menziesii* has an unequivocally negative response to HNO_3 concentrations common to ambient summer conditions in the Los Angeles air basin. They believed it was very likely that HNO_3 contributed to the disappearance of this sensitive lichen species from the Los Angeles air basin, as well as other locations with arid conditions with high deposition loads (Riddell et al., 2008).

3.4.2.4. Summary of Phytotoxic Effects of Gaseous Nitrogen and Sulfur on Vegetation

Sulfur Dioxide

The evidence is sufficient to infer a causal relationship between exposure to SO_2 and injury to vegetation (Section 3.4.2.1). The current secondary standard for SO^2 is a 3-h average of 0.50 ppm, which is designed to protect against acute foliar injury in vegetation. There has been limited research on acute foliar injury since the 1982 PM-SO_X AQCD and there is no clear evidence of acute foliar injury below the level of the current standard.

Effects on growth and yield of vegetation are associated with increased SO^2 exposure concentration and time of exposure. The 1982 PM-SO_X AQCD concluded that more definitive concentration-response studies were needed before useable exposure metrics could be identified. The few new studies published since the 1982 PM-SO_X AQCD continue to report associations between exposure to SO^2 and reduced vegetation growth. However, most these studies have been performed outside the U.S. and at levels well above ambient concentrations observed in the U.S.

Nitrogen Oxide, Nitrogen Dioxide and PAN

The evidence is sufficient to infer a causal relationship between exposure to NO, NO_2 and PAN and injury to vegetation (Section 3.4.2.2). It is well known that in sufficient concentrations, NO, NO_2 and PAN can have phytotoxic effects on plants through decreasing photosynthesis and induction of visible foliar injury (U.S. EPA, 1993). However, the 1993 NO_X AQCD concluded that concentrations of NO, NO_2 and PAN in the atmosphere are rarely high enough to have phytotoxic effects on vegetation (U.S. EPA, 1993). Since the 1993 NO_X AQCD, very little new research has been done on these phytotoxic effects at concentrations currently observed in the U.S.

HNO_3

The evidence is sufficient to infer a causal relationship between exposure to HNO_3 and changes to vegetation (Section 3.4.2.3). Experimental exposure of HNO_3 resulted in damage to the leaf cuticle of pine and oak seedlings which may predispose those plants to other stressors such as drought, pathogens and other air pollutants (Bytnerowicz et al., 1998a; Bytnerowicz et al., 1998b). However, these tree seedling experiments used relatively short-term exposures at concentrations well above current ambient conditions. In lichen studies, several lines of evidence, including transplant and controlled exposure studies, indicate that past and current HNO_3 concentrations may be contributing to the decline in lichen

species in the Los Angles basin (Boonpragob and Nash, 1991; Nash and Sigal, 1999; Riddell et al., 2008). Current deposition of HNO_3 is contributing to N saturation of some ecosystems close to sources of photochemical smog (Fenn et al., 1998) such as the mixed conifer forests of the Los Angeles basin mountain (Bytnerowicz et al., 1999).

Table 3-28. Summary of recent studies of SO_2 exposure to plants.

Species	Exposure[a]	Endpoint(s)	Results	Reference
Scots pine (*Pinus sylvestris L.*); Norway spruce (*Picea abies (L.) Karst.*)	0, 50, 100, 150, 155 ppb SO_2 in growth chambers simulating natural weather in Finland in early June. The SO_2 concentrations represented the range of hourly SO_2 concentrations in the vicinity of industrial areas in Finland.	Concentrations of carbohydrates and secondary components	Exposure to SO_2 (100 and 155 ppb) reduced concentrations of glucose and fructose and increased concentrations of sucrose in pine needles. By contrast, one spruce clone had more glucose and fructose and less sucrose in needles exposed to 100 ppb SO_2, but in other spruces, no changes in sugar concentrations were detected in different SO_2 exposures (50–155 ppb). Exposure to SO_2 had no effects on concentrations of monoterpenes in pine or spruce needles. Concentration of total resin acids was significantly smaller in needles exposed to the greatest concentration of SO_2 (155 ppb), but no changes were detected in other exposures (50–150 ppb) in either tree species. Concentrations of palustric and neoabietic acids were affected by SO_2 in needles of pine (155 ppb SO_2) and clonal spruces (100 ppb SO_2). Exposure to SO_2 did not affect foliar concentration of total phenolics in pine and spruce seedlings. In exposure to 0, 50, 100 and 150 ppb SO_2, total phenolic concentration of spruce roots increased linearly with elevated SO_2 exposure level. By contrast, one spruce clone had decreased concentrations of phenolics in roots after exposure to 155 ppb SO_2.	Kainulainen et al. (1995)
Scots pine (*Pinus sylvestris L.*); Norway spruce (*Picea abies (L.) Karst.*)	Mature trees growing at a polluted (32 ppb SO_2) and low pollution (1 ppb SO_2) sites in Finland. In addition, seedlings were placed in the chambers and open-field plots in mid-Sept. 1991 and fumigated 8 hours daily, 5 days a week from 19 September to 15 Nov 1991 and from 19 May to 12 Oct 1992. Mean pollutant concentrations in the fumigated chambers during the 8–h exposure periods were 5–6 ppb SO_2 and 7–8 ppb NO_2. The mean pollutant concentrations not receiving the particular pollutant were ~2 ppb SO_2 and 5 ppb NO_2.	Response of needle S and N concentrations	Elevated concentrations of S were found in mature pine and spruce trees at polluted sites. The response of mature Scots pine to SO_2 differed from that of mature Norway spruce. The greater increase in the needle total S concentrations of pine suggested more abundant stomatal uptake of SO_2 compared to spruce. Mature pine was able to assimilate SO_4^{2-} derived from SO_2 into organic S more effectively than mature spruce at the high S and N deposition sites, whereas both pine and spruce seedlings accumulated S under $NO_2 + SO_2$ exposure.	Manninen et al. (2000)

Species	Exposure[a]	Endpoint(s)	Results	Reference
Mature red spruce (*Picea rubens Sarg*.)	Branches were fumigated in late summer of 1990 and 1991 in Canada. Four SO_2 treatment levels (0, 100, 200, 400 ppb)	Net photosynthesis, stomatal conductance, visible foliar injury	Net photosynthesis and stomatal conductance were found to decrease in direct proportion with cumulative foliar SO_2 absorption. Needle injury was observed in sun branches exposed to 200 and 400 ppb of SO_2 in 1990. Net photosynthesis was depressed by SO_2 regardless of branch position. Foliage subjected to high level SO_2 did not recover from SO_2 damage 1 year after treatment: needles had fallen off twigs and twig length of new foliage was reduced.	Meng et al. (1994)
Scots pine (*Pinus sylvestris L.)*; Norway spruce *(Picea abies (L.) Karst.)*	Open-air experiment, Finland- trees were exposed to F, N and S pollutants individually, or in mixtures, by spraying F and N compounds in aqueous solution and fumigating plants with gaseous SO_2, for 5 months in each of 3 consecutive growing seasons. SO_2 concentration among the trees varied between 35 and 140 ppb SO_2, depending on velocity and direction of the wind. Exact concentrations of SO_2 were not reported.	Visible symptoms, pollutant concentrations, ultrastructure of seedlings	Visible injury symptoms were most pronounced in combination exposures and whenever F was applied. Visible symptoms correlated well with needle pollutant concentrations. Exposure to F increased needle F contents particularly when F was applied with SO_2 or NH_4NO_3. This suggests that a reduction in N or SO_2 emissions, in F polluted areas, could improve the condition of conifers via decreased accumulation of phytotoxic F in the needles. Norway spruce needles accumulated 2–10 times as much S and F as those of Scots pine. In both species, exposure to SO_2 increased significantly the amount of cytoplasmic vacuoles, suggesting detoxification of excess sulphate or low pH. All exposures enhanced the accumulation of lipid bodies. Both visible symptoms and ultrastructural changes pointed to the more pronounced sensitivity of Norway spruce compared to Scots pine.	Wulff et al. (1996)
European Beech (*Fagus sylvatica L.*), Norway Spruce (*Picea abies (L.) Karst.*) European Silver Fir (*Abies alba Mill.*).	Weekly concentrations of SO_2, (averaging 3–42 ppb) and O_3 (10–90 ppb) was applied to trees in open-top chambers in Hohenheim, Germany, for almost five years.	Shoot length, leaf surface area, dry weight	Fumigation with SO_2 alone caused insignificant decreases of shoot length, total dry weight, and needle surface of spruce and fir. Fir trees fumigated with SO_2 in combination with O_3 showed lower rates of productivity compared to filtered control treatments. Beech was not as affected by SO_2 than with O_3 or $SO_2 + O_3$.	Billen et al. (1990)
Norway spruce (*Picea abies (L.*)	Weekly concentrations of SO_2, (averaging 3–42ppb) and O_3 (10–90 ppb) was applied to trees in open-top chambers in Hohenheim, Germany, for almost five years.	Ectomycorrhizal (EM) frequency, fine root structure, distribution of short roots	SO_2 resulted in higher percentages of non-mycorrhizal short root tips, and decreased number of living short roots. EM percentage decreased by 38% on SO_2 exposed roots.	Blaschke (1990)
European Beech (*Fagus sylvatica L.*), Norway Spruce (*Picea abies (L.) Karst.*) European Silver Fir (*Abies alba Mill.*).	Weekly concentrations of SO_2, (averaging 3–42 ppb) and O_3 (10–90 ppb) was applied to trees in open-top chambers in Hohenheim, Germany, for almost five years	Visible injury	In Jan to Feb 1985, after long frost, SO_2 treated fir showed development of tip necrosis, showing SO_2 inhibits frost resistance. No clear visible effects were found due to SO_2 alone on beech or spruce.	Arndt et al. (1990)

Species	Exposure[a]	Endpoint(s)	Results	Reference
European Beech (*Fagus sylvatica L.*), Norway Spruce (*Picea abies (L.) Karst.*) European Silver Fir (*Abies alba Mill.*).	Root samples taken in five-year Hohenheim Long Term Experiment in Germany from 2 tree groups. Each group of trees consisted of three younger (10–year-old) and five older (13–year-old) trees. Weekly concentrations of SO_2, (averaging 3–42 ppb) and O_3 (10–90 ppb) was applied to trees in open-top chambers.	Fine root and mycorrhizae production	In beech seedlings, SO_2 and $SO_2 + O_3$ resulted in reduced fine root production by 35% and 55%, respectively. SO_2 had no clear effect on fine root production in fir. SO_2 increased fine root production in spruce by 31%, but significantly reduced relative frequency of mycorrhizae (~20).	Wollmer and Kottke (1990)
Norway spruce (*Picea abies L. Karst.*) and fir seedlings (*Abies aiba Mill.*)	One- and two-year old seedlings exposed to low levels of SO_2 and O_3 in open-top chambers in five year experiment 1983 through 1988 in Hohenheim, Germany. SO_2 concentrations averaged weekly between 3–42 ppb and O_3 concentrations were between 10–90 ppb.	Visible symptoms, photosynthesis, transpiration	The twigs did not exhibit any visible sign of injury due to SO_2 treatments. Exposure of fir to SO_2 alone or in combination with O_3 resulted in a significant decrease in photosynthesis and transpiration. No changes either in photosynthesis or in transpiration were found in spruce under fumigation with SO_2 alone.	Schweizer and Arndt (1990)
Black sage (*Salvia mellifera*) CA sagebrush (*Artemisia californica*) Eastern Mojave buckwheat (*Eriogonum asciculatum*) CA brittlebush (*Encelia californica*)	SO_2 fumigation over 10 weeks, at 0, 50, 200, and 500 ppb, California	Number of inflorescences	Decreased inflorescences were observed at 50 ppb SO_2 for black sage, and at 200 ppb SO_2 for California sagebrush, Eastern Mojave buckwheat, and California brittlebush, with progressive declines as SO_2 concentration increased.	Westman et al. (1985)
Timothy grass (*Phleum pratense*)	Exposure to 120 ppb SO_2 for 40 days.	Leaf production, leaf senescence, dry weight (LAR), leaf-area ratio, specific leaf area (SLA)	Diminished leaf production and increased leaf senescence in seedlings exposed to 120 ppb SO_2 at 35 days. Exposure to 120 ppb SO_2 in seedlings over 40 days resulted in a 62% reduction in the dry weight of roots and 51% reduction in the dry weight of shoots, as well as a significant decline in leaf-area ratio and specific leaf area by the end of the experiment.	Mansfield and Jones (1985)
Mixed native prairie grassland	Exposed grasses to a control (~7 ppb) and three elevated levels of SO_2 (~21, 37, 64 ppb) over 5 year study.	Root and rhizome S concentrations, biomass, primary productivity, lichen cover, population	Year-to-year S accumulation did not appear to occur over the 5–year course of the treatment, though progressive increases in root and rhizome S concentrations were observed seasonally. No significant negative effects on either above-ground net primary productivity or below-ground biomass dynamics in grasses were observed, except a decrease in biomass for *Bromus japonicus*. Lichen cover declined after 1 year of exposure at the low treatment level.	Laurenroth and Milchunas, (1985)
Faba bean (*Vicia faba* L)	Experiment done in 3 different years (1986, 1986, 1988). Seasonal mean elevated exposures of SO_2 were 58 ppb in 1985, 22 ppb in 1986 and 26 ppb in 1988. Ambient concentrations were 6 ppb in 1985, 3 ppb in 1986 and 3 ppb in 1988.	Yield, leaf injury	Exposure to elevated SO_2 resulted in leaf injury in all three years. SO_2 exposure reduced yield by 17% in 1985, 7% in 1986 and 9% in 1988.	Kropff (1990)

[a]Concentration, Duration (hours, days)

Chapter 4. Summary and Conclusions

The previous chapters present the policy-relevant science pertaining to the emissions, atmospheric transformation and transport, deposition and ecological effects of NO_X and SO_X. Ecological effects are divided into broad categories of ecosystem types typically studied: terrestrial, wetlands, freshwater aquatic, and estuarine aquatic. Several NO_X and SO_X chemical species were considered because of their complex multi-phase and multi-species in both the atmosphere and the biosphere. For example, the atmospheric chemistry of NO_X and SO_X would be incomplete if only gas-phase compounds were considered; therefore, descriptions of current ambient concentrations and deposition amounts related to the particulate forms of N and S are given in Chapter 2. Similarly, the roles of other atmospheric pollutants including Hg, O_3, NH_3, and NH_4^+, and their interactions with NO_X and SO_X in the atmosphere and biosphere are also considered.

4.1. Source to Deposition

4.1.1. Chemical Families and Constituent Species

NO_X is the name given to the family of chemical species containing oxidized N, chief among which are NO, NO_2, HNO_3, and PAN in the gas phase. And because it has a prominent role in transporting N from the atmosphere to the biosphere, particulate NO_3^- is included in this ISA as well even though it is not a member of the oxidized N family of species as typically defined. Some of these oxidized N species are directly emitted; others are formed as secondary products from the emitted species.

Similarly, SO_X is the name for the family of chemical species containing oxidized S, including SO, SO_2, SO_3, and S_2O; however, of these gas-phase species, only SO_2 is present in concentrations relevant for atmospheric chemistry and environmental exposures. In addition, and as was the case with the NO_X species, particulate SO_4^{2-} is included in this ISA because of its dominant role in transferring S species from the atmosphere to the biosphere. Furthermore, this ISA includes extensive treatment of the reduced N chemical species NH_3 and NH_4—together given the chemical family name NH_X—because NH_X can play a crucial role controlling the transfer of total N and S to the biosphere on many levels of spatial extent. The most salient points from the foregoing chapters are summarized below.

4.1.2. Transport and Transformation

Convective processes and small-scale turbulence will both transport pollutants up and down throughout the PBL and the FT. Emitted NO_X, SO_X, NH_3 and other pollutants can be transported vertically by convection into upper part of the mixed layer on one day, and then transported overnight in a layer of elevated mixing ratios like a nocturnal low-level jet or the conveyor belts that characterize flows around frontal systems. Once pollutants are lofted to the middle and upper troposphere, they typically have a much longer lifetime and, with the generally stronger winds at these altitudes, can be transported long distances from their source regions. The length scale of this transport is highly variable owing to chemical and meteorological conditions encountered along the transport path. Transport of NO_X and SO_X from the boundary layer to the upper troposphere by convection, for example, usually dilutes high surface concentrations and extends species lifetimes by several days. During this transport time, the emitted and now chemically transformed pollutants can be entrained from aloft into the convective boundary layer

downwind as it grows with increasing insolation. In this way, the transported, transformed pollutants can be mixed back down to the surface.

CTMs are the prime tools for computing the emissions and interactions of NO_X, SO_X, NH_X and other pollutants; their transport and transformation, including production of secondary aerosols; the evolution of particle size distributions; and the deposition of pollutants to the surface. CTMs are driven by calculated pollutant emissions for primary species such as NO_X, SO_X, NH_3, and primary PM, and by computed meteorological fields produced by other numerical prediction models. Meteorological quantities such as winds and temperatures are taken from operational analyses, reanalyses, or numerical weather circulation models to determine both transport and emission components of the CTMs: higher temperatures, for example, will substantially alter the rates and chemical forms of some emitted N pollutants and the lofting of N and S pollutant plumes. Additional discussion of these processes and the general performance of CTMs is provided in Section 2.8.

The emitted, transported, and transformed pollutants reach the earth's surface where they can exert ecological effects largely through deposition. Wet and dry deposition are important removal processes for pollutants on all scales and so are included in all CTMs.

Wet deposition results from the incorporation of atmospheric particles and gases into cloud droplets and their subsequent precipitation as rain or snow, or from the scavenging of particles and gases by raindrops or snowflakes as they fall. Receptor surface properties like vegetation leaf surfaces have little effect on wet deposition, although leaves can retain liquid and solubilized particles containing S and N. In terrain containing extensive vegetative canopies, any material deposited by precipitation to the upper stratum of foliage is likely to be intercepted by several foliar surfaces before reaching the soil. This allows such processes as foliar uptake, chemical transformation, and re-suspension into the atmosphere to occur.

Dry deposition is a complicated and poorly characterized process that appears to be controlled by a highly varying complex of such variables as atmospheric stability, macro- and micro-surface roughness, particle diameter, and receptor surface characteristics. The general approach for dry deposition used in most CTMs is the resistance-in-series method described in Section 2.8.2. The range of particle sizes, the diversity of canopy surfaces, and the variety of chemical constituents in airborne particulates have made it difficult to estimate with precision dry particulate deposition totals for large expanses of the U.S.

Direct and indirect wet and dry deposition to specific locations like watersheds depend on air pollutant concentrations in the airshed above the watershed, but the shape and extent of the airshed is quite different from that of the watershed owing to the transport and transformation of emitted pollutants described above. In a watershed, everything that falls in its area, by definition, flows into a single body of water. An airshed, by contrast, is a theoretical concept that defines the source area containing the emissions that contribute a given level, often 50 or 75%, to the deposition in a particular watershed or to a given waterbody. Hence, airsheds are modeled domains containing the sources estimated to contribute a given level of deposition from each pollutant of concern. The principal NO_X airsheds and corresponding watersheds for several regions in the eastern U.S. are shown in Section 2.8.4.

4.1.3. Emissions and Atmospheric Concentrations

Total anthropogenic NO and NO_2 emissions in the U.S. in 2002 were 23.19 Tg. Combustion chemistry at EGUs contributed ~22% of these total and transportation-related sources, ~56%. Ambient annual NO_X concentrations have decreased ~35% in the period 1990–2005 to current annual average concentrations of ~15 ppb.

Biogenic NO_X sources are substantially smaller than anthropogenic ones and include biomass burning, lightning, and soils. The NO and N_2O emitted from soils as intermediate products from denitrification can evolve either naturally or as stimulated by addition of N containing fertilizers to crops and other soil management practices. N_2O, another member of the oxides of N family of compounds, is also a contributor to total U.S. GHG emissions: ~6.5% on a Tg CO_2e basis in 2005, and its U.S. emissions

decreased ~3% in the period 1990–2005, though there remains considerable interannual variation in this value.

Concentrations of NO_2 in the CONUS from non-anthropogenic sources in the U.S. and elsewhere in the world are <300 ppt over most of the CONUS and <100 ppt in the eastern U.S. on an annual average basis. The 24-h ambient NO_2 concentrations in CMSAs where most of the regulatory monitors are located and where most anthropogenic emissions originate were, on average, <20 ppb with a 99 percentile value <50 ppb for the years 2003–2005. Annual-average NO_2 concentrations over the CONUS are calculated to be <5 ppb for nearly all urban and rural and remote sites.

On a national scale, energy production at EGUs accounted for ~66% of total SO_2 emissions in the U.S. in 2001-2002; ~5% of total SO_2 is emitted by transportation-related sources, with on-road vehicles accounting for ~40 % of the transportation fraction and off-road diesel and marine traffic together accounting for the remainder. Ambient annual SO_X concentrations have decreased ~50% in the period 1990–2005 and now stand at ~4 ppb for both aggregate annual and 24-h average concentrations nation-wide.

Annual-average policy-relevant background SO_2 concentrations in the U.S. from uncontrolled sources here and elsewhere in the world are <10 ppt over most of the CONUS, or <1% of observed SO_2 concentrations everywhere except areas in the Pacific Northwest where geogenic SO_2 sources are particularly strong.

NH_3 emissions are chiefly from livestock and from soils as stimulated by addition of N-containing fertilizers to crops and other soil management practices. Confined animal feeding operations and other intensified agricultural production methods over a period of many decades have resulted in greatly increased volumes of animal wastes high in N; 30 to 70% of these wastes may be emitted as NH_3. This increase in NH_3 emissions, and the consequent increase in NH_4^+ concentration and deposition, correlates well with the local and regional increases in agricultural intensity. However, there remain no reliably consistent estimates of national average NH_3 concentrations owing to three complex issues: the high spatial and temporal variability in NH_3 emissions; the high uncertainty in the magnitude of those emissions; and the lack of real-time, ambient level NH_3 monitoring techniques. Nonetheless, U.S. national NH_3 emissions totals have been calculated taking into account these three drivers of uncertainty; for 2001-2002 that national NH_3 emissions total was ~4.08 Tg/yr.

4.1.4. Deposition

Increasing trends in urbanization, agricultural intensity, and industrial expansion during the previous 100 years have produced a nearly 10-fold increase in N deposited from the atmosphere. NO_X, chiefly from fossil fuel combustion, often dominates total N pollution in the U.S. and comprises ~50 to 75% of the total N atmospheric deposition.

For the period 2004–2006, the routine monitoring networks report the mean N deposition in the U.S. was greatest in the Ohio River Valley, specifically in the states of Indiana and Ohio, with values as high as 9.2 and 9.6 kg N/ha/yr, respectively. N deposition was lower in other parts of the East, including the Southeast and in northern New England. In the central U.S., Kansas and Oklahoma reported the highest deposition, 7.0 and 6.5 kg N/ha/yr, respectively.

N deposition primarily occurred in the form of wet NO_3^- and NH_4^+, followed with decreasing amounts of dry HNO_3, dry NH_4^+, and dry NO_3^-. Although deposition in most areas of the U.S. occurred in wet form, there were some exceptions, including parts of California where N deposition was primarily dry. Data are very sparse for the central U.S. between the 100th meridian and the Mississippi River; but where available, N deposition values there are lower than most of the eastern U.S., ranging from 4.1 to 5.3 kg N/ha/yr.

For the period 2004–2006, mean S deposition in the U.S. was greatest east of the Mississippi River with the highest deposition amount, 21.3 kg S/ha/yr, in the Ohio River Valley where most recording

stations reported 3 year averages >10 kg S/ha/yr. Numerous other stations in the East reported S deposition >5 kg S/ha/yr. Total S deposition in the U.S. west of the 100th meridian is relatively low, with all recording stations reporting less than 2 kg S/ha/yr and many reporting less than 1 kg S/ha/yr.

S was primarily deposited in the form of wet SO_4^{2-} followed in decreasing order by a smaller proportion of dry SO_2 and a much smaller proportion of dry SO_4^{2-}. However, these S data in the western U.S., like those for N deposition, are derived from networks with many fewer nodes in the West than in the East.

4.1.5. Field Sampling and Analysis

The instrumentation deployed at present in the routine regulatory monitoring networks for determination of gas-phase NO_2 and SO_2 concentrations is designed for determining compliance with the current NAAQS. But in applications for determining environmental effects, all these methods have important limitations which make them inadequate for fully characterizing the state of the atmosphere at present; for correctly representing the complex heterogeneity of N and S deposition across the landscape; and for realistically apportioning the contributions of reduced and oxidized forms of atmospheric N and S in driving observed biological effects at a national scale.

Routine NO_2 measurements by chemilumenescnce difference (the FRM) are contaminated by unknown and varying concentrations of higher-order oxidized N species, including gas-phase HNO_3, important itself for N deposition to the biosphere and also as a precursor to pNO_3. Moreover, dry deposition of NO, NO_2, and PANs is not at present estimated, but could be as much as 30% of total dry oxidized N deposition in areas near strong NO_X sources.

The present-day ambient annual average SO_2 concentrations are very near or even below the operating limit of detection of most of the FRM monitors in the largest regulatory network. This produces irresolvable uncertainty in these data which may be important for environmental effects from S compounds, since they result in some cases from exposures at these current low concentrations.

Routine field sampling techniques for NH_3 are at present limited to integrated values from several days to one week because higher frequency semi-continuous methods are not yet sufficiently robust to deploy in regulatory networks although passive NH_3 samplers show excellent potential. Estimates for the contribution of NH_3 to the total N deposition budget range as high as 30% of total N, and are perhaps the dominant source of reduced N.

Routine, regulatory, national-scale sampling and analysis for particulate-phase NO_3^-, SO_4^{2-}, and NH_4^+ are subject to positive and negative errors, chiefly from the loss or production of constituent species on the surface of the filter used for the long time-integrated measurement.

The coverage of the networks is very thin over large expanses of the interior U.S. and especially so west of the 100th meridian. This lack of monitored sites increases the likelihood that significant N and S deposition is now occurring at current atmospheric concentrations where no measurements are available, as predicted in numerical experiments with large-scale, first-principles models of atmospheric chemistry and physics and deposition, and as measured at some few selected special sites.

4.2. Acidification

Acidifying deposition includes gases and particles derived from SO_X, NO_X, and NH_X. The effects of acidifying deposition on ecosystems have been well studied over the past several decades and vulnerable areas have been identified for the U.S. The wealth of available data has led to the development of robust ecological models used for predicting soil and surface water acidification. The principal factor governing the sensitivity of terrestrial and aquatic ecosystems to acidifying deposition is geology.

Watersheds of acid-sensitive lakes and streams have geologic formations with low base cation supply. Other factors contribute to the sensitivity of soils and surface waters to acidifying deposition, including topography, vegetation, soil chemistry, land use, and hydrologic flowpath. Regional and ecosystem vulnerability to acidification results from sensitivity and exposure to acidifying deposition.

4.2.1. Terrestrial

In the 1982 PM-SO_X AQCD foliar and root uptake pathways for SO_X were described in detail, as well as the role of S as a nutrient. Though small amounts of SO_2 may be beneficial, it was understood that large amounts and high frequency of SO_2 exposure and S deposition can be detrimental in the long term. At that time, there were no documented observations or measurements of changes in natural terrestrial ecosystems that were directly attributed to acidic precipitation; however, changes still may have been occurring.

The 1993 NO_X AQCD documented few cases in which excessive atmospheric N deposition was linked to soil acidification, although the process of soil acidification was already well understood. Since the preparation of these assessments, direct links between NO_X and SO_X deposition and many adverse effects associated with ecosystem loading have been reported.

4.2.1.1. Biogeochemistry and Chemical Effects

The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in biogeochemistry related to terrestrial ecosystems. The strongest evidence for a causal relationship comes from studies of forested ecosystems, with supportive information on other plant communities, including shrubs and lichens (Section 3.2.2.1.). Grasslands are likely less sensitive to acidification than forests. Soil acidification occurs in response to inputs of sulfuric acid and nitric acid; the effect can be neutralized by weathering or base cation exchange. Soil acidification is a natural process, but is often accelerated by acidifying deposition. Acidifying deposition is important in decreasing concentrations of exchangeable base cations in soils. Despite recent decreases in acidifying deposition, there are widespread observations of ongoing soil acidification such as decreases in soil exchangeable base cations. The limited mobility of anions associated with naturally derived acidity (organic acids and carbonic acid) controls the rate of base cation leaching from soil under conditions of low atmospheric deposition of S and N. Because inputs of S and N in acidifying deposition provide anions that are more mobile in the soil environment than anions of naturally derived acids, these mineral acid anions can accelerate natural rates of base-cation leaching.

Nitrification is mediated by autotrophic bacteria that derive energy by oxidizing NH_4^+ to NO_3^-. Nitrification produces acidity in the form of HNO_3 as a byproduct, which contributes to the acidification of soils and surface waters.

There are three useful indicators of chemical changes and acidification effects on terrestrial ecosystems, with consistency and coherence seen among multiple studies, including soil base saturation, Al concentration, and C:N Ratio (see Table 4-1).

- Soil base saturation is the concentration of exchangeable bases as a percent of the total soil cation exchange capacity. Once base saturation decreases to a critical level (~15-20%), inputs of H_2SO_4 and HNO_3 result in exchange of inorganic Al.

- Inorganic Al is toxic to some tree roots. Plants affected by high inorganic Al concentrations in soil solution often have reduced root growth, which restricts the ability of the plant to take up water and nutrients, especially calcium (Parker et al., 1989).

- The C:N ratio of soil is used to indicate alterations to the N biogeochemical cycle. If the ratio falls below about 20 to 25, nitrification is stimulated resulting in net nitrification and increased acidity.

Table 4-1.   Chemical indicators of acidification to terrestrial ecosystems.

Reference	Indicator
SOIL BASE SATURATION	
Reuss (1983)	If base saturation is less than 15–20%, exchange ion chemistry is dominated by inorganic Al.
Cronan and Grigal (1995)	Base saturations below about 15% in the soil B-horizon could lead to effects from Al stress.
Lawrence et al. (2005)	Base saturation decreases from 30% to 20% in the upper soil B-horizon showed decreases in diameter growth of Norway spruce.
Bailey et al. (2004)	At Ca saturation less than 2% and Mg saturation less than 0.5% in the upper soil B-horizon, sugar maple mortality was observed.
ALUMINUM CONCENTRATIONS	
Johnson et al. (1991) Joslin and Wolfe (1992)	In soils with base saturation below about 20%, base cations reserves are so low that Al exchange dominates.
Eagar et al. (1996) Cronan and Grigal (1995)	There is a 50% risk of negative effects on tree growth if the molar ratio of Ca to Al in soil solution was 1.0. 100% risk for negative effects on growth at a molar ratio below 0.2.
Johnson et al. (1994a; 1994b)	Ca:Al ratios above 1.0 over the course of 4 years were found in a forest stand experiencing high mortality.
DeWitt et al. (2001)	Ca:Al ratios below 0.5 in a Norway spruce stand showed reduced Mg concentrations in needles in the third year.
C:N RATIO	
Aber et al. (2003) Ross et al. (2004)	Increased effects of nitrification occur only in soil with C:N ratio below about 20–25.

4.2.1.2. Biological Effects

The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in terrestrial biota. The strongest evidence for a causal relationship comes from studies of terrestrial systems exposed to elevated levels of acidifying deposition that show reduced plant health, reduced plant vigor, and loss of terrestrial biodiversity. In multiple studies, consistent and coherent evidence shows that acidifying deposition can affect terrestrial ecosystems by causing direct effects on plant foliage and indirect effects associated with changes in soil chemistry (Section 3.2.2.3). Biological effects of acidification on terrestrial ecosystems are generally attributable to Al toxicity, decreased ability of plant roots to take up nutrient cations and elevated leaching of Ca^{2+} from conifer needles. There are several indicators of stress to terrestrial vegetation (see Table 3-3), including percent dieback of canopy trees, dead tree basal area (as a percent), crown vigor index, and fine twig dieback.

Species Level

- Changes in soil chemistry (e.g., depletion of soil base cations, Al toxicity to tree roots, leaching of base cations into drainage water) have contributed to high mortality rates and decreasing growth trends of red spruce trees (*Picea rubens*) in some areas of the eastern U.S. over the past three decades (see Red Spruce, Section 3.2.2.3).

- Acidifying deposition, in combination with other stressors, is a likely contributor to the decline of sugar maple (*Acer saccharum*) trees that occur at higher elevation, in some portions of the eastern U.S., on geologies dominated by sandstone or other base-poor substrate, and that have base-poor soils (see Sugar Maple, Section 3.2.2.3).

- Lichens and bryophytes are among the first species affected by acidifying deposition in the terrestrial ecosystem. Effects of SO_2 on lichens include reduced photosynthesis and respiration, damage to the algal component of lichen, leakage of electrolytes, inhibition of N fixation, reduced potassium absorption, and structural changes.

- Data are insufficient to draw general conclusions for other species.

Community Level

- Species loss and reduced biodiversity of forests, shrubs, and meadow plant communities may occur in response to acidifying deposition; however, such effects are likely more related to the nutrient enrichment effects of N deposition.

4.2.1.3. Regional Vulnerability and Sensitivity

There has been no systematic national survey of terrestrial ecosystems to determine the extent and distribution of terrestrial ecosystem sensitivity to the effects of acidifying deposition. However, one preliminary national evaluation estimated that ~15% of forest ecosystems in the U.S. exceeds the estimated critical load of wet and dry deposition of S and N by >250 eq/ha/yr (McNulty et al., 2007).

Forests of the Adirondack Mountains of New York, Green Mountains of Vermont, White Mountains of New Hampshire, the Allegheny Plateau of Pennsylvania, and high-elevation forest ecosystems in the southern Appalachians are the regions most sensitive to terrestrial acidification effects from acidifying deposition (Section 3.2.4.2). While studies show some recovery of surface waters, there are widespread measurements of ongoing depletion of exchangeable base cations in forest soils in the northeastern U.S. despite recent decreases in acidifying deposition.

4.2.2. Aquatic

In the 1982 PM-SO_X AQCD, the evidence on acidifying deposition and its role in the acidification of aquatic ecosystems was assessed. The most vulnerable regions were identified, including the Adirondack Mountains of New York. Significant changes were reported in aquatic ecosystems with increasing acidity, particularly as the pH decreases below ~5.5. It was concluded that: changes in community structure occur at all levels in the food web; bacterial decomposition is reduced and fungi that feed on organic debris may become dominant in aquatic communities; organic matter accumulates rapidly, tying up nutrients and limiting nutrient mineralization and cycling; phytoplankton productivity may be reduced because of changes in nutrient cycling and increased acidity; biomass and total productivity of benthic macrophytes and algae may increase, in part because of increased lake transparency; andspecies diversity and total numbers of species of aquatic plants and animals (especially invertebrates and fish species) are reduced, and acid-tolerant species predominate.

In the 1993 NO_X AQCD a much-expanded body of evidence was available on the role of N deposition in the acidification of aquatic ecosystems. This was especially the case with respect to episodic acidification, which is far more common than chronic acidification and has been well documented for streams and lakes in the eastern U.S. The most well known examples are in the Adirondack and Catskill Mountains of the Northeast, as well as in the Great Smoky Mountains of the Southeast. Instances of episodic acidification were also reported in the western U.S. but to a much lesser extent than in the East.

4.2.2.1. Biogeochemistry and Chemical Effects

The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in biogeochemistry related to aquatic ecosystems. The strongest evidence for a causal relationship comes from studies of changes in surface water chemistry including concentrations of SO_4^{2-}, NO_3^-, sum and surplus of base cations, ANC, inorganic Al, Ca, and surface water pH (see Section 3.2.2.1). Surface water chemistry integrates the sum of upstream soil and water processes and reflects the results of watershed-scale terrestrial effects of S and N deposition, including N saturation, forest decline, and soil acidification (Stoddard et al., 2003). In many cases, surface water chemistry indicates the effects of acidification on biotic species and communities found in fresh water ecosystems.

The status of surface water chemistry can be examined and reported as chronic chemistry or episodic chemistry. Chronic chemistry refers to annual average conditions, which are often represented as summer and fall chemistry for lakes, and as spring baseflow chemistry for streams. Episodic chemistry refers to conditions during rainstorms or snowmelt when proportionately more drainage water is routed through upper soil horizons, which tend to provide less neutralizing of atmospheric acidity as compared with deeper soil horizons. Surface water chemistry has lower pH and ANC during storm runoff or snowmelt than during baseflow conditions. One of the most important effects of acidifying deposition on surface water chemistry is the short-term change in chemistry that is termed "episodic acidification." Some streams may have chronic or average chemistry that is suitable for aquatic biota, but be subject to occasional episodic acidification with lethal consequences. Episodic declines in pH and ANC are nearly ubiquitous in drainage waters throughout the eastern U.S., caused partly by acidifying deposition and partly by natural processes.

Acidification effects on aquatic biota are often evaluated using measures of either inorganic Al or pH. ANC is also used because it is an indicator of acid-base status (although ANC does not relate directly to the health of biota). The usefulness of ANC lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, Ca, SO_4^{2-} and inorganic Al.

Sulfate, Nitrate, and Base Cations

Changes in water chemistry resulting from acidifying deposition typically include changes in SO_4^{2-}, NO_3^-, and base cation concentrations. Each plays an important role in the acid-base chemistry of water; none, however, are directly toxic at concentrations commonly encountered in surface waters (Table 4-2).

- Sulfate is the primary inorganic anion found in most acid-sensitive waters. Continued decreases in S emissions should cause further decreases in SO_4^{2-} concentrations in surface waters. However, the rate of decrease in surface water SO_4^{2-} concentrations may be delayed as accumulated S leaches from watershed soils in some regions of the country, especially the southern Appalachian Mountains.

- The importance of NO_3^- as an agent of acidification varies by region, but is particularly important during periods of high hydrologic flow from soils to streams, such as those that occur during snowmelt and rain events. The relationship between N deposition and surface water NO_3^- concentration is complex and involves the terrestrial and aquatic cycling of N and other elements. NO_3^- contributes to the acidity of many lakes and streams in the eastern U.S. However, there is no apparent relationship between recent trends in N deposition and trends in NO_3^- concentrations in these surface waters (in contrast to observed responses for S deposition and SO_4^{2-} concentrations). This suggests that the time scales of N saturation may be longer than previously considered (e.g., centuries, rather than decades). Nevertheless, long-term retention of N deposited in forested regions and consequent dampening of deposition effects on surface waters is unlikely to continue (Aber et al., 2003).

- Decreases in base cation concentrations in eastern U.S. surface waters over the past two to three decades are ubiquitous and are closely tied to trends in SO_4^{2-} concentrations. Rates of base cation depletion have been similar to those for SO_4^{2-} plus NO_3^- in most areas (Shenandoah National Park is a notable exception). Decreasing trends in base cation concentrations do not necessarily indicate further acidification or recovery of surface waters, but may indicate either lower base cation leaching rates in soils or depletion of base cations from the soil system.

Acid Neutralizing Capacity, Aluminum, and pH

Acidification of surface water causes changes in ANC, Al concentration, and pH. Low pH and high inorganic Al concentration can be directly toxic to aquatic biota (Section 3.2.3).

- ANC reflects the difference between base cations and anions of strong acids in solution; it is the most widely used measure of acid sensitivity, acidification, and chemical recovery of surface waters in response to changes in acidifying deposition. Acidic waters are defined as those having ANC equal to or below zero. Waters with ANC of <50 µeq/L are considered "extremely acid-sensitive" (Schindler, 1988), and are vulnerable to episodic acidification (DeWalle et al., 1987; Eshleman, 1988). Lake and stream ANC values decreased throughout much of the 20th century in a large number of acid-sensitive lakes and streams throughout the eastern U.S. Since ~1990, the ANC of many affected lakes and streams has increased slightly. The number of acidic surface waters has decreased in some areas of the Northeast, but not in the central and southern Appalachian Mountains.

- Dissolved inorganic Al is an important chemical indicator of the effects of acidifying deposition on surface water because it is toxic to aquatic life and generally does not leach from soils in the absence of acidification. When pH falls below approximately 5.5, inorganic Al generally becomes a greater health risk to biota. Limited data suggest that acid-sensitive regions of the northeastern U.S. have elevated inorganic Al concentrations in surface waters induced by years of acidifying deposition, posing a threat to aquatic life. Concentrations have decreased slightly in some surface waters in the northeastern U.S. during the last two decades in response to decreased levels of acidifying deposition.

- The pH of freshwater streams and lakes is a common measure used to link acidification to adverse effects on aquatic biota. Decreases in pH below values of 6.0 typically result in species loss of benthic invertebrates, plankton species, and fish. A number of synoptic surveys indicated loss of species diversity and absence of several fish species in the pH range of 5.0 to 5.5. If pH decreases to lower values, there is a greater likelihood that more aquatic species could be lost without replacement, resulting in decreased richness and diversity.

Table 4-2. Chemical indicators of acidification in surface water.

Reference	Indicator
SULFATE	
Driscoll et al. (2001a)	Acidifying deposition at Hubbard Brook Experimental Forest in New Hampshire contributed to a nearly four-fold increase in stream SO_4^{2-} concentration between 1850 and 1970.
Stoddard et al. (2003)	Widespread decreasing trends in SO_4^{2-} concentrations were documented by U.S. EPA during the period 1990–2000 in the eastern U.S. including New England lakes (1.77 µeq/L/yr), Adirondack lakes (2.26 µeq/L/yr), Appalachian streams (2.27 µeq/L/yr), and Upper Midwest lakes (3.36 µeq/L/yr).
NITRATE	
Driscoll and Newton (1985)	NO_3^- concentrations in 20 Adirondack lakes in the early 1980 averaged 12% of SO_4^{2-} concentrations.
Lovett et al. (2000)	Baseflow NO_3^- concentrations in 1994–97 were an average of 37% of SO_4^{2-} concentrations in 39 Catskill streams.
Murdoch and Stoddard (1993)	During high-flows in Catskill streams NO_3^- concentrations periodically equaled or exceeded SO_4^{2-} concentrations.
Webb et al. (2004)	Average concentrations of NO_3^- in most southeastern streams tend to be considerably less than SO_4^{2-} concentrations.
Cook et al. (1994)	Very high NO_3^- concentrations in streamwater were documented at high elevations in the Great Smoky Mountains in North Carolina.
BASE CATIONS	
Likens et al. (1996)	Approximately linear increasing relationship between concentrations of base cations and $SO_4^{2-}+ NO_3^-$ concentrations in Hubbard Brook streams from 1964 to 1969, then a reversal in 1970 and a decreasing trend up to 1994.
Lawrence et al. (1999)	Decreasing concentrations of base cations at a rate that exceeded decreases in concentrations of $SO_4^{2-}+ NO_3^-$ in Catskill Mountain streams from 1984 to 1997.
ACID NEUTRALIZING CAPACITY	
Sullivan et al. (2006b)	Model simulations suggest that none of the lakes in the Adirondack target lake population were chronically acidic or had ANC less than 20 µeq/L under preindustrial conditions. By 1980, there were hundreds of such lakes.
Stoddard et al. (2003)	Tendencies during the 1990s toward increasing surface water Gran ANC in all glaciated regions of the eastern U.S. (i.e., New England, Adirondacks, Northern Appalachian Plateau) and Upper Midwest; and decreasing Gran ANC in the Ridge/Blue Ridge province.
SURFACE WATER ALUMINUM	
Gensemer and Playle (1999)	Found that organically complex aluminum (organic Al) can occur in surface waters as a result of natural soil and hydrologic processes, but this form of Al is not harmful to aquatic life.
Gensemer and Playle (1999)	Demonstrated that inorganic Al has been found to be toxic to plant and animal species throughout the food web.
Baldigo et al. (2007)	20% mortality of young-of-the-year brook trout during a 30–day period with a median inorganic Al concentration of 2 µmol/L. 90% mortality occurs over 30 days with a median inorganic Al concentration of 4.0 µmol/L.
Lawrence et al. (2007)	49 of 195 streams (25%) in the western Adirondack region had inorganic Al concentrations above 2.0 µM during August base flow.

PH	
Haines and Baker (1986) Baker et al. (1990b)	pH values for biological effects have been summarized for a variety of aquatic organisms; common threshold values for pH are 5.0, 5.5, and 6.0.
Charles et al. (1989) Sullivan et al. (1990) Cumming et al. (1992; 1994)	25 to 35% of the Adirondack lakes larger than 4 ha have been acidified since preindustrial time. An estimated 80% of the Adirondack lakes that had pH less than 5.2 in the mid-1980s were inferred to have experienced large declines in pH and ANC since the previous century. About 30 to 45% of the lakes with pH between 5.2 and 6.0 have also acidified.
Gbondo-Tugbawa et al. (2002)	PnET-BGC modeling at Hubbard Brook estimated that past stream pH (circa 1850) was probably about 6.3, compared with just above 5.0 in 2000.
Stoddard et al. (2003)	An increase in the hydrogen ion concentration of Appalachian streams (0.08 µeq/L/yr) and Upper Midwest lakes (0.01 µeq/L/yr) was reported. No trends were found in New England lakes or Appalachian streams in this study.

4.2.2.2. Biological Effects

The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in aquatic biota. The strongest evidence for a causal relationship comes from studies of aquatic systems exposed to elevated levels of acidifying deposition that support fewer species of fishes, macroinvertebrates, and diatoms (Section 3.2.3.3). Consistent and coherent evidence from multiple species and studies shows that acidification can result in the loss of acid-sensitive species, and there is evidence of a biological gradient in effects in that more species are lost with greater acidification. Biological effects are linked to changes in water chemistry including ANC, inorganic Al, and pH. Decreases in ANC and pH and increases in inorganic Al concentration contribute to declines in taxonomic richness of zooplankton, macroinvertebrates, and fish. Chemical changes can occur over both long- and short-term time scales, with additional effects on biological systems. Short-term (hours or days) episodic changes in water chemistry can have biological effects, including reduced fish condition factor, changes in species composition, and declines in aquatic species richness across multiple taxa, ecosystems and regions.

Species Level

- High levels of acidification (to pH values below 5) virtually eliminate all mayflies, crustaceans, and mollusks from some streams.

- In general, populations of salmonid fish are not found at pH levels less than 5.0, and smallmouth bass (*Micropterus dolomieu*) populations are usually not found at pH values less than 5.5 to 5.2.

- Twenty percent mortality of young-of-year brook trout were documented during a 30-day period with a median inorganic Al concentration of 2 µmol/L (Baldigo et al., 2007). It was estimated that 90% mortality would occur over 30 days with a median inorganic Al concentration of 4.0 µmol/L.

Community Level

- Community-level effects were observed in the Adirondacks and Shenandoah National Park where taxonomic richness is lower in lakes and streams having low ANC and pH.

- Decreases in pH and increases in inorganic Al concentrations have reduced the species richness of plankton, invertebrates, and fish in acid-affected surface waters.

- In the Adirondacks, a positive relationship exists between the pH and ANC in lakes and the number of fish species present in those lakes. A number of synoptic surveys indicated suggested loss of species diversity and absence of several sensitive fish species in the pH range of 5.0 to 6.0 (Section 3.2.4.4).

- In Shenandoah National Park streams, the fish species richness decreased with decreasing stream ANC. On average, richness is lower by one fish species for every 21 µeq/L decrease in ANC (Section 3.2.4.5).

- Short-term episodes of acidification are particularly harmful to aquatic biota. Early life stages are more sensitive to acidic conditions than the young-of-the-year, yearlings, and adults. Episodes are most likely to affect biota if the water had pre-episode pH above 5.5 and minimum pH during the episode of less than 5.0. Episodic acidification can have long-term adverse effects on fish populations.

4.2.2.3 Regional Vulnerability and Sensitivity

The effects of acidifying deposition have been assessed by several national surveys since the 1980s, including the National Surface Water Survey and the National Stream Survey in the mid-1980s, the Wadeable Streams Assessment (WSA) in 2004, the U.S. EPA Long-Term Monitoring program beginning in 1983, and Temporally Integrated Monitoring of Ecosystems probability surveys beginning in 1991. These surveys indicate that acidifying deposition has acidified surface waters in the southwestern Adirondacks, New England uplands, low-silica eastern Upper Midwest, forested Mid-Atlantic Highlands, and Mid-Atlantic Coastal Plain (Section 3.2.4.2).

In the U.S., the Northeast and Mountainous West regions contain many of the surface waters most sensitive to acidification. Levels of acidifying deposition in the West are low in most areas, acidic surface waters are rare, and the extent of chronic surface water acidification that has occurred to date has been very limited. However, episodic acidification does occur. In both the west and the northeast, the most severe acidification of surface waters generally occurs during spring snowmelt. On average, spring ANC values of acid-sensitive surface waters in New England, the Adirondacks, and the northern Appalachian Plateau were on average 30 µeq/L lower than summer values between 1990 and 2000. This implies that lakes and streams in these regions would need on average to recover to chronic ANC values above ~30 µeq/L or more before they could be expected not to experience acidic episodes (Stoddard et al., 2003).

In 2004, the U.S. EPA conducted a national WSA survey and found that, overall, less than 1% of the 1,020,000 km of stream in the target population was acidic due to acidifying deposition. No acidic streams were observed in the Mountainous West, Xeric West, Upper Midwest, Northern Plains, Southern Plains, or Temperate Plains ecoregions. Streams that were acidified from acidifying deposition were found in the Northern Appalachians (2.8% of 96,100 km of stream), and the Southern Appalachians (1.8% of 287,000 km). Very low ANC (0 to 25 µeq/L) streams, likely exposed to episodic acidification, were found in the Northern Appalachians (2.7% of 96,100 km of stream), the Coastal Plain (6.3% of 119,000 km), and the Mountainous West (0.6% of 204,000 km). Stream surveys were not conducted in the Adirondacks or New England.

It is important to address surface water recovery in response to reduced acidifying deposition over the past few decades. The following summarizes recent regional trends in acidification recovery.

About one-quarter to one-third of the lakes and streams that were chronically acidic during summer in the 1980s were no longer chronically acidic in 2000. These improvements in water chemistry are largely attributed to decreases in S deposition. Throughout the northeastern U.S., the concentration of SO_4^{2-} in surface waters has decreased substantially in response to decreased emissions and atmospheric deposition of S. Decreased SO_4^{2-} concentrations of a third or more in lakes and streams have been commonly observed.

Data from U.S. EPA monitoring programs show that the following important changes in lake and stream chemistry occurred during the 1990s in response to S and N emissions reductions: SO_4^{2-} concentration decreased as a percentage of total ion concentration in surface waters; ANC increased modestly in three of the five regions included in surface water efforts; dissolved organic carbon and associated natural organic acidity increased, perhaps toward more natural pre-disturbance concentrations, as surface water acidity contributed from acidifying deposition decreased; and inorganic, and potentially toxic, Al concentrations appear to have decreased slightly in some sensitive aquatic systems.

Despite these improvements, some regions and specific locations remain sensitive to acidifying deposition. For example, in the Adirondacks, the current rates of N and S deposition exceed the amount that would allow recovery of the most acid-sensitive lakes. In the Shenandoah, past SO_4^{2-} has accumulated in the soil and is slowly released from the soil into stream water, where it causes acidification, making parts of this region sensitive to current loading. Numerical models specifically calibrated to these locations and conditions suggest that the number of acidic streams will increase under the current deposition rates.

4.2.3. Ecosystem Services

Acidification of ecosystems is primarily driven by NO_X, NH_X and SO_X. Ecosystem services, as defined by Hassan et al. (2005), are broadly grouped into four main categories (see Section 3.1.3). The specific effects of acidification on ecosystem services may include:

- **Supporting**: altered nutrient cycling, decreased biodiversity, decline of productivity

- **Provisioning**: decline in the richness, abundance, and/or health of fish, other aquatic species and some terrestrial trees

- **Regulating**: decline in water and soil quality

- **Cultural**: decline in forest aesthetics, fishing, ecotourism and cultural heritage values related to ecosystem integrity and biodiversity

4.3. Nitrogen Nutrient Enrichment

NO_X and NH_X are the main contributors to N deposition across the U.S (see Chapter 2). Given the complexity of the N cycle, a broadly applicable and well-tested predictive model of the ecological effects of N deposition is not available. However, there is substantial empirical information for specific ecosystems and endpoints about ecological and biogeochemical responses to N deposition. The most commonly used experimental designs are N addition, N deposition gradient, and observational studies that evaluate relationships between effects and changing pollution levels over time (see Table 4-4 and Table 3-25). N addition experiments often use NH_4NO_3 or $(NH_4)_2SO_4$ additions to simulate the chemical species in atmospheric N_r deposition. Deposition gradient experiments often only measure oxidized and reduced forms of N. Therefore, publications addressing N additions or deposition often do not include

data on all components of N_r. Thus throughout this Section, causality determinations are made on effects of N deposition that incorporate evidence related to various forms of N.

The different ecosystem types that occur across the U.S. have a broad range of sensitivity to N deposition. In general, N deposition to terrestrial ecosystems causes accelerated growth rates in some species, which may lead to altered competitive interactions among species and nutrient imbalances, ultimately affecting biodiversity. The onset of these effects occurs with N deposition levels as low as 3 kg N/ha/yr in sensitive terrestrial ecosystems. In aquatic ecosystems, N that is both leached from the soil and directly deposited can pollute surface water. This causes alteration of the diatom community at levels as low as 1.5 kg N/ha/yr in sensitive freshwater ecosystems. In estuarine and near coastal marine ecosystems, total N loading, of which atmospheric deposition is a contributing factor, promotes eutrophication. Eutrophication is a serious problem in many coastal areas of the U.S.

Factors that govern the sensitivity of terrestrial ecosystems to nutrient enrichment from N deposition include the degree of N-limitation to plant growth, rates and form of N deposition, elevation, climate, species composition, length of growing season, and soil N retention capacity. Critical N loads are described for European ecosystems (see Section 3.3.7.1). The range of critical loads in Europe varies by ecosystem type: terrestrial ecosystems are between 5-30 kg N/ha/yr; freshwater wetlands are between 5-35 kg N/ha/yr; inland surface waters are between 5-20 kg N/ha/yr; coastal habitats are between 20-25 kg N/ha/yr; and marine habitats are between 30-40 kg N/ha/yr. Less is known about the extent and distribution of the terrestrial ecosystems in the U.S. that are most sensitive to the effects of nutrient enrichment from atmospheric N deposition; however available data for quantified relationships between loading and ecological effects are discussed in Section 3.3.7.2 and in Table 4-4. Table 4-4 summarizes field studies of the ecological effects of N deposition and N addition. It includes 51 studies that were conducted in the U.S. and 8 that were conducted in Europe and Asia since the last UNECE critical loads assessment. The ecosystem types from the U.S. include coastal sage scrub, desert, sub-alpine forest, coniferous forest, mixed hardwood forest, chaparral, oak savanna, grassland, freshwater lakes and freshwater wetlands. Endpoints include lichen, mycorrhizae, herbaceous and woody vascular plant species, algae and multiple biogeochemical indicators. Critical loads are available for few ecosystems and endpoints in the U.S.

4.3.1. Terrestrial

The 1993 NO_X AQCD concluded that N deposition may cause important effects on terrestrial systems, and that the effects are often due to total N loading, not just that the oxidized forms. N deposited to an N-deficient ecosystem is generally expected to increase growth. If N is deposited on an ecosystem with adequate N or saturated with N, NO_3^- leaching is expected to occur. Much of the information presented in the 1993 NO_X AQCD was based on results from studies of forest ecosystems. N saturation was known to be more common in older forests. Disturbances such as fire and harvesting would push ecosystems to a state more removed from a condition of N saturation. Fertilization was known to increase growth in N-deficient forests in the short-term, but little was known about long-term effects of N fertilization and the differential growth effects on various tree and herbaceous plant species. It was known that plants do not necessarily benefit from added N. When N increases to the point that it is no longer limiting, deficiencies of other nutrients can occur (Aber et al., 1989).

A few studies documented the deleterious effects of excessive N on tree growth and grassland biodiversity. Alpine ecosystems were identified as particularly sensitive to N deposition. The studies published since the 1993 NO_X AQCD generally support its conclusions confirm findings of previous studies, provide more information on the long-term effects of N deposition, and expand the knowledge of effects to include more ecosystems and species.

4.3.1.1. Biogeochemical Effects

N cycling

The evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemical cycling of N in terrestrial ecosystems (Section 3.3.2.1). This is supported by numerous observational, deposition gradient and field addition experiments. N deposition disrupts the nutrient balance of ecosystems with numerous biogeochemical effects. The chemical indicators that are typically measured include NO_3^- leaching, C:N ratio, N mineralization, nitrification, denitrification, foliar N concentration, and soil water NO_3^- and NH_4^+ concentrations. Note that N saturation does not need to occur to cause adverse effects on terrestrial ecosystems. However, in some regions N saturation is a plausible mechanism for net nitrification and associated NO_3^- leaching in drainage water. Substantial leaching of NO_3^- from forest soils to stream water can acidify downstream waters (see Section 3.2) and deplete soils of nutrient base cations, especially Ca and Mg (Likens et al., 1998).

- Two of the primary indicators of N enrichment in forested watersheds are the leaching of NO_3^- in soil drainage waters and the export of NO_3^- in stream water, especially during the growing season (Stoddard, 1994).

- There is consistent and coherent experimental evidence that NO_3^- leaching can be induced by chronic addition of N (Edwards et al., 2002b; Kahl et al., 1999; Kahl et al., 1993; Peterjohn et al., 1996, Norton et al., 1999). Several N-exclusion studies in Europe demonstrated that decreases in N deposition produced immediate reductions in NO_3^- leaching from forest stands (Gundersen et al., 1998; Quist et al., 1999).

- In upland forested areas in the U.S., most N received by atmospheric deposition is retained in soil, and lesser amounts (7–16%) are retained in plant biomass (Nadelhoffer et al., 1999a). Several different data compilations indicate consistent and coherent results that 80% to 100% of N deposition is retained or denitrified within terrestrial ecosystems that receive less than about 8–10 kg N/ha/yr (Aber et al., 2003; Dise and Wright, 1995; Kristensen et al., 2004; MacDonald et al., 2002; Sullivan, 2000b).

- In the West, mixed conifer forests and chaparral watersheds with high smog exposure in the Los Angeles Air Basin also are N-saturated and exhibit the highest stream water NO_3^- concentrations within wildlands in North America (Bytnerowicz and Fenn, 1996; Fenn et al., 1998). In the mixed conifer forests of the Sierra Nevada and San Bernardino mountains, a critical load for increased NO_3^- leaching has been calculated to be 17 kg N/ha/yr. Several studies in the Rocky Mountains indicate that the capacity of alpine catchments to sequester N is exceeded at levels greater than 5-10 kg N/ha/yr (Baron et al., 1994; Williams and Tonnesen, 2000).

- Aber et al. (2003) found that surface water NO_3^- concentrations exceeded 1 µeq/L in watersheds receiving about 9 to 13 kg N/ha/yr of atmospheric N deposition. The lakes and streams found to have high NO_3^- concentration were those receiving N deposition above this range, but responses were variable among those receiving high N deposition. Above this range, mean NO_3^- export increased linearly with increasing deposition at a rate of 0.85 kg NO_3^- kg N/ha/yr for every 1 kg N/ha/yr increase in deposition, although there was considerable variability in N retention among watersheds at higher rates of deposition.

- Activities or disturbances such as logging or fire that export large quantities of N from the site alter future N availability and site propensity to achieve N saturation (Chanasyk et al., 2003).

C cycling

The evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemical cycling of C in terrestrial ecosystems (Section 3.3.3.1). The most extensive evidence on

the interactions between N deposition and C cycling is available for forest ecosystems. Experimental N addition studies show a range of responses in terms of tree mortality and productivity. In general, moderate to high additions of N lead to either no significant change in growth rates or transient growth increases (generally at deposition rates lower than 10 kg N/ha/yr), followed by increased mortality, especially at higher rates of fertilization (see Section 3.3.3.1). This group of studies shows coherence in effects, and indicates the presence of a biological gradient in responses with increasing N deposition.

Due to the complexity of interactions between the N and C cycling, the effects of N on C budgets (quantified input and output of C to the ecosystem) are variable. Regional trends in NEP of forests have been estimated through models based on gradient studies (Magnani et al., 2007). There have been critiques of the method and the magnitude of these reported effects (Sutton et al., 2008b). N addition was found to slightly increase ecosystem C in a meta-analysis that examined the effects of N fertilization ranging from 25.5 to 200 kg N/ha/yr on forest ecosystem C content (see Section 3.3.3.1). In the western U.S., atmospheric N deposition has been shown to cause increased litter accumulation and carbon storage in above-ground woody biomass, which in turn may lead to increased susceptibility to more severe fires (Fenn et al., 2003a).

Less is known regarding the effects of N deposition on C budgets of non-forest ecosystems. A meta-analysis, including 16 observations from 9 publications, conducted to evaluate the relationship between N addition ranging from 16 to 320 kg N/ha/yr and C sequestration of non-forest ecosystems showed that N addition has no significant effect on net ecosystem exchange of non-forest ecosystems.

N deposition also affects the patterns of C allocation because most growth occurs above ground. This increases the shoot-to-root ratio, which can be detrimental to the plant because of decreased resistance to environmental stressors, such as drought and windthrow (Braun et al., 2003; Fangmeier et al., 1994b; Krupa, 2003; Minnich et al., 1995).

N_2O and CH_4 flux

The evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemical flux of N_2O in terrestrial ecosystems (Section 3.3.4.2). Terrestrial soil is the largest source of N_2O, accounting for 60% of global emission (Johnson, 2002). In a meta-analysis of 80 observations of terrestrial ecosystems that received chemical forms of N (NH_4^+, NO_3^-, NH_4NO_3, and urea) and addition rates (10 to 562 kg N/ha/yr), N addition resulted in a two-fold increase in N_2O emission. The response of N_2O emission to N addition for coniferous forest, deciduous forest and grasslands was significant (see Section 3.3.4.2).

The evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemical flux of CH_4 in terrestrial ecosystems (Section 3.3.4.1). Non-flooded upland soil is the largest biological sink for atmospheric CH_4, consuming about 6% of the atmospheric CH_4 (Le Mer and Roger, 2001). A meta-analysis was performed on a data set of 41 observations including four forms of N (NH_4^+, NO_3^-, NH_4NO_3 and urea) and the addition rates ranging from 10 to 560 kg N/ha/yr. The results indicated that N addition reduced CH_4 uptake, but this inhibition was significant only for coniferous and deciduous forests (see Section 3.3.4.1).

4.3.1.2. Species Richness, Composition and Biodiversity

The evidence is sufficient to infer a causal relationship between N deposition on the alteration of species richness, species composition and biodiversity in terrestrial ecosystems. The most sensitive terrestrial taxa are lichens. Empirical evidence indicates that lichens in the U.S. are adversely affected by deposition levels as low as 3 kg N/ha/yr. Alpine ecosystems are also sensitive to N deposition, changes in an individual species (*Carex rupestris*) were estimated to occur at deposition levels near 4 kg N/ha/yr and modeling indicates that deposition levels near 10 kg N/ha/yr alter plant community assemblages. A summary of N deposition effects are presented below, organized by ecosystem type.

Lichens

There is consistent and coherent evidence indicating that lichen communities are affected by current levels of N deposition. Sensitive lichens are frequently used as indicators of air pollution and atmospheric deposition levels. In addition to being good subjects for biomonitoring, they constitute important components of the forest ecosystem by contributing to biodiversity, regulating nutrient and hydrological cycles, and providing habitat elements for wildlife (McCune and Geiser, 1997); see Section 3.3.5.

Lichens that contain a cyanobacterial photobiont appear to be more sensitive to adverse effects from atmospheric N deposition than most other lichens (Hallingbäck, 1991; Hallingbäck and Kellner, 1992). The decline of lichens containing cyanobacteria in parts of northern Europe has been associated with N deposition in the range of 5 to 10 kg N/ha/yr (Bobbink et al., 1998). In the U.S., lichen species are negatively affected by N inputs as low as 3 to 8 kg N/ha/yr (Fenn et al., 2003a).

In the San Bernardino Mountains, California, up to 50% of lichen species that occurred in the region in the early 1900s have disappeared (Fenn et al., 2003a; Nash and Sigal, 1999). The critical load has been calculated for lichen communities in mixed conifer forests in California at 3.1 kg N/ha/yr (Fenn et al., 2008).

The Pacific Northwest retains widespread populations of pollution-sensitive lichens (Fenn et al., 2003a). In this area, lichen communities are beginning to show evidence of changes in response to increased N pollution, including decreased distribution of sensitive lichen taxa, and their replacement with nitrophilous species (Geiser and Neitlich, 2007).

Alpine Plant Communities

Consistent and coherent evidence indicates that alpine plant communities are among the most sensitive terrestrial communities to atmospheric N deposition. Factors that govern the sensitivity of alpine tundra to N deposition include low rates of primary production, short growing season, low temperature, and wide variation in moisture availability in the alpine environment (Bowman et al., 1993; 1994; Bowman and Fisk, 2001; Fisk et al., 1998). Alpine herbaceous plants are generally considered N-limited and changes in alpine plant productivity and species composition have been noted in response to increased N inputs (Vitousek et al., 1997; Bowman et al., 2006). Alpine plant communities have also developed under conditions of low nutrient supply, in part because soil-forming processes are poorly developed, and this also contributes to their N-sensitivity.

The western U.S. contains extensive land areas that receive low levels of atmospheric N deposition, interspersed with hot spots of relatively higher N deposition that typically occur downwind of large metropolitan centers and agricultural areas. Some of these areas of higher N deposition occur at high elevation. Results from several studies suggest that the capacity of Rocky Mountain alpine catchments to sequester N is exceeded at input levels less than 10 kg N/ha/yr (Baron et al., 1994; Williams, 1999). Changes in an individual species (*Carex rupestris*) were estimated to occur at deposition levels near 4 kg N/ha/yr. Changes in the plant community were estimated to occur at deposition levels near 10 kg N/ha/yr. (Bowman et al., 2006). In comparison, critical loads for alpine plant communities in Europe are between 5-15 kg N/ha/yr (Bobbink et al., 2003).

Grasslands

Consistent and coherent evidence for reduced biodiversity in response to N deposition is reported for grasslands in the U.S. and Europe. Clark and Tilman (2008) evaluated the effects of chronic N addition over 23 years in Minnesota prairie-like successional grasslands and in native savanna grassland and found species numbers declined at the lowest addition level (10 kg N/ha/yr added to 6 kg N/ha/yr of ambient deposition). The authors calculated the critical load as 5.3 kg N/ha/yr with an inverse prediction interval of 1.3–9.8 kg N/ha/yr.

Change in species composition in response to N deposition has been observed regardless of soil type in European grasslands. Such effects have been found in calcareous, neutral, and acidic environments, species-rich heaths, and montane-subalpine grasslands (Bobbink et al., 1992b; 1998; Stevens, 2004).In a transect of 68 acid grasslands across Great Britain, covering the lower range of ambient annual N deposition (5 to 35 kg N/ha/yr) chronic N deposition significantly reduced plant species richness. Species richness declined as a linear function of the rate of inorganic N deposition, with a reduction of one species per 4 m^2 quadrant for every 2.5 kg N/ha/yr of chronic N deposition. The critical loads for ten different types of grasslands in Europe ranged between 10 and 30 kg N/ha/yr, above which changes in species composition were reported (Bobbink et al., 2003) (See Section 3.3.7.1).

In the San Francisco Bay area of California, which receives N deposition levels of 10 to 15 kg N/ha/yr, exotic nitrophilous grasses have displaced native grass species, likely due to greater N availability from deposition and from the cessation of grazing, which previously exported N out of the system (Fenn et al., 2003b).

Forests

Forests include overstory trees, understory herbaceous plants and mycorrhizae. There is very little information on the effect of N deposition on the biodiversity of overstory trees within forests in the U.S. This is due to the long life span and slow growth of trees, which makes such changes difficult to detect. A study of the northern edge of the Great Plains (southern Canada), showed that increasing N deposition over a range of 8 to 22 kg N/ha/yr to aspen-dominated and boreal forests increase forest expansion into the grasslands (Kotchy and Wilson 2001). More is known concerning the effects of N deposition on understory herbs, however most of the evidence is from Europe, where alteration of species composition is known to occur over the gradient of N deposition ranging from 6 to 20 kg N/ha/yr for acid tolerant species and a decline in the cover and abundance of ericaceous shrubs along a gradient from 3 to 12 kg N/ha/yr (Gilliam, 2006a). Loss of mycorrhizal diversity was recorded for Alaskan coniferous forest over a gradient of 1 to 20 kg N/ha/yr, and studies in oak savanna ecosystems in Minnesota show N addition decreases mycorrhizal diversity (Avis et al., 2003).

Arid and Semi-arid Grasslands

Alteration to arid and semi-arid plant communities resulting from experimental N fertilization have been reported in the Colorado Plateau, Joshua Tree National Park in California, and the coastal sage scrub community (CSS) of Southern California.

Results from several lines of evidence showed increased biomass of non-native plant species over native species; decreased soil moisture under some conditions; and increased fire risk where dense grasses replaced shrub cover.

In some areas of the CSS of Southern California, dry N deposition may be upwards of 30 kg N/ha/yr (Bytnerowicz and Fenn, 1996). Native shrub and forb seedlings in this plant community are unable to compete with dense stands of exotic grasses, and thus are gradually replaced by the grasses, especially following disturbances such as fire (Cione et al., 2002; Eliason and Allen, 1997; Yoshida and Allen, 2001). The CSS community in California has been declining in land area and in shrub density for the past 60 years and is being replaced in many areas by Mediterranean annual grasses (Allen et al., 1998; Padgett and Allen, 1999; Padgett et al., 1999}. N deposition is considered a possible cause or contributor to this ecosystem alteration.

Egerton-Warburton and Allen (2000) discerned a shift in arbuscular mycorrhizal community composition with decreased species richness and diversity along a deposition gradient (2 to 57 µg N/g as soil NO$_3^-$). These shifts in mycorrhizal fungal communities may facilitate replacement of native plant communities by Mediterranean annual grasslands in CSS.

A coherent body of evidence suggests that N deposition may be contributing to greater fuel loads and thus altering the fire cycle in a variety of ecosystem types (Fenn, 2003b). Invasive grasses, which can be favored by high N deposition, promote a rapid fire-cycle in many locations (D'Antonio and Vitousek,

1992). The increased productivity of flammable understory grasses increases the spread of fire and has been hypothesized as one mechanism for the recent conversion of CSS to grassland in California (Minnich and Dezzani, 1998).

Deserts

Consistent and coherent evidence shows that N fertilization alters desert plant communities in the Chihuahuan Desert, Jordana Basin, Mojave Desert, and the Great Basin. N additions stimulate plant growth and cause the observed invasion of some exotic plant species and associated changes in ecosystem function, especially where water supply is adequate. There is little evidence evaluating biological responses across deposition gradients. However there are numerous field experiments that evaluate N addition levels ranging from 10-100 kg N/ha/yr. This is within the range of deposition that occurs in the U.S., which may be as high as 30–90 kg N/ha/yr downwind of major urban and agricultural areas (Fenn et al., 2003). Increased grass biomass has also been associated with increased fire frequency in the Mojave Desert (Brooks, 1999; Brooks and Esque, 2002; Brooks et al., 2004). This effect is most pronounced at higher elevation, probably because the increased precipitation at higher elevation contributes to greater grass productivity. In some cases, precipitation may be a more limiting factor than N to plant growth in deserts. Increased N supply at lower elevation in arid lands can only increase productivity to the point at which moisture limitation prevents additional growth. Fire was relatively rare in the Mojave Desert until the past two decades, but now fire occurs frequently in areas that have experienced invasion of exotic grasses (Brooks, 1999).

4.2.3. Transitional

Anaerobic conditions of waterlogged soils in wetlands result in slow decomposition of organic matter and accelerated denitrification. N cycles of two types of wetland, ombrotrophic bogs and coastal salt marshes, were discussed in 1993 NO_X AQCD. Ombrotrophic bogs are generally considered the most sensitive to atmospheric N deposition because they are nutrient poor, with a closed N cycle in which the predominant source of N is rainfall. The 1993 NO_X AQCD found that the three main ecological effects of N deposition on wetland ecosystem are: increasing primary production; modifying microbial processes; and reducing biodiversity. Recent studies support and extend the conclusions in the 1993 NO_X AQCD, especially with regard to the effects of N deposition on species diversity.

4.3.2.1. Biogeochemical Effects

The contribution of N deposition to total N load varies among wetland types. A wetland is more vulnerable to N deposition as the relative contribution of N deposition to its total N load increases. For example, in freshwater wetland ecosystems atmospheric deposition is the main source of N to the ecosystem while N deposition is a minor contributor to N load in many coastal estuarine wetlands.

N Cycling

The evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemical cycling of N (Section 3.3.2.2). N deposition contributes to total N load in wetlands. The chemical indicators that are typically measured include NO_3^- leaching, N mineralization, and denitrification rates. N dynamics in wetland ecosystems are variable in time, among types of wetlands and environmental factors, especially water availability (Howarth et al., 1996). A wetland can act as a source, sink, or transformer of atmospherically deposited N (Devito et al., 1989) and these functions can vary with season and with hydrological conditions. Vegetation type, physiography, local hydrology, and

climate all play significant roles in determining source/sink N dynamics in wetlands (Arheimer and Wittgren, 1994; Devito et al., 1989; Koerselman et al., 1993; Mitchell et al., 1996).

N mineralization has been shown to increase with N addition, and this can cause an increase in wetland N export to adjacent surface water (Groffman, 1994). In general, leaching losses of NO_3^- in water derived directly from wetlands are often small because of NO_3^- removal by denitrification. Elevated N inputs to wetlands will often increase the rate of denitrification (Broderick et al., 1988; Cooper, 1990; Dierberg and Brezonik, 1983). This decreases environmental effects associated with increased N supply to soils and drainage waters; however it increases the emissions of greenhouse gases (e.g., N_2O) to the atmosphere. Denitrification appears to be negligible in wetland environments that are typically nutrient (including N) poor, such as some bogs and fens (Morris, 1991).

C Cycling

The evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemical cycling of C. A meta-analysis that included wetlands with other non-forest ecosystems indicated no effect of N deposition on overall net ecosystem exchange of C (See Section 3.3.3). In other words, any gain in C capture by photosynthesis was offset by ecosystem respiration and C leaching. There were not enough studies to evaluate wetlands as a separate category. There is evidence that above and below ground C exchange processes are affected by N deposition. In *Sphagnum*-dominated ombrotrophic bogs, higher N deposition resulted in higher tissue N concentrations and greater NPP (Aldous, 2002), but lower bulk density. A study of 23 ombrotrophic peatlands in Canada with deposition levels ranging from 2.7 to 8.1 kg N/ha/yr showed peat accumulation increases linearly with N deposition; however in recent years this rate has begun to slow indicating limited capacity for N to stimulate accumulation (Turunen et al., 2004). Soil respiration has been studied in European countries under a natural gradient of atmospheric N deposition from 2 to 20 kg N/ha/yr. They found enhanced decomposition rates for material accumulated under higher atmospheric N supplies resulted in higher carbon dioxide (CO_2).

In intertidal wetlands, primary production of plant species typically increases with N addition, however most studies apply fertilizer treatments that are several orders of magnitude larger than atmospheric deposition (Mendelssohn, 1979; Darby et al., 2008; Wigand et al., 2003, Tyler et al., 2007). N fertilization experiments in salt marsh ecosystems show biomass stimulation from 6 to 413% with application rates ranging from 7 to 3120 kg N/ha/yr (U.S. EPA, 1993a).

Increases in biomass linked to N deposition, have also increased evapotranspiration rates (Howes, 1986). This changed the soil water balance of water and may influence the direction of plant community succession. Model results suggest 7 kg N/ha/yr is the threshold for an oligotrophic bog to become a mesotrophic bog dominated by trees, as found in the 1993 NO_X AQCD.

N_2O and CH_4 flux

The evidence is sufficient to infer a causal relationship between N deposition and the alteration of N_2O flux in wetland ecosystems. Nineteen observations of the effects of different N forms (NH_4^+, NO_3^-, NH_4NO_3, and urea) and addition rates (15.4 to 300 kg N/ha/yr) on wetland N_2O emissions were evaluated in a meta-analysis (see Section 3.3.4.2; Mendelssohn, 1979). The results indicated that N addition increased the production of N_2O by about two-fold.

The evidence is sufficient to infer a causal relationship between N deposition and the alteration of CH_4 flux in wetland ecosystems. Wetlands are generally net sources of CH_4, but some wetlands can be net sinks depending on environmental conditions such as drainage and vegetation (Crill et al., 1994; Saarnio et al., 2003). A meta-analysis was performed on a data set of 17 observations to assess the effects of N additions on CH_4 fluxes (see Section 3.3.4.1). This data set included four forms of N (NH_4^+, NO_3^-, NH_4NO_3 and urea) and the addition rates ranged from 30 to 240 N kg N/ha/yr (see Section 3.3.4.1). The results indicated that N addition increased CH_4 production from the wetlands, but had no significant effect on CH_4 uptake of wetlands.

4.3.2.2. Biological Effects

The evidence is sufficient to infer a causal relationship between N deposition and the alteration of species richness, species composition and biodiversity in wetland ecosystems (Section 3.3.5.2). Wetlands contain a high number of rare plant species. Excess N deposition can cause shifts in wetland community composition by altering competitive relationships among species, which potentially leads to effects such as decreasing biodiversity, increasing non-native species establishment and increasing the risk of extinction for sensitive and rare species.

Changes in plant species composition caused by elevated atmospheric N deposition haven been demonstrated in Europe. Achermann and Bobbink (2003), see Table 3-24, evaluated the empirical evidence linking N deposition to wetland species composition and biodiversity to develop the following critical loads in Europe: raised and blanket bogs = 5-10 kg N/ha/yr; poor fens = 10-20 kg N/ha/yr; rich fens 15-35 kg N/ha/yr; mountain rich fens 15-25 kg N/ha/yr; pioneer and low-mid salt marshes 30-40 kg N/ha/yr.

Some wetland species are adapted to low-N environments. High levels of atmospheric N deposition increase the risk of decline and extinction of those sensitive species. In general, these include the genus *Isoetes sp.,* of which three species are federally endangered; insectivorous plants like the endangered green pitcher *Sarracenia oreophila;* and the genus *Sphagnum*, of which there are 15 species listed as endangered by eastern U.S. states. Roundleaf sundew (*Drosera rotundifolia*) is also susceptible to elevated atmospheric N deposition (Redbo-Torstensson, 1994). This plant is native to, and broadly distributed across, the U.S. and is listed as endangered in Illinois and Iowa, threatened in Tennessee, and vulnerable in New York . In the U.S., *Sarracenia purpurea* can be used as a biological indicator of local N deposition in some locations (Ellison and Gotelli, 2002). *S. purpurea* is a perennial pitcher plant native to Canada and the eastern U.S. that grows in nutrient-poor peatlands and is sensitive to changes in N availability. Based on the annual demographic rates, a non-stationary matrix model forecasted that the extinction risk within the next 100 years increased substantially if N deposition rate increase (1-4.7%) from the rate of 4.5-6.8 kg N/ha/yr (Gotelli and Ellison, 2002).

4.3.2.3. Regional Vculnerability and Sensitivity

Bogs are among the most sensitive wetland ecosystems to N deposition. In the U.S., peat-forming bogs are most common in areas that were glaciated, especially in portions of the Northeast and Upper Midwest (U.S. EPA, 1993a).

N input and output rates of fens are intermediate between bogs and coastal marshes. N deposition could drastically change species composition, increase primary productivity and increase methane emission in fens (Aerts and de Caluwe, 1999; Pauli et al., 2002).

Atmospheric N inputs contribute to eutrophication problems in coastal marshes at many locations. However marine inputs of N are typically higher than direct atmospheric input. Models of sources of N to wetland ecosystems are not yet available.

The effect of N deposition on wetland ecosystems depends on the fraction of rainfall in its total water budget and the sensitivity to N deposition was suggested as bogs (70-100% rainfall) >fens (55-83% rainfall) >intertidal wetlands (10-20% rainfall) (Morris, 1991).

4.3.3. Freshwater Aquatic

The 1993 NO_X AQCD concluded that productivity of fresh water is usually limited by the availability of phosphorus (P). However, it was noted that high inputs of P from anthropogenic sources could lead to N limitation. The ratio of dissolved N to total phosphorus (molar basis) was used as an

indicator for nutrient limitation, with values less than 2 indicating N limitation. The proportions of N limited lakes showed a wide regional variation: Pacific Northwest (27.7%), Upper Midwest (19%), Northeast (5%), and Southeast (2.5%). All sub regions of the West contain substantial numbers of N limited lakes.

4.3.3.1. Biogeochemical Effects

N Cycling

The evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemical cycling of N in freshwater aquatic ecosystems (Section 3.3.2.3). N deposition is the main source of N enrichment to headwater streams, lower order streams and high elevation lakes. The chemical indicators that were studied included NO_3^- and DIN concentration in surface waters as well as Chl a:total P ratio. Elevated surface water NO_3^- concentrations occur in both the eastern and western U.S. Bergstrom and Jansson (2006) report a significant correlation between N deposition and lake biogeochemistry by identifying a correlation between wet deposition and [DIN] and Chl a: Total P. Recent evidence provides examples of lakes and streams that are limited by N and show signs of eutrophication in response to N addition.

C Cycling

The evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemical cycling of C in freshwater aquatic ecosystems (Section 3.3.3.3). If growth of the autotrophic community of a freshwater stream is N-limited, then N addition will stimulate C-capture via photosynthesis often altering the C cycle. Moreover, a freshwater lake or stream must be N-limited to be sensitive to N-mediated eutrophication. Elser et al. (2008) in a meta-analysis of over 600 experiments found that N-limitation occurs frequently in freshwater ecosystems, in contrast to the traditional paradigm. There are also many examples of fresh waters that are N-limited or N and P co-limited (See Annex C). Bergström and Jansson (2006) concluded that most lakes in the northern hemisphere are limited by N in their natural state.

Numerous studies investigate the relationship between N concentration of freshwater and primary productivity (reported as Chl a, NPP, or an index such as the lake chemistry ratio of DIN:TP) and atmospheric N deposition. Typically N addition experiments of lake and stream bioassays in which N was added to waters in field or laboratory to measure the response are conducted. A meta-analysis of enrichment bioassays in 62 freshwater lakes of North America found algal growth enhancement from N amendments to be common in slightly less than half the studies (Elser et al., 1990). Gradient studies of undisturbed northern temperate, mountain, or boreal lakes, that generally receive low levels of atmospheric N deposition found strong relationships between N-limitation and productivity where N deposition was low, and P and N+P limitations where N deposition was higher (Fenn, 2003b; Bergström et al., 2005; Bergström and Jansson, 2006). One such study in Sweden found, the lowest productivity at sites where wet N deposition was about 1.3 kg N/ha/yr; increasing productivity occurred at deposition levels greater than 2.2 kg N/ha/yr (Bergström et al., 2005).

4.3.3.2. Biological Effects

The evidence is sufficient to infer a causal relationship between N deposition and the alteration of species richness, species composition and biodiversity in freshwater aquatic ecosystems (Section 3.3.5.3). Increased N deposition can cause a shift in community composition and reduce algal biodiversity, especially in sensitive oligotrophic lakes.

In the West, a hindcasting exercise determined that the change in Rocky Mountain National Park lake algae that occurred between 1850 and 1964 was associated with an increase in wet N deposition that was only about 1.5 kg N/ha (Baron, 2006). Similar changes inferred from lake sediment cores of the Beartooth Mountains of Wyoming also occurred at about 1.5 kg N/ha deposition (Saros et al., 2003).

Some freshwater algae are particularly sensitive to added nutrient N and experience shifts in community composition and biodiversity with increased N deposition. For example, two species of diatom (a group of algae), *Asterionella formosa* and *Fragilaria crotonensis*, now dominate the flora of at least several alpine and montane Rocky Mountain lakes and sharp increases have occurred in Lake Tahoe (Baron et al., 2000; Interlandi and Kilham, 1998; Saros et al., 2003; Saros et al., 2005; Wolfe et al., 2001a; Wolfe et al., 2003). The timing of this shift has varied, with changes beginning in the 1950s in the southern Rocky Mountains and in the 1970s or later in the central Rocky Mountains. These species are opportunistic algae that have been observed to respond rapidly to disturbance and slight nutrient enrichment in many parts of the world.

Extremely high NO_3^- concentrations can have direct adverse effects on fish, invertebrates and amphibians, but the concentrations required to elicit such effects are typically more than 30 times higher than those that would commonly be attributable to atmospheric deposition. For example, mortality of rainbow trout eggs and fry occurred after 30-day incubations in concentrations greater than 79 µg N/L; adverse effects on amphibians and insects occur at even higher concentrations.

4.3.3.3. Regional Vulnerability and Sensitivity

Eutrophication effects on freshwater ecosystems from atmospheric deposition of N are most likely to occur in lakes and streams that have low productivity, low nutrient levels and that are located in the most undisturbed areas.

- In the western U.S., high-elevation lakes are considered the most sensitive aquatic ecosystems to N deposition. Some examples include the Snowy Range in Wyoming, the Sierra Nevada Mountains, and Lake Tahoe in California, and the Colorado Front Range.

- The most severe eutrophication from N deposition effects are expected downwind of major urban and agricultural centers.

4.3.4. Estuarine Aquatic

The 1993 NO_X AQCD concluded that the primary effect of N enrichment effect on aquatic ecosystems is eutrophication of estuarine and near-coastal marine waters, which results in an increase of algal biomass and changes in community composition. Recent studies generally support and expand upon the conclusions of 1993 NO_X AQCD. The data for estimating the contribution of N deposition to the nutrient budget of aquatic ecosystems were very sparse and mainly limited to the Chesapeake Bay before 1993. The contribution of N deposition to estuarine eutrophication is now better understood in the Chesapeake Bay and other estuaries.

4.3.4.1. Biogeochemical Effects

A recent national assessment of eutrophic conditions in estuaries found that 65% of the assessed systems had moderate to high overall eutrophic conditions and generally received the greatest N loads from all sources, including atmospheric and land-based sources (Bricker et al., 2007). Estuarine and coastal marine ecosystems experience a range of ecological problems associated with nutrient enrichment.

Because the productivity of estuarine and near shore marine ecosystems is generally limited by the availability of N, they are susceptible to eutrophication effect of N deposition.

N Cycling

The evidence is sufficient to infer a causal relationship between N_r deposition and the biogeochemical cycling of N (Section 3.3.2.4). The N load from atmospheric deposition is estimated to comprise 10% to 40% of the total input of N to many coastal estuaries, and could be higher for some. Atmospheric N loads to great waters and estuaries in the U.S. are estimated to range from 2 to 8% for Guadalupe Bay, TX on the lowest end to ~72% for the St. Catherines-Sapelo estuary, GA (Castro et al., 2003) on the highest. At Chesapeake Bay, where N and S deposition and ecological effects have been extensively studied, total atmospheric deposition of atmospheric NO_3 is estimated to contribute from 20% to 30% of total N and 14% of the NH_4 loadings to the Bay.

Estimates of total N loadings to estuaries are computed using measurements of wet and dry N deposition where these are available and interpolated with or without the use of air quality models. Direct atmospheric inputs (directly to the water surface) of Nr to coastal waters are essentially equal to or greater than those contained in riverine flow in the absence of deposition and may contribute from 20 to >50% of N loadings to these systems: 11, 5.6, and 5.6 kg N/ha for the Northeast Atlantic coast of the U.S., the Southeast Atlantic coast of the U.S., and the U.S. Eastern Gulf of Mexico, respectively.

It is unknown if current levels of atmospheric deposition alone are sufficient to cause eutrophication. In general, estuaries tend to be N-limited (Elser et al., 2008), and many currently receive high levels of N input from human activities to cause eutrophication (Howarth et al., 1996; Vitousek and Howarth, 1991). The most widespread chemical indicators of eutrophication are submerged aquatic vegetation, Chl *a*, algal blooms, macroalgae and dissolved O_2.

C Cycling

The evidence is sufficient to infer a causal relationship between N deposition and alteration to the biogeochemical cycling of C (Section 3.3.3.4). Estuaries and coastal waters tend to be N-limited and are therefore inherently sensitive to increased atmospheric N loading (D'Elia et al., 1986; Howarth and Marino, 2006; Elsner et al., 2007). This is at least partly because denitrification by microbes found in estuarine and marine sediments releases much of the added N inputs back into the atmosphere (Vitousek et al., 1997). However, other limiting factors occur in some locations and during some seasons. Levels of N limitations are affected by seasonal patterns. N-limited conditions are likely to be found during the peak of annual productivity in the summer.

Numerous studies evaluate the relationship between N loading, eutrophication and ecological endpoints including Chl *a* concentration, macroalgal abundance, dissolved O_2, nuisance or toxic and algal blooms In the national estuary condition assessment, high Chl *a* concentration was the most widespread documented indicator of eutrophication (Bricker et al., 2007) (see Figure 3-42).

Excess N inputs will affect the Si:N ratio in water. If the Si:N ratio decreases below about 1, the marine food web structure would be expected to change, with decreasing diatom-to-zooplankton-to-higher tropic level ratios and increasing abundance of flagellated algae.

Table 4-3.   Indicators of estuarine eutrophication.

Primary Symptom	Description
Chl *a*	Excess N input will stimulate primary productivity and Chl *a* concentration indicator of phytoplankton biomass
Macroalgal Abundance	Macroalgal blooms were moderate or high for half of the nation's assessed estuaries (Bricker et al., 2007). Macroalgal blooms can cause the loss of important submerged aquatic vegetation by blocking sunlight.
Dissolved O_2	Dissolved O_2 concentration decreases with increasing algal abundance under elevated N, because microbes consume O_2 as they decompose dead algae. Increased atmospheric N deposition could stimulate the development of hypoxic or anoxic zones. The northern Gulf of Mexico is the largest documented zone of hypoxic coastal water in U.S.
Nuisance/Toxic Algal Blooms	Excess N input can cause nuisance or toxic algal blooms, which release toxins in the water that can poison aquatic animals and threaten human health. About one third of the nation's assessed estuary systems exhibited a moderate or high symptom expression for nuisance or toxic algae (Bricker et al., 2007).

Source: Bricker et al. (2007).

4.3.4.2. Biological Effects

The evidence is sufficient to infer a causal relationship between N deposition and the alteration of species richness, species composition and biodiversity in estuarine ecosystems (Section 3.3.5.4). Increased N deposition can cause shifts in community composition, reduced hypolimnetic DO, reduced biodiversity, and mortality of submerged aquatic vegetation. The form of deposited N can significantly affect phytoplankton community composition in estuarine and marine environments. Small diatoms are more efficient in using NO_3^- than NH_4^+. Increasing NH_4^+ deposition relative to NO_3^- in the eastern U.S. favors small diatoms at the expense of large diatoms. This alters the foundation of the food web. Submerged aquatic vegetation is important to the quality of estuarine ecosystem habitats because it provides habitat for a variety of aquatic organisms, absorbs excess nutrients, and traps sediments. Nutrient enrichment is the major driving factor contributing to declines in submerged aquatic vegetation coverage. The Mid-Atlantic region is the most heavily impacted area in terms of moderate or high loss of submerged aquatic vegetation due to eutrophication. Indicators to assess the eutrophic condition of estuarine and coastal waters are given in Table 4-3. Because estuaries receive N from multiple sources, it is unknown if N deposition alone could cause estuary eutrophication.

4.3.4.3. Regional Vulnerability and Sensitivity

The most eutrophic estuaries were generally those that had large watershed-to-estuarine surface area, high human population density, high rainfall and runoff, low dilution, and low flushing rates (Bricker et al., 2007). The national estuary condition assessment conducted by Bricker et al. (2007) found the most eutrophic estuaries occurred in the mid-Atlantic region and the estuaries with the lowest degree of eutrophication were in the North Atlantic. Other regions had mixtures of low, moderate, and high degree of eutrophication. The regional assessment results from the report of Bricker et al. (2007) are summarized in Section 3.3.8.

The Chesapeake Bay is the largest estuary in the U.S. Its watershed covers 64,299 square miles and the surface area of the bay and its major tributaries is 4,479 square miles (Pyzik et al., 2004). The

Chesapeake Bay is perhaps the best-documented case study in the U.S. of the effects of human activities on estuarine eutrophication. Recent studies (Boyer et al., 2002; Howarth, 2007) indicated that atmospheric deposition makes a substantial contribution (about 25%) to the overall N budget of Chesapeake Bay. Human disturbances, such as landscape changes, have exacerbated the negative impacts of N deposition by reducing N removal and retention in the upper watershed region. Anthropogenic N inputs have substantially altered the trophic condition of Chesapeake Bay over the last 50 to 100 years. Signs of eutrophication in the bay include high algal production, low biodiversity, and large hypoxia and anoxia zones. Submerged aquatic vegetation was once abundant in Chesapeake Bay, covering about 200,000 acres along the shallows and shorelines. Increased nutrient inputs caused submerged aquatic vegetation declines since the mid-1960s, and had fallen to about 38,000 acres by 1984. Eutrophication has been implicated in declines and disappearance of striped bass (*Morone saxatilis*) and blue crab (*Callinectes sapidus*) in the Chesapeake Bay.

4.3.5. Ecosystem Services

Some valuation studies assess the effects of N enrichment from multiple sources (see Annex F). There are no publications at this time which focus on the ecosystem services specifically affected by N deposition. The evidence reviewed in this ISA illustrates that N deposition can affect ecosystem services in the following categories (defined by Hassan et al., 2005):

- Supporting: nutrient cycling, biodiversity

- Provisioning: forest yields, fishing yields in estuaries

- Regulating: water quality, air quality, climate regulation (interactions with greenhouse gases CO_2, N_2O, CH_4), fire frequency and intensity, disease resistance

- Cultural: swimming, boating, recreation, biodiversity

4.4. Direct Phytotoxic Effects

4.4.1. Sulfur Dioxide

The evidence is sufficient to infer a causal relationship between exposure to SO_2 and injury to vegetation (Section 3.4.2.1). The current secondary standard for SO_2 is a 3-h average of 0.50 ppm, which is designed to protect against acute foliar injury in vegetation. There has been limited research on acute foliar injury since the 1982 PM-SO_X AQCD and there is no clear evidence of acute foliar injury below the level of the current standard.

Effects on growth and yield of vegetation are associated with increased SO_2 exposure concentration and time of exposure. The 1982 PM-SO_X AQCD concluded that more definitive concentration-response studies were needed before useable exposure metrics could be identified. The few new studies published since the 1982 PM-SO_X AQCD continue to report associations between exposure to SO_2 and reduced vegetation growth. However, most these studies have been performed outside the U.S. and at levels well above ambient concentrations observed in the U.S.

4.4.2. NO, NO$_2$ and PAN

The evidence is sufficient to infer a causal relationship between exposure to NO, NO$_2$ and PAN and injury to vegetation (Section 3.4.2.2). It is well known that in sufficient concentrations, NO, NO$_2$ and PAN can have phytotoxic effects on plants through decreasing photosynthesis and induction of visible foliar injury (U.S. EPA, 1993a). However, the 1993 NO$_X$ AQCD concluded that concentrations of NO, NO$_2$ and PAN in the atmosphere are rarely high enough to have phytotoxic effects on vegetation (U.S. EPA, 1993a). Since the 1993 NO$_X$ AQCD, very little new research has been done on these phytotoxic effects at concentrations currently observed in the U.S.

4.4.3. HNO$_3$

The evidence is sufficient to infer a causal relationship between exposure to HNO$_3$ and changes to vegetation (Section 3.4.2.3). Experimental exposure of HNO$_3$ resulted in damage to the leaf cuticle of pine and oak seedlings, which may predispose those plants to other stressors such as drought, pathogens, and other air pollutants (Bytnerowicz et al., 1998a, b). However, these tree seedling experiments used relatively short-term exposures at concentrations well above current ambient conditions. In lichen studies, several lines of evidence, including transplant and controlled exposure studies, indicate that past and current HNO$_3$ concentrations may be contributing to the decline in lichen species in the Los Angles basin (Boonpragob and Nash, 1991; Nash and Sigal, 1999; Riddell et al., 2008). Current deposition of HNO$_3$ is contributing to N saturation of some ecosystems close to sources of photochemical smog (Fenn et al., 1998) such as the mixed conifer forests of the Los Angeles basin mountain (Bytnerowicz et al., 1999).

4.5. Mercury Methylation

The evidence is sufficient to infer a causal relationship between S deposition and increased methylation of Hg, in aquatic environments where the value of other factors is within adequate range for methylation (Section 3.4.1.4). The main agent of Hg methylation is SO_4^{2-}-reducing-bacteria, and experimental evidence from laboratory to mesocosm scales has established that only inconsequential amounts of MeHg can be produced in the absence of SO_4^{2-}. These experimental results are highly coherent with one another, and with observational studies at larger scales. Changes in the amount of SO_4^{2-} present have been shown to be followed by commensurate changes in MeHg, and mechanistic links have been established between variation in SO_4^{2-} and variation in methylation of Hg.

Quantification of the relationship between SO_4^{2-} and methylation of Hg in natural settings has proved difficult because of the presence of multiple interacting factors in aquatic environments where SO_4^{2-} and Hg are present. The amount of MeHg produced has been shown to vary with O_2 content, temperature, pH, and supply of labile organic carbon. In some watersheds, such as high altitude lakes in the western U.S., where no effect of changes in SO_4^{2-} deposition have been recorded on methylation of Hg. This is because one or several interacting factors were not present in the amounts required for methylation to occur at more than inconsequential rates. Watersheds with conditions known to be conducive to Hg methylation can be found in the northeastern U.S. and southeastern Canada, but significant biotic Hg accumulation has been observed in other regions that have not been studied as extensively, and where a different set of conditions may exist.

Hg is a highly neurotoxic contaminant, and enters the food web in the methylated form. MeHg is then concentrated in higher trophic levels, including fish eaten by humans, with undesirable consequences for affected species, and for populations that consume large amounts of fish. Once MeHg is present, other

variables influence how much of it accumulates in fish. Current evidence indicates that increased S deposition very likely results in MeHg accumulation in fish.

Table 4-4.   Summary of N deposition levels and corresponding ecological effects.

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
U.S.						
Coastal sage scrub	Level = 9.8 to 35 kg N/ha/yr Species = nitrate as HNO_3/NO_3 Measure = referred to Padgett et al. (1999)	60 kg N/ha/yr; as NH_4NO_3 between Jan. and March 1994, 1995, 1996 in two 30 kg N/ha/yr applications	N addition caused a shift in arbuscular mycorrhizal community composition with decreased species richness and diversity promoting a shift from shrub to grasslands	California		Egerton-Warburton and Allen (2000)
Coastal sage scrub	Level = not reported Species = not reported Measure = not reported	50 ml N solution (10 µg/g NH_4NO_3; Or 50 µg/g NO_3^-; Or 50 µg/g NH_4^+) every 2 weeks from March to May, 1997	No evidence that decline in native coastal sage scrub and increase in exotic grass is due to mycorrhizal response to increased NO_3^-	Southern California	*Artemisia californica* (native); *Bromus madritenis spp.* Rubens (exotic)	Yoshida and Allen (2001)
Coastal sage scrub	Level = Up to 30 kg N/ha/yr Species = not reported Measure = referred to Bytnerowicz et al. (1987); Fenn et al. (2003a)	60 kg N/ha/yr; as NH_4NO_3	Soil inoculum from high N deposition site caused native shrub growth depression likely due to mycorrhizal fungi response. Growth of exotic grass may be promoted by soil inoculum from high N deposition site.	Western Riverside County Multispecies Reserve; University of California Riverside Botanical Gardens	*Artemisia californica* (native); *Bromus madritenis* spp. Rubens (exotic)	Siguenza et al. (2006)
Desert	Level = 30 kg N/ha/yr Species = not reported Measure = referred to Bytnerowicz et al. 1987	Two additions of 16 kg N/ha/yr, one as NH_4NO_3 and one as an NPK treatment	N addition increased biomass of non-native plants by ~54%, decreased native species biomass by about ~39%	Mojave desert	Creosote bush (*Larrea tridentate*), invasive grasses *Bromus madritensis* spp. Rubens, and *Schismus* spp.; and the forb *Erodium cicutarium*	Brooks (2003)

---

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

[2] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Desert	Level = 1.71 to 2.45 kg N/ha/yr Species = NH_4NO_3; Measure = field study for 16 years with network of six funnel precipitation collectors	Long term experiment: 100 kg N/ha/yr as granular NH_4NO_3 to 10 plots 2x/year since Dec. 1995; Single season experiment: 20 kg N/ha/yr to 40 plots once	Long term: increased the cover of warm season grasses and decreased the cover of legumes; Short term: increased N lead to significant plant community structure change, especially in blue and black grama grassland patch types	Chihuahuan Desert	Blue and black grama (*Bouteloua gracilis* and *Bouteloua eropoda*, respectively)	Baez et al. (2007)
Forest (sub-alpine)	Level = 3.6 and 3.5 kg N/ha/yr on east slope; 1.1 kg N/ha/yr on west slope Species = not reported Measure = referred to Williams et al. (1998); NADP 1999; Stottlemyer et al. (1997)	No addition	Compared to west side, east side had lower C:N, lignin:N, and higher N:Mg, N:P, foliar [N], soil [N], N mineralization rates and lake water [NO_3].	Eastern vs. Western slope of Continental Divide in Rocky Mountains.	Englemann spruce-subalpine fir forests	Baron et al. (2000)
Forest (sub-alpine)	Level = 1-2 kg N/ha/yr on west slope; 3-5kg N/ha/yr on east slope Species = not reported Measure = unspecified	No addition	East side had decreased soil organic horizon C:N and foliar C:N, and increased foliar N concentration, foliar N:Mg, foliar N:P and potential net mineralization; Englemann spruce forest biogeochemistry altered	Eastern vs. Western slope of Continental Divide in Rocky Mountains.	Englemann spruce	Rueth and Baron (2002)
Forest	Level = 1.2 to 23 kg N/ha/yr-dry dep and 0.8 to 45 kg N/ha/yr-wet dep Species = NO_3^- and NH_4^+ Measure = various citations	No addition	N saturation observed at 25–45 kg N/ha/yr of total inorganic N deposition. Where N saturation occurred, high NO_3^- concentrations in streamwater, soil, leaves; high NO emissions; high foliar N:P.	California-Los Angeles Air Basin		Bytnerowicz and Fenn (1996)

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Forest (coniferous)	Level = 2 study sites: CP = 18.8 kg N/ha/yr BF= 2.9 kg N/ha/yr Species = NO_3^- and NH_4^+ Measure = throughfall and fog water	No addition	Site nearest to urban area (Los Angeles) received much more N deposition, as well as other pollutants (i.e. S deposition), and received much more fog, coinciding with much more wet deposition of N in that site Ecosystem was N saturated, as evidenced by high streamwater NO_3^- concentration, 151 and 65 µeq/L at upper and lower ends, respectively, of Devil Canyon West Fork	San Bernardino Mountains, California	Coniferous forest	Fenn et al. (2000)
Forest (mixed-chaparral, hardwood, coniferous)	Level = 11 to 40 kg N/ha/yr Species = NO_3^- and NH_4^+ Measure = throughfall (Fenn, 2002a)	No addition	DIN export was scale dependent, with highest export occurring in watersheds of ~150–ha. Differences attributed to temporal asynchrony between N availability and biological demand	San Bernardino Mountains, CA	Mixed forest- chaparral, hardwood, coniferous	Meixner and Fenn (2004)
Forest (coniferous)	Level = 8 kg N/ha/yr and 82 kg N/ha/yr Species = not reported Measure = referred to Fenn et al. (2002a)	0, 50, 150 kg N/ha/yr annually from 1996 to 2002	Tree mortality was 9% higher and beetle activity 50 % higher for unfertilized trees at the high deposition site compared to the low pollution site. Tree mortality and beetle activity increased 8% and 20%, respectively under highest N fertilization rates at the low deposition site	San Bernardino Mountains, CA	Ponderosa pine	Jones et al. (2004)

---

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Forest (chaparral)	Level = 35 kg N/ha/yr Species = not reported Measure = taking mean of two methods (estimation methods using data in situ and published data; NADP)	No addition	Continued high export (~3 kg N/ha/yr) of NO_3^- in stream water (15 year) after prescribed burn indicates that chaparral ecosystem did not recover N-retention capabilities after disturbance	San Dimas Experimental Forest (40 km NW of LA), San Gabriel Mountains, CA	Chamise (*Adenostoma fasiculatum*), *Ceanothus spp.*, live oak (*Quercus agrifolia*)	Meixner et al. (2006)
Forest (conifer)	Level = 1.2 to 71.1 kg N/ha/yr Species = NO_3^- and NH_4^+ Measure = throughfall (Fenn and Poth, 2004)	No addition	Empirical critical load for adverse impacts on lichen at 3.1 kg N/ha.yr. Enhanced NO_3^- leaching calculated with N deposition above 17 kg N/ha/yr. Lowered litter C:N and increases foliar N also observed at highly polluted sites.	California mixed conifer forests	Lichens, Ponderosa pine	Fenn et al. (2008)
Forest	Level = 20 to 35 kg N/ha/yr Species = NO_3^- Measure = field studies and NuCM, a nutrient cycling model (Fenn et al., 1996)	No addition	Areas with higher deposition had increased NO_3^- leaching, increased soil acidity, and decreased base cation saturation.	Southern California		Fenn et al. (2003)
Forest	Level = 3.2 to 5.5 kg N/ha/yr Species = not reported Measure = data from Loch Vale, a NADP/NTN monitoring station and Campbell et al. (2000)	25 kg N/ha/yr of NH_4NO_3	N addition increased N concentration in foliar and organic soil horizon	Fraser Experimental Forest, Colorado	Spruce	Rueth et al. (2003)
Forest	Level = 1.7 kg N/ha/yr Species = not reported Measure = referred to Stottlemyer and Troendle 1992, Stottlemyer et al. 1997	25 kg N/ha/yr of NH_4NO_3	N addition doubled N mineralization rates and stimulated nitrification	Loch Vale watershed, Colorado	Old-growth spruce	Rueth et al. (2003)

---

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

[2] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Forest (alpine)	Level = 50 kg N/ha/yr Measure =referred to Sievering et al. (1996); Theodose and Bowman (1997); Fisk et al. (1998)	200 kg N/ha/yr in 1993 and 1994; No fertilizer in 1995; 100 kg N/ha/yr as $(NH_4)_2SO_4$ in 1996 and 1997 Nutrient amendments consisted of a mixture a mixture of $(NH_4)_2)NO_3$ and $(NH_4)_2SO_4$ for the N plots	N deposition increased plant foliage productivity but reduced species richness. The reduction of species is best explained by changes in soil chemistry that resulted directly or indirectly from N additions	Niwot Ridge, Colorado	Alpine tundra: sedge *Kobresia myosuroides. Acomastylis rossii, Polygonum viviparurn Trifolium*. More mesic tundra-*A. rossii* and *Deschumnpsia caespitosa*. Snow bed-*D.caespitosa*, *Sibbaldia rocurnbens*, *Rifolium parryi*	Seastedt and Vaccaro (2001)
Forest	Level = 11.5 to 25.4 kg N/ha/yr Species = NO_3^- and NH_4^+ Measure = 16 IMPROVE monitoring sites and 11 NADP/NTN wet dep. sites	No addition	Concentrations of N in lichen thallus were highest at eastern and westernmost sites where N deposition was highest, implicating both agricultural (east) and urban (west) sources;	Columbia River Gorge, OR/WA	Lichens	Fenn at al. (2007).
Forest (maple-dominated hardwood)	Level = 5 to 8 kg N/ha/yr Species = not reported Measure = NADP 2006	30 kg N/ha/yr as $NaNO_3$	Arbuscular mycorrhizal fungal biomass, storage structures and lipid storage declined in response to N addition	Northern Michigan	Maple-dominated hardwood- Sugar maple (*Acer saccharum*)	van Diepen et al. (2007)
Forest	Level = 3.3 to 12.7 kg N/ha/yr Species = not reported Measure = at NERC, 29 Jan 2003, compiled data sets and used them in stats model by Ollinger et al., 1993, or used published values	No addition	At deposition levels above approximately 7–10 kg N/ha/yr, stream NO_3^- concentration increase with increasing deposition Soil C:N and nitrification flux increased with N deposition N deposition did not alter foliar chemistry	Northeastern U.S.		Aber et al. (2003)
Forest	Level = 5.4 kg N/ha/yr Species = not reported Measure = McNulty and Aber (1993)	15.7 to 31.4 kg N/ha/yr as NH_4Cl-N or $NaNO_3^-$N	Forest trees in plots receiving <20 kg N/ha/yr had high rate of growth initially followed by a decline, and forests trees in plots receiving >25 kg N/ha/yr showed moderate rates of decline.	Vermont	Red spruce	McNulty et al. (1996)

---

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Forest (herbaceous layer)	Level = 7 kg N/ha/yr Species = not reported Measure = Shepard et al. (1989)	14 and 28 kg N/ha/yr as crystalline $(NH_4)_2SO_4$	N addition decreased herbaceous cover under hardwoods	Adirondack Park, New York	Mixed hardwood – American beech, sugar maple, and yellow birch	Hurd et al. (1998).
Forest (ectomycorrhiza)	Level = 3.5–7.8 kg N/ha/yr in wet N deposition Species = not reported Measure = NADP data	Greenhouse study: 3 rates of N applications (0, 35, 140 kg N/ha).	Ectomycorrhizal abundance and richness declined along increasing N deposition transect under pitch pine. The decline in richness was significantly correlated with the N deposition rate. In greenhouse study, pine seedling biomass was inversely related to N addition.	New Jersey Pine Barrens	Pitch pine	Dighton et al. (2004).
Forest	Level = Wet plus dry deposition 600 eq ha/yr for N and 900 equiv./ha/yr for S Species: not reported Measure =Kahl et al. (1999)	25.2 kg N/ha for 10 years.	After 10 years of treatment, basal area increment of sugar maple was enhanced 13 to 104%, whereas red spruce was not significantly affected. The increase in sugar maple radial growth was attributed to a fertilization effect from the $(NH_4)_2SO_4$ treatment	Bear Brook, Maine	Sugar maple; red spruce	Elvir et al. (2003)
Forest	Level = 17 kg N/ha/yr Species = not reported Measure = referred to Adams et al. (1993)	35.5 kg N/ha/yr and 40.5 kg S/ha/yr fertilized annually $(NH_4)_2SO_4$ (17 years)	N addition enhanced growth of black cherry and yellow poplar during the first 7 years, but reduced growth of these species in years 9 to 12, with no change in red maple or sweet birch	Fernow Experimental Forest, West Virginia	Mixed hardwood- red oak, red maple, tulip poplar, black cherry, sweet birch	DeWalle et al. (2006)

---

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Forest (mixed hardwood)	Level = 17 kg N/ha/yr Species = not reported Measure = referred to Adams et al. (1993)	35 kg N/ha/yr $(NH_4)_2SO_4$ (16 years)	Possible declining growth vigor in red maple, and to lesser extent black cherry and tulip poplar. Observed interspecific differences in growth and plant nutrition responses suggest eventual changes in species composition under increasing N saturation.	Fernow Experimental Forest, West Virginia	Mixed hardwood- red oak, red maple, tulip poplar, black cherry, sweet birch	May et al. (2005)
Forest (mixed hardwood)	Level = 17 kg N/ha/yr Species = not reported Measure = referred to Adams et al. (1993)	35 kg N/ha/yr $(NH_4)_2SO_4$ (12 years)	N addition altered response of N-processing microbes to environmental factors, becoming less sensitive to seasonal changes in soil moisture and temperature	Fernow ExperimentalExperimental Forest, West Virginia	Mixed hardwood- red oak, red maple, tulip poplar, black cherry, sweet birch	Gilliam et al. (2001).
Forest (herbaceous layer)	Level = 17 kg N/ha/yr Species = not reported Measure = referred to Adams et al. (1993)	35 kg N/ha/yr $(NH_4)_2SO_4$ (4 years)	Increased foliar N in over-story tree species and *Viola rotundifolia* and decreased foliar Ca^{2+} and Mg^{2+}, in response to 4 years of treatment. Nitrification rates were equally high in soils of all watersheds; Results support earlier studies that high amounts of ambient N deposition brought about N saturation on untreated watersheds at the Fernow Experimental Forest	Fernow Experimental Forest, West Virginia	*Viola rotundifolia Michx*	Gilliam et al. (1996)

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Forest (herbaceous layer)	Level = 17 kg N/ha/yr Species = not reported Measure = referred to Adams et al. (1993)	35 kg N/ha/yr $(NH_4)_2SO_4$ (6 years)	no significant impact on the herbaceous layer under hardwoods	Fernow Experimental Forest, West Virginia	Mixed hardwood	Gilliam et al. (2006b)
Forest	Level = 6.6 to 8 kg N/ha/yr Measure = regional extrapolation from NADP sites. Ollinger et al. (1993); and estimates from Munger et al. (1996).	50 and 150kg N/ha/yr for 15 years	Mortality of red pine reached 56% in 15 years in the pine high N plot, and biomass accumulation has stopped altogether. The high N hardwood stand shows increased above-ground NPP, but excess N availability and a severe drought in 1995 contributed to mortality of 72% of red maple trees by 2002. Species importance and litterfall patterns were altered in several plots after 1995. Roots, foliage and wood have diminished as net sinks for added N, re-emphasizing the role of soils in N retention. DIN was not detected in soil water of high N hardwood plot until the 15th year. Losses of inorganic N remain high in the high N plots (higher in pines than hardwoods) and low N plots in the pine stand also have measurable DIN losses. Foliar and fine root N concentrations are elevated significantly	Harvard Forest	Red pine *(Pinus resinosa Ait.)*, black and red oak (*Quercus velutina Q. rubra*) black birch (*Betula lenta*), red maple (*Acer rubrum*), American beech (*Fagus grandifolia*) and black cherry (*Prunus serotina*)	Magill et al. (2004)

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Forest (herbaceous layer)	Level = 6.6 to 8 kg N/ha/yr Measure = regional extrapolation from NADP sites. Ollinger et al. (1993); and estimates from Munger et al. (1996).	50 and 150kg N/ha/yr	Following 7 years of N additions, density and biomass of herb layer species had declined by 80% and 90%	Harvard Forest	Understory of red pine	Rainey et al. (1999)
Forest (mixed hardwood and coniferous)	Level = 6.6 to 8 kg N/ha/yr Measure = regional extrapolation from NADP sites. Ollinger et al. (1993); and estimates from Munger et al. (1996).	50 and 150kg N/ha/yr.	Wood production increased (hardwood) and decreased (coniferous) Foliar N increased 25% (hardwood) and 67% (coniferous); NO_3^- leaching increased continuously over 6–year study in coniferous forest, but was unchanged in hardwood forest, most (85–99%) of added N was retained, primarily in recalcitrant soil pool. Of the retained N, 50–83% appears to be in the long-term, recalcitrant soil pool.	Harvard Forest	Red pine (*Pinus resinosa Ait.*) stand and mixed hardwood stand	Magill et al. (1997).

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Oak savanna	Level=5.3 kg N/ha/yr Species = not reported Measure = NADP 2003	54 , and 170 kg N/ha/yr (16–yr addition of NH_4NO_3)	N addition decreased total ectomycorrhizal fungal diversity by 50% and changed species composition.	Minnesota	Native oak savannah: bur oak (*Quercus macrocarpa Michaux*) and pin oak (*Q.ellipsoidalis E.J. Hill*), ectomycorrhizal fungi	Avis et al. (2003)
Grassland	Level = 6 kg N/ha/yr Species = 58% NH_4, 42% NO_3 Measure = CASTN35 for total inorganic (wet plus dry) N deposition; local wet deposition from the on-site NADP monitoring station	10, 20, 34, 54 or 95 kg N/ha/yr at 3,5,5,7, and 9 years respectively from 1982 to 2004	Reduced relative number of species at every deposition level. Species numbers were reduced more per unit of added N at lower addition rates, suggesting that chronic but low-level N deposition may have a greater impact on diversity than previously thought. Chronic (23 year) N addition (10 kg N/ha/yr) reduced plant species numbers by 17% relative to controls receiving ambient. Critical load calculated at 5.3 kg N/ha/yr with an inverse prediction interval of 1.3–9.8 kg N/ha/yr	Cedar Creek Biological Station, Minnesota	Species = rich mixture of native C_4 grasses and forbs (full list at http://www.cedarcreek.umn.edu/)	Clark and Tilman (2008)
Grassland	Level = not reported Species = not reported Measure = not reported	0, 54.4, and 272 kg N/ha/yr NH_4NO_3 added twice a yr for 18 years	Most of the forbs were lost from the high N plots, and two grass species, *P. pratensis* and *A. repens*, dominated. Loss of plant diversity in areas of high N. N addition changed composition of soil microbial community; increased bacterial and decreased fungal fatty acid methyl ester activity	Cedar Ck, LTER, Minnesota	*P. pratensis, A. repens, and Schizachyrium scoparium*	Bradley et al. (2006)

---

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Grassland	Level = 10–15 kg N/ha/yr in San Jose grasslands; 4–6 kg N/ha/yr at peninsula sites Species = not reported Measure = referred to Blanchard et al., (1996)	No addition	Dry N deposition from smog contributes to grass invasion. Soil N limits grass invasion on serpentinitic solids. Grazing cattle select grasses over forbs, and grazing lead to a net export of N as cattle are removed for slaughter. Decreased populations of the bay checkerspot butterfly due to invasion of grasses after cattle grazing.	San Francisco Bay area, California	Bay checkerspot butterfly/ serpentinitic grasslands	Weiss (1999)
Grassland	Level = 10–15 kg N/ha/yr Species = not reported Measure =referred to Weiss 1999	No addition	N deposition displaced native grass species by exotic nitrophilous grasses. Low levels of soil N normally limit grass invasion in serpentinitic soils, but in ungrazed areas with experimental N fertilization or high N deposition, the introduced grasses crowd out many native species.	San Francisco Bay area, California	Serpentinitic grasslands	Fenn et al. (2003).
Grassland	Level = not reported Species = not reported Measure = not reported	70 kg N/ha/yr divided into a liquid $Ca(NO_3)_2$ pulse with the first autumn rains and a time-release pellet application (Osmocote) in January of each yr for 3 years.	After three years, N addition suppressed plant diversity, forb production, and forb abundance in association with enhanced grass production	Jasper Ridge Biological Preserve, California	*Avena barbata*, *Bromushordeaceus*, *Lolium multiflorum*, *Avena fatua*, and *Bromus diandrus, Anagallis arvensis, Geranium dissectum, Erodium botrys, Vicia sativa, Crepis vesicaria*	Zavaleta et al. (2003).

---

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Grassland (alpine)	Level =6 kg N/ha/yr Species = not reported Measure = not reported	20, 40, 60 kg N/ha/yr for 8 years	N deposition caused changes of plant species composition within 3 years of the initiation of the experiment and were significant at all levels of N addition. Changes in net nitrification were detectable at levels above 20 kg N/ha/yr. N addition increased NO_3^- leaching and NO_3^- concentration in soil water. Changes in the plant community, based on the first axis of a detrended correspondence analysis, were estimated to occur at deposition levels near 10 kg N/ha/yr.	Colorado Front Range	Alpine dry meadows dominated by the sedge *Kobresia myosuroides*, with a mix of perennial forbs, sedges, and grasses making up the remainder of the community.	Bowman et al. (2006)
Grassland	Level = 5 kg N/ha/yr Measure =referred to Sievering et al. (1996); Theodose and Bowman (1997); Fisk et al. (1998)	200 kg N/ha/yr In 1993 and 1994; No fertilizer in 1995; 100 kg N/ha/yr as $(NH_4)_2SO_4$ in 1996 and 1997; As a mixture of NH_4NO_3 and $(NH_4)_2SO_4$	Increased plant biomass and tissue N concentration	Niwot Ridge, Colorado	Alpine tundra: sedge *Kobresia myosuroides. Acomastylis rossii, Polygonum viviparurn Trifolium*. More mesic tundra-*A.* Rossii and *Deschumnpsia caespitosa*. Snow bed-D. casepitosa, *Sibbaldia procurnbens*, *Trifolium parryi*	Seastedt and Vaccaro (2001)
Grassland	Level = not reported Species = not reported Measure = not reported	0, 10, 40, 70, and 100 kg N/ha/yr for 75 days	N addition increased growth. Native species gained more height at every level of N availability compared to exotics	Greenhouse study	Two N. American natives (Blue grama, western wheatgrass), and Four exotics, (cheatgrass, leafy spurge, Canada thistle, Russian knapweed)	Lowe et al. (2002)

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Grassland	Level = 5 kg N/ha/yr Measure =referred to Sievering et al. (1996) Theodose and Bowman (1997); Fisk et al. (1998)	25 kg N/ha/yr with biweekly additions of 2 g of NH_4NO_3 dissolved in deionized water for 2 years	N addition caused a community shift towards greater dominance of hairgrass in wet alpine meadows.	Niwot Ridge, Colorado	Alpine tundra: sedge Kobresia myosuroides. *Acomastylis rossii, Polygonum viviparurn Trifolium.* More mesic tundra-*A.* *Rossii* and *Deschumnpsia caespitosa.* Snow bed-*D.caespitosa, Sibbaldia procurnbens,* Trifolium	Bowman et al. (1995); Burns, (2004).
Lake (alpine)		No addition	By analysis of a lake sediment cores for a 400 year time interval, the study shows a typical alpine lake diatom flora, consisting mainly of small *Fragilaria sensu* lato species, dominated until approximately 1995, at which time *Fragilaria crotonensis* and *Cyclotella bodanica var. lemanica* rapidly increased to 30% each of the total assemblage. The shifts appear indicative of both increased N loading to these systems as well as changes in thermal stratification patterns	Beartooth Lake, Minnesota	Diatoms: *Fragilaria sensu* lato, *Fragilaria crotonensis, Cyclotella bodanica var. lemanica*	Saros et al. (2003)
Lake (alpine)	Deposition values back to 1900 (0.5 kg N/ha/yr) were calculated using 19 years (1984-2003) of measured values from Loch Vale (Colorado, USA; NADP site CO98)	No addition	The mean wet N-deposition values of 1.5 kg N/ha/yr (1950-1964) corresponded with the alteration of diatom assemblages attributed to N deposition in alpine lakes in Rocky Mountain National Park. This value becomes the critical load defining the threshold for ecological change from eutrophication.	Loch Vale, Colorado	Diatoms	Baron (2006)

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Lake	Level= 2.5 - 3.5 kg N/ha/yr at elevations greater than 2,500m; <2.5 kg N/ha/yr at elevations less than 2,500m Measure= NADP sites in the five-state (WY, CO, UT, AZ and NM) region of the intermountain West for the period 1992-1996 Species=not reported	No addition	The deposition of inorganic N in wetfall increased at the rate of 0.32 kg N/ha/yr from 1984 to 1997 at the Niwot Ridge NADP site; Annual loading of NO_3^- increased with elevation; Current level of N deposition in wetfall decreased surface water pH and ANC, and resulted in episodic acidifycation and NO_3^- leakage.	Green Lakes Valley of the Colorado Front Range		Williams and Tonnessen (2000)
Lake	Level = 2 kg N/ha/yr Measure = NAPD site from 1981 through 1996	N additions in semi-continuous laboratory bioassays of mixed diatom assemblages,	Increasing N shifted diatom species in alpine lakes.	Rocky Mountain , Colorado	Diatoms:Stephanodiscus *minutulus*, *Stephunodiscus niugarue*, and *Cyclotella bodanica*.	Interlandi and Kilham (1998)
Surface waters	Level = 8–10 kg N/ha/yr Measure = NADP from 1982 to 1994	No addition	Chronic N deposition resulted in increased N leaching.	Eastern U.S./ New England and Adirondack lakes		Stoddard (1994)
Surface waters	Level = 4.71 kg N/ha/yr –200% increase in NO_3^- loading from wet deposition over the prior decade, increasing from 8 kg N/ha/yr for 1985–1987 to 16.5 kg N/ha/yr 1990-1992 Species= not reported Measure = NADP	No addition	A shift in from an N-limited system to an N-saturated system. Many lakes having (NO_3^-) concentrations greater than 10 íequiv/L. Increasing atmospheric deposition of N with elevation is causing a change from N limitation to P limitation in the highest-elevation bristlecone pines	Niwot Ridge/Green Lakes, Colorado Front Range		Williams et al. (1996)
Wetland (freshwater)	Level = 10 to14 kg N/ha/yr	Hawley Bog: 2 treatments of 0.1 or 1.0 mg NH_4-N/L every 2 weeks between June 1 and Sept 30 for 1998, 1999, and 2000	Negative population growth rate of pitcher plant	Hawley Bog (MA) Molly Bog (VA)	*Sarracenia purpurea*	Gotelli and Ellison (2002; 2006)

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Coastal-Marine		Discontinuously diluted N limited cultures, which were pulsed with NO_3^- every 3 days;	Large diatoms became dominant when nitrate was supplied as the only N source once in 3 days. Sinking rate of the nitrate grown population was higher (0.12 m/day) than that of the ammonium grown population (0 m/day).		Marine phytoplankton	Stolte et al. (1994)
Variable	Variable	60–120 kg N/ha/yr variable range across 23 different experiments	Soil CEC and temperature were the strongest contributors to multivariable explanation of species richness response to experimental N addition in 23 studies throughout the U.S. Greater plant species loss was associated with lower soil CEC, colder temperature and larger production increases	Variable	Variable	Clark et al. (2007)

CHINA AND EUROPE

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Forest	Level = 3 kg N/ha/yr Species = not reported Measure = not reported	30 years of annual additions of NH_4NO_3 in 3 treatments: N1 and N_2 (34 and 68 kg N/ha/yr) and 20 years of N3 (108 kg N/ha/yr), plus a control	Stimulate stemwood production in all levels of N addition until 7 years into experiment; thereafter the second and third treatments (with medium and high N addition) decreesed stemwood production and the first treatment (the lowest amount of N addition) continued to increase stemwood production throughout experiment	Northern Sweden	Scots pine	Högberg et al. (2006)
Forest (boreal)	Level = 3–12 kg N/ha/yr Species = not reported Measure = MATCH model of N-deposition for 1996; surveys in permanent plots in the National Forest Inventory	No addition	N deposition decreased the abundance and cover of ericaceous shrubs	Sweden	Vaccinium species (*Ericaceae*)	Strengbom et al. (2003)

---

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Forest	Level= not reported Species= not reported Measure=not reported	22 years of annual additions of NH_4NO_3 in four treatments: N0 (control); N1 (30-60 kg N/ha/yr), N2 (60-120 kg N/ha/yr) and N3 (90-180 kg N/ha/yr)	The early increase in growth rates was reduced at the highest N level and partly also at the middle level. N retention in ecosystem was high at the lowest level of N addition, while considerable N lost from the sites at higher levels, indicating N saturation.	North Sweden	Scot pine	Tamm et al. (1995)
Forest	Level: wet deposition from 1965-1990: <u>Norrliden</u> (S:5.5-7.2kg S/ha/yr; NH_4-N: 1.3-1.9 kg N/ha/yr; NH_3-N: 1.6-2.2 kg/ha/yr) <u>Lisselbo</u> (S:5.2-6.7kg S/ha/yr; NH_4-N: 1.2-1.9 kg N/ha/yr; NH_3-N: 1.4-1.9 kg/ha/yr) Species: S, NH_4 and NH_3 Measure=not reported	Norrliden: 60-120kg N/ha/yr from 1971 to 1988 Lisseblo: 40-120kg N/ha/yr from 1969 to 1988	N normally is a growth-limiting factor in boreal forest, but regular N additions can induce boron and magnesium deficiency, and low internal concentrations in the trees, e.g., of potassium and phosphorus.	Norrliden in northern Sweden and Lisselbo in southern Sweden	Scot pine	Tamm et al. (1999)
Lake	Wet DIN = 1.3–11 kg N/ha/yr Total N = 1–4 and 9–18 kg N/ha/yr Species = wet DIN and total N Measure = SEPAs use of MATCH model	No addition	Increased lake concentrations of inorganic N caused P limitation in summer and increased eutrophication with increased lake algal productivity	Sweden		Bergström et al. (2005)
Wetland	Level = 0.2 – 0.3 g $N/m^2/a$ (2 – 3 kg N/ha/yr) Species = NH_4^+ and NO_3^- Measure = refers to Ruoho-Airola et al. 1998	Cumulative addition of 3 g $N/m^2/a$ (30 kg N/ha/yr) as NH_4NO_3 on six occasions during growing season	Increased NH_4NO_3 affected comp. of moss layer, specifically decreasing *Sphagnum balticum*, and caused decrease in litter and an increase of a Vaccinium species	Eastern Finland	*Sphagnum sp.*, *Eriophorum vaginatum*, *Carex pauciflora*, *Vaccinium oxycoccos*, *Scheuchzeria palustris*	Saarnio et al. (2003)

---

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Type of Ecosystem	Ambient N Deposition (kg N/ha/yr)[1]	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Wetland	Level = not reported Species = not reported Measure = not reported	240 kg N/ha/yr as NH_4NO_3 applied in field experiment where 3 of 6 plots received treatment every 2 weeks for 2 years	N addition increased above ground biomass and abundance of *Deyeucia angustifolia*, stimulated CO_2 and CH_4, and N_2O emissions from *D. angustifolia* wetlands. N_2O emissions significantly influenced by N addition.	Northeast China	*Deyeucia angustifolia*	Zhang et al. (2007)
Wetland	Level = 2 to 20 kg N/ha/yr Species = not reported Measure = national precipitation monitoring programs of each country and refer to the 3 years prior to peat sampling in experiment	No addition	Decomposition rates for material accumulated under higher atmospheric N supplies resulted in higher CO_2 emissions and dissolved organic carbon release	Nine European countries	Species like Sphagnum	Bragazza et al. (2006)

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

---

[1] Ambient N deposition information is divided into three categories: Level = deposition rate; Species = chemical species of N that were measured; Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Annex A. Ecosystem Monitoring and Models

A.1. Introduction

A tremendous amount of research has been conducted in the U.S., and elsewhere, over the past three decades on the ways in which atmospheric deposition of sulfur (S) and nitrogen (N) affect the health, condition, and vitality of aquatic, transitional, and terrestrial ecosystems. Much of this work has focused on developing a better understanding of acidification and nutrient enrichment processes. Some of this work has been highly quantitative allowing researchers to determine key process rates in multiple ecosystem compartments. Nevertheless, quantification of overall ecosystem response requires a higher level of process rate aggregation. It is important to develop quantitative understanding of the extent of past ecosystem effects in response to atmospheric S and N deposition, the extent to which conditions will worsen or recover under continued or reduced deposition levels, and the sustained loads of deposition that would be required to prevent further ecosystem damage and to allow damaged ecosystems to recover. This kind of quantitative understanding cannot evolve directly out of process-based research. It requires development of mathematical models that encode process knowledge and link it in such a way as to pro-duce quantitative estimates of change in resource conditions over time in response to changes in the major forcing functions, including atmospheric deposition, climate, and landscape disturbance. As described in this Annex, many such models have been developed and used to estimate past and future changes in ecosystem condition. Such models cannot be validated, per se, because environmental systems are never closed and because important processes yield conflicting, often opposing, results. Therefore, a model can produce the right answer for the wrong reason (Oreskes et al., 1994). Similarly, a particular process may not be important at a particular site where a model is tested, but assume much greater importance elsewhere. For these reasons, it is critical that environmental models be tested and confirmed at multiple locations that exhibit differing conditions and pollutant loads before they are used as the foundation for public policy (Sullivan, 2000a).

Some of the best data with which to test and confirm environmental models are derived from long-term monitoring sites. These are locations where one or more attributes of a natural ecosystem compartment (i.e., surface water, soil, plants) is periodically sampled and analyzed over a long period of time. Such data are often especially valuable for sites, which experience rather large changes in one of the forcing functions (often atmospheric deposition). This enables evaluation of the extent to which the model accurately captures the dynamics of ecosystem response(s) that occur. Because many environmental attributes undergo rather substantial intra- and inter-annual variability in response to climatic variation and other changes, a long period of record is required before a monitoring data set can be used for evaluation of ecosystem response or for model confirmation.

Long-term monitoring data provide not only data with which to test model projections, but also a reality check on scientific understanding of damage and recovery processes. If observed (monitored) changes are not in agreement with process understanding, it is possible or perhaps likely that one or more key processes is not well understood or well formulated in the model.

This Annex summarizes the primary long-term monitoring sites and programs in the U.S., and the principal mathematical models used to simulate environmental responses to atmospheric S and N deposition. Quantitative data derived from the model projections and from trends analyses of the monitoring data provide an important part of the foundation for evaluating the past, current, and future effects of S and N deposition, and expected recovery as emissions levels decrease in the future.

A.2. Ecosystem Monitoring

The effects of acidic and N nutrient deposition on ecosystems require long-term study. Changes in ecosystems often occur gradually, and sustained monitoring of key variables provides the principal record of change over time. Monitoring data are also useful for establishing a baseline of resource conditions and determining if short-term events were unusual or extreme (Lovett et al., 2007). There are limited monitoring programs and data to document ecosystem responses to changes in atmospheric deposition in the past. It is often difficult to sustain funding for ecosystem monitoring, perhaps because results are produced slowly and because results are seldom viewed as novel. Nevertheless, monitoring data provide some of the best means for evaluating the completeness of the scientific knowledge base and for testing how robust our projections of future conditions might be. This section describes some of the more important and useful monitoring programs for evaluating the effects of N and S deposition on ecosystems in the U.S.

There are long-term monitoring sites scattered throughout the U.S. where samples are periodically collected and analyzed to determine the condition of aquatic, transitional, or terrestrial ecosystem elements. Some have been in operation for only a short period of time; others have continued for decades. None extend back far enough to have documented resource conditions before the advent of high levels of atmospheric S and N deposition. Some of the monitoring sites exist as an individual entity, or small collection of sites, often established primarily for research purposes. Despite the research focus, many of these long-term research sites include collection of monitoring data. Other long-term monitoring sites exist as part of large regional programs with a specific focus on long-term monitoring. The most significant individual monitoring sites and networks are discussed below.

Lovett et al. (2007) reviewed the characteristics of successful environmental monitoring programs, and argued that monitoring is a fundamental part of environmental science and policy. Their analysis underscored the fact that environmental monitoring costs little relative to the value of the resources that it protects and the policy that it informs. Monitoring data also have substantial added value because they can be used for multiple purposes, including various research objectives.

Ecosystems also require long-term study because most changes occur slowly. When more rapid change does occur, for example in response to an extreme event, a long-term record is needed to put the effects of the extreme event into proper context.

A.2.1. Environmental Monitoring and Assessment Program

The EMAP began regional surveys of the nation's surface waters in 1991 with a survey of northeastern U.S. lakes. Since then, EMAP and Regional-EMAP (REMAP) surveys have been conducted on lakes and streams throughout the country. The objective of these EMAP surveys is to characterize ecological condition across populations of surface waters. EMAP surveys are probability surveys where sites are picked using a spatially balanced systematic randomized sample so that the results can be used to make estimates of regional extent of condition (e.g., number of lakes, length of stream). EMAP sampling typically consists of measures of aquatic biota (fish, macroinvertebrates, zooplankton, and periphyton), water chemistry, and physical habitat.

Of particular interest with respect to acidic deposition effects were two EMAP surveys conducted in the 1990s, the Northeastern Lake Survey and the Mid-Atlantic Highlands Assessment of streams (MAHA). The Northeastern Lake Survey was conducted in summer from 1991 to 1994 and consisted of 345 randomly selected lakes in the states of New York, New Jersey, Vermont, New Hampshire, Maine, Rhode Island, Connecticut, and Massachusetts (Whittier et al., 2002). To make more precise estimates of the effects of acidic deposition, the sampling grid was intensified to increase the sample site density in the Adirondacks and New England Uplands areas known to be susceptible to acidic deposition. The MAHA study was conducted on 503 stream sites from 1993 to 1995 in the states of West Virginia, Virginia,

Pennsylvania, Maryland, Delaware, and the Catskill Mountain region of New York (Herlihy et al., 2000). Sampling was done during spring baseflow. Sample sites were restricted to first through third order streams as depicted on the U.S. Geological Survey (USGS) 1:100,000 digital maps used in site selection. To make more precise estimates of the effects of acidic deposition, the sampling grid was intensified to increase the sample site density in the Blue Ridge, Appalachian Plateau, and Ridge section of the Valley and Ridge ecoregions. Results from both of these surveys were used to develop and select the sampling sites for the Temporally Integrated Monitoring of Ecosystems (TIME) program, which is described below.
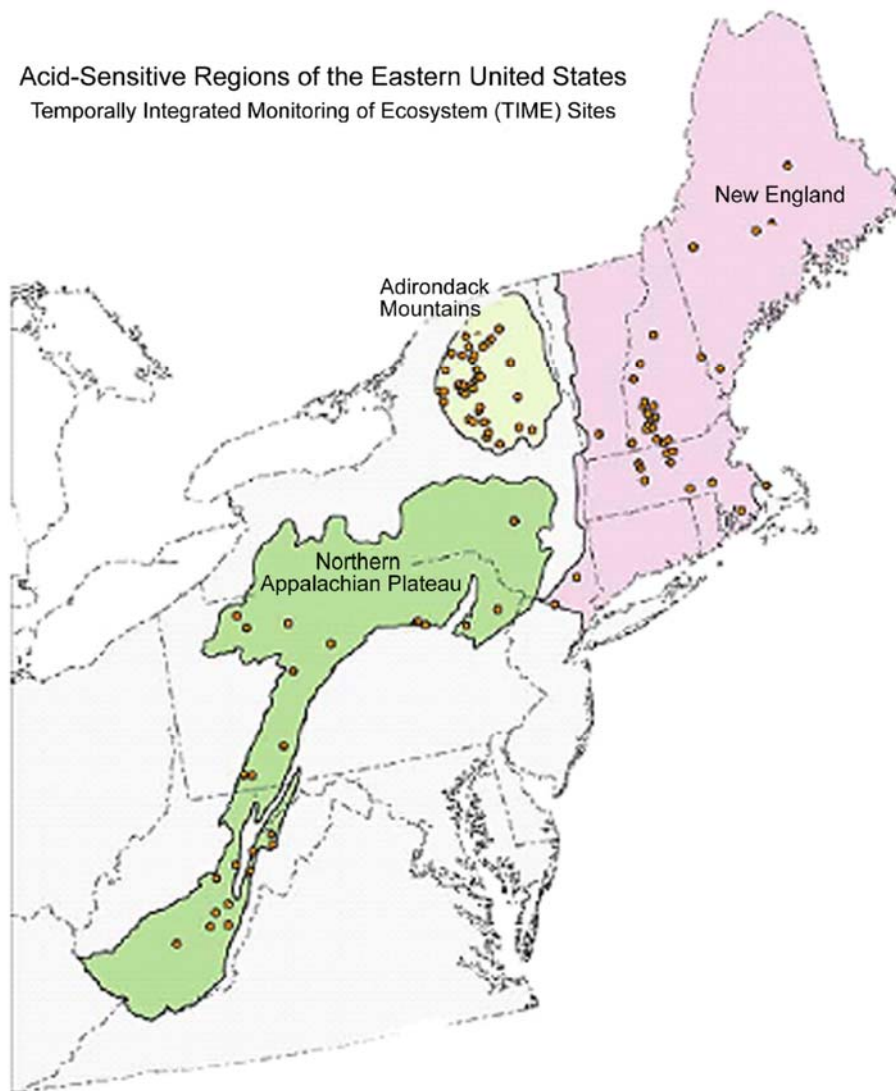
Source: Stoddard et al. (2003).

Figure A-1. Location of acid-sensitive regions of the northern and eastern U.S. These are regions for which statistical survey data are available in the 1990s, and locations of individual TIME sites used in trend analysis.

A.2.2. Surface Water Chemistry Monitoring

There are two surface water chemistry monitoring programs, administered by the U.S. EPA, that are especially important to inform the assessment of aquatic ecosystem responses to changes in atmospheric deposition. These are the TIME program (Stoddard et al., 2003) and the Long-term Monitoring (LTM) program (Ford et al., 1993; Stoddard, 1998a). These efforts focus on portions of the U.S. most affected by the acidifying influence of S and N deposition, including lakes in the Adirondack Mountains of New York and in New England, and streams in the Northern Appalachian Plateau and Blue Ridge in Virginia and West Virginia. Both projects are operated cooperatively with numerous collaborators in state agencies, academic institutions and other federal agencies. The TIME and LTM projects have slightly different objectives and structures, which are outlined below. Stoddard et al. (2003) conducted a thorough trends analysis of the TIME and LTM data.

A.2.2.1. TIME Project

At the core of the TIME project is the concept of probability sampling, whereby each sampling site is chosen statistically from a pre-defined target population. Collectively, the monitoring data collected at the sites are representative of the target population of lakes or streams in each study (Figure A-1). The target populations in these regions include lakes and streams likely to be responsive to changes in acidic deposition, defined in terms of acid neutralizing capacity (ANC), which represents an estimate of the ability of water to buffer acid. It can be either calculated (calculated ANC = sum of base cations – sum of mineral acid anions, where all concentrations are in μeq/L) or titrated in the laboratory (Gran ANC). Measurement of Gran ANC uses the Gran technique to find the inflection point in an acid-base titration of a water sample (Gran, 1952). In the Northeast, the TIME target population consists of lakes with a Gran ANC less than 100 μeq/L. In the Mid-Atlantic, the target population is upland streams with Gran ANC less than 100 μeq/L. In both regions, the sample sites selected for future monitoring were selected from the EMAP survey sites in the region (Section A.2.1) that met the TIME target population definition.

Each lake or stream is sampled annually (in summer for lakes; in spring for streams), and results are extrapolated with known confidence to the target population(s) as a whole using the EMAP site population expansion factors or weights (Larsen and Urquhart, 1993; Larsen et al., 1994; Stoddard et al., 1996; Urquhart et al., 1998). TIME sites were selected using the methods developed by the EMAP (Herlihy et al., 2000; Paulsen et al., 1991). The TIME project began sampling northeastern lakes in 1991. Data from 43 Adirondack lakes can be extrapolated to the target population of low-ANC lakes in that region. There are about 1,000 low-ANC Adirondack lakes, out of a total population of 1830 lakes with surface area greater than 1 ha. Data from 30 lakes (representing about 1,500 low-ANC lakes, out of a total population of 6,800) form the basis for TIME monitoring in New England. Probability monitoring of Mid-Atlantic streams began in 1993. Stoddard et al. (2003) analyzed data from 30 low-ANC streams in the Northern Appalachian Plateau (representing about 24,000 km of low-ANC stream length out of a total stream length of 42,000 km).

The initial 1993−1995 EMAP-MAHA sample in the Mid-Atlantic was not dense enough to obtain enough sites in the TIME target population in the Blue Ridge and Valley and Ridge ecoregions. In 1998, another denser random sample was conducted in these ecoregions to identify more TIME sites. After pooling TIME target sites taken from both MAHA and the 1998 survey, there are now 21 TIME sites in the Blue Ridge and Ridge and Valley that can be used for trend detection in this aggregate ecoregion in the Mid-Atlantic in addition to the Northern Appalachian Plateau ecoregion.

A.2.2.2. Long-Term Monitoring Project

As a complement to the statistical lake and stream sampling in TIME, the LTM project samples a subset of generally acid-sensitive lakes and streams that have long-term data, many dating back to the early 1980s (Figure A-2). These sites are sampled 3 to 15 times per year. This information is used to characterize how some of the most sensitive of aquatic systems in each region are responding to changing deposition, as well as giving information on seasonal variation in water chemistry. In most regions, a small number of higher-ANC (e.g., Gran ANC greater than 100 μeq/L) sites are also sampled, and help separate temporal changes due to acidic deposition from those attributable to other disturbances (e.g., climate, land use change). Because of the availability of long-term records (more than two decades) at many LTM sites, their trends can also be placed in a better historical context than those of the TIME sites, where data are only available starting in the 1990s.

Monitored water chemistry variables include pH, ANC, major anions and cations, monomeric aluminum (Al), silicon (Si), specific conductance, dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC). The field protocols, laboratory methods, and quality assurance procedures are specific to each team of investigators. This information is contained in the cited publications of each research group. The EMAP and TIME protocols and quality assurance methods are generally consistent with those of the LTM cooperators. Details of LTM data from each region are given below.
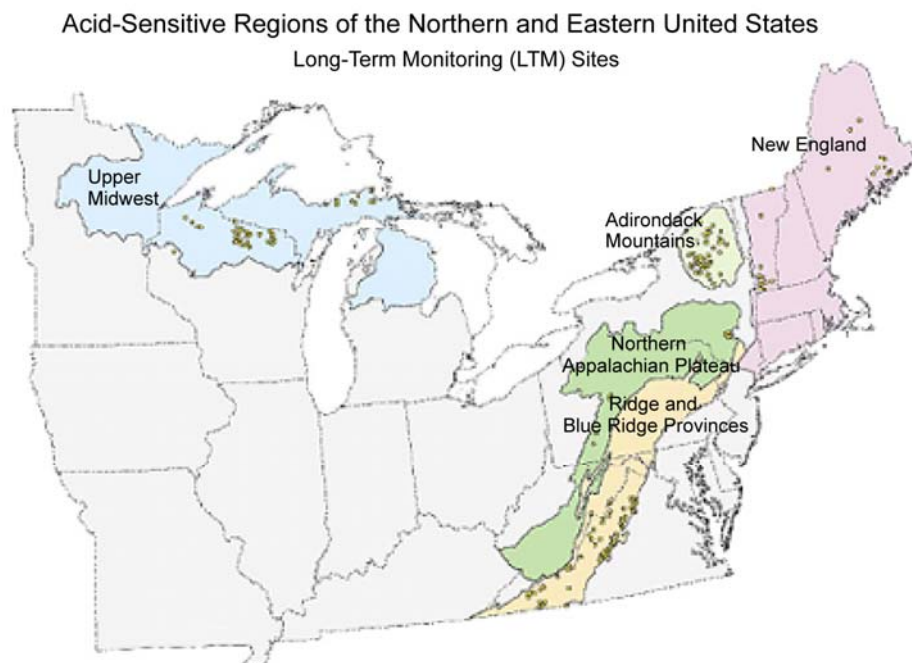
Source: Stoddard et al. (2003).

Figure A-2.   Location LTM sites used in the 2003 Surface Water report.

New England Lakes: The LTM project collects quarterly data from lakes in Maine (sampled by the University of Maine; (Kahl et al., 1991; Kahl et al., 1993) and Vermont (data collected by the Vermont Department of Environmental Conservation; Stoddard and Kellogg, 1993; Stoddard et al., 1998a). Data from 24 New England lakes were available for the trend analysis reported by Stoddard et al. (2003) for the time period 1990 to 2000. In addition to quarterly samples, a subset of these lakes have outlet samples

collected on a weekly basis during the snowmelt season; these data are used to characterize variation in spring chemistry. Most New England LTM lakes have mean Gran ANC values ranging from –20 to 100 µeq/L; two higher ANC lakes (Gran ANC between 100 and 200 µeq/L) are also monitored.

Adirondack Lakes: The trend analysis of Stoddard et al. (2003) included data from 48 Adirondack lakes, sampled monthly by the Adirondack Lake Survey Corporation (Driscoll and Van Dreason, 1993; Driscoll and Paostek, 1995) a subset of these lakes are sampled weekly during spring snowmelt to help characterize spring season variability. Sixteen of the lakes have been monitored since the early 1980s; the others were added to the program in the 1990s. The Adirondack LTM dataset includes seepage and drainage lakes, most with Gran ANC values in the range of –50 to 100 µeq/L; three lakes with Gran ANC between 100 µeq/L and 200 µeq/L are also monitored.

Appalachian Plateau streams: Stream sampling in the Northern Appalachian Plateau is conducted about 15 times per year, with the samples spread evenly between baseflow (e.g., summer and fall) and high flow (e.g., spring) seasons. Data from four streams in the Catskill Mountains (collected by the U.S. Geological Survey; (Murdoch and Stoddard, 1993) and five streams in Pennsylvania (collected by Pennsylvania State University (DeWalle and Swistock, 1994a) were analyzed by Stoddard et al. (2003). All of the Northern Appalachian LTM streams have mean Gran ANC values in the range –25 to 50 µeq/L.

Upper Midwest lakes: Forty lakes in the Upper Midwest were originally included in the LTM project, but funding in this region was terminated in 1995. The Wisconsin Department of Natural Resources (funded by the Wisconsin Acid Deposition Research Council, the Wisconsin Utilities Association, the Electric Power Research Institute and the Wisconsin Department of Natural Resources) has continued limited sampling of a subset of these lakes, as well as carrying out additional sampling of an independent subset of seepage lakes in the state. The data reported by Stoddard et al. (2003) included 16 lakes (both drainage and seepage) sampled quarterly (Webster et al., 1993) and 22 seepage lakes sampled annually in the 1990s. All of the Upper Midwest LTM lakes exhibit mean Gran ANC values from –30 to 80 µeq/L.

Ridge/Blue Ridge streams: Data from the Ridge and Blue Ridge provinces consist of a large number of streams sampled quarterly throughout the 1990s as part of the Virginia Trout Stream Sensitivity Study (Webb et al., 1989), and a small number of streams sampled more intensively (as in the Northern Appalachian Plateau). A total of 69 streams, all located in the Ridge section of the Ridge and Valley province, or within the Blue Ridge province, and all within the state of Virginia, had sufficient data for the trend analyses by Stoddard et al. (2003). The data are collected cooperatively with the University of Virginia and the National Park Service. Mean Gran ANC values for the Ridge and Blue Ridge data range from –15 to 200 µeq/L, with 7 of the 69 sites exhibiting mean Gran ANC greater than 100 µeq/L.FIA field personnel collect soil data during the Phase 3 field season, which begins in early June and ends in September. Soil samples are sent to the laboratory immediately after collection where they are stabilized by air drying. Laboratory analyses are conducted throughout the fall and winter following the field season. On-plot measurements include soil compaction and bare soil observations. Soil compaction, the percentage of the soil surface exhibiting evidence of soil compaction as well as the type of compaction, is measured by ocular estimation. The relative amount of bare soil is also estimated. Field measurements related to erosion and compaction estimates are made on all four subplots on the Phase 3 field plot. Soil samples are collected on FIA sample plots along soil sampling lines adjacent to subplots 2, 3, and 4. Soils are collected if the soil sampling location is in a forested condition. A total of five samples are collected on each plot (three forest floor, two mineral soil). The entire forest floor layer is sampled from a known area after measuring the thickness of the litter and duff layers at the north, south, east, and west edges of a 12–inch diameter sampling frame. Only organic material that is <one-fourth-inch diameter is collected; rocks and larger woody materials are discarded before collection.

Once the forest floor has been removed, mineral and organic soils are sampled volumetrically by collecting cores from two depths: 0 to 4 inches and 4 to 8 inches. The texture of each layer is estimated in the field and characterized as organic, loamy, clayey, sandy, or coarse sandy. Following soil sampling, the depth to any restrictive horizon within the top 20 inches is estimated using a soil probe. Soil samples are mailed to the regional laboratory for physical and chemical analysis.

In the lab, mineral soil samples collected from FIA plots are analyzed for a suite of physical and chemical properties including:

- Bulk density, water content, and coarse fragment (>2–mm) content
- pH (water and 0.01 M $CaCl^2$)
- Total carbon
- Total inorganic carbon (carbonates) (pH >7.5 soils only)
- Total N
- Exchangeable cations (Na, K, Mg, Ca, Al, Mn)
- Extractable sulfur and trace metals (Sr, Ba, Mn, Ni, Cu, Zn, Cd, Pb)
- Extractable P (Bray 1 method for pH <6 soils, Olsen method for pH >6 soils)

Forest floor and litter samples are analyzed for:

- Bulk density and water content
- Total carbon
- Total N

Soil chemical and physical properties can be highly variable in the field and are expensive to analyze. As a result, interpretation of soil chemical data is confounded by spatial variability within the plot. In addition, depending upon the soil type, both the number of samples and the methods used in collecting these samples may vary between plots, complicating compilation and estimation procedures. Finally, soil samples reflect conditions only in the forest floor and upper 20 cm of the soil. In many systems, the upper portion of the soil profile is likely to be more responsive to disturbance, providing a useful index for monitoring changes in soil properties over time.

A.2.3. USGS Monitoring Programs

A.2.3.1. National Water Quality Assessment Program

The National Water Quality Assessment (NAWQA) Program was created in 1991 by the USGS to assess the nation's water quality in 51 study units defined primarily by major drainage divides. These units comprise approximately 50% of the conterminous U.S. Its major of the program are to determine the condition of the nation's streams, rivers, and ground water; whether these conditions are changing over time; and how these conditions are affected by natural features and human activities.

The major priority of the NAWQA Program since its inception has been on watersheds that have experienced impacts from agriculture and various forms of development. The location of sites, sampling frequency, and types of measurements taken, all reflect this priority. Each study unit runs on a 9–year cycle, with approximately one-third of the study units beginning the cycle every 3 years. Each 9–year cycle is comprised of 3 years of intensive data collection and 6 years of low-level assessment. Three types of sampling sites are established within each study unit: integrator sites, indicator sites, and synoptic sites. Integrator sites are located on major rivers at points that drain much or the entire study unit. Indicator sites drain large fractions of the study unit that are representative of a particular landscape or land use type. Some indicator sites are also located to evaluate point sources of water pollution, and some are located downstream of undisturbed drainages to provide reference, or background conditions. Reference indicator sites are generally located too low in the drainage basin for assessment of surface water

acidification. Sites associated with synoptic studies are chosen for improving spatial resolution of data collection within the study unit. The strategies for site selection, sampling, and analysis for synoptic sites are issue-specific and keyed to hydrologic conditions, times, and places of specific interest for the targeted water quality issue.

During the 3 year intensive sampling period, integrator and indicator sites are sampled multiple times, both periodically and in association with high flows. The sampling approach for synoptic studies varies depending on the issue of interest, but is usually done within the second or third year of the intensive sampling period. During the six years of the low-level assessment, sampling usually involves base-flow sampling of high priority integrator sites, and possibly some sampling of indicator sites.

Water quality measurements vary among study units, but usually include pathogens, nutrients (including N and S), trace elements, pesticides, industrial organics, suspended sediment, salinity, temperature, acidity, and dissolved O_2.

NAWQA studies have resulted in over 1000 reports on an extensive list of water quality issues, including freshwater and marine eutrophication associated with N pollution. None deal with acidification, however. Program details and access to publications can be obtained at http://water.usgs.gov/nawqa/.

A.2.3.2. Hydrologic Benchmark Network

The Hydrologic Benchmark Network (HBN) was started in 1963 by the USGS and gradually grew to include 57 river gauging stations and 1 lake-stage station in 39 states by 1990. Most of the stations have been established at the outlet of watersheds that were virtually free of human activities, located in places such as in national parks and forests, wilderness areas, or nature preserves. Streamflow was initially monitored continuously at each station, and samples were collected every month for water-quality analyses that included concentrations of nutrients and all major ions. The frequency of water sampling at HBN stations was decreased to quarterly in 1986 because of budgetary restrictions. Sampling was discontinued in October 1997, except for a small study in the eastern U.S. that focused on the initial response of rivers to decreases in industrial emissions mandated by the CAAA of 1990 (http://www.epa.gov/oar/oaq_caa.html/).

All HBN watersheds were evaluated in 2002 to determine whether upstream development had made them unsuitable as reference watersheds. The 36 sites that best met the network criteria were selected for continued streamflow monitoring, and water sampling was reinitiated at 15 of those 36 sites. In 2003, 15 of the original HBN stations were equipped with refrigerated, automated samplers and telemetry systems that allow program coordinators to monitor stream conditions and adjust sampling frequency and capture unique stream conditions or special sampling needs. The automated sampling system is designed to collect samples through a wide range of flow conditions and to transmit data by satellite. About 25 water samples are collected annually at each HBN water quality station and refrigerated on site until retrieved by field personnel who visit the sites regularly. The most recent trends analysis was done by Clow and Mast (1999) to evaluate long-term trends in stream chemistry with respect to the CAA. The program is further described in a fact sheet that can be found at: http://ny.water.usgs.gov/pubs/fs/fs20053135/.

A.2.3.3. New York City Water Quality Network

The New York District of the U.S. Geological Survey operates a water quality network throughout the water supply watershed for New York City, in the Catskill Mountains region. The purpose of the network is to provide stream flow and water quality data at key locations within the watershed. There are currently 34 sites throughout the network at which stream flow data are collected, and at thirteen of those sites stream water quality data are also collected. The water quality network is composed of paired "nodes" consisting of one or more "upper nodes" that provide water quality of undeveloped, forested

watersheds, and "lower nodes" that provide downstream water quality data that may reflect some level of development within the watershed.

Water quality sampling for this program began at the 13 sites in 1998–99. Water samples are collected biweekly and during high flow for approximately 6 storms per year. All water samples are analyzed for concentrations of nutrients and major ions. Because streams in this area are also affected by acidic deposition, acid-neutralizing capacity and 3 forms of Al are also measured. Further details on the program are available at: http://ny.cf.er.usgs.gov/nyc/unoono.cfm.

A.2.3.4. Catskill Long-Term Monitoring Sites

Within the Catskill Mountains region of New York State, stream samples are collected and stream flow is measured at three locations within the Neversink River basin, and at one site on Rondout Creek. Water samples are collected biweekly and during most storms. These sites are currently part of the U.S. EPA LTM program, but also are affiliated with other programs. Sampling at two of the four sites began in the mid 1980s, whereas sampling at the remaining two sites began in 1991. The primary purpose of these sites is to monitor effects of acidic deposition on stream chemistry. The full suite of analytes needed to assess acidic deposition effects are measured on these water samples.

A.2.3.5. Buck Creek, New York

Stream flow and water chemistry are monitored at three locations within Buck Creek watershed, in the western Adirondack Region of New York. Samples are collected biweekly and during most storms at each location. Sampling began in 1998 at two sites and 2001 at the third site. The full suite of analytes needed to assess acidic deposition effects is measured on these water samples. Measurements of ANC and pH were also collected at one site weekly for the period of 1991 to 2001 (Lawrence et al., 2004). Recent data from Buck Creek are presented in Lawrence et al. (2007). Buck Creek is the only stream within the acidified region of the Adirondacks where base flow and storm samples are collected in conjunction with flow monitoring.

A.2.4. NSF Long-Term Ecological Research Network

The Long-Term Ecological Research (LTER) program constitutes a loose network of 26 sites (Table A-1), funded by the National Science Foundation (NSF). There is increasing concern over such globally significant problems as loss of biodiversity, climate change, destruction of forests, depletion of stratospheric ozone, regional air and water pollution, and soil erosion. The research conducted at the various LTER sites has examined and continues to examine aspects of these problems and provides scientific information which has been invaluable in the formation of public policy. Site locations and research activities are summarized in (Table A-1). A few of the sites that have been used most extensively for evaluation of long-term effects of N and sulfur deposition are discussed in greater detail below.

Table A-1.   LTER site locations and basic site description information.

Site	Landsat WRS	Institutional Affiliations	Principal Biome/ Main Communities	Research Topics
H.J. Andrews Experimental Forest (AND) 44.2, −122.2	Path 46 Row 29; Lat/Long: 44°14'N/ 122°11'W	Oregon State University; USDA Forest Service Pacific Northwest Research Station	Temperate coniferous forest. Douglas-fir/western hemlock/ western red cedar; true fir and mountain hemlock; streams	Successional changes in ecosystems; forest-stream interactions; population dynamics of forest stands; patterns and rates of decomposition; disturbance regimes in forest landscapes
Arctic Tundra (ARC) 68.6, −149.6	Path 73, Row 12; Lat/Long: 68°38'N/ 149°34'W	The Ecosystem Center, Marine Biological Laboratory; Universities of Alaska, Massachusetts, Minnesota, Cincinnati, and Kansas; Clarkson University	Arctic tundra, lakes, streams. Tussock tundra; heath tundra; riverine willows; oligotrophic lakes; headwater streams	Research topics: Movement of nutrients from land to stream to lake; changes due to anthropogenic influences; controls of ecological processes by nutrients and by predation
Baltimore Ecosystem Study (BES) 39.1, −76.3	Path 15, Row 33; Lat/Long 38°54" 04' (N), 76°52" 04' (W)	Institute of Ecosystem Studies; USDA Forest Service, Johns Hopkins University; University of Maryland; Baltimore County and College Park; University of North Carolina; Parks and People Foundation; US Geological Survey; Yale University	Eastern deciduous forest/ Suburban Agriculture fringe, urban parks, residential and commercial patches, riparian and stream habitats	Patch dynamics of built, social, biological, and hydrological components of the metropolitan area; feedback's between social, economic, and ecological components of an urban ecosystem; effect of infrastructure and development on fluxes of nutrients, energy, and water in upland, stream, and coastal regions of metropolitan Baltimore
Bonanza Creek Experimental Forest (BNZ) 64.8, −148.0	Path 69, Row 15; Lat/Long: 64°45'N/ 148°00'W	University of Alaska; Institute of Northern Forestry, USDA Forest Service, Pacific Northwest Research Station	Taiga. Areas of boreal forest including permafrost-free uplands and permafrost-dominated north slopes and lowlands; floodplain seres	Successional processes associated with wildfire and floodplains; facilitative and competitive interactions among plant species throughout succession; plant-mediated changes in resource and energy availability for decomposers; herbivorous control of plant species composition; hydrologic regime and stream ecology
Cedar Creek Natural History Area (CDR) 45.4, −93.2	Path 27, Row 28; Lat/Long: 45°24'N/ 93°12'W	University of Minnesota	Eastern deciduous forest and tallgrass prairie. Old fields; oak savanna and forest, conifer bog; lakes; pine forest; wetland marsh and carr	Successional dynamics; primary productivity and disturbance patterns; nutrient budgets and cycles; climatic variation and the wetland/upland boundary; plant-herbivore dynamics

Central Arizona - Phoenix (CAP) 33.5, −11.2	Path 36, Row 37 and Path 36, Row 36° These have been used by CAP although Path 37, Row 37 is centered more closely in the City of Phoenix	Arizona State University (Main and West)	Sonoran Desert scrub. Urban parks, residential, interior remnant desert patches, commercial and industrial patches, urban fringe, regulated river and floodplain (dry), effluent-dominated river	Interactions of ecological and socio-economic systems in an urban environment; influence of land use change on ecological patterns and processes; movement of nutrients through highly manipulated, urban flowpaths; interactions of introduced and native species in urban environment; millennium- and century-scale geomorphic change in landforms and interaction with engineered landscapes
Coweeta Hydrologic Laboratory (CWT) 35.0, −83.5	Path 18, Row 36; Lat/Long: 35°00'N/ 83°30'W	University of Georgia; USDA Forest Service, Southeastern Forest Experiment Station	Eastern deciduous forest. Hardwood forests and white pine plantations	Long-term dynamics of forest ecosystems including forest disturbance and stress along an environmental gradient; stream ecosystems along an environmental gradient; and the riparian zone as a regulator of terrestrial-aquatic linkages
Harvard Forest (HFR) 42.5, −72.2	Path 13, Row 30; Lat/Long: 42°32'N/ 72°10'W	Harvard University; Universities of New Hampshire and Massachusetts; The Ecosystem Center, Marine Biological Laboratory	Eastern deciduous forest. Hardwood-white-pine-hemlock forest; spruce swamp forest; conifer plantations	Long-term climate change, disturbance history and vegetation dynamics; comparison of community, population, and plant architectural responses to human and natural disturbance; forest-atmosphere trace gas fluxes; organic matter accumulation, decomposition and mineralization; element cycling, fine root dynamics and forest microbiology
Hubbard Brook Experimental Forest (HBR) 43.9, −71.8	Path 13, Row 29; Lat/Long: 43°56'N/ 71°45'W	Yale, Cornell, and Syracuse Universities; Institute of Ecosystem Studies; USDA Forest Service, Northeastern Forest Experiment Station	Eastern deciduous forest. Northern hardwood forests in various developmental stages, spruce-fir forests; streams and lakes	Vegetation structure and production; dynamics of detritus in terrestrial and aquatic ecosystems; atmosphere-terrestrial-aquatic ecosystem linkages; heterotroph population dynamics; effects of human activities on ecosystems
Jornada Experimental Range (JRN) 32.5, −106.8	Path 33, Row 37; Lat/Long: 32°30'N/ 106°45'W	New Mexico State University; USDA ARS Jornada Experimental Range; Duke University; NOAA, RTP, NC; University of New Mexico; Dartmouth College, NH; Oregon Graduate Center; Texas Technological University; SUNY Buffalo; University of Keele, UK; Kings College, London, UK; U.S. EPA-EMAP, Las Vegas, NV	Hot desert. Playa, piedmont, and swale; bajada, basin, mountain and swale shrubland; mesquite dunes	Desertification; factors affecting primary production; animal-induced soil disturbances; direct and indirect consumer effects; vertebrate and invertebrate population dynamics; grazing effects on ecosystem structure and function; biodiversity and ecosystem function; small mammal effects on soil and vegetation heterogeneity; soil microbial processes; surface hydrology; trace gas emissions from soils; eolian processes

W.K. Kellogg Biological Station (KBS) 42.4, −5.4	Path 21, Row 31; Lat/Long: 85°24'W/ 42°24'N	Michigan State University, Michigan Agricultural Experiment Station	Row-crop agriculture. Conventional and organic-based corn-soybean-wheat cultivation; perennial biomass cultivation; native successional communities	Ecological interactions underlying the productivity and environmental impact of production-level cropping systems; patterns, causes, and consequences of microbial, plant, and insect diversity in agricultural landscapes; gene transfer, community dynamics, biogeochemical fluxes
Konza Prairie Research Natural Area(KNZ) 39.1, −94.6	Path 28, Row 33; Lat/Long: 39°05'N/ 96°35'W	Kansas State University	Tallgrass prairie. Tallgrass prairie; gallery forest; prairie stream	Effects of fire, grazing and climatic variability on ecological patterns and processes in tallgrass prairie ecosystems, use of remotely sensed data and geographic information systems to evaluate grassland structure and dynamics
Luquillo Experimental Forest (LUQ) 18.3, −65.8	Path 4, Row 47 and 48; Lat/Long: 18°18'N/ 65°47'W	Center for Energy and Environment Research, University of Puerto Rico; Institute of Tropical Forestry, USDA Forest Service, Southern Experiment Station	Tropical rainforest. Tabonuco forest; palo Colorado forest; palm brake; dwarf forest and montane streams	Patterns of and ecosystem response to different patterns of disturbance; land-stream interactions; effect of management on ecosystem properties; integration of ecosystem models and geographic information systems
McMurdo Dry Valleys - Antarctica (MCM) −78.0, +165.0	Path 56, Row 116	Desert Research Institute, Reno, Nevada; U.S. Geological Survey, Boulder, Colorado	Polar desert oases	Microbial ecosystem dynamics in arid soils, ephemeral streams, and closed basin lakes; resource and environmental controls on terrestrial, stream and lake ecosystems; material transport between aquatic and terrestrial ecosystems; ecosystem response to greater hydrologic flux driven by warming climate
Niwot Ridge/ Green Lakes Valley (NWT) 40.1, −105.6	Path 34, Row 32; Lat/Long: 40°03'N/ 105°37'W	Institute of Arctic and Alpine Research, University of Colorado	Alpine tundra; Fellfield; meadow; herbaceous and shrub tundras; cliffs and talus; glacial lakes; streams and wetlands	Patterns and controls of nutrient cycling; trace gas dynamics, plant primary productivity and species composition; geomorphology, and paleoecology
North Temperate Lakes (NTL) 46.0, −89.7 and 43.1, 89.4	Path 25, Row 28 and Path 24, Row 30 Lat/Long: 46°00'N/ 89°40'W and 89°24/ 43°06	Center for Limnology, University of Wisconsin-Madison, Wisconsin	Northern temperate lakes in glacial landscapes in urban, agricultural and forested watersheds. Oligotrophic, dystrophic and eutrophic lakes; temporary forest ponds; warm and cold streams; sphagnum-leatherleaf bog; conifer swamp; mixed deciduous and coniferous forests	Physical, chemical and biological limnology; hydrology and geochemistry; climate forcing; producer and consumer ecology; ecology of invasions; ecosystem variability; lakescape and landscape ecology

Palmer Station (PAL) Antarctica −64.7, −64.0	Path 219 , Row 105; Lat/Long: 64°40'S/ 64°W	University of California, Santa Barbara; Old Dominion University	Polar marine. Coastal and open ocean pelagic communities; seabird nesting areas	Oceanic-ice circulation and models; sea-ice dynamics; biological/physical interactions; effect of sea ice on primary production, consumer populations and apex predators; bio-optical models of primary production; spatial distribution and recruitment in consumer populations; seabird population dynamics and reproductive ecology
Plum Island Sound (PIE) 42.67, −70.99	Path 12, Row 30; Lat/Long: 42°40'/ 70°59' Site has the following X and Y bounds in decimal coordinates: X min = −71.22 X max = −70.75. Y min = 42.50 Y max = 42.83. The total area is approximately 37 km x 37 km or 1369 km^2	The Ecosystems Center, Marine Biological Laboratory; Universities of South Carolina and New Hampshire; Massachusetts Audubon; Wells, Maine, NERRS	Coastal estuary	Linkages between land and coastal waters involving organic carbon and organic N inputs to estuarine ecosystems from watersheds with various land covers and uses
Sevilleta National Wildlife Refuge (SEV) 34.3, −106.8	Path 33, Row 36; To acquire entire site area, Path 32, Row 36, Path 32, Row 37 and Path 33, Row 37 are also needed. Lat/Long: 34°19'/ 106°62'W	University of New Mexico; U.S. Fish and Wildlife Service	Multiple: intersection of subalpine mixed-conifer forest/meadow, riparian cottonwood forest, dry mountainland, grassland, cold desert, hot desert. Conifer savanna; creosote bush; desert grassland; mesquite and sand dunes; Great Basin shrub and shortgrass steppes; tallgrass swales; riparian communities	Landscape and organism population dynamics in a biome tension zone; semiarid watershed ecology; climate change; biospheric/atmospheric interactions; paleobotany/ archaeology; microbial role in gas flux; and control of landscape heterogeneity; scale effects on spatial and temporal variability
Shortgrass Steppe (SGS) 40.8, −104.8	Path 33, Row 32; Lat/Long: 40°49'N/ 104°46'W	Colorado State University; USDA Forest Service; USDA Agricultural Research Service	Floodplain; shrubland; saltmeadow	Soil water; above- and belowground net primary production; plant population and community dyna-mics; effects of livestock grazing; soil organic matter accumulation and losses, soil nutrient dynamics; and ecosystem recovery from cultivation
Virginia Coast Reserve (VCR) 37.5, −74.8	Path 14, Row 34; Lat/Long: 37°30'N 75°40'W	University of Virginia	Coastal barrier islands. Sandy intertidal; open beach; shrubthicket; mature pine forest; salt marsh; estuary	Holocene barrier island geology; salt marsh ecology, geology, and hydrology; ecology/ evolution of insular vertebrates; primary/ secondary succession; life-form modeling of succession

A.2.4.1. Hubbard Brook Experimental Forest

The Hubbard Brook Ecosystem Study (HBES) at Hubbard Brook Experimental Forest (HBEF) is the longest-running precipitation and stream chemistry (1963 to present) monitoring program in the U.S.

(see http://www.hubbardbrook.org). HBEF was established in 1955 as a major center for hydrologic research in New England. The site is located within the boundaries of the White Mountain National Forest in central New Hampshire. The 3138–ha, bowl-shaped valley has hilly terrain, ranging from 222 to 1015 m elevation. The HBES originated in 1960 with the intention of applying the small watershed approach to the study of element fluxes and cycles. The goal of the study is to develop a better understanding of ecological patterns and processes that characterize the northern forest in eastern North America, and its response to both natural and human disturbances. In 1987, HBEF joined the NSF's LTER network (http://www.lternet.edu). Hubbard Brook is renowned for its long-term record of measurements, landscape-scale experiments of whole watersheds, and the involvement of scientists from diverse disciplines and institutions.

The HBEF is entirely forested, mainly with deciduous northern hardwoods: sugar maple (*Acer saccharum*), beech (*Fagus grandifolia*), and yellow birch (*Betula alleghveniensis*), and some white ash (*Fraxinus americana*) on the lower and middle slopes. Other less abundant species include mountain maple (*Acer spicatum*), striped maple (*Acer pensylvanicum*), and trembling aspen (*Populus tremuloides*). Red spruce (*Picea rubens*), balsam fir (*Abies balsamea*), and white birch (*Betula papyrifera* var. *cordifolia*) are abundant at higher elevations and on rock outcrops. Hemlock (*Tsuga canadensis*) is found along the main Hubbard Brook. Pin cherry (*Prunus pensylvanica*), a shade intolerant species, dominates all sites for the first decade following a major forest disturbance. Logging operations ending around 1915–1917 removed large portions of the conifers and better quality, accessible hardwoods. The present second-growth forest is even-aged and composed of about 80 to 90% hardwoods and 10 to 20% conifers.

The HBEF is an oblong basin about 8 km long by 5 km wide. Hubbard Brook is the single major stream draining the basin. Numerous smaller tributary streams of varying size drain into Hubbard Brook including Watershed 6 (WS-6), which is the biogeochemical reference watershed.

One of the strengths of the HBES is the long-term monitoring program. Table A-2 lists the major parameters included in the HBES long-term monitoring study. The monitoring data illustrate that short-term observations can be misleading and that decades of monitoring may be required to detect real changes in complex ecosystems. The long-term record at the HBEF provides: insight into ecosystem function; empirical data for testing models and generating hypotheses; a record of extreme or unusual events; and information that is relevant to regional national and global environmental issues.

Table A-2. **Current long-term monitoring data sets developed through the Hubbard Brook Ecosystem Study**

PHYSICAL/HYDROLOGIC MONITORING
- Instantaneous streamflow (9 stations)
- Daily precipitation (24 stations)
- Class A weather station data
- Weekly snow depth on snow courses
- Daily soil temperature and moisture

AIR CHEMISTRY
- (SO_2, HNO_3, particulates, ozone)

MIRROR LAKE
- Instantaneous streamflow (3 inlets,outlet)
- Daily precipitation (2 stations)
- Weekly chemistry (3 inlets, outlet)
- Bi-monthly limnology (temp, chemistry, plankton)

SOLUTION CHEMISTRY
- Weekly bulk precipitation (6-10 stations)
- Monthly soil solution WS5, WS6
- Weekly stream at weirs of WS19
- Monthly stream within WS5, WS6

ORGANISMS
- Bird populations
- Phytophagous insect populations WS2, WS4, WS5, WS6
- Vegetation biomass, chemistry

SOILS
- Forest floor mass, chemistry (WS6, WS5; 5-yr intervals)
- Chemical and physical properties from soil pits (WS5)
- Chemical and physical properties from soil bags

Some of the monitoring is done on experimentally manipulated watersheds. There are nine gauged watersheds at the HBEF, four of which have been treated experimentally. A tenth ungauged watershed was also treated. Table A-3 includes summary data on the various watersheds. Datasets for long-term monitoring can be found at http://www.hubbardbrook.org/data/dataset_search.php. The datasets most often used to examine ecosystem response to ambient deposition of N and S are from WS-6 and Mirror Lake, since they have not been experimentally manipulated. Watershed 6 is the biogeochemical reference catchment at HBEF where monitoring began in June 1963. Measured stream chemistry parameters include major anions and cations, pH, silica, dissolved organic and inorganic carbon, specific conductance, dissolved O_2, ANC, and PO_4. Stream chemistry data can be accessed at http://www.hubbardbrook.org/data/dataset.php?id=8. The normal sampling interval for WS-6 is weekly, with more frequent samples taken at times of increased discharge.

Table A-3.   Study watersheds at HBEF.

WS	Area (ha)	Slope (°)	Aspect	Elevation (m)	Gauge Type	Initial Yr.
1	11.8	18.6	S22°E	488–747	V-notch weir	1956
2	15.6	18.5	S31°E	503−716	V-notch weir	1957
3	42.4	12.1	S23°W	527–732	V-notch weir	1957
4	36.1	15.6	S40°E	442–747	V-notch weir	1960
5	21.9	15.4	S24°E	488–762	V-notch weir, San Dimas flume	1962
6	13.2	15.8	S32°E	549–792	V-notch weir, San Dimas flume	1963
7	77.4	12.4	N16°W	619–899	V-notch weir, San Dimas flume	1965
8	59.4	14.0	N12°W	610–905	V-notch weir, San Dimas flume	1968
9	68.4		NE	685–910	V-notch weir	1995
10	12.1		SE	470–595	None	1970

Monitoring of streamflow and water chemistry has shown that the study watersheds have similar characteristics. Within each watershed there are a variety of soils, vegetation, microtopographical features, and micro-climate. Nevertheless, the composition of these variables seems to be similar from watershed-to-watershed. Thus, the effects of experimental manipulations of watersheds can be adequately evaluated by comparison with neighboring unmanipulated watersheds.

The most conspicuous streamflow characteristic is the seasonal shift from large volume of flow in spring to very low flow in late summer and early autumn. These yearly highs and lows reflect seasonal spring snowmelt that often occurs over a few days or weeks and the slow progressive decrease in flow from the transpirational draft in summer, respectively. The numerous streams in the HBEF range from small ephemeral channels that often dry up during summer to a large perennial 5th-order stream (Hubbard Brook).

Mirror Lake is a 15–ha oligotrophic clearwater lake adjacent to HBEF. The lake normally mixes in spring and fall, and is ice-covered from about December 1st to April 15th each year. Part of the drainage

to the lake originates in the Experimental Forest. The lake water is dilute, slightly acidic, and quite clear, with low productivity and low concentrations of nutrients in the water. Numerous studies have been conducted on Mirror Lake since the mid-1960s, including extensive physical, chemical, biological, and paleoecological research (Likens, 1985). Data are available since 1967 for lakewater concentrations at discrete depths for base cations, pH, and dissolved O_2. Ammonium, major anions, phosphate, and dissolved silica have been measured routinely since 1970, although some data are available before these dates for each solute. Other standard monitoring data include temperature and specific conductance at each depth. Before 1990, not all records had complete solute arrays. Since 1990, DIC and ANC have also been measured on a routine basis, although some prior data do exist for those parameters. The usual sampling interval for Mirror Lake is four to six times each year, especially at times of maximum and minimum thermal stratification. Data for Mirror Lake and inlet and outlet streams can be found at: http://www.hubbardbrook.org/data/dataset_search.php.

The soils, vegetation, and climate at the HBEF are characteristic of the northern hardwood forest complex, which spans much of the north-central and northeastern U.S. and southeastern Canada. Streamflow and stream chemistry reflect the landscape characteristics of the drainage area. Consequently, results from the relatively small watersheds at the HBEF are to a first approximation representative of a much larger regional area. During the scientific debate that occurred before passage of the CAAA of 1990, the trends in sulfate (SO_4^{2-}) concentrations in streamwater and precipitation at HBEF were very influential in convincing scientists and policy makers that decreasing S emissions would yield large decreases in the concentration of SO_4^{2-} in precipitation and streamwater in the northeastern U.S. (Lovett et al., 2007). Monitoring data collected since 1963 (Figure A-3) played a major role in development of the watershed-ecosystem concept and methods for analyzing and understanding watershed biogeochemical cycles (Bormann and Likens, 1967; Likens et al., 1978; Likens and Bormann, 1995; Lovett et al., 2007).

An extensive effort has been made to bring together some of the results of research that had been done at Hubbard Brook over the last several decades. Over the duration of the HBES there have been six books and more than 1,000 papers published. In addition, more than 500 abstracts were published and more than 100 graduate theses completed. A complete list of titles is available at http://www.hubbardbrook.org/pubs/pub_search.php. To date, four synthesis volumes have been completed (Bormann and Likens, 1979; Likens et al., 1977; Likens, 1985, 1992).
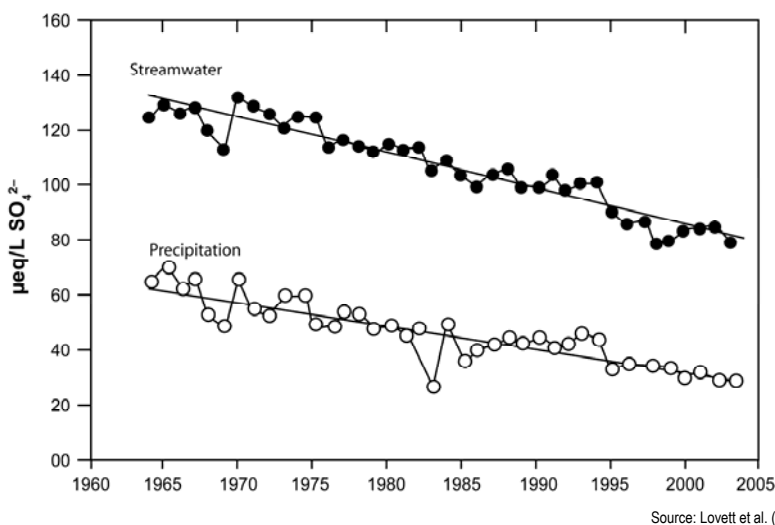
Source: Lovett et al. (2007); updated from Likens et al. (2002).

Figure A-3. **Long-term record of SO_4^{2-} concentration in streamwater and precipitation at Watershed 6 of HBEF.**

A.2.4.2. Coweeta

The Coweeta LTER research program (http://coweeta.ecology.uga.edu/) in North Carolina is based in the eastern deciduous forest of the Blue Ridge Physiographic Province of the southern Appalachian Mountains. The program entails long-term cooperation between the University of Georgia and the U.S. Department of Agriculture (USDA) Forest Service Coweeta Hydrologic Laboratory. The research program centers on the effects of disturbance and environmental gradients on biogeochemical cycling, and the underlying watershed ecosystem processes that regulate and respond to those cycles. Coweeta represents one of the longest continuous environmental studies of any North American landscape.

The research at Coweeta focuses largely on how water, soil, and forest resources respond to management practices, natural disturbances, and the atmospheric environment. It also aims to identify practices that mitigate impacts on these watershed resources. Current topics of emphasis include analyses of long-term changes in hydrology, nutrient cycling, and productivity in response to management practices and natural disturbances; assessment of prescribed burning effects on the forest environment; interdisciplinary implementation of ecosystem management on the national forests; effects of climatic change on productivity; impacts of atmospheric deposition on forest processes and ecosystems; cumulative effects of land use practices on water quality; physiological studies of forest carbon balance and competition; and biodiversity.

Investigators at the Coweeta Hydrologic Laboratory have recorded N dynamics of streams and precipitation in mature mixed hardwood-covered watersheds since 1972. Research has been conducted on responses to management practices such as clearcutting, selective cutting, conversion of native hardwood to coniferous forest, and old-field succession. Reference watersheds were characterized as in a transition phase between stage 0 and stage 1 of watershed N saturation. Evidence for stage 3 of N saturation, where the watershed is a net source of N rather than a N sink, was found for the most disturbed watershed at Coweeta.

The Coweeta Basin comprises 2185 hectares within the Blue Ridge geologic province in North Carolina. The laboratory has been dedicated to forest hydrology research since its establishment in 1933. Elevations range from 679 to 1592 m. More than 50 km of streams drain the area.

Coweeta is the first major mountain range contacted by air masses moving over the industrialized Piedmont region to the south. Analyses of precipitation chemistry have shown the influence of both local and regional activities on nutrient inputs to forest ecosystems.

Since Coweeta was established, 32 weirs have been installed on streams. Seventeen of these weirs are currently operational. Stream gauging was initiated on most watersheds between 1934 and 1938, and stream chemistry measurements date back to 1968.

Research has been conducted on eight mixed hardwood control areas and 13 catchments where forest management prescriptions have been applied. Past treatments have included varying intensities of cutting, ranging from light selection through clear-cutting; conversion of hardwoods to grass and subsequent succession to hardwoods; multiple-use management; mountain farming; and the application of herbicides and fertilizers.

Research and monitoring data from Coweeta has been extensively analyzed and reported in the scientific literature. Example recent publications include Swank and Vose (1997), Grossman et al. (1998), Schofield et al. (2001), and Scott and Helfman (2001).

Long-term changes in soils have been identified in reference and managed watersheds over two decades (Knoepp and Swank, 1994). For example, changes in exchangeable soil cation content varied with aspect: concentrations decreased on a north-facing slope but were stable on a south-facing slope. The demonstrated impacts of forest management practices have varied considerably. Soils in a white pine plantation showed stable C levels, but cations declined.

Commercial sawlog harvest resulted in large increases in soil C and cation concentrations, which remained elevated for 17 years. Whole-tree harvest resulted in decreased soil C for the next 14 years. Clearly soil response to harvest varies with type of harvest and site. Long-term studies like these have

proven useful in guiding ecosystem management projects in the southern Appalachians (Meyer and Swank, 1996).

A.2.4.3. Walker Branch

Walker Branch Watershed is located on the U.S. Department of Energy's Oak Ridge Reservation in Tennessee. The 97.5 ha Walker Branch watershed has been the site of long-term, intensive environmental studies since the late-1960s (see http://walkerbranch.ornl.gov/).

The forest soils are acidic, very cherty, infertile, and permeable. They are formed over dolomitic bedrock, but retain little evidence of their carbonate parent material. The forest vegetation is primarily oak-hickory with scattered pine on the ridges and mesophytic hardwoods in the valleys.

Initially, the research and monitoring of Walker Branch centered primarily on the geologic and hydrologic processes that control the amounts and chemistry of water moving through the watershed. Past projects have included:

- watershed hydrology and forest nutrient dynamics,
- forest micrometeorology,
- atmospheric deposition,
- International Biological Program Eastern Deciduous Forest Biome Project,
- trace element cycling and stream nutrient spiraling, and
- effects of acidic deposition on canopy processes and soil chemistry.

These projects have all contributed to a more complete understanding of how forest watersheds function and have provided insights into the solution of energy-related problems associated with air pollution, contaminant transport, and forest nutrient dynamics. Available long-term data at this site include:

- Daily climate data
- Monthly climate data
- Precipitation
- Atmospheric deposition
- Stream discharge and annual runoff
- Stream chemistry
- Vegetation

A.2.5. Water, Energy, and Biogeochemical Budgets Program

The Water, Energy, and Biogeochemical Budgets (WEBB) Program was started in 1991 at five small watersheds in the U.S. to examine water, energy, and biogeochemical fluxes and to determine the effects of atmospheric deposition, climatic variables, and human influences on watershed processes. The five sites are at Loch Vale, Colorado; Luquillo Experimental Forest, Puerto Rico; Panola Mountain, Georgia; Sleepers River, Vermont; and Trout Lake, Wisconsin. These sites are supported, in part, by other programs in the USGS, other Federal and State Agencies, and Universities. Two of these sites, Loch Vale and Sleepers River, have been used extensively to evaluate the effects of atmospheric sulfur and N deposition, and are described here. Each of those sites is also part of the LTER network.

A.2.5.1. Sleepers River

The Sleepers River Research Watershed in northeastern Vermont was established by the Agricultural Research Service (ARS) of the USDA in 1959 and is now operated jointly by the USGS and the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), with collaboration from several other Federal agencies and universities (see http://nh.water.usgs.gov/projects/sleepers/index.htm). The USGS uses hydrologic measurements and chemical and isotopic tracing techniques to determine how water moves from the hillslope to the stream, and what processes cause chemical changes, including the neutralization of acid rain. Research results provide insights on how pollutants move through ecosystems, and how ecosystems may respond to climatic change.

The watershed is covered by 1 to 4 m of glacial till, a compacted fine silty material that formed underneath glacial ice as it moved overland. The till was formed primarily from local bedrock, which is a calcareous granulite/quartz-mica phyllite. About 60 to 80 cm of soil has developed in the till. Weathering of calcite in the till and bedrock causes highly buffered streamflow, compared to most streams in New England, and a nutrient-rich biological environment. Sleepers River is, therefore, an end member in regional biogeochemical cycling studies (Hornbeck et al., 1997).

The Sleepers River area has reverted from a predominately cleared, agricultural landscape to a mostly forested one. A Northern Hardwood forest, dominated by sugar maple, white ash, yellow birch, and beech, with lesser amounts of red spruce and balsam fir, now covers two-thirds of the area; the remaining open land is primarily pasture and hayfields. Dairy farming and logging are the primary human enterprises in the watershed. The average annual temperature is 6 °C and the average annual precipitation is 1.1 m, 20% to 30% of which falls as snow.

Sleepers River has one of the longest historical hydrologic and climatologic data bases for a cold-region area in the U.S., featuring measurements of precipitation and streamflow since 1959, snow depth and corresponding water content since 1960, soil frost depth since 1984 (Shanley and Chalmers, 1999), and ground-water levels since 1991. These and other measurements constitute a valuable resource for hydrologic modeling and for the evaluation of climatic changes. Sampling site locations are shown in Figure A-4.
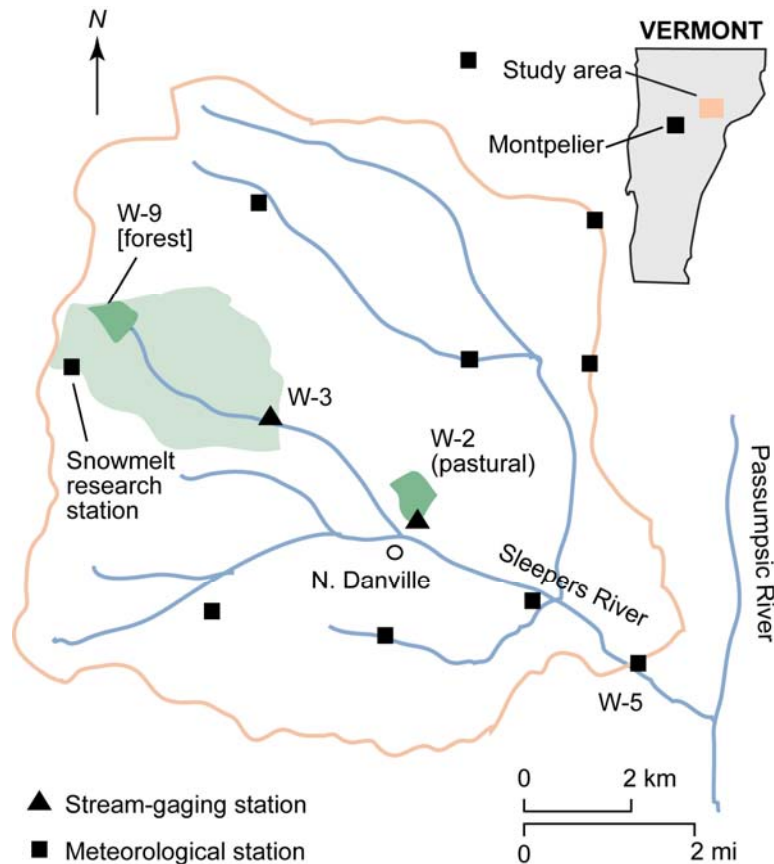
Figure A-4. Location of sampling stations in Sleepers River watershed, Vermont.

Recent research findings include the following:

- Precipitation is acidic, but streamflow is well-buffered from calcite weathering in till and bedrock.

- Infiltrating snowmelt causes ground water to rise into the permeable soil zone, where it moves rapidly downslope.

- Naturally occurring isotopic and chemical tracers indicate that "old" water dominates streamflow, and that water acquires solutes from weathering and biogeochemical processes along both deep and shallow flowpaths.

- Nitrate (NO_3^-) in streamflow is supplied primarily by mineralization and nitrification in the soil, rather than directly by the N content of precipitation.

The fate of NO_3^- in the forest ecosystem is being investigated by analysis of both the N and O isotopes of the NO_3^- ion. The isotopic composition of NO_3^- in streamflow matches that of NO_3^- produced by mineralization and nitrification in the soil, indicating that streamflow NO_3^- is derived from the soil and not from the rain or snowmelt that causes the high flow (Kendall et al., 1995). This finding suggests that most incoming atmospheric N is incorporated at least temporarily in the soil where it is utilized by the biota.

A.2.5.2. Loch Vale

The Loch Vale Watershed is a 661–ha alpine/subalpine basin located in the south-central Rocky Mountains, about 100 km northwest of Denver, Colorado. The basin is in a roadless area in Rocky Mountain National Park and is accessed by a 5–km hike or ski from the trailhead near Bear Lake. The western boundary of the basin is the Continental Divide; streams drain to the northeast. Basin elevations range from 4192 m (13,153 ft) at Taylor Peak to 3110 m (10,200 ft) at the outlet. There are two main subbasins in Loch Vale: Andrews Creek drains the northern subbasin, and Icy Brook drains the southern subbasin. These two creeks join above The Loch, which is the lowest of three lakes in the basin. Stream gauges are operated on Andrews Creek, Icy Brook, and at The Loch outlet. Water chemistry monitoring occurs at The Loch and on both inlet streams (see http://nh.water.usgs.gov/projects/sleepers/index.htm).

Large glaciers that covered much of Rocky Mountain National Park during the late Pleistocene sculpted the basin into characteristic glacial landforms, including steep U-shaped valleys, cirques, and arêtes. When the glaciers retreated about 12,500 years ago, they deposited till of varying thickness, which is confined mostly to the forested, lower part of the basin. Smaller, more recent glacial advances left younger till, talus, and rock deposits in the upper parts of the basin. The younger glacial and periglacial deposits are largely unvegetated.

Available water chemistry data include major ions, nutrients, DIC, DOC, and, for selected samples, a range of isotopes including $^{2}H/H$, $^{18}O/^{16}O$, $^{15}N/^{14}N$ and $^{18}O/^{16}O$ in nitrate ion, ^{35}S, $^{34}S/^{32}S$, $^{87}Sr/^{86}Sr$, ^{13}C, ^{12}C). Monitoring of precipitation and hydrology include the following elements:

- Precipitation: quantity — 3 sites continuous; chemistry, 1 site, biweekly.

- Stream discharge, 2 sites (Andrews Creek-Loch Vale, Icy Brook-Loch Vale).

- Stream chemistry, (Andrews Creek, Icy Brook-Loch Vale).

- Spring discharge, conductance, and temperature, 3 sites continuous.

- Spring water chemistry, 3 sites biweekly, 20–30 sites once during low-flow season.

- Soil lysimeters, 5 sites, biweekly to monthly during summer and fall.

- Snowpack amount and chemistry (depth, snow-water equivalent) basin-wide survey at maximum accumulation, index sites biweekly to monthly.

- Selected microenvironment runoff, e.g., rock outcrop, talus fields, weekly to monthly.

- Meteorology: 3 sites (wind speed, wind direction, air temperature, incoming and outgoing radiation, relative humidity), continuous.

- Gas flux (CO_2 and CH_4) in wetland, forest, and talus soils, weekly to monthly; CO_2 concentrations in surface waters at 10–15 sites several times annually.

- Snowmelt lysimeter discharge and chemistry, monitored for three years, currently inactive.

Atmospheric deposition of N to Loch Vale is high compared to most other sites in the Rockies, although considerably lower than most impacted sites in eastern North America and Europe. The alpine/subalpine ecosystem at Loch Vale exhibits symptoms of advanced watershed N saturation, indicating sensitivity to N deposition. Talus landscapes contribute substantially to N export in streamflow, and soil microbial processes are important in cycling N, even in areas such as talus that have little soil development. Research at this site indicates that N export is a function of both deposition and internal N-cycling processes that are affected by variability in climate.

A.2.6. Other Monitoring Programs

A.2.6.1. Bear Brook

The Bear Brook Watershed (BBW) is located in eastern Maine (44°52'15" latitude, 68°06'25" longitude), approximately 60 km from the Atlantic coastline. The BBW is a paired watershed study funded by the U.S. EPA since 1987 as part of The Watershed Manipulation Project (WMP) within the National Acid Precipitation Assessment Program (NAPAP) (see http://hydromodel.com/bbwm.htm; http://www.umaine.edu/DrSoils/bbwm/bbwm.html). As a long-term research watershed, the BBW includes bench-scale, micro-site, plot, and whole watershed investigations. The major purposes of the BBW project are to:

- Identify and quantify the major processes that control surface water acidity, with a major emphasis on the role of excess SO_4^{2-} and nitrate provided via atmospheric deposition and experimental application, and the rate of cation supply from chemical weathering and cation desorption.

- Assess the quantitative and qualitative responses at the watershed level to different (both increased and decreased) levels of acidic deposition.

- Evaluate the ability of existing models of water acidification to predict short- and long-term chemical variations in surface water chemistry and to predict watershed soil responses to increased and decreased loading of strong acids.

The watershed includes two first order streams: East Bear Brook (EBB) and West Bear Brook (WBB). On each stream, a catchment outlet was selected and gauged so that both streams have about the same catchment area (EBB = 10.7 ha and WBB = 10.2 ha). Since streams are close and face the same slope direction, the watersheds are geographically similar and are appropriate for a paired watershed studies. Both watersheds have a maximum discharge of about 0.01 mm/ha/s or 0.15 m^3/s. Annual water yield relative to incoming precipitation for WBB ranges from 68 to 77% and EBB ranges from 62–68%.

Stream channels in each watershed are well defined. Each stream bed is approximately 1 m wide at the weir and water flows over exposed bedrock in places. Elsewhere, the streambeds are comprised of boulders and gravel. Both streams have undergone intermittent dry periods during summer over the course of the study. One V-notch weir was constructed on each of the streams during winter 1987–1988. Mean discharge in each stream is about 0.13 cubic feet per second.

Sampling frequency at the weirs was every three weeks during the winter of 1986–1987 and at least weekly thereafter. On the basis of sampling conducted before beginning the manipulation experiment (1987–1989), the streams had the following characteristics: ANC, −5 to 90 μeq/L; air-equilibrated pH, 4.7 to 7.2; specific conductance of approximately 26 μS/cm; and DOC of 1 to 4 mg C/l.

Soils in the Bear Brook watersheds are primarily Spodosols. The average depth of the overburden in the watersheds is 0.5 m, with a range of 0 to 5.2 m. Soil pH (0.01M CaCl$_2$) values ranged from 2.9 in the O horizon, to 3.9 in the B horizon, to 4.4 in the C horizon. The bedrock is primarily metamorphosed and folded politic graded beds and quartzites, with granitic dikes. The surficial material is till.

The forest is comprised primarily of deciduous species with areas of conifers. Tree species include American beech (*Fagus grandifolia*), birch (*Betula* sp.), maple (*Acer* sp.), red spruce (*Picea rubens*), balsam fir (*Abies balsamea*), white pine (*Pinus strobus*), and hemlock (*Tsuga canadensis*). Coniferous stands, which occupy approximately 17% of the total watershed area, occur more commonly in the upper, steeper portions of the watersheds.

Although the Bear Brook project was intended as an experimental manipulation of West Bear Brook, there is also great value in the long-term monitoring data collected at East Bear Brook, the non-manipulated reference watershed. This two-decade long monitoring record provides information on the

response of an acid-sensitive low-order stream in Maine to changes that have occurred in atmospheric deposition since 1986.

Results of the Bear Brook project have been widely published (cf. Kahl et al., 1993b; Norton et al., 1999a, 1999b, 1994).

A.2.6.2. Shenandoah Watershed Study

The Shenandoah Watershed Study (SWAS) program is a monitoring and research network focused on low-order, high-gradient streams associated with public lands in western Virginia (see http://swas.evsc.virginia.edu/). The objectives of the program are to increase understanding of factors that govern biogeochemical conditions and stressor-response relationships in forested mountain watersheds of the central Appalachian region. Success in addressing these scientific and problem-oriented objectives has been achieved through development of a data collection network that accounts for spatial gradients, as well as temporal variation, in the chemical composition of the region's relatively undisturbed headwater streams.

The program is notable for the length of the continuous data record that has been obtained, including the longest-running record (28 years) of stream water composition and discharge in the National Park System. The SWAS component of the program, which now includes 14 streams in Shenandoah National Park, was initiated in 1979. The Virginia Trout Stream Sensitivity Study (VTSSS) component, which now includes 51 streams in National Forests and other conservation lands, was initiated in 1987. The distribution of SWAS-VTSSS study sites in relation to public lands is shown in Figure A-5

The SWAS-VTSSS program has been maintained as a cooperative effort involving the Department of Environmental Sciences at the University of Virginia, the National Park Service, the U.S. EPA, the USDA Forest Service, the U.S. Geological Survey, the Virginia Department of Game and Inland Fisheries, and Trout Unlimited. The monitoring sites account for ecological variation among the region's forested mountain watersheds with a data-collection strategy that represents: spatial variation through the distribution of hydrochemical monitoring within a lithologic classification system; and temporal variation through long-term data collection at fixed locations sampled at different frequencies.
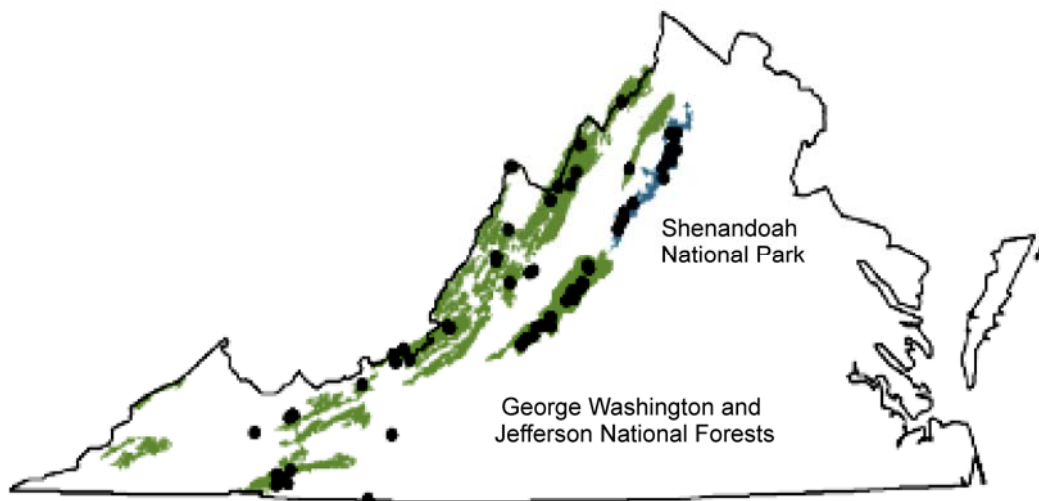
Figure A-5. **SWAS-VTSS Program Study Sites. The length of the stream water chemical composition record for SWAS-VTSSS study watersheds is 20 to 28 years. SWAS sites are located in Shenandoah National Park (shaded blue). VTSSS sites are mainly located in Virginia's National Forests (shaded green).**

The lithologic classification system includes 6 classes based on the physical and chemical properties of bedrock formations in the region. ANC and concentrations of related acid-base constituents in stream waters, as well as other biotic and abiotic properties of watersheds, differ among the lithologic classes.

The SWAS-VTSSS data collection framework is most-well developed in the Blue Ridge Mountains Province within Shenandoah National Park, where stream water composition data are collected seasonally at 14 sites, weekly at 6 sites, and every four hours during episodic high-flow conditions at 3 sites with continuous discharge gauging. Stream water composition data are collected on a seasonal basis at an additional 51 sites located outside of the Park, in both the Blue Ridge Mountains and Ridge and Valley Provinces.

Stream water samples collected through the SWAS and VTSSS programs are analyzed for ANC, pH, and the major anions (SO_4^{2-}, nitrate, and chloride) and cations (calcium, magnesium, potassium, and sodium) by methods appropriate for low-ionic strength natural waters. Both the SWAS and VTSSS sample streams were selected based on geographic distribution, representation of the major bedrock types underlying the mountain ridges in the region, and minimization of recent watershed disturbance. All but a few of the sample streams currently support reproducing populations of native brook trout. All of the sample streams supported brook trout populations historically.

Sustained data collection in a network constructed of intensively studied sites nested within a geographically extensive set of less intensively studied sites has allowed detection and interpretation of change that has occurred in a context of multiple time scales and stressors. Responses to multi-year changes in acidic deposition have been reflected in long-term trends in quarterly concentrations of SO_4^{2-}, ANC, and other acid-base constituents of streams in the network. Expectations for southeastern watersheds with soils that retain sulfur, for example, have been confirmed by the lack of regional improvement in stream water quality following reductions in acidic deposition mandated by the CAA. The acid-base chemistry of streams in the network also varies seasonally and on shorter time scales. Weekly and higher-frequency automated stream water sampling during periods of high runoff have supported the study of episodically more-acidic conditions, including the study of fish sensitivity with in-stream bioassays and development of models to predict severity and recurrence intervals.

By accounting for significant spatial gradients and temporal patterns in the region, the SWAS-VTSSS hydrochemical data collection program provides a basis for both observing and interpreting watershed-scale change, as well as an informed foundation for process-oriented research. Monitoring data and research findings obtained through the SWAS-VTSSS program have contributed to increased scientific understanding, as well as to policy formulation and implementation.

The mathematical model, Model of Acidification of Groundwater in Catchments (MAGIC), was first calibrated using data obtained for White Oak Run, a SWAS-VTSSS study stream in Shenandoah National Park. MAGIC is the most widely used acid-base chemistry model in the U.S. and Europe and the principal model used by the National Acid Precipitation Assessment Program in the 1980s to estimate future damage to lakes and streams in the eastern U.S. The MAGIC model has since been applied in a number of regional assessments that relied extensively on stream water and soils data obtained through the SWAS-VTSSS program. Among these are:

- The Southern Appalachian Mountain Initiative, a multi-state effort to evaluate alternative approaches to solving regional air-pollution problems. MAGIC projections indicated that even ambitious emission control strategies would not result in near-term recovery of the region's most acidified surface waters – a consequence of base-cation depletion in soils exposed to decades of acidic deposition.

- The Shenandoah Assessment, an assessment of acidification effects on aquatic systems in Shenandoah National Park. MAGIC reconstructions indicated that Park streams associated with base-poor bedrock lost about 70 µeq/L between 1900 and 1990. MAGIC projections indicated that some streams may recover given prospective reductions in acidic deposition, but others will not.

Data and findings provided through the SWAS-VTSSS program have also proven relevant to the evaluation and implementation of national air pollution control policies. The SWAS-VTSSS program provides data for the U.S. EPA long-term monitoring of surface water response to legislated reductions in sulfur emissions. Whereas SO_4^{2-} concentrations in surface water declined during the 1990–2000 period for four northeastern regions with sensitive surface waters, the SWAS-VTSSS study region, in contrast, experienced increasing stream-water SO_4^{2-} concentrations and continuing acidification.

Recent publications that were based on analyses of SWAS-VTSSS data include Cosby et al. (1991), Stoddard et al. (1993), Sullivan et al. (2003), and Webb et al. (2004).

A.2.6.3. Fernow

The Fernow Experimental Forest, established in 1934, is located just south of the city of Parsons in the most mountainous region of West Virginia. It is surrounded by the Monongahela National Forest, which comprises about 900,000 acres of rugged, hilly terrain. Most research at Fernow is focused on improvement of forest management (see http://www.fs.fed.us/ne/parsons/fefhome.htm).

Scientists at Fernow are developing information and techniques for sustainably managing hardwood forests in the central Appalachians. The mixed hardwood forest covers about 78% of West Virginia and supplies important timber products, provides recreational opportunities, and supports a diverse assemblage of wildlife and plant species.

The Fernow Experimental Forest was heavily logged between 1905 and 1911. The forest now contains about 1900 ha of second- and third-growth Appalachian hardwood stands, which are representative of average to better than average sites found on approximately 4 million ha of the forest type in West Virginia and surrounding states. At the lowest elevations, the original forests consisted mainly of hardwoods, with eastern hemlock (*Tsuga canadensis* [L.] Carr.) along stream bottoms and on north slopes. Forests at the higher elevations were dominated by red spruce (*Picea rubens* Sarg.) and hemlock. Small patches of pure spruce occurred on the tops of the mountains.

Elevations in the Fernow range from 533 to 1112 m, with slopes of 10% to 60%. A rock layer composed of fractured hard sandstone and shale underlies most of the Fernow. A majority of the soils are of the Calvin and Dekalb series, which originated from these rocky materials (loamy-skeletal mixed mesic Typic Dystrochrepts). On the southeastern part of the forest, Greenbrier limestone outcrops to produce a midslope zone of limestone soil of the Belmont series (fine-loamy mixed mesic Typic Hapludalfs). Almost all Fernow soils, including the sandstone, shale, and limestone soils, are well-drained, medium textured loams and silt loams. Average soil depth is about 1 m, and average soil pH is about 4.5.

A rainy, cool climate is typical on the Experimental Forest. Precipitation, which averages about 145 cm per year, is evenly distributed throughout the year. Mean annual temperature is about 9 °C, and the length of the growing season is approximately 145 days.

The forest types and conditions today reflect the site qualities and past history of the area. Oaks (*Quercus* spp.) are most common and are found on all sites along with American beech (*Fagus grandifolia* Ehrh.) and sweet birth (*Betula lenta* [L].). Excellent sites in coves and on north slopes support primarily northern red oak (*Quercus rubra* L.), sugar maple (*Acer saccharum* Marsh.), yellow-poplar (*Liriodendron tulipifera* L.), black cherry (*Prunus serotina* Ehrh.), white ash (*Fraxinus americana* L.), basswood (*Tilia americana* L.), cucumbertree (*Magnolia acuminata* L.), and beech. Fair sites on south and east slopes usually support oak stands composed of red oak, white oak (*Quercus alba* L.), chestnut oak (*Quercus prinus* L.), and scarlet oak (*Quercus coccinea* Muenchh.). Other fair site species include red maple (*Acer rubrum* L.), sweet birch, black gum (*Nyssa sylvatica* Marsh.), sassafras (*Sassafras albidum* Nutt.), and sourwood (*Oxydendrum arboreum* [L.] DC.). Good sites commonly support a mixture of excellent and fair site species. Black locust (*Robinia pseudoacacia* L.), sweet birch, and Fraser magnolia (*Magnolia fraseri* Walt.) are consistent but generally minor components of the forest on all sites. American chestnut was a major forest component until it was eliminated by the chestnut blight.

The Fernow Experimental Forest encompasses practically the entire Elk Lick Run drainage, which is about 5.8 km long and 3.5 km across at the widest point. Elk Lick Run has seven major tributaries including Big Spring, which drains a headwater limestone formation. Headwater areas on two of these tributaries have been gauged to show how forest management influences streamflow.

Research on the Fernow Experimental Forest by the Timber and Watershed Project scientists is done in cooperation with the Monongahela National Forest, West Virginia University, Marshall University, Pennsylvania State University, Virginia Tech, and the West Virginia Division of Natural Resources.

Scientific studies on the Fernow have followed two lines of research, with considerable overlap. Silvicultural research, focused mostly on mixed hardwood stands, addresses questions relating to regenerating, growing, tending, and harvesting trees and stands. Watershed research has addressed some of the more basic questions about water use by forests and forest hydrology, as well as critical issues affecting roads, best management practices, and forest management effects on water and soil resources. The Fernow also has been in the forefront of research on acidic deposition and N saturation. A whole-watershed acidification study has been conducted since 1989. Recently, research on threatened and endangered species has assumed a more prominent role, due to the presence of Indiana bat and running buffalo clover on the Fernow.

A.2.6.4. National Ecological Observatory Network

The National Ecological Observatory Network (NEON) is a continental-scale research platform that is primarily focused on discovering and understanding the impacts of climate change, land-use change, and invasive species on ecology. It will also generate data that will be useful for assessing effects of NO_X and SO_X deposition on ecosystems. NEON has not yet been implemented; it is described here because it represents an ambitious monitoring program that is expected to be very useful in the near future. NEON will gather long-term data on ecological responses of the biosphere to changes in land use

and climate, and on feedbacks with the geosphere, hydrosphere, and atmosphere. NEON is proposed as a national observatory, consisting of distributed sensor networks and experiments, linked by advanced cyber infrastructure to record and archive ecological data for at least 30 years. Using standardized protocols and an open data policy, NEON is intended to gather essential data for developing scientific understanding and theory required to manage the nation's ecological challenges. The program description is found at www.neoninc.org/.

A.3. Modeling

A.3.1. Principal Ecosystem Models Used in the U.S.

It is particularly difficult to study endpoints at the larger levels of biological organization (e.g., at the population, community, biogeochemical, and ecosystem-level) with monitoring studies. Geographic areas are larger, and timeframes are longer, rendering it difficult to obtain data in sufficient quantity to detect impacts unless they are exceptionally severe. Therefore, the most common approach to study endpoints at these scales is to develop and apply a model. Models may be calibrated using data from monitoring, survey, or laboratory or field experiments and are useful tools in predicting larger-scale, longer-term impacts. However, verifying the predictions and assessing the overall validity of the model can be challenging.

Some of the most frequently used ecosystem models designed to quantify effects of atmospheric N and S deposition are discussed below. It is important to note that the ecosystem models are parameterized for specific areas and may not be readily applicable to other locations without significant re-parameterization.

There are four principal models that are currently being used in the U.S. to assess the effects of S and N deposition on terrestrial and freshwater aquatic ecosystems: MAGIC, NuCM, PnET/BGC, and DayCent-Chem. Two models, SPARROW and WATERSN, are commonly used to evaluate N loading to large river systems and to estuaries. These six models are briefly reviewed in the following sections. Each review begins with a summary of the provenance and conceptual basis of the model and contains references to some of the published applications. This is followed by a more detailed description of the processes included in the model, the inputs required, and the output variables simulated by the model.

The ranges of process complexity, temporal resolution and spatial discretization represented in these models are considerable. These ranges make comparative summaries of inputs, outputs, and processes across the models problematic. The models are all currently in use because they are, in a sense, complementary to each other, with each providing an approach or satisfying requirements unique to their own structure and intended applications. As a result, there is no good way to develop satisfying comparative equivalences among the components of the various structures. It is also beyond the scope of this document to present the level of detail necessary to run any of the models. The descriptions below must of necessity be brief. References to appropriate texts designed to provide more detail are given for each model.

Following the discussion of the four models most frequently used in the U.S., there are brief descriptions of the most important models of S and N deposition effects that are being used in Europe and elsewhere.

A.3.1.1. MAGIC

The MAGIC model (Cosby et al., 1985a; 1985b; 1985c) is a mathematical model of soil and surface water acidification in response to atmospheric deposition based on process-level information

about acidification. MAGIC has been applied extensively in North America and Europe to both individual sites and regional networks of sites, and has also been used in Asia, Africa and South America. The utility of MAGIC for simulating a variety of water and soil acidification responses at the laboratory, plot, hillslope, and catchment scales has been tested using long-term monitoring and experimental manipulation data.
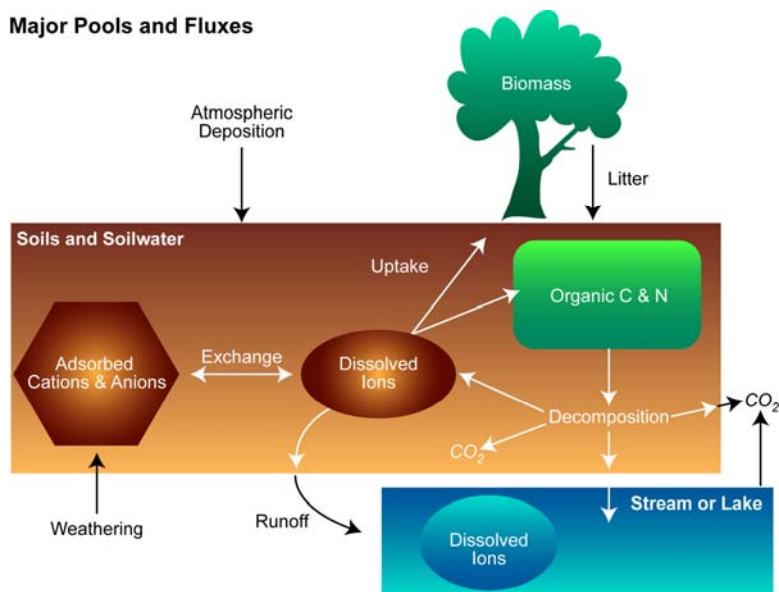
Figure A-6.   **Conceptual structure of the MAGIC model showing major pools and fluxes included in simulation of effects of S and N deposition.**

MAGIC has been widely used in policy and assessment activities in the U.S. and in several countries in Europe (e.g., Beier et al., 1995; Clair, 2004; Cosby, 1985b; Cosby et al., 1990, 1995, 1996; Ferrier et al., 2001; Hornberger et al., 1989; Jenkins et al., 1990; Moldan et al., 1998; Sullivan et al., 1998, 2006b; Whitehead et al., 1988, 1997; Wright et al., 1994, 1998).

MAGIC Model Structure

MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on surface water chemistry (see Figure A-6). The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in these waters. MAGIC consists of: a section in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving SO_4^{2-} adsorption, cation exchange, dissolution-precipitation- speciation of aluminum, and dissolution-speciation of inorganic carbon; and a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering, net uptake and loss in biomass and losses to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change of surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils.

Cation exchange is modeled using equilibrium (Gaines-Thomas) equations with selectivity coefficients for each base cation and aluminum. SO_4^{2-} adsorption is represented by a Langmuir isotherm. Aluminum dissolution and precipitation are assumed to be controlled by equilibrium with a solid phase of

aluminum trihydroxide. Aluminum speciation is calculated by considering hydrolysis reactions as well as complexation with SO_4^{2-}, fluoride and dissolved organic compounds. Effects of carbon dioxide on pH and on the speciation of inorganic carbon are computed from equilibrium equations. Organic acids are represented in the model as tri-protic analogues. Weathering rates are assumed to be constant. Two alternate mechanisms are offered for simulation of nitrate and ammonium in soils and water: either first order equations representing net uptake and retention; or a set of equations and compartments describing process-based N dynamics controlled by C and N pools and fluxes in the compartments.

      Atmospheric deposition fluxes for the base cations and strong acid anions are required as inputs to the model. These inputs are generally assumed to be uniform over the catchment. Atmospheric fluxes are calculated from concentrations of the ions in precipitation and the rainfall volume into the catchment. The atmospheric fluxes of the ions must be corrected for dry deposition of gas, particulates and aerosols and for inputs in cloud/fog water. The volume discharge for the catchment must also be provided to the model. In general, the model is implemented using average hydrologic conditions and meteorological conditions in annual or seasonal simulations, i.e., mean annual or mean monthly deposition, precipitation and lake discharge are used to drive the model. Values for soil and surface water temperature, partial pressure of carbon dioxide and organic acid concentrations must also be provided at the appropriate temporal resolution.

      The MAGIC model can be implemented as a one- or two-soil representation of a catchment with or without wetlands. Atmospheric deposition enters the soil compartment(s) and the equilibrium equations are used to calculate soil water chemistry. The water is then routed to the stream compartment, and the appropriate equilibrium equations are reapplied to calculate runoff chemistry. Input-output mass balance equations are provided for base cations and strong acid anions, and charge balance is required for all ions in each compartment (for complete details of the model see Cosby et al., 1985a, 1985b, 1985c; 2001).

      For most applications, model outputs for 15 stream water variables are used. These variables consist of the concentrations of 10 ions (H; Ca; Mg; Na; K; NH_4; SO_4^{2-}; NO_3; Cl; and total inorganic Al), the stream discharge (Q), stream pH, sum of base cation (SBC) concentrations (SBC = Ca + Mg + Na + K + NH_4), sum of mineral acid anion (SAA) concentrations (SAA = Cl + SO_4^{2-} + NO_3) and the charge balance acid neutralizing capacity (ANC = SBC – SAA). These variables are expressed in units of m/yr (or m/mo) for Q, μmol/L for inorganic Al, and μeq/L for all other variables. In addition, model output for 7 soil and soilwater variables are frequently used, the total base saturation and individual cation saturations for Ca, Mg, Na, and K, the soilwater pH and the Ca/Al ratio in soil water.

      The aggregated nature of the model requires that it be calibrated to observed data from a system before it can be used to examine potential system response. Calibrations are based on volume weighted mean annual or seasonal fluxes for a given period of observation. The length of the period of observation used for calibration is not arbitrary. Model output will be more reliable if the annual flux estimates used in calibration are based on a number of years rather than just one year. There is a lot of year-to-year variability in atmospheric deposition and catchment runoff. Averaging over a number of years reduces the likelihood that an "outlier" year (very dry, etc.) is used to specify the primary data on which model forecasts are based. On the other hand, averaging over too long a period may remove important trends in the data that need to be simulated by the model.

      The calibration procedure requires that stream water quality, soil chemical and physical characteristics, and atmospheric deposition data be available for each catchment. The water quality data needed for calibration are the concentrations of the individual base cations (Ca, Mg, Na, and K) and acid anions (Cl, SO_4^{2-}, and NO_3) and the pH. The soil data used in the model include soil depth and bulk density, soil pH, soil cation-exchange capacity, and exchangeable bases in the soil (Ca, Mg, Na, and K). The atmospheric deposition inputs to the model must be estimates of total deposition, not just wet deposition. In some instances, direct measurements of either atmospheric deposition or soil properties may not be available for a given site with stream water data. In these cases, the required data can often be estimated by: (a) assigning soil properties based on some landscape classification of the catchment; and

(b) assigning deposition using model extrapolations from some national or regional atmospheric deposition monitoring network.

Soil data for model calibration are usually derived as aerially averaged values of soil parameters within a catchment. If soils data for a given location are vertically stratified, the soils data for the individual soil horizons at that sampling site can be aggregated based on horizon, depth, and bulk density to obtain single vertically aggregated values for the site, or the stratified data can be used directly in the model.

Calibration of the model (and estimation of historical changes at the modeled sites) requires a temporal sequence of historical anthropogenic deposition. Current understanding of ecosystem responses to acidic deposition suggests that future ecosystem responses can be strongly conditioned by historical acid loadings. Thus, as part of the model calibration process, the model should be constrained by some measure of historical deposition to the site. However, such long-term, continuous historical deposition data may not exist. The usual approach is to use historical emissions data as a surrogate for deposition. The emissions for each year in the historical period can be normalized to emissions in a reference year (a year for which observed deposition data are available). Using this scaled sequence of emissions, historical deposition can be estimated by multiplying the total deposition estimated for each site in reference year by the emissions scale factor for any year in the past to obtain deposition for that year.

A.3.1.2. NuCM

The current NuCM model is based on the original Integrated Lake Watershed Acidification Study (ILWAS) model of the 1980s (cf. Chen et al., 1984; Gherini et al., 1985; Goldstein et al., 1984). NuCM was developed as an extension to the ILWAS model by investigators in the Integrated Forest Study see and the model code was written by Tetra-Tech, Inc. (Liu et al., 1991). NuCM was developed to explore potential effects of atmospheric deposition, fertilization and harvesting in forest ecosystems. Because NuCM was designed primarily for simulating the effects of atmospheric deposition on nutrient cycling processes, its construction emphasizes soil and soil solution chemistry (Liu et al., 1991). As a stand-level model, NuCM incorporates all major nutrient cycling processes (uptake, translocation, leaching, weathering, organic matter decay, and accumulation). Vegetation is divided into leaf, bole and root compartments for under- and overstory vegetation. NuCM simulates the cycling of N, P, K, Ca, Mg, Na, and S based on expected optimal growth rates (input by the user and reduced in the event of nutrient limitation), user-defined litterfall, weathering, N and S mineralization rates, soil minerals composition, initial litter, soil organic matter pools, and C/N ratios.

The model has been calibrated for different vegetation types, including a loblolly pine (*Pinus taeda* L.) stand at Duke University (Johnson et al., 1995), a mixed deciduous stand at Walker Branch (Johnson et al., 1993) and a red spruce (*Picea rubens Sarg.*) stand in the Great Smoky Mountains (Johnson et al., 1996). The NuCM model was used as part of the Southern Appalachian Mountain Assessment (Sullivan et al., 2002a).

NuCM Model Structure

In NuCM, the ecosystem is represented as a series of vegetation and soil components. The overstory consists of one generic conifer and one generic deciduous species of specified biomass and nutrient concentration (foliage, branch, bole, roots). For mixed species stands, average values for biomass and nutrient concentration by component must be used. NuCM also includes an understory, which can be divided into canopy, bole, and roots. Maximum potential vegetative growth in the model is defined by the user and is constrained in the model by the availability of nutrients and moisture. The forest floor is simulated from litterfall inputs and litter decay. Litterfall mass inputs are defined by the user, and litter decay is represented as a four stage process where: coarse litter decays to fine litter; fine litter decays to

humus and cations; humus decays to organic acids, NH_4^+, SO_4^{2-}, H^+, and CO_2; and organic acids decay to NH_4^+, SO_4^{2-}, H^+, and CO_2. Each stage is represented as a first-order equation.

The soil includes multiple layers (up to 10), and each layer can have different physical and chemical characteristics. The user defines bulk density, cation exchange capacity, exchangeable cations, adsorbed phosphate and SO_4^{2-}, and four soil minerals and their composition. These inputs define the initial soil exchangeable/adsorbed pools and total pools. Initial total soil N pools are simulated from litterfall and decay, as described above, and user-defined C/N ratios. Vegetation, litter, and soil pools change over a simulation in response to growth, litterfall and decomposition, and nutrient fluxes via deposition, leaching and weathering.

The processes that govern interactions among these pools include translocation, uptake, foliar exudation and leaching, organic matter decay, nitrification, anion adsorption, cation exchange and mineral weathering. Translocation, defined as the removal of nutrients from foliage before litterfall, is user-specified. Maximum uptake is calculated from biomass and nutrient concentrations; actual uptake is equal to this maximum value when sufficient nutrients are available and reduced when nutrients become limiting. Reduced uptake first allows reduced nutrient concentrations in plant tissues, then causes a reduction in growth. Foliar exudation and leaching rates are simulated as proportional to foliar concentrations using user-defined coefficients.

Mineral weathering reactions are described in the model using rate expressions with dependencies on the mass of mineral present and solution-phase hydrogen-ion concentration taken to a fractional power. Cation exchange is represented by the Gapon equation. The model simulates a tri-protic organic acid with a fixed charge density. Nitrification is represented in the form of a Michaelis–Menton rate expression. Phosphate adsorption is represented by a linear isotherm, and SO_4^{2-} adsorption is represented by a Langmuir adsorption isotherm.

Climate inputs to the NuCM model are through input meteorological files (typically 1 to 5 years long), which are repeated to generate long-term simulations. The meteorological files contain daily values for precipitation quantity, maximum and minimum air temperature, cloud cover, dewpoint, atmospheric pressure, and wind speed. Monthly soil temperature data are also required.

Precipitation is routed through the canopy and soil layers and evapotranspiration, deep seepage, and lateral flow are simulated. The movement of water through the system is simulated using the continuity equation, Darcy's equation for permeable media flow, and Manning's equation for free surface flow. Percolation occurs between layers as a function of layer permeability's and differences in moisture content. Nutrient pools associated with soil solution, the ion exchange complex, minerals, and soil organic matter are all tracked explicitly by NuCM.

Wet deposition is calculated from precipitation amounts and user-input air quality files which define precipitation concentrations on a monthly basis. Dry deposition is calculated from air concentrations in the air quality files combined with user-defined deposition velocities and simulated leaf areas. Leaching is calculated from soilwater percolation and simulated soil solution concentrations using the soil chemical and biological algorithms defined above for each soil horizon.

The only processes in the NuCM model that are explicitly temperature-dependent are evaporation, occurrence of precipitation as rainfall versus snowfall, snowpack melting, litter decay, and nitrification. Temperature affects processes such as cation exchange, mineral weathering, and uptake only indirectly. Precipitation effects are manifested strictly through the hydrologic simulations; none of the nutrient processes are dependent explicitly upon moisture.

A.3.1.3. PnET-BGC

PnET-BGC is an integrated dynamic biogeochemical model that simulates chemical transformations of vegetation, soil and drainage water. The PnET-BGC model was formulated by linking two submodels (vegetation and biogeochemical) to allow for the simultaneous simulation of major element cycles in forest and interconnected aquatic ecosystems. The vegetation submodel is based on PnET-CN

(Aber, 1992; Aber and Driscoll, 1997; Aber et al., 1997), a simple generalized model of monthly carbon, water, and N balances that provides estimates of net primary productivity, N uptake, and water balances. The biogeochemical submodel BGC (Gbondo-Tugbawa et al., 2001), expands PnET to include vegetation and organic matter interactions of other elements (Ca^{2+}, Mg^{2+}, K^+, Na^+, Si, S, P, Al^{3+}, Cl^-, and F^-), abiotic soil processes, solution speciation, and surface water process.

PnET-BGC was initially developed for and applied to the northern hardwood forest ecosystem. The model has been tested using vegetation, soil and water chemistry data from the Hubbard Brook Experiment Forest (HBEF) (Gbondo-Tugbawa et al., 2001). The model has subsequently been applied to intensively studied watersheds in the Adirondack and Catskill regions of New York and applied regionally to the Adirondacks (Chen and Driscoll, 2005b) and northern New England (Chen and Driscoll, 2005a, 2005c). PnET-BGC has also been used to evaluate the effects of current and future atmospheric deposition scenarios (Gbondo-Tugbawa, 2002a; Sullivan, 2006b).

PnET-BGC Model Structure

PnET/BGC simulates major biogeochemical processes, such as forest canopy element transformations, hydrology, soil organic matter dynamics, N cycling, geochemical weathering, and chemical equilibrium reactions in solid and solution phases, and allows for simulations of land disturbance (see Figure A-7) (Gbondo-Tugbawa et al., 2001). The model uses mass transfer relationships to describe weathering, canopy interactions and surface water processes. Chemical equilibrium relationships describe anion adsorption, cation exchange and soil solution and surface water speciation. Soil solution equilibrium reactions are described using the tableau approach (Morel and Hering, 1993). A more detailed description of the model can be found in Gbondo-Tugbawa et al. (2001).
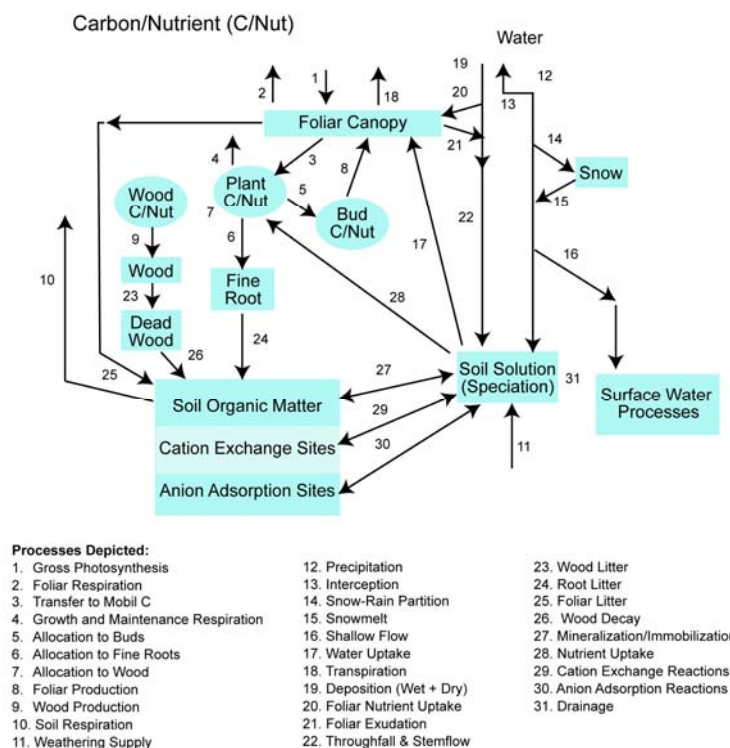
Figure A-7. The PnET-BGC model illustrating the compartments and flow paths of carbon and nutrients (C/Nut) within the model.

The model operates on a monthly time step and is applied at the stand to small-watershed scale. The process of photosynthesis, growth and productivity, litter production and decay, mineralization of organic matter, immobilization, and nitrification in PnET have been described in Aber and Federer (1992) and Aber et al. (1997). The BGC submodel uses the Gaines–Thomas formulation (White and Zelazny, 1986) to describe cation exchange reactions within the soil. The exchangeable cations considered in the model include Ca^{2+}, Mg^{2+}, Na^+, H^+, Al^{3+}, K^+, and NH_4^+. A pH-dependent adsorption isotherm is used to describe the SO_4^{2-} adsorption process. The speciation of monomeric aluminum is calculated in the model, including both organic and inorganic forms. Organic acids are described using a triprotic analogue (Driscoll et al., 1994b), and the total amount of organic acids is estimated as a certain fraction (based on the charge density) of DOC. The model simulates ANC in surface waters as an analogue to ANC measured by Gran plot analysis, by considering the contributions of DIC, organic anions and Al complexes (Driscoll et al., 1994b).

The PnET/BGC model requires inputs of climate, wet and dry deposition chemistry, and weathering data. Climate inputs consist of minimum and maximum air temperature, solar radiation, and precipitation. The model uses a constant dry-to-wet deposition ratio by default, but a variable ratio can also be applied (Chen and Driscoll, 2005b). The model inputs utilize canopy enhancement factors to depict the increased dry deposition observed in coniferous and mixed forest stands compared to hardwood forests. Deposition and weathering fluxes for all major elements are required as model inputs. Weathering rates are assumed to remain constant over time.

Calibration of PnET-BGC is based on empirical relationships and observations. The model uses historical reconstructions of climate, atmospheric deposition, and land disturbance to construct hindcasts of the response of forests to past acidic deposition. The model can also be used to predict the response of

acid-sensitive forest ecosystems to future changes in acidic deposition, for example in response to controls on atmospheric emissions. A detailed description of the model, including a detailed uncertainty analysis of parameter values, is available in Gbondo-Tugbawa et al. (2001).

A.3.1.4. DayCent-Chem

DayCent-Chem links two widely accepted and tested models, one of daily biogeochemistry for forest, grassland, cropland, and savanna systems, DayCent (Parton et al., 1998), and the other of soil and water geochemical equilibrium, PHREEQC (Parkhurst and Appelo, 1999). The linked DayCent/PHREEQC model was created to capture the biogeochemical responses to atmospheric deposition and to explicitly consider those biogeochemical influences on soil and surface water chemistry. The linked model expands on DayCent's ability to simulate N, P, S, and C ecosystem dynamics by incorporating the reactions of many other chemical species in surface water.

Hartman et al. (2007) et al. used DayCent-Chem to investigate how wet and dry deposition affect biological assimilation, soil organic matter composition, ANC and pH of surface waters, and also Al mobilization, soil base cation depletion, and base cation flux. Model results were tested against a long-term data set available from Andrews Creek in Loch Vale Watershed, Rocky Mountain National Park, Colorado.

DayCent-Chem Model Structure

DayCent is the daily time-step version of CENTURY, a non-spatial, lumped parameter model that simulates C, N, P, S, and water dynamics in the soil-plant system at a monthly timestep over time scales of centuries and millennia (Parton et al., 1994). CENTURY can represent a grassland, crop, forest, or savanna system with parameters that describe the site-specific plant community and soil properties. DayCent, the daily timestep version of CENTURY, adds layered soil temperature, a trace gas submodel, a more detailed soil hydrology submodel, and explicitly represents inorganic N as either NO_3^- or NH_4^+ (Del Grosso et al., 2001; Kelly et al., 2000; Parton et al., 1998). DayCent 5 is an object-oriented model written in the C++ programming language that implements a layered soil structure and algorithms to manage soil layers. The model is initialized with an organic soil depth and up to 10 soil layers, where each layer has a specified thickness, texture, bulk density, field capacity, wilting point, and saturated hydraulic conductivity.

PHREEQC is a model based on equilibrium chemistry of aqueous solutions interacting with minerals, gases, exchangers, and sorption surfaces. The model is written in the C programming language and has an extensible chemical database. Version 2.7 of PHREEQC is used in the linked DayCent-Chem model to compute aqueous speciation, ion-exchange equilibria, fixed-pressure gas-phase equilibria, dissolution and precipitation of mineral phases to achieve equilibrium, and irreversible aqueous mineral phase reactions. The aqueous model uses ion-association and Debye Huckel expressions. Ion-exchange reactions are modeled with the Gaines-Thomas convention and equilibrium constants are derived from Appelo and Postma (1993).

The DayCent-Chem model inputs are climate drivers consisting of daily precipitation, and minimum and maximum air temperatures. The model also requires daily atmospheric wet deposition concentrations for precipitation species Ca^{2+}, Cl^-, K^+, Mg^{2+}, Na^+, NH_4^+, NO_3^-, SO_4^{2-}, and H^+ and daily dry deposition amounts or dry/wet ratios for all precipitation species. Initial conditions for model simulations include: initial snowpack water content and chemical composition; initial soil solution concentrations; and initial exchangeable cations in each soil layer. Potential annual denudation rates for each mineral phase that could be dissolved in the soil, groundwater, or stream solutions must also be provided.

DayCent-Chem implements a geochemical submodel of layered pools and properties that provides information exchange, such as of water fluxes and solute concentrations, between the coupled models, and calculates daily geochemical outputs. The geochemical submodel defines soil layers and a

groundwater pool that correspond to those in Day-Cent 5's original soil class. Surface water concentrations are computed in a two-step process where solutes are first transported, and then PHREEQC undertakes solution reactions. At each timestep, the model updates exchangeable base cation pools and soil solutions in each soil layer, along with groundwater and stream solutions.

DayCent 5 output includes daily evapotranspiration; soilwater content; outflow; inorganic and organic C, N, P, and S stream fluxes; C, N, P, and S contents in soil and plant pools; net primary production (NPP); nutrient uptake; trace gas flux; and heterotrophic respiration. In addition to standard DayCent 5 outputs, at each daily timestep the model writes the solution chemistry for soil layers, groundwater, and stream.

A.3.1.5. SPARROW

SPAtially Referenced Regressions on Watersheds (SPARROW) is a hybrid statistical/deterministic model used to estimate pollutant sources and contaminant transport in surface waters. SPARROW can be used to estimate pollutant loading to downstream receiving waters for a number of water quality constituents. The model as constructed for evaluating N export to estuaries will be presented here.

SPARROW was first described by Smith et al. (1997) as a water quality model designed to reduce problems with interpreting watershed data as a result of sparse sampling, network bias, and basin hetero-geneity. SPARROW combines regression techniques and process information regarding contaminant transport and retention in watershed and riverine systems. Literature values for watershed retention rates are used; in-stream retention of N is estimated by a first-order decay function (Smith et al., 1997).

Others have developed similar regression models relating in-stream water quality measurements to watershed nutrient sources and basin attributes (Howarth et al., 1996; Jaworski et al., 1997; Mueller et al., 1997). These simple correlative models assume that contaminate sources and sinks are homogenously distributed and do not make a distinction between watershed and in-stream loss processes. SPARROW is distinct from these methods by incorporating spatial representation of basin attributes in the model. Model correlations between basin attributes and water quality measurements are strengthened by incorporating these spatial references (Alexander et al., 2001; Smith et al., 1997). Spatially referenced basin attributes include land use, point and non-point N sources, temperature, soil permeability, and stream density, among others. Figure A-8 shows the mathematical form of the SPARROW model (Preston and Brakebill, 1999).

$$L_i = \sum_{n=1}^{N} \sum_{j \varepsilon J(i)} \beta_n S_{n,j} e^{(-a'Z_j)} e^{(-\delta' Z_{i,j})}$$

where

$L_i =$ load in reach i;

$n, N =$ source index where N is the total number of considered sources;

$J(i) =$ the set of all reaches upstream and including reach i, except those containing or upstream of monitoring stations upstream of reach i;

$\beta_n =$ estimated source parameter;

$S_{n,j} =$ contaminant mass from source n in drainage to reach j;

$\alpha =$ estimated vector of land-to-water delivery parameters;

$Z_j =$ land-surface characteristics associated with drainage to reach j;

$\delta =$ estimated vector of instream-loss parameters; and

$T_{i,j} =$ channel transport characteristics.

Figure A-8.   **Mathematical form of the SPARROW model.**

Smith et al. (1997) provided an example of SPARROW model development for application to the conterminous U.S. Their exploratory model included five N sources and eight land surface characteristics as potential factors that deliver N from land to water. In-stream decay coefficients for three stream size classes were also tested for significance (Table A-4).

The final model resulted in the inclusion of each of the five N sources and three (temperature, soil permeability, and stream density) of the eight land to water delivery factors. Parameter selection was primarily based on statistical significance. Further discussion regarding the exclusion of precipitation and irrigated land, both of which were determined to be significant, can be found in Smith et al. (1997). Parameter estimates are evaluated for robustness through the use of bootstrap analysis.

The bootstrap procedure involves randomly selecting, with replacement, M monitored loads and associated predictor variables from among the observations in the data set (M is the number of monitored reaches in the reach network). Where a sampled observation has an upstream monitored load as one of its predictors, the monitored value is used, regardless of whether the upstream station appears in the bootstrap sample. Coefficient values are estimated from the bootstrap sample. The bootstrap process is repeated 200 times, resulting in 200 estimates of each coefficient. From these estimates, the mean coefficient value (called the bootstrap estimate), minimum confidence interval, and probability that the estimated coefficient has the wrong sign are determined (Smith et al., 1997).

Spatial referencing in the model occurs in two ways: land surface polygons are mapped in conjunction with nonpoint contaminant sources and the land-water delivery variables (temperature, soil permeability, stream density, etc.); and the stream reach network is mapped along with point sources, channel transport characteristics, and measured transport rates. The positive impacts of this spatial referencing can be quantified by eliminating the channel decay coefficients from the model and creating a new model with only the contaminant sources and land-water delivery variables in the original model (Smith et al., 1997). Removing this spatial reference provided by the reach network results in a model with significantly higher mean squared error and lower predictive capacity (Table A-5).

Table A-4. Parameter estimates, probability levels, and regression results of parametric and bootstrap regressions of total nitrogen at 414 national stream quality accounting network stations on basin attributes, for the Chesapeake Bay total nitrogen SPARROW model.

Model Parameters	Coefficient Units[a]	Exploratory Model		Final Model					
		Parametric Coefficient	P	Parametric Coefficient	Parametric P	Bootstrap Coefficient	Lower 90% CI[b]	Upper 90% CI[b]	Bootstrap p
NITROGEN SOURCE B									
Point sources	Dimensionless	0.4112	0.0004	0.3464	0.0049	0.4401	0.0864	0.8173	<0.005
Fertilizer application	Dimensionless	2.798	0.0154	1.278	0.0022	1.433	0.6149	2.373	<0.005
Livestock waste production	Dimensionless	1.340	0.1553	0.9723	0.0629	1.058	0.0859	1.919	0.005
Atmospheric deposition	Dimensionless	3.334	0.2513	6.465	0.0033	6.555	3.270	9.323	<0.005
Nonagricultural land	kg N/ha/yr	38.49	0.0154	14.67	0.0005	16.65	7.130	29.89	<0.005
LAND TO WATER DELIVERY A									
Temperature	oF−1	0.0228	0.0001	0.0196	0.0001	0.0198	0.0117	0.0259	<0.005
Slope[c]	%	0.2034	0.2187						
Soil permeability	h/cm	0.0295	0.0022	0.0442	0.0001	0.0447	0.0334	0.0572	<0.005
Stream density[c]	km−1	0.0205	0.0124	0.0215	0.0095	0.0243	-0.0003	0.0450	0.025
Wetland[d]	Dimensionless	0.7177	0.2962						
Irrigated land[e]	Dimensionless	1.101	0.0001						
Precipitation[f]	cm	38.52	0.0057						
Irrigated water use[g]	cm	0.0772	0.3117						

Model Parameters	Coefficient Units[a]	Exploratory Model		Final Model					
		Parametric Coefficient	P	Parametric Coefficient	Parametric P	Bootstrap Coefficient	Lower 90% CI[b]	Upper 90% CI[b]	Bootstrap p
IN-STREAM DECAYH Δ									
δ 1 (Q <28.3 m³/s)	D–1	0.2917	0.0001	0.3758	0.0001	0.3842	0.2981	0.4768	<0.005
δ 2 (28.3 m³/s <Q <283 m³ s)	D–1	0.1099	0.0001	0.1233	0.0001	0.1227	0.0621	0.1710	<0.005
δ 3 (Q >283 m³/s)	D–1	0.0352	0.1794	0.0406	0.1321	0.0408	0.0176	0.0685	0.015
R^2		0.8822		0.8743					
Mean square error		0.4310		0.4543					
Number of observations		414		414					

[a]Dependent variable (nitrogen transport) in kilograms per year. [b]Minimum bootstrap confidence intervals (CI). [c]Variable enters the model in reciprocal form. [d]Ratio of wetland area to total land area. [e]Ratio of irrigated land area to total cropland area. [f]Product of reciprocal precipitation and one minus the ratio of irrigated land area to total cropland area. [g]Ratio of irrigated land area to irrigated water use. [h]Decay coefficients fit separately for stream reaches with mean streamflow (Q) corresponding to indicated intervals. The streamflow interval breakpoints of 28.3 and 282 m3/s correspond to 1000 and 10,000 ft3/s, respectively . Source: Smith et al. (1997).

  SPARROW has also been applied to spatially identify N sources at the scale of the Chesapeake Bay watershed (Preston and Brakebill, 1999). A similar set of N sources, land-to-water delivery parameters, and in-stream loss rates to those used in Smith et al. (1997) were considered for this model (Preston and Brakebill, 1999). Only estimates for parameters that were used in the final model are given in Table A-6.
  The final model included five N sources, one land-to-water deliver parameter (soil permeability), and four in-stream loss rates (including reservoir retention). Comparisons between predicted and observed N loading provided an r^2 value of 0.961 (Preston and Brakebill, 1999). Because the data that are used in SPARROW are spatially referenced, model results can be mapped.

Table A-5. **Effect of spatial referencing on measures of regression model performance for predicting total N flux using the sparrow model.**

Model Components	Mean Square Error	R²
Includes full spatial referencing (SPARROW)[a]	0.4544	0.8743
Excludes in-stream decay and reservoir retention	0.9659b	0.7307

Table A-6.   **Parameter estimates, probability levels, and regression results for the Chesapeake Bay total N SPARROW model**

Explanatory Variables	Parameter Estimates	Probability Level
Nitrogen sources	β	
Point Sources	1.496	<0.005
Urban area (acres)	7.008	0.010
Fertilizer application (lb/yr)	0.2790	<0.005
Livestock waste production (lb/yr)	0.3361	<0.005
Atmospheric deposition (lb/yr)	1.024	<0.005
Land-to-water delivery	α	
Temperature (EF)	–	–
Precipitation (in)	–	–
Avg slope (%)	–	–
Soil permeability (in/h)	0.0754	0.095
Stream density (l/mi)	–	–
Wetland (%)	–	–
Instream loss (days)[a]	δ	
T1 (Q #200 ft^3/s)	0.7595	<0.005
T2 (200 ft^3/s < Q #1,000 ft^3/s)	0.3021	<0.005
T3 (Q > 1,000 ft^3/s)	0.0669	<0.005
Tu (reservoir retention)	0.4145	<0.005
R-squared	0.961	
Mean square error	0.1669	
Number of observations	79	

[a]T, travel time
Q, stream discharge
lb/yr, pounds per yr
°F, degrees Fahrenheit
in/h, inches per hour
ft^3/s, cubic feet per second
–, value not statistically significant

A.3.1.6. WATERSN

The Watershed Assessment Tool for Evaluating Reduction Strategies for Nitrogen (WATERSN) model is a steady-state numerical N budgeting model that estimates the amount of N exported to rivers and estuaries from forest, agricultural and urban land uses. The model is intended to provide an understanding of the relative contribution of N export from these land uses to estuaries, and to evaluate N

export reduction strategies that are specific to each land use type (Driscoll et al., 2007a). Figure A-9 shows a conceptual diagram of the N budgeting system used in WATERSN.

A detailed description of the original model calculations is provided in Castro et al. (2001). Subsequent model applications (Castro et al., 2003; Castro and Driscoll, 2002; Driscoll et al., 2003a; Whitall et al., 2004) have developed modifications to the approach originally described in Castro et al. (2001).

WATERSN uses calculations described in Jordan and Weller (Jordan and Weller, 1996) to estimate N inputs to the watershed/estuary system. Estimated anthropogenic sources of N inputs to the modeled watershed/estuary system include: crop and lawn fertilizer application; biotic N fixation by leguminous crops and pastures; atmospheric deposition of wet and dry inorganic N (NH_4^+, NO_3^-) net N import of food for human consumption; and net N import of feed for livestock (Castro and Driscoll, 2002).

Agricultural Areas

N available for water-borne export to estuaries from agricultural lands is determined as the difference between N inputs and outputs (Castro et al., 2001). Modeled N inputs to agricultural lands consist of wet and dry atmospheric NH_4^+ and NO_3^- deposition, N fertilization, biotic N fixation, and livestock waste (Castro and Driscoll, 2002). Wet and dry deposition are derived from NADP and CASTNet data. Average annual wet deposition rates of NH_4^+ and NO_3^- are taken from NADP sites in or near the study watersheds. Dry deposition of NH_4^+ and NO_3^- is calculated as an average of all CASTNet sites nearest to the study watersheds. WATERSN assumes that dry deposition of both NH_4^+ and NO_3^- to the estuary surface is 25% less than dry deposition to the watershed (Castro and Driscoll, 2002). Meyers et al. (2001) described the uncertainty of estimates of wet and dry deposition and considered it to be no less than a factor of 2. Estimates of N fertilization are taken from agricultural census data. WATERSN assumes that all fertilizer sold in a county is applied in that county. This is considered to be the most certain N input to the model (±25%) (Castro and Driscoll, 2002). WATERSN estimates both non-symbiotic and symbiotic N fixation for crops, pastures, hay fields and upland forests. Non-symbiotic rates were taken from literature values for crops, orchards, upland forests, and non-wooded pastures (Hendrickson, 1990; Stevenson, 1982; Woodmansee, 1978). Symbiotic rates of N fixation are based on type of legume, crop N harvest, N in unharvested portions of crops, soil N availability, and fertilization rate. These estimates are less certain than for N fertilization, but are noted as being a relatively minor N source in most of the study watersheds. Livestock waste was calculated as the difference between livestock consumption of N in feed and production of N in meat, milk, and eggs for human consumption (Jordan and Weller, 1996).
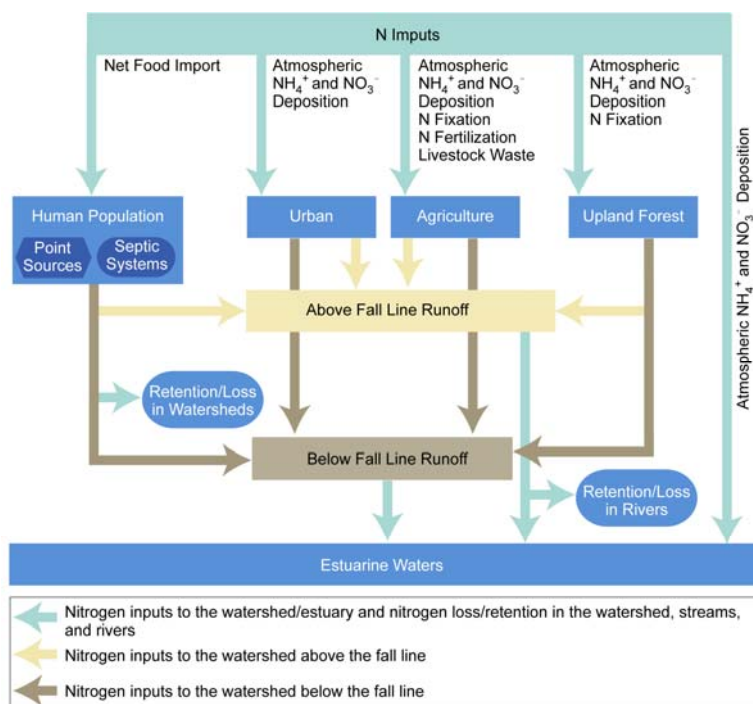
Source: Castro et al. (2003).

Figure A-9. Schematic diagram of the WATERSN approach to estimate the contribution made by different N sources to the total N inputs an estuary.

N outputs from agricultural land include crop harvest, pasture grazing, volatilization of NH_3 and denitrification. Data regarding crop harvest are obtained from agricultural census. N removed through crop harvest is estimated by multiplying the crop harvest by the percent N in each crop. Estimates for grazing are based on sheep, cattle, and horse populations (USDA online database in Castro and Driscoll, 2002, their dietary N requirements, and proportion of dietary N obtained from grazing (Jordan and Weller, 1996). NH_3 volatilization is assumed to be 10% of the N input from fertilizer and atmospheric deposition, and 20% of livestock manure inputs (Schlesinger and Hartley, 1992). Denitrification rates were originally estimated as 10 to 30% of the N inputs from fertilizer and atmospheric deposition and 20% of livestock N waste. Subsequent applications of WATERSN (Castro et al., 2003) modified denitrification rates from agricultural lands to vary with the mean watershed temperature and are based on a denitrification activity Q_{10} value of 2 (Maag et al., 1997; Stanford et al., 1975). A Q_{10} value of 2 suggests that the denitrification rate used by the model will change by a factor of 2 for every 10 degree change in temperature based on a direct relationship between temperature and denitrification.

Urban Areas

N inputs to urban areas include atmospheric and non-atmospheric sources. The total atmospheric N deposition input to urban areas is taken as the total (wet + dry) inorganic (NO_3^- and NH_4^+) N deposition rate to the watershed multiplied by the total urban area in the watershed. Non-atmospheric sources include point sources (primarily waste water treatment plants) and non-point sources (septic systems and pervious/impervious surface runoff) of N in urban areas (Castro et al., 2003).

N outputs from urban areas include waste water treatment plant effluent, septic system leachate, and total N runoff from pervious and impervious lands. Measured total N data are used to calculate N export for wastewater treatment plants that have available data. A strong regression relationship between measured total N discharged from wastewater treatment plants and human populations that use

wastewater treatment facilities is used to estimate total N discharges from wastewater treatment plants that do not have total N monitoring data available. Septic system output is determined by multiplying watershed specific human per capita N excretion rates by the human population of the watershed. WASTERSN assumes that 75% of this N is exported to the estuary (Castro and Driscoll, 2002). The soil water assessment tool (SWAT) is used to estimate non-point source non-atmospheric total N runoff from pervious and impervious urban lands. SWAT is a distributed parameter, continuous time model applicable at the watershed scale. Required inputs to SWAT include climatic variables, soil properties, elevation, vegetation information, and land use. SWAT is designed to predict land use and land management impacts on water, sediment, and agricultural yields in large watersheds (Castro and Driscoll, 2002). The model assumes that 75% of atmospheric N inputs to urban areas is exported to the estuary (Fisher and Oppenheimer, 1991). Alternatively, this N export term can be modified.

Upland Forests

N inputs to forests are assumed to be in the form of atmospheric deposition and non-symbiotic N fixation. Outputs from forests are estimated with a non-linear regression relationship between wet deposition of inorganic N and stream water export of dissolved inorganic nitrogen (DIN) developed using results from a multitude of forest watershed studies. Exported dissolved organic nitrogen (DON) was assumed to be equal to 50% of the inorganic N export (Castro and Driscoll, 2002).

Watershed and In-Stream N Retention

Model validation efforts using measured N fluxes from the USGS National Stream Quality Accounting Network (NASQAN) have shown that WATERSN tends to overestimate N export from watersheds to estuaries (Castro and Driscoll, 2002). These differences are not unexpected since WATERSN does not account for watershed and in-stream N sinks. Attempts have been made to improve flux estimates by accounting for watershed and in-stream N retention (Castro and Driscoll, 2002; Castro et al., 2001; 2003). A summary of the N retention rates applied to WATERSN in these studies is given in Table A-7.

Castro and Driscoll (2002) assumed that 30% of the total N that entered rivers above the fall line was lost during transport to the fall line and that inputs that enter the river below the fall line were not attenuated because of the relatively short travel times to the estuary (See Table A-7). This 30% in-stream N retention value represents the median retention value obtained in previous studies of northeastern U.S. rivers (Castro et al., 2001) and falls within the range of retention values estimated by Howarth et al. (1996) and Alexander et al. (2000). Castro and Driscoll (2002) also incorporated watershed N retention fractions specific to individual land uses. They assumed that 60% of the excess N from agricultural land and septic systems was lost (retained within the watershed) due to watershed processes. Support for this value of N retention was given by several reports of riparian N removal rates from agricultural land, ranging from about 50 to 90% (Jacobs and Gilliam, 1985; Jordan et al., 1993; Lowrance et al., 1983; Peterjohn and Correll, 1984). After incorporating these assumptions, predicted fluxes closely matched ($r^2 = 0.909$) measured fluxes.

Table A-7.   Summary of N retention rates used in recent WATERSN studies.

Study	Retention Type	% N Retention
Castro et al. (2001)	In Stream*	30%
	Agriculture	50%
Castro and Driscoll (2002)	In Stream*	30%

	Agriculture	60%
Castro et al. (2003)	Agriculture	40%
	Septic System	40%
	In Stream	Adjusted until predicted N flux matched observed fluxes

*In-stream N retention was only applied to lengths of river located above the "fall line." Below fall line N inputs to streams were assumed to not be attenuated due to the relatively short travel time to the estuary. The "fall line" is defined as the boundary between the Piedmont and Coastal Plain physiographic provinces in the eastern U.S.
Source: Castro and Driscoll (2002)

Driscoll et al. (2003a) applied WATERSN to investigate anthropogenic N loading to estuaries in the northeastern U.S. The objectives of the study were to apply WATERSN to quantify the inputs of Nr to the region (Figure A-10), discuss the ecological effects of regional elevated anthropogenic Nr inputs, and evaluate management options aimed at mitigating the effects of these elevated anthropogenic N inputs. Modeled N reduction scenarios included reductions atmospheric N emissions, increased N removal efficiencies of wastewater treatment plants, offshore pumping of wastewater, reductions in agricultural N runoff to surface waters, and an integrated management scenario consisting of a combination of N reductions from multiple sources. Other studies have applied WATERSN to address similar issues related to N loading to estuaries in other regions of the U.S. (Castro et al., 2003; Whitall et al., 2004; Whitall and Bricker, 2006).
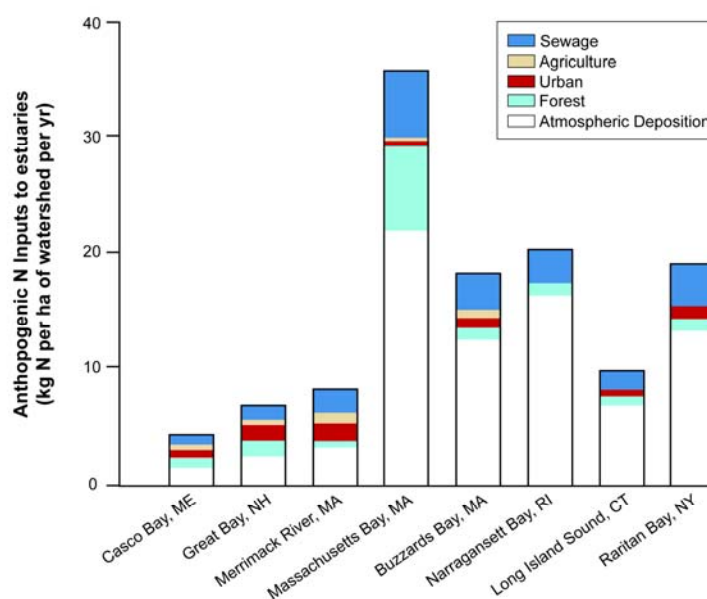
Source: Driscoll et al. (2003a).

Figure A-10.   WATERSN model estimates of anthropogenic N inputs to the estuaries of the northeastern U.S., in kilograms per hectare per year.

A.3.2. Additional Effects Models Used Widely in Europe

The models of the effects of S and N deposition described below have been used primarily in Europe. These descriptions are derived in part from the UNECE Convention of Long-Range Transboundary Air Pollution Modelling and Mapping manual (Posch et al., 2003).

A.3.2.1. The Very Simple Dynamic Model

The Very Simple Dynamic (VSD) soil acidification model is frequently used in Europe to simulate acidification effects in soils when observed data are sparse. It only includes weathering, cation exchange, N immobilization processes, and a mass balance for cations, sulfur and N. It resembles the model presented by Reuss (1980) which, however, did not consider N processes. In the VSD model, the various ecosystem processes have been limited to a few key processes. Processes that are not taken into account include canopy interactions; nutrient cycling processes; N fixation and NH_4 adsorption; SO_4^{2-} transformations (adsorption, uptake, immobilization, and reduction); formation and protonation of organic anions; and complexation of Al.

The VSD model consists of a set of mass balance equations, describing the soil input-output relationships, and a set of equations describing the rate-limited and equilibrium soil processes. The soil solution chemistry in VSD depends solely on the net element input from the atmosphere (deposition minus net uptake minus net immobilization) and the geochemical interaction in the soil (CO_2 equilibria, weathering of carbonates and silicates, and cation exchange). Soil interactions are described by simple rate-limited (zero-order) reactions (e.g., uptake and silicate weathering) or by equilibrium reactions (e.g., cation exchange). It models the exchange of Al, H, and Ca + Mg + K with Gaines-Thomas or Gapon equations.

Solute transport in VSD is described by assuming complete mixing of the element input within one homogeneous soil compartment with a constant density and a fixed depth. Since VSD is a single layer soil model neglecting vertical heterogeneity, it predicts the concentration of the soil water leaving this layer (mostly the rootzone). The annual water flux percolating from this layer is taken as being equal to the annual precipitation excess. The time step of the model is one year, and therefore seasonal variations are not considered. A detailed description of the VSD model can be found in Posch and Reinds (2003).

A.3.2.2. SMART

The Simulation Model for Acidification's Regional Trends (SMART) model is similar to the VSD model, but somewhat extended. It is described in De Vries et al. (1989) and Posch et al. (1993). As with the VSD model, the SMART model consists of a set of mass balance equations, describing soil input-output relationships, and a set of equations describing the rate-limited and equilibrium soil processes. It includes most of the assumptions and simplifications given for the VSD model; and justifications for them can be found in De Vries et al. (1989).

SMART models the exchange of Al, H, and divalent base cations using Gaines Thomas equations. Additionally, SO_4^{2-} adsorption is modeled using a Langmuir equation (as in MAGIC) and organic acids can be described as mono-, di-, or tri-protic. Furthermore, it does include a balance for carbonate and Al, thus allowing application to a range of site conditions, from calcareous soils to completely acidified soils that do not have an Al buffer left. Recently, a description of the complexation of aluminum with organic acids has been included. The SMART model has been developed with regional applications in mind, and an early example of an application to Europe can be found in De Vries et al. (1994).

A.3.2.3. SAFE

The Soil Acidification in Forest Ecosystems (SAFE) model has been developed at the University of Lund (Warfvinge et al., 1993) and a recent description of the model can be found in Alveteg and Sverdrup (2002). The main differences between the SMART and MAGIC models are: (a) weathering of base cations is not a model input, but it is modeled with the PROFILE (sub-)model, using soil mineralogy as input (Warfvinge and Sverdrup, 1992) SAFE is oriented to soil profiles in which water is assumed to move vertically through several soil layers (usually 4); and (c) Cation exchange between Al, H, and (divalent) base cations is modeled with Gapon exchange reactions, and the exchange between soil matrix and the soil solution is diffusion-limited.

The standard version of SAFE does not include SO_4^{2-} adsorption although a version, in which SO_4^{2-} adsorption is dependent on SO_4^{2-} concentration and pH has recently been developed (Martinson et al., 2003). The SAFE model has been applied to many sites and more recently also regional applications have been carried out for Sweden (Alveteg and Sverdrup, 2002) and Switzerland (Kurz et al., 1998).

A.3.3. Other Models

There are scores of models that can be useful in the context of developing a better understanding of the ecological effects of atmospheric S and N deposition. The preceding sections have summarized a relatively small number of models that are most commonly used for this purpose in the U.S. and Europe, in particular those that contribute to substantive conclusions presented in the ISA. There are many other models that are not covered in the discussion presented in this Annex. Several are highlighted in Table A-8.

Table A-8. **Some examples of models that could contribute to development of a better understanding of the ecological efforts of atmospheric S and N deposition, but that are not explicitly addressed in this annex.**

Model	Name	Type[1]	Support[2]	Reference[3]	Notes
QUAL2K		A	S	1	QUAL2K is one dimensional river and stream water quality model. QUAL2K assumes: that he channel is well-mixed vertically and laterally; steady state hydraulics; diurnal water-quality kinetics. QUAL2K addresses point and non-point loads, BOD/DO, non-living particulate organic matter (detritus); denitrification; sediment-water interactions; bottom algae; pH (both alkalinity and total inorganic carbon).
WASP7	Water Quality Analysis Simulation Program	A	S	2	WASP is a dynamic compartment-modeling program for aquatic systems, including both the water column and the underlying benthos. WASP allows the user to investigate 1, 2, and 3 dimensional systems, and a variety of pollutant types. The time varying processes of advection, dispersion, point and diffuse mass loading and boundary exchange are represented in the model. WASP also can be linked with hydrodynamic and sediment transport models that can provide flows, depths velocities, temperature, salinity and sediment fluxes.

Model	Name	Type[1]	Support[2]	Reference[3]	Notes
CE-QUAL-RIV1; CE-QUAL-R1; CE-QUAL-W2; CE-QUAL-ICM	Water quality models (river, reservoir, and estuary/ coastal) supported by USACE	A	N	3	CE-QUAL-R1 is a one-dimensional, vertical reservoir model and CE-QUAL-W2 is a two-dimensional (vertical and longitudinal), laterally averaged, hydrodynamic and water quality model. These two models are widely used by the Corps of Engineers, other federal and state agencies, the private sector, and agencies in other countries. CE-QUAL-RIV1 was developed for highly unsteady flow conditions, such as storm water flows and streams below peaking hydropower dams. CE-QUAL-ICM run in a 2D mode. This approach has been used for large, shallow waterways, harbors, and embayments.
RCA	Row Column AESOP	A	N	4	RCA evaluates the fate and transport of conventional and toxic pollutants in surface waterbodies in one, two, or three dimensions. RCA has been linked to various hydrodynamic models. Subroutines have been developed to model coliforms, pathogens, BOD/DO, simple and advanced eutrophication, wetland systems, and toxic contaminants. A sediment nutrient flux subroutine permits the coupling of the water column and sediment bed.
WARMS	Waterfowl Acidification Response Modeling System	A	N	McNicol et al. (1995), McNicol (2002)	WARMS includes an acidification model linked to fish and waterfowl models. WARMS uses pH, area, dissolved organic carbon, total P, and presence of fish to estimate preacidification, present and eventual steady-state values for pH, fish presence and waterfowl breeding parameters under proposed SO_2 emission scenarios.
GT-MEL	Georgia Tech hydrologic model and the Multiple Element Limitation model	I	N	5	GT-MEL is a spatially distributed, process-based ecohydrology model that links a land surface hydrology model with a terrestrial biogeochemistry model. GT-MEL differs from other available ecohydrology models in its simplicity, flexibility, and theoretical foundation. The coupled GT-MEL simulates the cycling and transport of water and nutrients (C, N and P) within hillslopes and watersheds. The model runs on a daily time step and can be applied to user-defined landscape units that may vary in shape and size (m^2 to km^2). Thus, GT-MEL can provide detailed spatial and temporal information on nutrient acquisition and turnover in plants and soils, and terrestrial flow pathways and discharge of water and nutrients to surface waters. The same set of model equations applies to any terrestrial ecosystem – agricultural crops, forests, grasslands, wetlands, tundra, etc. GT-MEL simulates the effects of multiple interacting stressors, including changes in land use, land cover, climate, and atmospheric CO_2 and N deposition.
ILWAS	Integrated Lake-Watershed Acidification Study	I	N	Gherini et al. (1985)	ILWAS was developed to predict changes in surface water acidity given changes in the acidity of precipitation and dry deposition. The model routes precipitation through the forest canopy, soil horizons, streams and lakes using mass balance concepts and equations which relate flow to hydraulic gradients. The physical-chemical processes which change the acid-base characteristics of the water are simulated by rate (kinetic) and equilibrium expressions and include mass transfers between gas, liquid and solid phases.

Model	Name	Type[1]	Support[2]	Reference[3]	Notes
THMB/IBIS		I	N	6, 7	THMB is a mechanistic simulation model of large river systems that has been used recently in combination with a dynamic terrestrial ecosystem model IBIS to quantify nitrate flux in the Mississippi River Basin. The coupled models simulate time-varying flow and storage of water and N in rivers, wetlands, and reservoirs, based on major source inputs, subsurface drainage and N leaching, topography, and precipitation and evaporation. Evaluations of the model in the Mississippi basin indicated that the model accurately simulated inter-annual variability in the water and N budget from 1960 to 1994.
BIOME-BGC	Biome-BGC is a multi-biome generalization of FOREST-BGC	T	N	8	Biome-BGC is a computer program that estimates fluxes and storage of energy, water, carbon, and N for the vegetation and soil components of terrestrial ecosystems. The primary model purpose is to study global and regional interactions between climate, disturbance, and biogeochemical cycles.
DNDC	Denitrification-decomposition model	T	N	9	DNDC was initially developed to quantifying nitrous oxide (N2O) emissions from agricultural soils in the U.S. The capability of the model to simulate soil biogeochemistry also allows DNDC to model emissions from other ecosystems through linkages with vegetation models; the model can be applied from field site to regional scales. The core of DNDC is a soil biogeochemistry model.
EPIC	Agricultural dynamic simulation model	T	N	11	EPIC is a widely used dynamic simulation model that describes the influence of agricultural management on crop productivity and erosion. The model has been used in studies of climate change, agricultural management and policy, and water-quality. EPIC simulates N cycling processes in soils-including mineralization, nitrification, immobilization, NH_3 volatilization and denitrification, runoff and subsurface leaching based on physical principles and parameter values derived from extensive model testing and specific field validation.
GLEAMS	Groundwater Loading Effects of Agricultural Management Systems	T	N	12	GLEAMS was developed from both EPIC and CREAMS and employs a more explicit description of soil water content. In GLEAMS, the concentration of nitrate-N removed via denitrification is a function of the factors describing the soil water content, the soil temperature, and the organic C content. Under this formulation, denitrification only occurs if the soil water content is greater than a parameter related to the soil water content at field capacity and saturation. The fraction of soil nitrate- N lost to denitrification increases quickly as soil water content increases beyond the field capacity. The EPIC and GLEAMS method of simulating denitrification neglects denitrification that may occur in anaerobic micro-zones when the soil is not at field capacity or saturation.
Hole-in-the-pipe	Hole-in-the-pipe	T	N	Davidson et al. (2000)	The Hole-in-Pipe model relates the emissions of nitrous oxides to common soil processes. It regulates soil emissions of NO and N_2O at two levels: 1st, the rate of N cycling through ecosystems, which is symbolized by the amount of N flowing through the pipes, affects total emissions of NO and N_2O; 2nd, soil water content and perhaps other factors affect the ratio of N_2O:NO emissions, symbolized by the relative sizes of the holes through which nitric oxide and nitrous oxide "leak." Soil water content is so important because it controls the transport of O_2 into soil and the transport of NO, N_2O, and N_2

Model	Name	Type[1]	Support[2]	Reference[3]	Notes
MERLIN	Model of Ecosystem Retention and Loss of Inorganic Nitrogen	T	N	Cosby et al. (1997), Kjonaas and Wright (1998)	MERLIN is a catchment-scale mass-balance model of linked carbon and N cycling in ecosystems for simulating leaching losses of inorganic N. It considers linked biotic and abiotic processes affecting the cycling and storage of N. The model is aggregated in space and time and contains compartments intended to be observable and/or interpretable at the plot or catchment scale. The structure of the model includes the inorganic soil, a plant compartment, and two soil organic compartments. Fluxes in and out of the ecosystem and between compartments are regulated by atmospheric deposition, hydrological discharge, plant uptake, litter production, wood production, microbial immobilization, mineralization, nitrification, and denitrification. N fluxes are controlled by carbon productivity, the C:N ratios of organic compartments and inorganic N in soil solution. Inputs include time series, constants, rates, source terms, and soil characteristics (Cosby et al., 1997).
NLM	Waquoit Bay Nitrogen Loading Model	T	N	RTI International (2001)	The Waquoit Bay Nitrogen Loading model estimates inputs from different N sources to defined land use categories and then estimates losses of N in various compartments of the watershed ecosystem, including the groundwater. This empirical N loading model produces long-term average output. It is not currently endorsed by a federal agency but has been published in peer-reviewed journals. Most applications of the model have focused on the Cape Cod area of Massachusetts. The empirical data for this model are specific to that area and the model simulates N transport exclusively in the subsurface (i.e., overland transport is not considered).
Simple Mass Balance Method/Steady State Mass Balance	"Mass balance approach"	T	N	Bhattacharya et al. (2004), Likens et al. (1996), Rodriguez and Macias (2006)	Examples of two mass balance approaches are: Simple Mass Balance: This model is based on a balance of inputs and outputs of N according to the equation: $N_{dep} + N_{fix} = N_i + N_u + N_{ad} + N_{de} + N_{fire} + N_{eros} + N_{vol} + N_{le}$ where the subscripts denote: dep (deposition); fix (fixation); i (immobilization); u (uptake); ad (adsorption); de (denitrification); fire (N loss during combustion); eros (erosion); vol (volatilization); le (leaching). Steady State Mass Balance: This method is the most commonly used method for analysis of critical loads of acid deposition. Its basic principle is based on identifying the long-term average sources of acidity and alkalinity in order to determine the maximum acid input that will balance the system at a biogeochemical safe-limit. Several assumptions have been made in the steady state calculations. First, it is assumed that ion exchange is at steady state and there is no net change in base saturation or no net transfer of ANC from soil solution to the ion exchange matrix. It is assumed that for N there is no net denitrification, adsorption or desorption and the N cycle is at steady state. Sulfate is also assumed to be at steady state: no sulfide oxidation, sulfate uptake, sulfate permanent fixation or sulfate reduction are significant. Simple hydrology is assumed where there is straight infiltration through the soil profile.

Model	Name	Type[1]	Support[2]	Reference[3]	Notes
HSPF/LSPC	Hydrological Simulation Program - FORTRAN	T*	S	12, 13	HSPF simulates watershed hydrology and water quality for conventional and toxic pollutants. HSPF incorporates watershed-scale ARM and NPS models into a basin-scale analysis framework that includes fate and transport in stream channels. It is a comprehensive model of watershed hydrology and water quality that allows the integrated simulation of land and soil contaminant runoff processes with In-stream hydraulic and sediment-chemical interactions. LSPC is a simplified version of HSPF. Although LSPC was designed to provide a less data intensive alternative to HSPF for modeling very large scale watersheds, it can also be used to model smaller, more detailed watersheds. The primary disadvantage of this simplified version of HSPF is that the developers eliminated the atmospheric deposition routines found in HSPF. For each model run, it automatically generates comprehensive text-file output by subwatershed for all land-layers, reaches, and simulated modules, which can be expressed on hourly or daily intervals. Output from LSPC has been linked to other model applications such as EFDC, WASP, and CE-QUAL-W2.
PLOAD	Pollutant Loading Model	T*	S	14	PLOAD is part of U.S. EPA's BASINS (Better Assessment Science Integrating Point and Nonpoint Sources) program and estimates nonpoint pollution sources on an annual basis. PLOAD can be combined with geographic information system (GIS)–based data coverages to rapidly estimate N loading to the bay using pass-through rates based on land uses from U.S. EPA guidance documents, literature, or other studies. This model is not precipitation driven; it does it include N speciation. However, the model does capture differences in N transport for different land uses in the watersheds.
SWAT	Soil and Water Assessment Tool	T*	S	van Griensven and Bauwens (2001), 15	SWAT is a public domain river basin scale model actively developed and primarily supported by the USDA (and included within U.S. EPA BASINS framework), that quantifies the impact of land management practices in large, complex watersheds. SWAT is a physically based model that applies to all land uses and to include stormwater runoff in its calculations. The model simulates NH_3, nitrate, and organic N throughout the waterbodies and vegetation in the modeled system. At this time SWAT only accepts the nitrate concentration in the rain as the N atmospheric component.
WARMF	Watershed Analysis Risk Management Framework	T*	S	16	WARMF includes a GIS-based watershed model that calculates daily runoff, shallow groundwater flow, hydrology and water quality of a river basin. A river basin is divided into a network of land catchments (including canopy and soil layers), stream segments, and lake layers for hydrologic and water quality simulations. Inputs include meteorology, air quality, point source, reservoir release, and flow diversion data. WARMF also includes two watershed approach modules for Consensus building and TMDL calculation.

Model	Name	Type[1]	Support[2]	Reference[3]	Notes
DRAINMOD		T*	N	17	DRAINMOD quantifies N losses and transport from agricultural lands with shallow water tables where artificial drainage systems are used. Watershed-scale versions of DRAINMOD have been developed and evaluated based on data collected on a NC coastal plain. DRAINMOD is based on water balances in the soil and at the soil surface. It uses functional methods to quantify infiltration, subsurface drainage, surface drainage, evapotranspiration, seepage, freezing, thawing, snowmelt, and seepage. The model predicts the water table depth and soil water contents above the water table, drainage rates and the other hydrologic components on an hourly and daily basis for long periods of hydrologic record. Hydrologic predictions of the model have been tested and found to be reliable for a wide range of soil, crop, and climatological conditions.
INCA		T*	N	Wade et al. (2005)	INCA is a water and N mass balance simulation model; it estimates the integrated effects of point and diffuse N sources on stream nitrate and ammonium concentrations and loads and also estimates the N loads related to processes in the plant/soil system. It has been most commonly applied to watersheds within the UK, but more recently has been modified for use in other European watersheds. INCA quantifies plant uptake of nitrate and ammonium, nitrification, denitrification, and mineralization and immobilization within each land-use type and subcatchment. Biogeochemical reactions are limited to the soil zone from which water and N are leached to deeper groundwater.
LWWM	Linked Watershed/Waterbody Model	T*	N	18	The original release of the LWWM coupled the RUNOFF Block of the U.S. EPA SWMM model (Version 4.21) with the U.S. EPA's Water Quality Analysis Program (WASP5). All components were accessed via a user-friendly operating shell. The LWWM included a GIS interface based on Arc/INFO to automate the reduction of spatial data within a watershed (i.e., land use and soils) for input into the RUNOFF Block of SWMM. The LWWM included pre-processors for inputting data into the RUNOFF Block of SWMM, WASP5 (Eutro and Toxi), and two hydrodynamic models associated with WASP5 (RIVMOD and DYNHYD5), as well as a graphical post-processor for the review of output from all model components. The post-processor was also the means by which nonpoint source loading files from RUNOFF were mapped to WASP segments.
ReNuM[a]	Regional Nutrient Management Model	T*	N	19	ReNuMa is based on the Generalized Watershed Loading Function (GWLF) model that has been used widely for purposes such as TMDL development. ReNuMa improves on GWLF by incorporating Net Anthropogenic N Inputs (NANI) accounting system. The model now considers atmospheric deposition, fertilizer application, septic system effluents, N fixation, and denitrification.
RHESS		T*	N	Boyer et al. (2006b)	RHESS has been used to explore N dynamics at the watershed scale. RHESSys simulates the coupled effects of C, N, and hydrological processes by coupling biogeochemical dynamics from the BIOME_BGC and the NGAS model used in DAYCENT. Streamflow is based on the implementation of variable source-area concepts based on topography, quantifying routing of water through the landscape from patch to patch using either a lumped topographic approach adapted from TOPMODEL or a distributed approach adapted from the DHSVM model

Model	Name	Type[1]	Support[2]	Reference[3]	Notes

[1]Type: A = aquatic; I = integrated aquatic/terrestrial; T = terrestrial; T* = watershed

[2] Support: S = currently supported by U.S. EPA; N = currently not supported by U.S. EPA

[3]Websites:

1: River and Stream Water Quality Model (QUAL2K); http://www.epa.gov/athens/wwqtsc/html/qual2k.html

2: U.S. EPA's WASP Website; http://epawasp.com/

3: U.S. Army Core of Engineers Environmental Laboratory - Water Quality Models; http://el.erdc.usace.army.mil/products.cfm?Topic=model&Type=watqual

4: Hydroqual: Row Column AESOP (RCA) Modeling Code Description and Technical Capabilities; http://www.hydroqual.com/pdf/RCA_Desc_doc.pdf

5: Woods Hole Marine Lab, Ecosystems Center MEL home page http://ecosystems.mbl.edu/Research/Models/mel/welcome.htmll

6: IBIS (Integrated Biosphere Simulator); http://water.usgs.gov/software/hspf.html

7: THMB (Terrestrial Hydrology Model with Biogeochemistry) - formerly HYDRA; http://www.sage.wisc.edu/download/HYDRA/hydra.html

8: Biome-BGC: Terrestrial Ecosystem Process Model, Version 4.1.1; http://www.daac.ornl.gov/MODELS/guides/biome-bgc_guide.html

9: Denitrification Modeling Workshop: Model Summary; http://marine.rutgers.edu/BGC/RCNsite/WS1/WS1models/DNDC-2.pdf

10: EPIC Fact Sheet; http://www.brc.tamus.edu/epic/epfact2004.htm

11: GLEAMS Y2K Update Website; http://www.tifton.uga.edu/sewrl/Gleams/gleams_y2k_update.htm

12: U.S. EPA's HSPF Website; http://www.epa.gov/ceampubl/swater/hspf/

13: USGS's Water Resources Applications Software: HSPF Website; http://water.usgs.gov/software/hspf.htm

14: U.S. EPA's Better Assessment Science Integrating Point & Nonpoint Sources (BASINS) Website; http://www.epa.gov/waterscience/basins/

15: Soil & Water Assessment Tool; http://www.brc.tamus.edu/swat/

16: US EPA's Watershed Analysis Risk Management Framework (WARMF) Website; http://www.epa.gov/athens/wwqtsc/html/warmf.html

17: DRAINMOD Download Website; http://www.bae.ncsu.edu/soil_water/drainmod/

18: Linked Watershed Waterbody Model at the Southwest Florida Water Management District; http://www.swfwmd.state.fl.us/software/lwwm.htm

19: Regional Nutrient Management (ReNuMa) at Cornell University College of Agriculture and Life Sciences;
http://www.eeb.cornell.edu/biogeo/nanc/usda/renuma.htm

Annex B. Acidification Effects

B.1. Effects on Biogeochemical Processes along Acidification Pathways

B.1.1. Atmospheric Deposition and Canopy Interaction

Inputs of N and S in wet, dry, and occult deposition first interact with the vegetative canopy. This interaction can occur a few centimeters above the ground in some alpine or grassland ecosystems to over 100 m above the ground in some forest canopies. In the canopy, deposited pollutants (especially N) can be taken up by the plants or by organisms that live within the canopy or on the leaf surface. Most of the deposited S moves as throughfall to the soil where it can be temporarily, or permanently, adsorbed on the soil. Sulfur that is not adsorbed on the soil moves readily into drainage water.

Earlier reviews (i.e., Hosker and Lindberg, 1982; Taylor et al., 1988) summarized information on the deposition of N to vegetation surfaces and interactions between pollutant deposition and canopy and leaf surfaces. Deposited N that is not taken up within the canopy then falls to the ground as throughfall, where plants, bacteria, and fungi compete for it. This competition for deposited N has long been known to play an important role in determining the extent to which N deposition will stimulate plant growth and the degree to which added N is retained within the ecosystem (U.S. EPA, 1993a). The available surface area of vegetation, onto which N gasses readily diffuse, has a significant effect on the dry deposition of N (Heil and Bruggink, 1987). Coniferous forests tend to increase deposition rates (both dry and wet) relative to deciduous forests, and landscape features such as elevation, aspect, and forest edge can play an important role in creating high levels of variability in deposition rates in complex terrain (Weathers et al., 2000).

B.1.2. Interactions with Soil

Air pollution is not the sole cause of soil acidity. High rates of soil acidification occur in low-deposition regions of the western U.S. because of internal soil processes, including tree N uptake and nitrification associated with extensive N fixation, for example on sites occupied by red alder trees (*Alnus rubra*) (Johnson et al., 1991a). Acidic deposition is not a necessary condition for having acidic soils, as evidenced by the common occurrence of acidic soils in unpolluted forests of the northwestern U.S. and Alaska (Johnson et al., 1991a).

B.1.2.1. Sulfur Retention and Release

Soils in the U.S. that most effectively adsorb SO_4^{2-} occur south of the maximum extent of glaciation that occurred during the most recent ice age. (Rochelle and Church, 1987). Sulfate adsorption is strongly pH dependent, and a decrease in soil pH resulting from acidic deposition can enhance the ability of soil to adsorb SO_4^{2-} (Fuller et al., 1987).

Considerable effort in the 1980s went into the computation of S budgets for watersheds and forest plots, to evaluate S retention and release. These budgets were subject to complications from fluxes that could not be measured directly, such as dry deposition and weathering, but generally indicated net S

retention at sites south of the line of glaciation—a result attributed to net adsorption of SO_4^{2-} (Cappellato et al., 1998; Rochelle et al., 1987). Through the 1990s little or no decrease in SO_4^{2-} concentrations occurred in streams below the glaciation line, despite regional decreases in atmospheric deposition of S (Webb et al., 2004). This lack of response has been generally attributed to the net release of adsorbed SO_4^{2-}, resulting from a shift in equilibrium between the adsorbed and solution phases under conditions of decreased atmospheric inputs of SO_4^{2-}. This interpretation is supported by a decrease in concentrations of adsorbed SO_4^{2-} from 1982 to 1990 in a Piedmont soil in South Carolina that received decreasing levels of S deposition during this period (Markewitz et al., 1998). This same soil also experienced an increase in adsorbed SO_4^{2-} from 1962 to 1972 (Markewitz et al., 1998). The only published S budget more recent than 1992 for an unglaciated site in the U.S. (Castro and Morgan, 2000) also suggests a net release of SO_4^{2-}. This upland Maryland watershed released 1.6 times more SO_4^{2-} than measured in throughfall in 1996–97. Additional information was obtained in the German study of Martinson et al. (2005) in which a "clean-roof" was used to exclude acidic deposition since 1989. Data collection enabled calibration of a model that predicted elevated concentrations of desorbed SO_4^{2-} in soil water for at least several decades. Although decreased levels of deposition are most likely resulting in net SO_4^{2-} desorption, limited research is available on sulfate desorption over time periods relevant to the time scale of decreased levels of S deposition (Johnson and Mitchell, 1998).

Numerous S budgets were also compiled in the 1980's for glaciated sites, and results generally indicated that inputs approximately equaled outputs on an annual basis (Rochelle et al., 1987). Little or no S retention at glaciated sites was attributed to relatively low SO_4^{2-} adsorption capacity in soils. Balanced S budgets implied that decreases in atmospheric deposition of S would lead directly to decreases in SO_4^{2-} leaching, and the strong correlation between decreases in atmospheric deposition and decreases in SO_4^{2-} concentrations in surface waters is widely recognized as an indication of this direct linkage (Stoddard et al., 2003). However, considerable evidence also indicates that S inputs in glaciated ecosystems do not behave conservatively, but instead are cycled through microbial and plant biomass (Alewell and Gehre, 1999; David et al., 1987; Likens et al., 2002). As a result, large quantities of S are stored in organic forms within the soil. David et al. (1987) found that annual S deposition (wet plus dry) at a site in the central Adirondack region of New York was about 1% of the organic S pool in the soil. Houle et al. (2001) estimated that annual S deposition at 11 sites in North America ranged from 1% to 13% of the organic S pool in soil.

Courchesne et al. (2005) measured a downward trend in water-soluble SO_4^{2-} from 1993 to 2002 in glaciated soils in Quebec, and attributed this response to net desorption of SO_4^{2-} rather than release of organically associated S. However, during this period, deposition of SO_4^{2-} was essentially unchanged. They attributed this discrepancy to a delay in the release of adsorbed SO_4^{2-} in response to a decrease in S deposition over the previous decade. These authors did not provide a mechanism to explain how desorption can continue under conditions of constant SO_4^{2-} inputs, however. On the basis of the abundant evidence of biological S cycling, it seems more likely that the delay observed by Courchesne et al. (2005) is the result of biological controls over the release of S.

Much of the organic S stored in soil is in carbon–bonded forms that are relatively unreactive, but can be mineralized to SO_4^{2-} in oxic conditions, typically found in moderately well-drained to well-drained soils (Johnson and Mitchell, 1998). Furthermore, strong correlations have been shown between levels of atmospheric deposition of S and concentrations of S in soil (Driscoll et al., 2001b; Novák et al., 2001). Long-term increases in concentrations of total S in soils that are at least partially attributable to increases in organic S have also been documented (Knights et al., 2000; Lapenis et al., 2004). The study of Houle et al. (2001) did not find a relation between these factors, however. A Swedish "clean-roof" study also provides some insights into the role of organic S in possibly delaying recovery (Mörth et al., 2005). After 9 years of pre-industrial levels of S deposition, the amount of S in runoff still exceeded inputs by 30%. Most of the S in runoff was attributed to mineralization of organic S in the O horizon.

B.1.2.2. Base Cation Depletion

Base cations are common in rocks and soils, but largely in forms that are unavailable to plants. There is a pool of bioavailable base cations (termed exchangeable base cations) that are adsorbed to negatively charged surfaces of soil particles. They can enter solution by exchanging with other dissolved cations including acidic cations such as H^+ or Al^{3+}. Base cations in this pool are gradually leached from the soil in drainage water, but are constantly resupplied through weathering. Weathering slowly breaks down rocks and minerals, releasing base cations to the pool of adsorbed base cations in the soil. The balance between base cation supply and base cation loss determines whether the pool of available base cations is increasing or decreasing in size. Net forest growth can also potentially lower exchangeable base cation concentrations through uptake of nutrient cations (Ca, Mg, and K), but these cations remain in the terrestrial ecosystem and can become available in the future through mineralization or canopy leaching. It has long been known that leaching of base cations by acidic deposition might deplete the soil of exchangeable bases faster than they are resupplied (Cowling and Dochinger, 1980). However, base cation depletion of soils had not been demonstrated at the time of the 1982 PM-SO_X AQCD (U.S. EPA, 1982b).

Data that clearly showed soil base cation depletion in the U.S. did not become available until the 1990s, although decreases in exchangeable Ca^{2+} concentrations between the periods 1947 to 1950 and 1987 to 1988 had been identified in European soils through repeated sampling (Billett et al., 1990; Falkengren-Grerup and Eriksson, 1990). In the only repeated sampling in the U.S. in which the original soil sample pre-dated acidic deposition, Johnson et al. (1994b) documented a decrease in exchangeable Ca^{2+} concentrations in both the O (combined Oa and Oe horizons) and B horizons from 1930 to 1984. Richter et al. (1994) also observed Ca^{2+} depletion in the B horizon from 1960 to 1990, in repeated sampling of Piedmont soil in South Carolina. The studies of Johnson et al. (1994b) and Richter et al. (1994) acknowledged the potential role of acidic deposition in causing the loss of Ca^{2+}, but focused on net forest growth as the primary cause.

Through reanalysis of archived soils, Lawrence et al. (1995) measured decreases in concentrations of exchangeable Ca^{2+} and acid-extractable Ca^{2+} in Oa horizons of spruce stands from 1969–70 to 1987–92 and presented relationships in soil chemistry that were not consistent with changes expected from vegetation uptake effects, but that could be explained by acidic deposition. Drohan and Sharpe (1997) also observed a decrease in Ca^{2+} concentrations in Oa and A horizons at 11 sites across Pennsylvania that were sampled in 1957 or 1959 and again in 1993, although effects of vegetation and acidic deposition were not distinguished.

A thorough soil re-sampling study in the U.S. was conducted by Bailey et al. (2003) in northwestern Pennsylvania. Between 1967 and 1997, pronounced decreases, attributed largely to acidic deposition, were measured in exchangeable Ca^{2+} and Mg^{2+} concentrations in Oa/A horizons and throughout the B horizon. Courchesne et al. (2005) found higher concentrations of exchangeable Ca^{2+} in the O horizon (combined Oe and Oa horizons) in 2002 than in 1994 at one of three sampling areas within a 5.1 ha watershed, but no significant differences at the other two locations. No significant differences were found for exchangeable Mg^{2+} at the three locations in the O horizon. In the upper 10 cm of the B horizon, no significant differences were found in exchangeable Ca^{2+}, but at two of three locations, exchangeable Mg^{2+} concentrations were lower in 2002 than in 1994. The 8–yr interval between sampling in this study is the shortest time in which changes in exchangeable base cations have been reported for North American soils.

In a regionally designed assessment of changes in soil-exchange chemistry, Sullivan et al. (2006b) found that base saturation and exchangeable Ca^{2+} concentrations in the Adirondack region of New York had decreased in the upper 10 cm of the B horizon between the mid 1980s and 2003, in watersheds of lakes with ANC less than 200 µeq/L. Soil chemistry in 36 lake watersheds in the mid 1980s was compared to soil chemistry in 32 lake watersheds in 2003. Although this study did not involve repeated sampling of the same sites, the comparison could be made on a regional basis because the sampling locations were selected randomly in both the mid 1980s and in 2003, and a large and similar number of sites were included in both samplings.

In a widely cited article, Likens et al. (1996) used a watershed mass balance approach to estimate changes in ecosystem Ca^{2+} pools at HBEF and found a sustained decrease in exchangeable Ca^{2+} concentrations from 1963 to 1993. The maximum depletion rate occurred in 1972, at the estimated peak in acidic deposition levels. The dependence on Ca:Na ratios to estimate Ca^{2+} weathering fluxes in this analysis adds uncertainty to the magnitude of changes reported for the exchangeable Ca^{2+} pool (Bailey et al., 2003). Two additional mass balance studies used Sr isotopes to evaluate changes in soil Ca^{2+} pools and fluxes. The study of Bailey et al. (1996) estimated substantial depletion rates in a watershed in the White Mountains of New Hampshire. Miller et al. (1993) estimated that inputs from weathering and atmospheric deposition approximately equaled leaching losses at a site in the Adirondack Mountains in New York. The different findings in these two studies are related to differences in the mineralogical composition of the respective soils. However, the Miller et al. (1993) study also estimated that 50 to 60% of the Ca^{2+} in vegetation and the forest floor was derived from the atmosphere, despite the fact that the weathering flux was estimated to be three times the rate of atmospheric inputs. This result suggests that Ca^{2+} supply from weathering in the lower profile is not reaching the upper soil where most root activity occurs, and that Ca^{2+} depletion has occurred in the upper soil.

The study of Yanai et al. (1999) investigated changes in Ca^{2+} and Mg^{2+} concentrations and content in northeastern hardwood stands over time intervals ranging from 10 to 21 years. The general conclusion of this study was that little or no change in O horizon (Oi, Oe, and Oa horizons) exchange chemistry occurred. However, a decrease in exchangeable Ca^{2+} concentrations in the Oa horizon was observed in this study at the HBEF from 1978 to 1997, although no change was observed in this soil in exchangeable Mg^{2+} concentrations, or Ca^{2+} or Mg^{2+} content in the Oa horizon. Results of this study were complicated by high spatial variability and differences in field sampling techniques between the original collection and the resampling (Yanai et al., 1999). Yanai et al. (2005) also found little difference over 15 years in exchangeable and extractable Ca^{2+} and Mg^{2+} concentrations in Oa horizons at 6 sites, and in O horizons (combined Oe and Oa horizons) at 13 sites, in hardwood stands in New Hampshire. In this study, it was also estimated that a difference greater than 50% would be needed to be statistically detected due to a large degree of spatial variability. Although most repeated sampling studies did identify decreases in exchangeable base cations in the Oa or O horizon, the results of Yanai et al. (2005) indicated that this change may not occur at all sites and may be difficult to detect in some soils due to inconsistencies in identifying horizon separations during sampling.

Through direct and inferred evidence of Ca^{2+} depletion, and additional research on soil processes, a detailed understanding of the mechanisms of Ca^{2+} depletion has developed over the past two decades. Ulrich (1983) explained Ca^{2+} depletion as a three-stage process in which buffering of acidity in the mineral soil is first accomplished by weathering of carbonates and other mineral forms that weather relatively rapidly. Once these mineral forms are depleted, buffering is accomplished largely by cation exchange, in which H^+ is substituted for base cations and concentrations of exchangeable base cations decrease. Once the buffering capacity provided by cation exchange is depleted, acid neutralization is accomplished by weathering of crystalline minerals that contain large amounts of silicon (Si) and Al and relatively small amounts of base cations. At this stage, Al is mobilized within the soil and exchangeable Al concentrations increase. The shift in acid buffering from base cation exchange to alumino-silicate weathering and exchangeable Al was documented in Russian soils sampled three times over 75 years (Lawrence et al., 1995).

The effect of decreasing concentrations of exchangeable base cations on cation leaching in mineral soil was shown in simulation modeling by Reuss (1983). Below a base saturation of 20%, leaching of Ca^{2+} decreases substantially and becomes less sensitive to variations in acid inputs as base saturation decreases further. This relationship was later shown experimentally by Lawrence et al. (1999). Samples from the upper B-horizon in nearly all of the Adirondack lake watersheds sampled by Sullivan et al. (2006b) had base saturation values less than 20%, as did soils at 11 sites in New York, Vermont, New Hampshire, and Maine in a regional study of mature spruce-fir forests (David and Lawrence, 1996). Exchangeable Ca^{2+} concentrations (expressed as a percentage of cation exchange capacity [CEC]) in the regional spruce-fir study were weakly correlated with an estimate of the relative weathering potential of

parent material in the upper 10 cm of the B horizon ($r^2 = 0.44$). However, these factors were strongly correlated in the Oa horizon ($r^2 = 0.92$) (Lawrence and David, 1997). Because mineral weathering in the B horizon is the primary source of soil Ca^{2+}, a strong relationship between weathering potential and exchangeable Ca^{2+} concentrations would be expected in this horizon. The weak correlation suggests that concentrations of Ca^{2+} had decreased into the Al-buffering range sometime in the past. The parent material signature in the Oa horizon was likely maintained through vegetative recycling—uptake of Ca^{2+} from the O and B horizons, followed by transport back into the O horizon in litterfall.

In summary, evidence from repeated sampling and studies of soil processes indicate that decreases in exchangeable base cation concentrations in both Oa and B horizons are common and widespread in the eastern U.S. Factors such as logging and net forest growth are likely to have contributed to this decrease in varying degrees, but acidic deposition has played a major role (Huntington, 2000; Lawrence et al., 1987). The magnitudes and rates at which Ca^{2+} depletion has occurred are less clear.

These base cation depletion issues relate directly to the chemical recovery potential of acidified soils and surface waters. Replenishment of exchangeable base cation concentrations on soils will require that inputs from weathering and atmospheric deposition exceed losses from leaching and vegetative uptake. Inputs of Ca^{2+} from atmospheric deposition decreased sharply in the east through the 1980s (Hedin et al., 1994), and have remained relatively stable since that time (http://nadp.sws.uiuc.edu/). Atmospheric deposition of SO_4^{2-} currently remains several factors higher than that of Ca^{2+} even at sites where SO_4^{2-} levels are relatively low (http://nadp.sws.uiuc.edu/), so chemical recovery at current acidic deposition levels will require inputs of base cations from weathering that are considerably greater than inputs from the atmosphere.

Because of the importance of weathering to the base-cation status of soils, a great deal of effort has been made to estimate in situ weathering flux with a variety of methods (Bailey et al., 2003; Likens et al., 1996; Miller et al., 1993). The complexity and variability of factors that affect weathering flux rates, such as soil mineralogy, particle surfaces, soil organic matter, moisture flux, and a host of other factors that are difficult to quantify, add large uncertainties to weathering flux estimates. Weathering rates estimated in geochemical models are generally assumed to be constant overtime, but lower weathering rates were observed in a soil sampled in 1987 than in the same soil sampled and archived in 1949–50 (Zulla and Billett, 1994). Further complexity in weathering flux rates results from the possible role of mycorrhizae in penetrating silicate minerals to extract base cations while remaining isolated from the soil solution (Blum et al., 2002; van Breemen et al., 2000). Lastly, as yet unidentified sources of base cations may exist in forest soils. Bailey et al. (2003) found that elevated rates of Ca^{2+} loss from forest harvesting continued for 30 years after disturbance, but the source of the additional Ca^{2+} being lost could not be identified. Until estimates of in situ weathering fluxes are better constrained and more data become available from repeated soil sampling, predictions of recovery of exchangeable base cation concentrations will be highly uncertain.

B.1.2.3. Aluminum Mobilization

Through the natural process of podzolization, dissolved organic acids derived from partially decomposed organic matter in the O horizon move into the mineral soil where they weather soil particles and release Al into solution. As soil solution moves deeper into the profile, acidity is neutralized and Al is deposited as a secondary mineral or more likely as an organic Al (Al_o) complex (De Coninck, 1980). The limited mobility of organic anions results in retention of most Al within the mineral soil (often in the Bh horizon). Complexation with dissolved organic matter can increase the mobility of Al within the soil and lead to transport of organic Al into surface waters from shallow soils that are high in organic matter (Lawrence et al., 1987).

Increased concentrations of exchangeable Al in the mineral soil have been identified through repeated sampling in the U.S. and Europe over periods ranging from 17 years to 41 years in studies by Billet et al. (1990), Bailey et al. (2005), Falkengren-Grerup and Eriksson (1990), and Lawrence et al.

(1995). In areas of Europe with excessively high acidic deposition levels, evidence of Al depletion in the mineral soil has also been found (Lapenis et al., 2004; Mulder et al., 1989), but Al depletion has not been documented in the U.S.

Increases in exchangeable Al concentrations in the O horizon have been documented over periods from 17 to 30 years (Bailey et al., 2005; Drohan and Sharpe, 1997; Lawrence et al., 1995), although the study of Yanai et al. (2005) did not find consistent changes in Oa horizons over 15 years.

Numerous papers have evaluated solubility controls on Al in both the mineral soil and the O horizon. These papers have commonly related Al solubility to gibbsite ($Al(OH)_3$) or a gibbsite-like mineral to determine if inorganic Al concentrations could be predicted from gibbsite solubility constants and pH (Cronan and Goldstein, 1989; David and Driscoll, 1984; Johnson et al., 1981; Lawrence and David, 1997). These efforts have shown that inorganic Al concentrations are often undersaturated with respect to gibbsite and do not support Al-trihydroxide as the primary control in natural systems. Gibbsite solubility should therefore be considered a useful point of reference in evaluating Al-solubility rather a mineral form that is an important control of Al solubility in natural systems.

Through the 1990s, evidence accumulated to indicate that secondary Al in the mineral soil is in a form associated with organic matter, and in some soils, imogolite (Berggren and Mulder, 1995; Dahlgren and Walker, 1993; Mulder and Stein, 1994; Simonsson, 1998; Skyllberg, 1999). Organic matter also plays a major role in controlling Al solubility in O horizons. This interaction has been described by Cronan et al. (1986) in O horizons through the bound Al ratio, which reflects the equivalents of adsorbed Al per mol of carboxyl groups (Cronan et al., 1986). Tipping et al. (1995) described Al solubility on organic and mineral soil horizons through equilibrium humic ion binding. Each of these approaches has had success in describing dissolved Al concentrations in organic soils as a function of pH through formulations that rely on concentrations of solid-phase organic bound Al. Further work has shown these relationships to be specific to the particular horizon, and the pool sizes of Al and humic substances (Lofts et al., 2001). However, inputs of acidity may alter concentrations of solid-phase organic bound Al (Lawrence and David, 1997). Changes in atmospheric deposition levels may therefore shift these relationships over time as soils further acidify or recover.

B.1.2.4. Soil Acidification

In the B horizon of soils north of the maximum extent of glaciation, CEC is largely derived from organic matter, whereas in older southern soils the surface charge of highly weathered clay minerals is the primary source of CEC. The CEC derived from organic matter is pH-dependent. Decreases in pH result in a decreases in CEC. In both cases, the CEC of the B horizon is much lower than in organic-rich surface horizons (Oa or A horizons). Less acidity from organic matter and a limited capacity for buffering due to low CEC makes the B horizon more susceptible to a lowering of pH from acidic deposition, and decreases in pH lower the CEC, further reducing the acid-buffering capacity from cation exchange. Two studies in the U.S. have provided measurements to assess changes in soil pH in the B horizon from acidic deposition. Bailey et al. (2005) found lower pH values in the upper B horizon in northwestern Pennsylvania soils in 1967 than in 1997, at 50 cm depth (p <0.001) and at 100 cm depth (p <0.001), which were largely attributable to acidic deposition. Markewitz et al. (1998) also found pronounced decreases in soil pH down to 60 cm in highly weathered Piedmont soils from 1962 to 1990. The latter study was conducted in a former cotton field in which loblolly pines were planted in 1956–57. Forest regrowth undoubtedly played a large role in the soil pH changes that were measured, but atmospheric deposition was estimated to account for 38% of the H^+ inputs during the 28 years that elapsed between measurements.

Other studies in Europe have found similar decreases in soil pH of the B horizon that could be attributed, at least in part, to acidic deposition. These include the study of Lawrence et al. (1995) in northwestern Russia, which documented decreases in soil pH in the B horizon down to 90 cm, from 1926 to 1964, and further decreases from 1964 to 2001. Acidic deposition was identified as the probable

primary cause of decreasing pH in this study. The study of Lawrence et al. (1995) also observed a decrease in CEC in this soil, as did a previous study of Russian soils (Lapenis et al., 2004). The decrease in pH was likely to have contributed to the decreased CEC of these soils, but a more important factor may have been a decrease in organic carbon concentrations that was also measured. To our knowledge, data to assess possible changes in CEC in soils in the U.S. has not become available, but change in CEC has implications for recovery potential of soils from acidic deposition effects (Sullivan et al., 2006a). Increased CEC driven by increases in pH could foster soil recovery by increasing the opportunity for adsorption of base cations, as soil solution becomes less acidic. Decreases in soil organic matter driven by climate and/or vegetation changes, such as those seen in Russian soils, would result in a decrease in acid-buffering capacity through cation-exchange. There are currently no data in the U.S. that indicate increases in soil pH associated with recent declines in acidic deposition levels. These data limitations make future projections of recovery of soil pH highly uncertain.

B.1.2.5. Nitrogen Saturation

Severe symptoms of N saturation, have been observed in high-elevation, nonaggrading spruce-fir ecosystems in the Appalachian Mountains, as well as in the eastern hardwood watersheds at Fernow Experimental Forest near Parsons, WV and throughout the northeastern U.S. Mixed conifer forests and chaparral watersheds with high smog exposure in the Los Angeles Air Basin also are N-saturated and exhibit the highest stream water NO_3^- concentrations documented within wildlands in North America (Bytnerowicz and Fenn, 1996; Fenn et al., 1998).

Some examples of N-saturated forests in North America, including estimated inputs and outputs, are shown in Table B-1 (Fenn et al., 1998). The Harvard Forest hardwood stand in western Massachusetts absorbed >900 kg N/ha without significant NO_3^- leaching during an 8–yr N amendment study (Fenn et al., 1998). In contrast, NO_3^- leaching losses were high at the Harvard Forest pine sites. In the 8–yr experimental study, NO_3^- leaching was observed in the pine stand after the first year (1989) in the high-N application plots, and further increases were observed in 1995 and 1996. The hardwood stand did not show significant increases in NO_3^- leaching until 1996. The differences in response of the pine and hardwood stands indicate that the mosaic of community types across the landscape must be considered when evaluating landscape-scale responses to N deposition (Magill et al., 2000).

Utilization of N in the terrestrial ecosystem is accomplished through complex interactions between plants and microbes that are not fully understood (Schimel and Bennett, 2004). Long-term N retention is largely accomplished by incorporation of N into soil organic matter through biological assimilation (Aber et al., 1998), and to a lesser extent by abiotic processes that are not well understood (Dail et al., 2001). The forms in which N is assimilated by plants and microbes are determined by availability, as described in Schimel and Bennett (2004). In the most N-limited ecosystems, competition between plants and microbes is high and N is assimilated primarily in depolymerized organic forms, resulting in low mineralization rates and minimal buildup of inorganic N in the soil. Increased availability of N increases the mineralization rate, which enhances competition between plants and microbes for available NH_4^+ produced by mineralization. Further increase in the availability of N (for example by high levels of atmospheric N deposition) lessens competition for NH_4^+ between plants and microbes and leads to increased production of NO_3^- by autotrophic nitrifying bacteria. Some of this NO_3^- can be taken up by plants and microbes, but because much of the N demand is satisfied by NH_4^+ under these conditions, NO_3^- tends to be mobile within the soil, enabling it to leach to drainage water. Based on the definitions of Aber et al. (1989, 1998) and Stoddard (1994), the first stage of N saturation is reached when competition between plants and microbes for NH_4^+ has decreased to the point that net nitrification occurs.

Substantial leaching of NO_3^- from forest soils to streamwater can acidify downstream waters (Webb et al., 1995), eutrophy estuaries and marine waters (Fisher and Oppenheimer, 1991), and deplete soils of nutrient base cations, especially Ca^{2+} and Mg^{2+} (Likens et al., 1998). Considerable evidence is available to link N deposition to acidification of soils. Much of this evidence comes from the northeastern

U.S., where increased accumulation of N in soil is suggested by a strong positive correlation between atmospheric deposition levels and total N concentration in the Oa horizon, at sites in New York, Vermont, New Hampshire, and Maine (Driscoll et al., 2001b). Further evidence that atmospheric deposition has increased availability of N in soil is shown by a strong negative correlation between atmospheric deposition levels and the C:N ratio of the Oa horizon in this region (Aber et al., 2003). If the C:N ratio falls below about 25, nitrification is stimulated, resulting in elevated NO_3^- in surface waters (Aber et al., 2003). Similar results were found in Europe, where a C:N ratio of 24 was identified as the critical level below which nitrification occurred (Emmett et al., 1998).

Analyses have been conducted in the northeastern U.S. and Europe to examine the relationships between N deposition and NO_3^- leaching to surface waters. The relationship between measured wet deposition of N and streamwater output of NO_3^- was evaluated by Driscoll et al. (1989) for sites in North America (mostly eastern areas), and augmented by Stoddard (1994). The resulting data showed a pattern of N leaching at wet inputs greater than approximately 5.6 kg N/ha/yr. Stoddard (1994) presented a geographical analysis of patterns of watershed loss of N throughout the northeastern U.S. He identified approximately 100 surface water sites in the region with sufficiently intensive data to determine their N status. Sites were coded according to their presumed stage of N retention, and sites ranged from Stage 0 (background condition) through Stage 2 (chronic effects). The geographic pattern in watershed N retention depicted by Stoddard (1994) followed the geographic pattern of N deposition. Sites in the Adirondack and Catskill Mountains in New York, where N deposition was about 11 to 13 kg N/ha/yr, were typically identified as Stage 1 (episodic effects) or Stage 2. Sites in Maine, where N deposition was about half as high, were nearly all Stage 0. Sites in New Hampshire and Vermont, which received intermediate levels of N deposition, were identified as primarily Stage 0, with some Stage 1 sites. Based on this analysis, a reasonable threshold of N deposition for transforming a northeastern site from the "natural" Stage 0 condition to Stage 1 would correspond to the deposition levels found throughout New Hampshire and Vermont, approximately 8 kg N/ha/yr. This is in agreement with the interpretation by Driscoll et al. (1989), which would probably correspond to total N inputs near 8 to10 kg N/ha/yr. This is probably the approximate level at which episodic aquatic effects of N deposition would become apparent in many watersheds of the eastern U.S.

Analysis of data from surveys of N outputs from 65 forested plots and catchments throughout Europe were conducted by Dise and Wright (1995) and Tietema and Beier (1995). Below the throughfall inputs of about 10 kg N/ha/yr, there was very little N leaching at any of the study sites. At throughfall inputs greater than 25 kg N/ha/yr, the study catchments consistently leached high concentrations of inorganic N. At intermediate deposition values (10 to 25 kg N/ha/yr), Dise and Wright (1995) observed a broad range of watershed responses. Nitrogen output was most highly correlated with N input ($r^2 = 0.69$), but also significantly correlated with S input, soil pH, percent slope, bedrock type, and latitude. A combination of N input (positive correlation) and soil pH (negative correlation) explained 87% of the variation in N output at the study sites (Dise and Wright, 1995).

The threshold level of atmospheric deposition that causes release of NO_3^- to surface waters was identified by Aber et al. (2003) as approximately 7 kg N/ha/yr for the northeastern U.S. In watersheds receiving N deposition above this level, concentrations of NO_3^- in surface waters were positively correlated with atmospheric deposition, whereas most watersheds with deposition less than 7 kg/ha/yr had little or no NO_3^- (undetectable at most sites) in their surface waters (Aber et al., 2003). The threshold value of 7 kg/ha/yr was based on atmospheric deposition levels for the base of forested watersheds. When scaled to include higher deposition levels expected at upper elevations this value was estimated to equal about 10 kg/ha/yr, similar to the European estimate of Dise et al. (1998).

The common deposition threshold for release of NO_3^- to surface waters in forested watersheds found in the northeastern U.S. and Europe represents an important advance in relating N inputs to ecosystem effects, but a considerable amount of variability in ecosystem response has also been demonstrated. Lovett et al. (2000) found that 39 watersheds in the Catskill region of New York State retained from 49% to 90% of atmospheric N inputs. Castro and Morgan (2000) showed that NO_3^- export

from watersheds in eastern North America can range from nearly 0 to over 400 eq/ha/yr in watersheds that receive similar levels of inorganic N in wet deposition in the range of 400 to 500 eq/ha/yr.

Experimental additions of N to plots and watersheds have also demonstrated variations in terrestrial retention of N. Additions of N (approximately twice ambient deposition) to hardwood watersheds in Maine (25 kg N/ha/yr) and West Virginia (35.5 kg N/ha/yr), which were releasing NO_3^- to surface waters before the additions, resulted in substantial increases in NO_3^- concentrations in soil water and stream water within the first treatment year (Kahl et al., 1993; Peterjohn et al., 1996) Additions of 25 kg N/ha/yr to spruce plots in Vermont (ambient bulk deposition 5.4 kg N/ha/yr), in which net nitrification did not occur before treatment, triggered net nitrification in the second year of treatment, whereas nitrification was not triggered until the third year in plots receiving 19.8 kg N/ha/yr (McNulty et al., 1996). Similar results to these were seen in two studies from Colorado. Additions of 25 kg N/ha/yr to old-growth spruce plots in Loch Vale watershed (ambient bulk deposition ~4–5 kg N/ha/yr) doubled N mineralization rates and stimulated nitrification, while the addition of the same amount to plots receiving ambient bulk deposition of ~2.0 kg N/ha/yr in Fraser Experimental Forest elicited no microbial response but significantly increased foliar and organic soil horizon N (Rueth et al., 2003). A comparison study of old-growth spruce plots across a depositional gradient in Colorado found mineralization rates to be higher where N deposition ranged from 3 to 5 kg N/ha/yr than where N deposition ranged from 1 to 2 kg N/ha/yr, with measurable nitrification rates at sites with the highest deposition amounts (Rueth and Baron, 2002). In marked contrast to these results, concentrations of NO_3^- plus NH_4^+ were not detected until the seventh year in hardwood plots in Harvard Forest, which received additions of 150 kg N/ha/yr (Magill and Aber, 2004). Concentrations of ($NO_3^- + NH_4^+$) in hardwood plots receiving 50 kg N/ha/yr were not yet detectable in the 15th year of treatments. The same treatments were applied to red pine (*Pinus resinosa*) plots, which exhibited elevated concentrations of ($NO_3^- + NH_4^+$) in soil water after 1 year of 150 kg N/ha/yr doses, and after 5 years of 50 kg N/ha/yr doses.

In general, deciduous forest stands in the eastern U.S. have not progressed toward N-saturation as rapidly or as far as spruce-fir stands. Deciduous forests may have a greater capacity for N retention than coniferous forests. In addition, deciduous forests tend to be located at lower elevation and receive lower atmospheric inputs of N. Many deciduous forests have higher rates of N uptake and greater N requirement than spruce-fir forests. Decreased growth and increased mortality have more commonly been observed in high-elevation coniferous stands than in lower elevation hardwood forests, and these differences have been partially attributed to excess inputs of N (Aber et al., 1998). Indeed, many of the lower elevation deciduous stands are N-deficient and are therefore likely to benefit (i.e., grow faster), at least up to a point, with increased inputs of N.

There are examples of N saturation in lower-elevation eastern forests, especially in West Virginia. For example, progressive increases in streamwater NO_3^- and Ca^{2+} concentrations were measured at the Fernow Experimental Forest in the 1970s and 1980s (Adams et al., 1997, 2000; Edwards and Helvey, 1991; Peterjohn et al., 1996). This watershed has received higher N deposition (average throughfall input of 22 kg/ha/yr of N in the 1980s) than is typical for low-elevation areas of the eastern U.S., however (Eagar et al., 1996), and this may help to explain the observed N saturation.

Varying responses to N additions reflect differences in N status of the treatment sites. These variations have most often been attributed to disturbance history, dating back a century or more (Goodale and Aber, 2001). Sites which have undergone disturbances that cause loss of soil N, such as logging, fire, and agriculture, tend to be most effective at retaining atmospheric and experimental inputs of N. Nitrogen retention capability often decreases with stand age, which suggests that older forests are more susceptible than younger forests to becoming N-saturated (Hedin et al., 1995). Aber et al. (1998) surmised that land use history may be more important than cumulative atmospheric deposition of N in determining the N status of a forest ecosystem.

Although considerable progress has been made in understanding the factors that control N retention, efforts to quantify net N retention through known processes have not been fully successful. Assimilation of N by mycorrhizae followed by exudation as dissolved organic matter was proposed by

Aber et al. (1998) as a possible explanation for unaccounted conversion of inorganic N into soil organic matter. However, Frey et al. (2004) found that elevated N inputs reduced active mycorrhizal biomass, fungal diversity and fungal:bacterial biomass ratios. These results suggested a decreased role for mycorrhizae in fixation of N under elevated N inputs.

Abiotic transformation of inorganic N into soil organic matter has also been proposed as a possible mechanism to explain high rates of N retention in soil, and some evidence has been presented to support this possibility. Dail et al. (2001) observed retention of $^{15}NO_3^-$ and $^{15}NO_2$ in sterile soil, but the method of sterilization may have increased dissolved organic carbon (DOC) concentrations and artificially increased the opportunity for formation of soluble organic N compounds. Davidson et al. (2003) developed the ferrous wheel hypothesis to explain incorporation of inorganic N into organic matter. The hypothesized mechanism involves conversion of NO_3^- to NO_2^- through oxidation of Fe_2^+. Testing of this hypothesis in situ was not found in the literature, but the small amount of Fe_2^+ that typically occurs in the forest floor, where presumably much of the conversion to organic N occurs, may limit the importance of this pathway. Fitzhugh et al. (2003) showed that NO_2^- produced in the first step of nitrification may be directly converted to soluble organic N rather than becoming fully oxidized to NO_3^-. However, concentrations of introduced $^{15}NO_2$ in this experiment were several orders of magnitude higher than that normally seen in forest soils. Therefore, the evidence at this time for abiotic retention of N is not fully convincing, and the importance of this process requires further research.

In addition to our limited understanding of N retention mechanisms, there is no direct information on ecosystem recovery from N saturation in the U.S. This may be at least partly because atmospheric deposition of N has been relatively stable in the eastern U.S. over the past two to three decades. An important source of information on N recovery responses has been provided by the European NITREX study, which reduced ambient N deposition for 5 years with roofs constructed over experimental plots in Germany and The Netherlands. At the German site, deposition was reduced from approximately 38 kg N/ha/yr to levels that varied from 10 to 20 kg N/ha/yr. At the Dutch site, deposition was reduced from 45 kg N/ha/yr to levels that varied from 1 to 10 kg N/ha/yr. At both of these sites, deposition levels before the experiment were approximately three to four times greater than the highest deposition levels commonly found in the eastern U.S., whereas after the reduction, levels at the Dutch site fell within the range of deposition in the eastern U.S. over the past two decades, and values at the German site were somewhat higher than this range (Emmett et al., 1998; Ollinger et al., 1993). The decrease in ambient N inputs resulted in a marked decrease in N outputs at each site within 2 to 3 years. The responses at the two sites were somewhat different, however. At the Dutch site, outputs of N exceeded inputs both before and after experimental reduction of inputs. At the German site, inputs exceeded outputs before and after reduction of inputs, but outputs were more similar to inputs after the reduction. At both sites, outputs after the reduction in deposition remained two to three times higher than outputs commonly measured in the eastern U.S.

Thus, atmospheric deposition of N has increased N availability in soils, which has led to increased nitrification and associated acidification of soil and soil water. The N retention capacity of soils is strongly dependant on land-use history, however, so the relationships between N deposition and ecosystem N status and percent of terrestrial retention are variable. In general, however, atmospheric deposition of 10 kg N/ha/yr or higher is required for appreciable amounts of NO_3^- to leach to surface waters in the eastern U.S. and northern Europe. Future projections of chemical recovery from N-driven acidification are uncertain because retention mechanisms are not fully understood, and there are only limited data on recovery responses. European experiments that reduced inputs of N found decreased outputs of N within 2 to 3 years, which indicates a relatively rapid response to decreased deposition levels. However, these studies are difficult to directly apply to the U.S. because deposition levels were much higher at the European sites before the experiment, and the 5–yearr duration of the experiments only demonstrated recovery to levels of N saturation that are higher than the more heavily affected sites in the eastern U.S.

High concentrations of lake or streamwater NO_3^-, indicative of ecosystem saturation, have been found at a variety of locations throughout the U.S., including the San Bernardino and San Gabriel

Mountains within the Los Angeles Air Basin (Fenn et al., 1996), the Front Range of Colorado (Baron et al., 1994; Williams et al., 1996a, 1996b), the Allegheny Mountains of West Virginia (Gilliam et al., 1996), the Catskill Mountains of New York (Murdoch and Stoddard, 1992; Stoddard, 1994), the Adirondack Mountains of New York (Wigington et al., 1996), and the Great Smoky Mountains in Tennessee (Cook et al., 1994). All of these regions, except Colorado, received relatively high (more than about 10 kg N/ha/yr) atmospheric deposition of oxidized N throughout the 1980s and 1990s. In contrast, the Front Range of Colorado receives less than about 4 or 5 kg N/ha/yr of total (wet plus dry) deposition (Sullivan et al., 2005), less than half of the total N deposition received at these other locations. The cause of N-saturation at high-elevation western watersheds that receive low to moderate levels of atmospheric deposition has been a subject of debate. High concentrations of NO_3^- in surface waters in the western U.S. are not widespread. Nitrate concentrations during the fall sampling season were low in most western lakes sampled in the Western Lakes Survey (WLS). Only 24 sampled lakes were found to have NO_3^- concentrations greater than 10 µeq/L. Of those, 19 lakes were situated at high elevation, most above 3,000 m. Cold temperatures in such lakes undoubtedly play an important role in maintaining high NO_3^- concentrations by limiting biological uptake processes. The high NO_3^- concentrations are likely to affect acid-base chemistry only where ANC is low. Eight lakes showed high NO_3^- (>10 µeq/L) and low ANC (<50 µeq/L), all of which occurred at elevations higher than 3,100 m. Four were located in Colorado, two in Wyoming, and one each in California and Utah. In all cases, pH was above 6.5 and ANC was greater than or equal to 15 µeq/L. Such lakes are sensitive to episodic pulses of NO_3^- acidity; such pulses have been reported from Colorado Front Range lakes (Williams and Tonnessen, 2000). Episodic acidification of western lakes could be important biologically.

In the Uinta Mountains of Utah and the Bighorn Mountains of central Wyoming, 19% of the lakes included within the WLS had NO_3^- >10 µeq/L. This suggests that N deposition in these areas may have exceeded the capability of these systems to assimilate N. It is unknown if these concentrations of NO_3^- represent effects from anthropogenic sources or if this constituted a natural condition associated with inhibited NO_3^- assimilation in cold alpine environments.

Williams et al. (1996a; 1996b) contended that N-saturation is occurring throughout high-elevation catchments of the Colorado Front Range. Many lakes in the Colorado Front Range have chronic NO_3^- concentrations greater than 10 µeq/L and concentrations during snowmelt are frequently much higher, due at least in part to leaching from tundra, exposed bedrock, and talus areas. Although biological N demand may be high in subalpine forests, uptake is limited in alpine areas by large N inputs from snowmelt, steep watershed gradients, rapid water flushing, extensive areas having little or no soil development, and limitations on the growth of phytoplankton in some alpine lakes by factors other than N (e.g., phosphorus, temperature) (Baron et al., 1994).

B.1.2.6. Nitrate Leaching

Nitrate leaching losses from soils to drainage waters are governed by a complex suite of ecosystem processes in addition to N inputs from atmospheric deposition. In particular, mineralization and nitrification processes play important roles in regulating the quantity of, and temporal variability in, the concentration of NO_3^- in soil solution, and consequently leaching losses from the rooting zone (Johnson et al., 1991b, 1991c; Joslin et al., 1987; Reuss and Johnson, 1985)(Johnson et al., 1991b; 1991c). Thus, NO_3^- leaching is mostly under biological control and typically shows pronounced seasonal variability (Van Miegroet and Johnson, 1993). Peak concentrations of NO_3^- in soil solution appear to be largely responsible for the potentially toxic peaks in Al concentration that sometimes occur in soil solution, although SO_4^{2-} may also play a role by serving to elevate chronic Al concentrations (Eagar et al., 1996).

High leaching of NO_3^- in soil water and streamwater draining high-elevation spruce-fir forests has been documented in numerous studies in the Southern Appalachian Mountain region (Joslin et al., 1992; Joslin and Wolfe, 1992b, 1994; Nodvin et al., 1995; Van Miegroet et al., 1992). This high NO_3^- leaching has been attributed to a combination of high N deposition, low N uptake by forest vegetation, and

inherently high N release from soils. Forest age is another major factor-affecting uptake, with mature forests requiring minimal N for new growth and, hence, often exhibiting higher NO_3^- leaching that younger, faster growing stands (Goodale and Aber, 2001). Old-growth red spruce stands in the Southern Appalachians have been demonstrated to have significantly slower growth rates than stands younger than 120 years (Smith and Nicholas, 1999). The latter feature is associated with low C:N ratios in mineral soil, high N mineralization potential and high nitrification (Eagar et al., 1996; Joslin et al., 1992).

In most terrestrial ecosystems in the U.S., N is strongly retained and there is limited mobility of NO_3^-. Exceptions to this pattern tend to occur in spatially limited regions that receive high levels of total N deposition (higher than about 10 to 20 kg N/ha/yr) and in alpine and subalpine environments that have little soil or vegetative development over substantial portions of the watersheds.

B.1.3. Interactions with Transitional Ecosystems

B.1.3.1. Sulfur Storage and Release in Transitional Ecosystems

Although S is generally mobile in upland soils in most parts of the U.S., wetlands act as both sources and sinks of atmospherically deposited S. Wetlands retain and release S in response to variations in hydrology, which in turn affect oxidation and the reduction process in wetland soils. Ito et al. (2005) evaluated the influence of land cover types on SO_4^{2-} fluxes in Adirondack lake watersheds. They found that SO_4^{2-} concentration in drainage water decreased in association with increased wetland area within the lake watershed (adj. $r^2 = 0.58$, $p \geq 0.001$). They attributed this observed pattern to dissimilatory SO_4^{2-} reduction in anaerobic wetland soils.

Sulfur storage in wetland soils to some degree prevents or delays the acidification of downstream surface waters with mineral acidity. However, the water table in wetland areas typically drops during drought conditions, and this allows development of aerobic conditions in surface wetland soils. Under aerobic conditions, stored S is re-oxidized to SO_4^{2-}, which can then be rapidly mobilized under high-flow conditions that occur in response to rainfall or snowmelt. This can cause substantial episodic pulses of acidity in surface waters that receive drainage water from wetlands. Thus, wetlands buffer downstream receiving waters against chronic acidity to some degree, but can be an important source of periodic episodes of more extreme acidity.

B.1.3.2. Organic Acidity in Transitional Ecosystems and Downstream Surface Waters

Organic acids in fresh water originate from the degradation of biomass in upland areas, wetlands, near-stream riparian zones, the water column, and stream and lake sediments (Hemond, 1994). The watersheds of surface waters that have high concentrations of organic matter (DOC >about 400 µM) often contain extensive wetlands and/or extensive organic-rich riparian areas (Hemond, 1990; Sullivan, 2000a).

Organic acids contributed by wetlands to downstream drainage waters can influence surface water acid-base chemistry, particularly in dilute waters having moderate to high (greater than about 400 µM) DOC concentrations. Organic acids in surface waters include a mixture of functional groups having both strong and weak acid character. Some lakes and streams are naturally acidic as a consequence of organic acids contributed to solution by wetlands. The presence of organic acids also provides buffering to minimize pH change in response to changes in the amount of SO_4^{2-} and NO_3^- derived from acidic deposition.

There are many lakes and streams that are chronically acidic or low in ANC mainly due to the presence of organic acids. In many cases, the principal source of these organic acids is the wetlands within the watershed. The NAPAP (Sullivan et al., 1992) concluded that about one-fourth of all acidic lakes and streams surveyed in the National Surface Water Survey (NSWS) (Kaufmann et al., 1988;

Linthurst et al., 1986a) were acidic largely as a consequence of organic acids. A survey of 1400 lakes in the Adirondack Mountains by the Adirondack Lake Survey Corporation (ALSC) (Kretser et al., 1989), which included many small lakes and ponds (1 to 4 ha) having relatively high DOC, revealed that about 38% of the lakes had pH <5 due to the presence of organic acids, and that organic acids generally depressed the pH of Adirondack lakes by 0.5 to 2.5 pH units in the ANC range of 0 to 50 µeq/L (Baker et al., 1990a).

Specification of the acid-base character of water high in DOC is somewhat uncertain. Attempts have been made to describe the acid-base behavior of organic acids using a single H^+ dissociation constant (pK_a), despite the fact that organic acids in natural waters are made up of a complex mixture of acidic functional groups. A portion (perhaps one-third) of the acidity in organic acids is quite strong, with some ionization occurring at pH values well below 4.0 (Driscoll et al., 1994b; Hemond, 1994). A number of modeling approaches have been used to estimate the acidity of organic acids in fresh waters, often as simple organic acid analogs having different pK_a values (Oliver et al., 1983; Perdue et al., 1984; Driscoll et al., 1994b).

The importance of naturally occurring organic acids as agents of surface water acidification was reinforced by a modeling study (Sullivan and Eilers, 1996) that showed that inclusion of organic acids in the Model of Acidification of Groundwater in Catchments (MAGIC) had a substantial effect on model predictions of surface water pH, even in waters where DOC concentrations were only moderate. MAGIC hindcasts of pre-industrial lakewater pH of Adirondack lakes showed poor agreement with diatom inferences of pre-industrial pH when organic acids were not considered in the MAGIC model (Sullivan and Eilers, 1996). Revised MAGIC hindcasts of pre-industrial lakewater pH that included an organic acid representation (Driscoll et al., 1994b) showed considerably closer agreement with diatom inferences (Figure B-1). The mean difference between MAGIC and diatom estimates of pre-industrial pH was reduced from 0.6 pH units to 0.2 pH units when organic acids were included in the model, and the agreement for individual lakes improved by up to a full pH unit (Sullivan et al., 1996a).

Rosenqvist (1978) and Krug et al. (1985) hypothesized that a significant component of the mobile acid anions contributed from atmospheric deposition (e.g., SO_4^{2-}, NO_3^-) replace organic anions that were previously present in solution. Under this anion substitution hypothesis, the net result of acidic deposition is not so much an increase in cations (including potentially toxic H^+ and Al^{n+}) as much as an exchange of SO_4^{2-} and NO_3^- anions for organic anions, with little or no change in ANC and pH. This hypothesis has received some support from paleolimnological studies, which suggested historic decreases in DOC concentrations during the period of lakewater acidification in the 1900s (Davis et al., 1985; Dixit et al., 2001; Kingston and Birks, 1990). Other studies have found a decrease in organic acidity which was at least partly attributable to the extent of organic acid protonation. David et al. (1999) measured a decrease in organic anion concentrations in stream water in response to the experimental whole-watershed acidification experiment at the Bear Brook Watershed in Maine. Wright et al. (1993) concluded that ANC increases in a small watershed in Norway, where rates of acidic deposition were experimentally reduced, were limited by the increasing role of organic acids that accompanied decreasing acid deposition load.

Complexation of organic acids by metals (Almer et al., 1974; Cronan and Aiken, 1985; Dickson, 1978; Lind and Hem, 1975) and pH-dependent changes in dissociation of organic acids (Oliver et al., 1983; Wright et al., 1988a) are probably important components of the organic acidity response. Loss of DOC in response to acidic deposition can also cause a shift in Al species composition towards lesser complexation with organic ligands. Such a shift from AL_o to Al_i increases toxicity of the Al to aquatic biota (Baker and Schofield, 1982). Changes in pH can alter the charge density of organic solutes and thus influence organic contributions to acidity (Wright et al., 1988a, 1988b). David et al. (1999) found that the charge density of organic acids decreased by about 1 µeq/L/mg C at West Bear Brook in Maine, in response to 6 years of experimental acidification, probably due to greater protonation of organic acid anions at the lower pH. Similar results were reported by Lydersen et al. (1996) at Lake Skjervatjern in Norway. Values of the organic acid charge density in the ALSC lakes in the Adirondack Mountains

increased with increasing pH between pH values of 5.0 to 7.0 due to the presence of weakly acidic functional groups (Driscoll et al., 1994b).
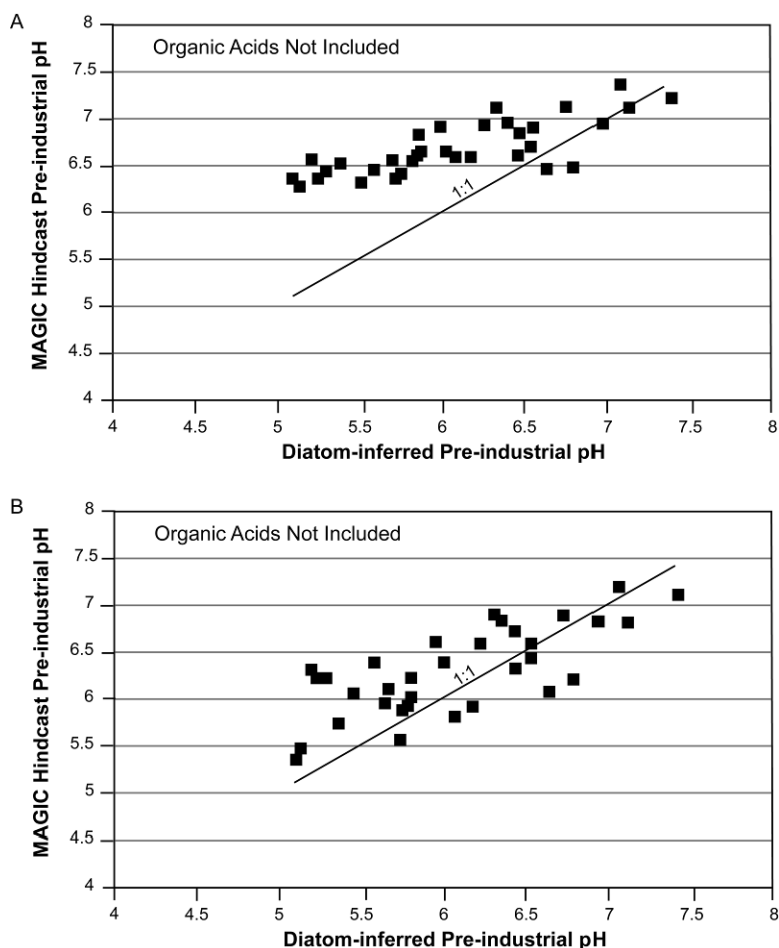
Source: Sullivan et al. (1996).

Figure B-1.   MAGIC model hindcast estimates of pre-industrial pH versus diatom-inferred pH for 33 statistically selected Adirondack lakes: a) without including organic acid representation in the MAGIC simulations, and b) including a triprotic organic acid analog model in the MAGIC simulations.

Hedin et al. (1990) artificially acidified a small, moderately high-DOC (725 μM C) stream with H_2SO_4 at HBEF in New Hampshire. Streamwater pH (4.4) was near the range of reported average pK_a values for organic acids, suggesting that the capacity of organic acids to buffer mineral acidity should be high. The acid loading rate was adjusted to achieve an increased streamwater SO_4^{2-} concentrations of 150 μeq/L at the downstream sampling point 108 m below the point of acid addition. Adjustments were made for dilution by soil water or inflow from small tributaries. Although streamwater DOC did not change significantly, the concentration of organic anions (as calculated from the charge balance) decreased by 17 μeq/L. Thus, the overall capacity of organic anions to neutralize mineral acid inputs offset about 11% of the added acid (Hedin et al., 1990). This experiment only considered interactions between mineral acid and organic matter within the stream. Any additional buffering that may have been provided within the terrestrial catchment was not represented in the experimental design. Also, any

possible catchment-mediated influences of the experimental acidification on organic acid properties or terrestrial DOC mobilization were excluded from the experiment because the acid was not applied to the catchment soils.
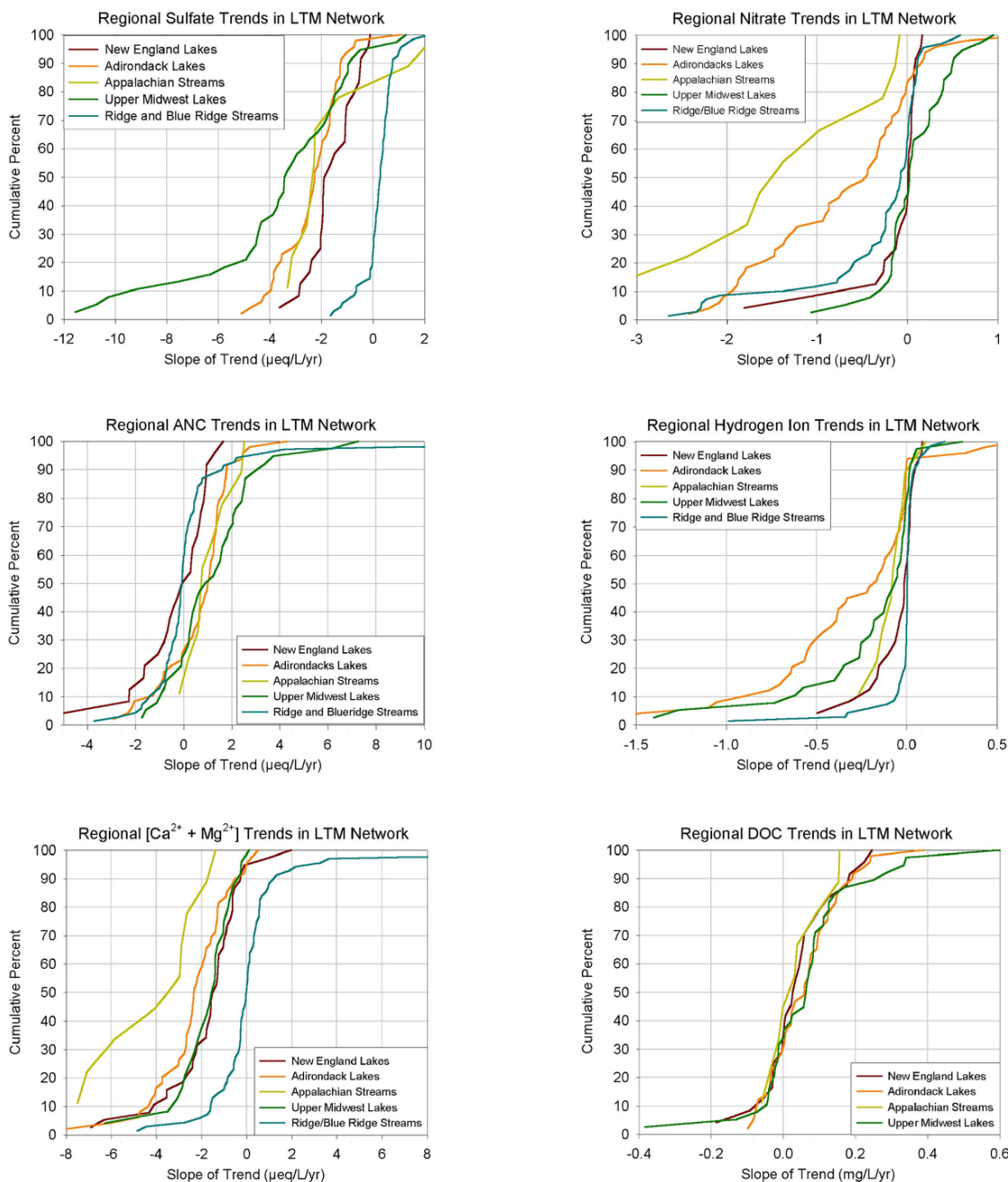
Source: Stoddard et al. (2003).

Figure B-2. **Cumlative frequency diagram (distribution) of slopes for SO_4^{2-}, NO_3^-, Gran ANC, hydrogen ion, $[Ca^{2+} + Mg^{2+}]$, and DOC concentrations in LTM surface water monitoring sites, by region, for the period 1990–2000. The Ridge/Blue Ridge Province did not have sufficient DOC data to allow trend analysis.**

Results of a resurvey of 485 Norwegian lakes sampled in both 1986 and 1995 provided evidence in support of an increase in organic acid anion concentrations in association with decreased lakewater SO_4^{2-} concentration (Skjelkvåle et al., 1998). The organic acid anion concentration increased by an amount equal to between 9% and 15% of the decrease in SO_4^{2-} concentration in the four regions of the country most heavily affected by the decrease in S deposition during the intervening 10 year period. Lakewater SO_4^{2-} concentrations decreased by 9 µeq/L (western and northern Norway) to 20 to 21 µeq/L (eastern and southern Norway). Only in mid-Norway, where average SO_4^{2-} concentration decreased by only 6 µeq/L, did the organic acid anion concentration remain unchanged between 1986 and 1995 (Skjelkvåle et al., 1998).

Recent monitoring data have shown that DOC and organic acid anion concentrations in many lakes and streams in the U.S. have increased in association with decreased S deposition. It is likely that a high percentage of this DOC originates from wetland soils within the monitored watersheds. This result appears to be partly responsible for the limited lakewater ANC and pH recovery that has occurred at many locations. The response of surface waters to changes in acidic deposition has included a general increase in surface water DOC (Figure B-2). All regions of the eastern U.S. analyzed by Stoddard et al. (2003) that had sufficient DOC data for analysis exhibited increases in DOC concentrations during the 1990s. All regional trends were significant with the exception of the Northern Appalachian Plateau, the region with the lowest median DOC concentration. The median increase in DOC of 0.05 mg/L/yr reported by Stoddard et al. (2003) corresponds to an overall increase of about 10% across study regions, similar to trends reported elsewhere in the northern hemisphere (Evans and Monteith, 2002; Skjelkvåle et al., 2001). This suggests a common cause. Both climate warming and decreasing acidic deposition are possible causal agents.

B.2. Factors That Determine Ecosystem Sensitivity

B.2.1. Transitional Ecosystems

B.2.1.1. Wetlands and Peatlands

Wetlands and peatlands often contain highly acidic soils. Their acidity is mainly attributable to the presence of large quantities of naturally occurring organic materials. Fulvic and humic acids, formed during the breakdown of organic matter, contribute substantial organic acidity to soil and surface waters in wetland and peatland environments. In the case of ombotrophic bogs and poor fens, there is also a scarcity of base cations, which would serve to buffer both organic and mineral acidity.

Because wetland and peatland vegetative communities are adapted to high levels of natural organic acidity, it is unlikely that S or N deposition would cause any acidification-related effects at levels of acidic deposition commonly found in the U.S. Nevertheless, wetlands are closely tied to a number of important biogeochemical processes that regulate watershed response to acidic deposition. The major interactions are described below.

High concentrations of DOC in brownwater lakes and streams are often due to the influence of wetlands on hydrography within the watershed. This presence of high concentrations (higher than about 500 µM) of DOC can substantially reduce the pH and ANC of surface waters, buffer those waters against pH changes in response to added mineral acidity, and form stable complexes with dissolved Al, thereby reducing its toxicity to aquatic life. Therefore, the response of surface waters to acidic deposition is strongly influenced by the extent of upstream and shoreline wetland development.

Wetlands also serve as a (sometimes-temporary) sink for atmospheric S and N. Chemical reduction reactions and biological uptake contribute to S and N storage in wetland soils. Oxidation during drought periods, when water levels recede, followed by flushing from wetland to downstream surface water during subsequent storm flow, can cause substantial pulses of mineral acidity in downstream receiving waters. On a chronic basis, the concentration of SO_4^{2-} (and associated acidity) in surface water can be substantially lower as a consequence of dissimulatory S reduction in upslope wetlands. On an episodic basis, wetlands can contribute to wide fluctuations in downstream surface water acid-base chemistry. Such fluctuations can include pulses of acidity that may be toxic to aquatic biota.

Wetlands provide anaerobic substrate for S-reducing bacteria. These bacteria are also partly responsible for the increased rate of mercury (Hg) methylation that is known to occur in wetlands. As a consequence, fish in lakes drained by wetlands often have much higher concentrations of tissue methyl mercury, as compared with fish in lakes that lack watershed wetlands (Driscoll et al., 2007b).

B.2.1.2. Ponds

The factors that determine the sensitivity of ponds to acidification from acidic deposition are generally similar to those that determine the sensitivity of lakes (discussed in the following section). In general, however, ponds and small lakes tend to exhibit low ANC and pH at a greater frequency than do larger lakes (Sullivan et al., 1990b). This pattern is mainly a consequence of the higher concentrations of DOC frequently found in ponds as compared with larger lakes. In addition, because larger bodies of water tend to have larger watersheds, there is a greater likelihood that they will integrate conditions across a broader landscape, increasing the possibility of receiving at least a moderate level of base cation supply (Sullivan et al., 1990b). Thus, where lakes are acid-sensitive, it is likely that ponds are also acid-sensitive. However, synoptic databases of pond acid-base chemistry are generally not available.

B.2.2. Streams and Lakes

Acidic deposition that falls as precipitation directly on the lake surface may eventually be neutralized by in-lake reduction processes which are controlled in part by hydraulic residence time. Natural hydrologic events also alter acidification and neutralization processes during snowmelt and change flowpaths during extended droughts (Webster et al., 1990).

Leaching of base cations by acidic deposition can deplete the soil of exchangeable bases. The importance of this response has recently been widely recognized because most watersheds are not exhibiting much ANC and pH recovery of drainage water in response to recent large decreases in S deposition. This limited recovery can be at least partially attributed to decreased base cation concentrations in surface water. This understanding of the base cation response has developed slowly. During the 1980s, the generally accepted paradigm of watershed response to acidic deposition was analogous to a large-scale titration of ANC (Henriksen, 1984). Atmospheric inputs of acidic anions were believed to result in movement of those anions through soils into drainage waters with near proportional loss of surface water ANC. This view was modified by Henriksen (1984), who suggested that a modest component of the added SO_4^{2-} (up to a maximum of about 40%) could be charge-balanced by increased mobilization of base cations from soils, and the remaining 60% to 100% of the added SO_4^{2-} resulted in loss of ANC in surface waters. During the latter part of the 1980s, it became increasingly clear that a larger component (>40%) of the added SO_4^{2-} was in fact neutralized by base cation release in most cases and the ANC (and therefore also pH) of surface waters typically did not change as much as was earlier believed. This understanding developed in large part from paleoecological studies (Charles et al., 1990b; Sullivan et al., 1990b), which indicated that past changes in lakewater pH and ANC had been small relative to estimated increases in lakewater SO_4^{2-} concentrations since pre-industrial times (Sullivan, 2000a). The belief that changes in acidic deposition were accompanied mainly by changes in ANC and

pH has been replaced by the realization that changes in SO_4^{2-} were accompanied mainly by changes in base cations. Thus, surface waters have not been acidified as much by historical deposition as was earlier believed. Furthermore, surface water ANC and pH should not be expected to show substantial chemical recovery upon reduced emissions and deposition of S and N. The magnitude of the base cation response has clearly limited the extent of surface water acidification caused by acidic deposition. However, this same response has contributed to base cation deficiencies in some soils, with associated adverse terrestrial effects.

B.2.3. Other Types of Ecosystems

There has been little work on the rates of atmospheric deposition to urban ecosystems despite extensive data on concentrations and chemical reactions of air pollutants in cities (U.S. EPA, 2004). Nevertheless, urban ecosystems are often subjected to large rates of deposition of anthropogenic pollutants (Lovett et al., 2000a). Decades of research on urban air quality indicate that cities are often important sources of emissions of NO_X, SO_X, and dust. Urban N deposition may affect nutrient cycles and soil acid-base chemistry in vegetated areas in and around cities, but such possible effects have not been studied sufficiently to draw conclusions about sensitivities or effects.

To determine the patterns of atmospheric deposition and throughfall in the vicinity of a large city, Lovett et al. (2000a) measured bulk deposition, oak forest throughfall, and particulate dust at sites along a transect within and to the north of New York City. They found that throughfall N was twice as high in the urban areas compared with suburban and rural areas. Most of the urban dry deposition of NO_3^- was from gaseous NO_X. Because there is limited biological uptake of throughfall N in an urban setting, it is believed that a relatively high (but unknown) percentage of N deposited to the urban landscape leaches to surface waters. Aquatic effects associated with N leaching from urban environments would be expected to be most pronounced near coastal cities. This is because atmospheric deposition to near-coastal urban environments can provide a substantial N load to estuaries and near shore oceanic environments, which tend to be N-limited. See further discussion in ISA Section 3.3.2.4.

B.3. Distribution and Extent of Ecosystem Effects

B.3.1. Terrestrial Ecosystems

Coniferous forests, with soils that are naturally more acidic, generally have lower pH and base saturation than soils in deciduous forests (Fernandez et al., 2003). In a paired watershed study at Bear Brook Watershed in Maine, one watershed with mixed coniferous and deciduous species received $(NH_4)_2SO_4$ corresponding to about 25 kg N/ha/yr and 29 kg S/ha/yr. After a decade of experimental acidification, the treated watershed had 66 kg/ha/yr less exchangeable Ca^{2+} and 27 kg/ha/yr less exchangeable Mg^{2+} than the untreated watershed (Fernandez et al., 2003). Soils under conifers (red spruce, balsam fir [*Abies balsamea*], hemlock [*Tsuga canadensis*]) appeared to be more sensitive to acidification than those under hardwoods (American beech [*Fagus grandifolia*], yellow birch [*Betula alleghaniensis*], sugar, and red maples [*Acer rubrum*]). The hardwoods demonstrated no significant effects from $(NH_4)_2SO_4$ addition. Differences in response to acid treatment among vegetation covers were most pronounced in upper soil (O horizon and upper 5 cm of the B horizon). The study did not distinguish between effects from NH_4^+ versus SO_4^{2-} additions.

Kozlowski (1985) suggested that plants and soils act as sinks for SO_2 deposition at low exposures of 1 to 4 $\mu g/m^3$, with no discernible effects on ecosystem structure at those levels. Shugart and McLaughlin (1985) cautioned that forest responses to SO_2 and other stressors are strongly controlled by the successional dynamics of impacted forests. Thus, efforts to better understand and quantify forest dynamics and development will be paramount to predicting chronic pollution effects.

Results of N fertilization studies have been used to infer the response of forests to atmospheric N deposition. Such studies were reviewed by Johnson (1991) and U.S. EPA (1993a), illustrating that forests can respond differently to periodic large pulsed fertilizer inputs, as compared with steady, low-level inputs from atmospheric deposition. For example, multiple or continuous inputs of N may stimulate populations of nitrifying bacteria (U.S. EPA, 1993a). This might be expected to modify the competitive interactions between trees and microbes and affect both the forest growth response and the extent of NO_3^- leaching and associated acidification.

In the southern Appalachian Mountains, acidification sensitivity has been evaluated for two common tree species: red spruce (sensitive) and loblolly pine (*Pinus taeda*; insensitive). Dendro-chronological analyses of tree cores collected for permanent plots in the Great Smoky Mountains National Park (37 trees cores from low elevation [~1500 m]; 35 tree cores from high elevation sites [~2000 m]), demonstrated a positive correlation between temporal and spatial trends in red spruce growth and acidic deposition, with a greater response in trees on ridges than in draws. Ridges are naturally more acidified, receive higher levels of acidic deposition, and have shallower soils with lower base saturation (Webster et al., 2004).

Loblolly pine seems to have low susceptibility to adverse effects from acidic deposition. A simulated acid addition experiment showed no significant effect of acidification on foliar nutrition in loblolly pine seedlings, at application levels of 21 to 26 kg/ha SO_4-S and 8 to 10 kg/ha NO_3^-N (Baker et al., 1994). Loblolly pines grown on old agricultural fields showed signs of N deficiency over 25 years of growth despite atmospheric deposition of 5 to 10 kg N/ha/yr (Richter et al., 2000).

In the northeastern U.S., two species of coniferous tree (red spruce and red pine) have been shown to be sensitive to acidification. Aber et al. (2003) reported a decrease in C:N ratio from about 35 to about 25 along an increasing N deposition gradient of 3 to12 kg N/ha/yr across the Northeast. At the Harvard Forest LTER site, at chronic experimental N addition levels of 50 and 150 kg N/ha/yr, Magill et al. (2004) found 31% and 54% decreases, respectively, in red pine growth after 15 years of chronic N application. No additive effect of S was seen after 11 years of a combined N and S treatment, with an application of 74 kg S/ha/yr and 50 kg N/ha/yr. There were no significant differences in baseline measurements between the low N and combined N and S treatments.

Recent evidence indicates that mortality in red spruce in the southern Appalachian Mountains is not abnormal when compared to historical rates, and that Fraser fir stands killed by the balsam woolly adelgid (*Adelges piceae*) are largely being replaced by vigorous re-growth of young stands of that species (Van Miegroet et al., 2007). To what extent spruce or fir mortality in the southern Appalachian Mountains will be replaced with a species mix similar to that existing before the mortality remains to be seen.

At the Fernow Experimental Forest in West Virginia, $(NH_4)_2SO_4$ inputs of 54 kg N/ha/yr and 61 kg S/ha/yr (application plus ambient atmospheric deposition), each about three times the ambient deposition level, were applied to one watershed for 4 years. Few differences in soil and forest floor chemistry were found in response to the N addition, although pH was significantly lower in the treatment watershed, corresponding to increased base-flow concentrations of NO_3^- and Ca^{2+} (Gilliam et al., 1996).

Deciduous forests show variable responses to acidification depending on the tree species present. Along an increasing N deposition gradient in the northeastern U.S., from 4.2 to 11.1 kg N/ha/yr, Lovett and Rueth (1999) found a twofold increase in mineralization in soils of sugar maple stands, but no significant relationship between increased deposition and mineralization in American beech stands. This difference might be attributable to the lower litter quality in beech stands. Thus, sugar maple appears to be more susceptible to effects of increasing deposition and concomitant soil acidification from either direct leaching of NO_3^- or enhanced nitrification. For northeastern hardwoods, Aber et al. (2003) found a

decrease in C:N ratio from 24 to 17 over a deposition gradient of 3 to 12 kg N/ha/yr. This decrease was similar but less steep than the decrease seen in conifers.

Across an 800 km pollution gradient (3 to 11 kg SO_4 -S/ha/yr; 2 to 4 kg NO_3 -N/ha/yr) in northern hardwood forests, with maples dominant, Pregitzer et al. (1992) found a 200 to 300 µg/g increase in foliar S, and litter fall S content ranged from 872 to 1356 µg/g. While foliar N did not change across the gradient, litterfall N was correlated with changing deposition. Pregitzer and Burton assert that their data did not suggest a causal link between acid deposition and forest decline. Decline would be impossible to document in the short 5–year time frame of their study. They did, however, assert that their results supported the plausibility of altered tree nutrition across large geographic regions due to atmospheric deposition.

B.3.2. Transitional Ecosystems

Wetlands are common in many areas that contain acid-sensitive surface waters. For example, wetlands constitute about 14% of the land surface in the Oswegatchie/Black River watershed in the southwestern Adirondack Mountains (Ito et al., 2005), one of the regions of the U.S. most affected by surface water acidification from acidic deposition. There are no studies, however, that have documented the extent or magnitude of acidification effects of S and N deposition on wetland ecosystems in the U.S.

The topic of acidification effects on wetlands is not well represented in the literature, and therefore the distribution of ecosystem effects for these systems is not presented. Because levels of natural organic acidity tend to be high in wetland soils and water, it is not likely that such ecosystems are affected by the levels of acidic deposition commonly encountered in the U.S. It is more likely that atmospheric deposition affects wetlands via nutrient N enrichment pathways. (See Discussion in ISA Sections 3.3.2.2 and 3.3.5.2) Gorham et al. (1987) hypothesized that acidic deposition to mineral-poor fens might cause depletion of exchangeable base cations and decreased pH of soil water. This mechanism was suggested as a possible cause of transition from mineral-poor fen to *Sphagnum* bog. Such an effect has not been observed in response to acidic deposition at levels found in the U.S.

Synoptic surveys of ponded waters generally are restricted to lakes larger than 1 ha, 4 ha, or 10 ha. Reasons for this limitation are varied and can include the perception that larger lakes are more important, the failure of regional topographic map coverages to include the smaller lakes and ponds, and the fact that smaller lakes tend to be much more numerous than larger lakes within the major lake districts of the U.S. In general, if the larger lakes in a given region are sensitive to acidification, the smaller ponds would also be expected to be sensitive. In most cases, data to demonstrate this are not available.

Ponds that have been observed to be sensitive to acidic deposition have been found in the Adirondack Mountains in New York (Kretser et al., 1989) and the Mount Zirkel Wilderness Area located in the Colorado Rockies (Campbell et al., 2004). Acid-sensitive ponds are likely to be found elsewhere as well.

B.3.3. Aquatic Ecosystems

In most regions of the U.S., most lakes and streams are not highly sensitive to existing levels of ambient air pollution. In addition, air pollution levels are generally decreasing in many parts of the country, especially in the eastern U.S., in response to federal and state air pollution control regulations. Therefore, the highly sensitive, and acidified, systems tend to be restricted to a relatively small percentage of the overall aquatic resource base. There are exceptions to this generalization, such as for example in Monongahela National Forest, WV, where a high percentage of the streams are acid-sensitive and highly acid-affected (Sullivan et al., 2002b). Similarly, a high percentage of Adirondack lakes (and presumably

also streams) are acid-sensitive and have been acidified by atmospheric deposition of S and N (Driscoll et al., 1991).

Studies to assess relationships between atmospheric deposition loading (N and S) and the estimated or expected extent, magnitude, and timing of aquatic acidification effects (NAPAP, 1998; U.S. EPA, 1995a; Van Sickle and Church, 1995) often employ a "weight of evidence" evaluation of the relationships between deposition and effects, as followed by NAPAP in the Integrated Assessment (IA) (NAPAP, 1991).

Several kinds of evidence were used in the IA to assess the extent and magnitude of acidification in sensitive regions of the U.S. These included:

- results of watershed simulation models that projected past or future chemical changes in response to changes in S deposition

- empirical biological dose/response models

- improved relationships between surface water chemistry and ambient acidic deposition

- trend analyses of long-term monitoring chemical data in regions that have experienced large recent changes in acidic deposition levels

- paleolimnological reconstructions of past water chemistry using fossil remains of algae deposited in lake sediments

- results from whole-watershed or whole-lake acidification or deacidification field experiments

Evidence from each type of study contributes to understanding of the quantitative importance of acidification and neutralization processes and their effects on the chemistry and biology of affected ecosystems.

B.3.3.1. Status of Surface Waters – Regional Overview

In the NSS, DOC concentrations were much higher in lowland coastal streams, compared with inland streams. National Stream Survey data also supported the hypothesis that atmospheric sources and watershed retention of S control regional patterns in streamwater SO_4^{2-} concentrations. Most NSS watersheds retained the vast majority of the total N loading from wet deposition. The 1986 data suggested, however, that some atmospherically deposited N may have been reaching streams in the northern Appalachians (Kaufmann et al., 1991).

In the 1990 NAPAP State of Science/Technology (SOS/T) summary, Baker et al. (1991a) identified six high interest subpopulations that accounted for most of the U.S. surface waters that were acidic with acidic deposition having been identified as the likely source (Figure B-3; Table B-2):

- Southwestern Adirondacks

- New England Uplands

- Low Si Eastern Upper Midwest

- Forested Mid-Atlantic Highlands

- Mid-Atlantic Coastal Plain

- Northern Florida Highlands

Stream data for the NSS was unavailable for three of these high-interest areas: the Adirondacks, New England, and Upper Midwest. The national WSA data indicated that acidic streams in the Upper Midwest are likely to be rare but there are acidic streams in the Adirondacks/New England region. Specific areas of interest within the other three high-interest regions are described below.

In addition to the large water chemistry databases developed by the U.S. EPA, there are also some important supplemental databases in some regions. For example, based on results of lake surveys conducted during the 1980s, about 70% of the known acidic lakes in Maine were either seepage type or high elevation (Kahl et al., 1991). The Maine seepage lake dataset includes 120 of the estimated 150 lakes in Maine that meet the following criteria: located in sand and gravel mapped by the USGS or Maine Geological Surveys; depth at least 1 m; and area at least 0.4 ha (1 ac). Sampling was conducted in 1986–87 and 1998–2000, and included at least one fall index sample for each lake. There were 87 lakes with Gran ANC less than 100 µeq/L.

The Maine high elevation lake dataset includes 90 lakes above 600 m elevation. Sampling was conducted during the periods 1986–88 and 1997–99. The study included the vast majority of Maine lakes that are at least 1 m deep and at least 0.4 ha (1 ac) in area. There were 64 lakes with Gran ANC less than 100 µeq/L.
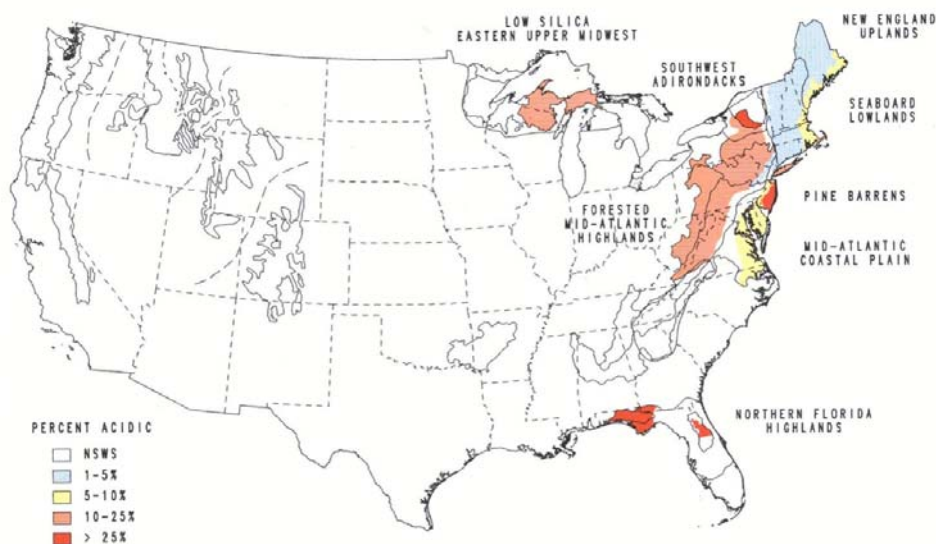
Figure B-3. **Location and percentage of acidic surface waters in U.S. high-interest subpopulations with respect to acidic deposition effects. Estimates are for the upstream reach ends in the NSS data. Population estimates in the Mid-Atlantic Highlands apply only to the forested watersheds, while estimates in the eastern Upper Midwest apply only to low-silica (≥ 1 mg/L) lakes. Figure taken from Figure 9–106 in the 1990 NAPAP SOS/T report.**

B.3.3.2. Recent Changes in Surface Water Chemistry

Surface water acid-base chemistry monitoring throughout the eastern U.S. occurs primarily in two EPA programs: the Temporally Integrated Monitoring of Ecosystems (TIME) project (Stoddard, 1990) and the Long-Term Monitoring (LTM) project (Ford et al., 1993; Stoddard et al., 1998a). Both projects are operated in cooperation with numerous state agencies, academic institutions and other federal agencies. Each is described below.

The regions represented by the LTM and TIME monitoring programs (Table B-3) are estimated to contain 95% of the lakes and 84% of the streams in the U.S. that have been anthropogenically acidified by acidic deposition. The Adirondacks had a large proportion of acidic surface waters (14%) in the NSWS; from 1984 to 1987, the ALSC sampled 1,469 Adirondack lakes greater than 0.5 ha in size and estimated

that many more (26%) were acidic (Driscoll et al., 1991). The higher percentage of acidic lakes in the ALSC sample was due to inclusion of smaller lakes and ponds (1 to 4 ha in area), many of which were acidic as a consequence of naturally occurring organic acids (Sullivan et al., 1990a). The proportions of lakes estimated by NSWS to be acidic were smaller in New England and the Upper Midwest (5% and 3%, respectively), but because of the large numbers of lakes in these regions, there were several hundred acidic waters in each of these two regions.

The Valley and Ridge Province and Northern Appalachian Plateau had 5% and 6% acidic sites, respectively. The only potentially acid-sensitive region in the eastern U.S. not assessed in the Stoddard et al. (2003) report was Florida, where the high proportion of naturally acidic lakes, and a lack of long-term monitoring data, make assessment of the effects of acidic deposition problematic (Stoddard et al., 2003).

The TIME project is structured as a probability sampling. Each site is chosen statistically to be representative of a target population. In the Northeast (New England and Adirondacks), this target population consists of lakes with Gran ANC <100 µeq/L, which are those likely to be most responsive to changes in acidic deposition. In the Mid-Atlantic, the target population is upland streams with ANC <100 µeq/L. Each lake or stream is sampled annually, and results are extrapolated to the target populations (Larsen and Urquhart, 1993; Larsen et al., 1994; Stoddard et al., 1996; Urquhart et al., 1998). The TIME project began sampling northeastern lakes in 1991. Data from 43 Adirondack lakes can be extrapolated to the target population of about 1,000 lakes having ANC <100 µeq/L, out of a total population of 1,830 lakes with surface area >1 ha. Data from 30 lakes representing about 1,500 lakes having ANC <100 µeq/L, out of a total population of 6,800 lakes, are included in the TIME program in New England.

As a compliment to lake and stream sampling in the statistical populations of lakes in TIME, the LTM project samples a subset of sensitive lakes and streams with long-term data, many dating back to the early 1980s. Each LTM site is sampled 3 to 15 times per year, and the resulting data are used to characterize the response of the most sensitive aquatic systems in each region to changing levels of acidic deposition. In most regions, a small number of higher ANC (e.g., Gran ANC >100 µeq/L) sites are also sampled. Because of the long-term records at most LTM sites, their trends can also be placed in a better historical context than those of TIME sites, where data are only available from the 1990s. Monitoring results from the LTM project have been widely published (DeWalle and Swistock, 1994; Driscoll et al., 1995; Driscoll and Van Dreason, 1993; Kahl et al., 1991, 1993; Murdoch and Stoddard, 1993; Stoddard et al., 1998; Stoddard and Kellogg, 1993; Webster et al., 1993). Overall results were summarized by Stoddard and Kellog (1993).

Monitoring data from the LTM and TIME projects were used to evaluate recent changes in lake and stream chemistry from 1990 to 2000 in many of the sensitive areas of the eastern U.S. including New England, the Adirondack Mountains, the Northern Appalachian Plateau, the Ridge and Blue Ridge provinces of Virginia, and the Upper Midwest (Stoddard et al., 2003). There are also substantial numbers of acid-sensitive streams in the Blue Ridge Province in North Carolina and portions of South Carolina and Tennessee that have been affected by acidic deposition but that were not included in this analysis. In general, the results of the TIME/LTM data analysis suggest that about one-quarter to one-third of the lakes and streams that were chronically acidic in the 1980s were no longer chronically acidic in the year 2000. However many still had low ANC and were potentially susceptible to episodic acidification (Stoddard et al., 2003).

Stoddard et al. (2003) found little evidence of regional change in the acidity status of lakes in New England or streams in the Ridge/Blue Ridge regions. Furthermore, none of the study regions showed an increase in the number of chronically acidic waters, even though there was a decline in base cation concentrations and a likely increase in natural organic acidity (Stoddard et al., 2003). An important caveat in this analysis is that changes in Gran ANC used in the analysis were based on the median change of all sites in a region (Table B-4). However, as shown in (Table B-5), the rates of ANC increase were generally more rapid in chronically acidic lakes with ANC less than 0 µeq/L and streams with ANC between 0 and

25 μeq/L. If acidic sites are recovering more rapidly than the population of sites as a whole, then the estimates of change in the number of acidic lakes and streams presented would be conservative.

While general estimates for large regions are useful in providing a broad picture of the extent and status of surface water acidity, specific results from studies within those regions can help isolate trends and determine the specific mechanisms that contribute to change. The following sections report on the current status, past acidification, and potential future conditions for lakes and streams in acid sensitive areas of the Northeast, Southeast, Upper Midwest, and Western U.S.

B.3.4. Regional Assessments

B.3.4.1. Northeastern Surface Waters

Current Status

The Adirondacks and New England are two of the most acid sensitive and intensively studied regions in the Northeast. The glaciated soils and location downwind from emissions sources have made these areas the subject of intense scientific study over the past four decades. Most of this research has focused on lake ecosystems, though important stream studies have been undertaken at specific research sites and more regional stream survey work is being conducted. As discussed below, the surface water chemistry in these areas integrates atmospheric deposition, local geology, and upland watershed characteristics.

Available surface water datasets for Adirondack lakes include TIME, EMAP, and ALSC, each of which is useful for documenting chemical status and recent chemical changes. Population estimates from the TIME dataset suggest that 13.0% of Adirondack lakes (238 lakes) were chronically acidic in the early 1990s during baseflow conditions in the summer. By applying an approximate rate of change in Gran ANC of +0.8 μeq/L/yr to these estimates (based on trend slopes for TIME and LTM data, (Table B-6), Stoddard et al. (2003) projected that approximately 8.1% of the population (149 Adirondack lakes) remained chronically acidic in 2000. This finding suggests that roughly 38% of lakes in the Adirondacks that were chronically acidic in the early 1990s were not chronically acidic a decade later. Certain caveats need to be included with the results of this analysis, however. Summertime baseflow sampling reflects the least acidic conditions experienced throughout the year. In addition, LTM trends, which are based on year-round sampling, may not be representative of trends in the summer-only sampling of the TIME program, and the rate of change determined through the TIME program was not controlled for possible differences in flow conditions between the two sample periods. Lastly, the ANC value of 0 μeq/L/yr used to define acidic waters has been shown to be below the level needed to protect aquatic ecosystems in the Adirondack region (Baldigo et al., 2007; Lawrence et al., 2007).

A study by Driscoll et al. (2001b) used EMAP data from 1991 to 1994 to evaluate the extent of acidic lakes in the Adirondacks for that period. The EMAP survey is a probability based survey representative of lakes with surface area greater than 1 ha (1,812 lakes). The survey was conducted during low-flow summer conditions, and the results therefore likely reflect the highest ANC values for the year. Results from the survey indicate that 10% of the population of Adirondack lakes were chronically acidic (ANC values of less than 0) and 31% were sensitive to episodic acidification (ANC values between 0 and 50) during the study period (Driscoll et al., 2001b).

The ALSC conducted a comprehensive survey of Adirondack lakes greater than 0.2 ha in surface area between 1984 and 1987 (Kretser et al., 1989). Of the 1,489 lakes surveyed, 24% had summer pH values below 5.0, 27% were chronically acidic (ANC <0), and an additional 21% were probably susceptible to episodic acidification (ANC between 0 and 50) (Driscoll et al., 2007a).

For the New England region, the TIME population data indicates that 5.6% of the population (386 lakes) in New England exhibited Gran ANC <0 μeq/L during the period of 1991 to 1994. This result is

similar to the EMAP findings which indicate that 5% of lakes in New England and in the eastern Catskill region of New York had ANC values less than 0 µeq/L. The EMAP analysis also estimated that an additional 10% of the population had low ANC values, between 0 and 50 µeq/L, and were probably sensitive to episodic acidification (Driscoll et al., 2001b).

Both TIME and LTM data from the New England region indicate that only a small increase in Gran ANC had occurred during the reported monitoring period (+0.3 µeq/L/yr). As a result, it is estimated that the proportion of chronically acidic lakes decreased only 0.1% from 5.6% to 5.5% over the previous 10 years (Table B-4) (Stoddard et al., 2003).

State surveys within New England provide additional information on the variation in lakewater chemistry across the region. In Maine, approximately 100 clearwater lakes in that state have been classified as acidic, based on surveys conducted by the U.S. EPA and the University of Maine (Kahl et al., 1999). An estimated 13% of the high-elevation lakes in Maine are acidic, compared to less than 1% of Maine lakes (>4 ha) represented in EPA's Eastern Lakes Survey (ELS) (Kahl et al., 1991; Linthurst et al., 1986a). Most acidic lakes in Maine are either seepage lakes located in sand and gravel deposits, or high-elevation lakes located above 600 m elevation. Roughly 60% of the acidic lakes are seepage lakes. The acid-sensitive seepage lakes are located in mapped sand and gravel deposits, are at least 1 m deep, and are at least 0.4 ha (1 acre) in surface area. About 45 of the 150 lakes of this type in Maine are acidic (Kahl et al., 1999).

Whereas lakes in the Adirondacks and New England have been intensively studied, there are no published data which describe the status of streamwater acid-base chemistry at a regional scale, except for the Catskill Mountains.

In the absence of regional streamwater studies, insights can be gained from site-specific long-term studies in the region. The HBEF has one of the longest continuous records of precipitation and streamwater chemistry in the U.S. Compared to model hindcast approximations, current conditions at HBEF indicate that soil percent base saturation has decreased in response to acidic deposition and because of accumulation of nutrient cations by forest vegetation. Further, acidic deposition has contributed to a nearly fourfold increase in stream SO_4^{2-} concentration; a decrease in ANC from positive to negative values; a decrease in stream pH to 5.0; and an increase in stream Al, largely occurring as the inorganic form which has been shown by Lawrence at al. (2007) to be an unequivocal indication of the effects of acidic deposition. Driscoll et al. (2001b) estimated that roughly 6% of lakes and streams in the Northeast are considered more sensitive to acidic deposition than the stream monitored at HBEF (Driscoll et al., 2001b).

Past Acidification

There are limited surface water data that directly document historic conditions and the response to atmospheric deposition since the time of the Industrial Revolution (Charles, 1991). To address this gap, scientists use sediment cores from lakes and detailed computer models to try to reconstruct past conditions as well as understand the mechanisms that contribute to changing conditions.

Paleolimnological Studies

Paleolimnological studies use the remains of diatoms and other algae embedded in lake sediments to reconstruct historical water chemistry. In the Adirondack Mountains and northern New England, both diatom and chrysophyte algal remains in sediment cores have been used to evaluate patterns of past acidification in a large number of lakes.

Major findings of the Paleoecological Investigation of Recent Lakewater Acidification (PIRLA)-I and PIRLA-II research programs in the Adirondack Mountains suggested that: Adirondack lakes had not acidified as much since pre-industrial times as had been widely believed before 1990; many Adirondack lakes with ambient pH greater than 6.0 had not acidified historically, whereas many of the lakes having pH less than about 6.0 had acidified; many of the lakes having high pH and ANC had increased in pH and ANC since the previous century; and the average F-factor for acid-sensitive Adirondack lakes was near

0.8 (Charles et al., 1990b; Sullivan et al., 1990). The results of these studies had major effects on scientific understanding of the extent to which lakes had acidified in response to acidic deposition. The view of surface water acidification as a large-scale titration of ANC (Henriksen, 1980, 1984) was replaced by the realization that base cation concentrations typically changed more than ANC in response to acidic deposition. This realization also modified expectations for chemical recovery of surface waters as acidic deposition levels have decreased (Sullivan, 2000).

Diatom and chrysophyte reconstructions of pH and ANC for a statistically selected group of Adirondack lakes suggested that about 25% to 35% of the Adirondack lakes that are larger than 4 ha had acidified since preindustrial time (Cumming et al., 1992). Low-ANC lakes of the southwestern Adirondacks acidified the most, probably due to low initial buffering capacity and high rainfall and deposition of S and N in that area. Cumming et al. (1992) estimated that 80% of the Adirondack lakes that had ambient pH ≥ 5.2 had experienced large declines in pH and ANC since the previous century, and that 30% to 45% of the lakes with pH between 5.2 and 6.0 had also acidified.

Cumming et al. (1994) reported the results of chrysophyte inferences of pH in recently deposited lake sediments to assess acidification timing for 20 low-ANC Adirondack lakes. Lakes that were inferred to have acidified since about 1900 tended to be small, high-elevation lakes with lower inferred pre-industrial pH than the group of study lakes as a whole. These were probably the most acid-sensitive and were the first to acidify with increasing acidic deposition. Husar and Sullivan (1991) estimated that S deposition was about 4 kg S/ha/yr at that time. These lakes are located in the high peaks area and in the southwestern portion of Adirondack Park. A second category of acidification response included high-elevation lakes that were historically low in pH (<5.5) but that acidified further beginning about 1900. The third identified type of response included lakes with pre-industrial pH in the range of about 5.7 to 6.3 that started to acidify around 1900 but showed their greatest pH change around 1930 to 1950. The final category included lakes that were not inferred to have acidified. They had pre-industrial pH around 6.0 and are located at lower elevation.

Davis et al. (1994) conducted paleolimnological studies of 12 lakes in northern New England that were low in pH and ANC. Past logging, forest fire, and vegetation composition in the watersheds were estimated from oral and written historical information, aerial photographs, and tree ring analyses. Lake sediment cores were collected and analyzed for pollen, diatoms, and chemistry to reconstruct past lake conditions for several hundred years. All 12 lakes were historically low in pH and ANC, with diatom-inferred pre-industrial ANC of –12 to 31 µeq/L. The inferred pH and ANC values of the lakes were relatively stable throughout the one to three centuries of sediment record before watershed disturbance by Euro-Americans. From the early 19th into the 20th century, however, all of the lakes showed increased diatom-inferred pH changes of about 0.05 to 0.6 pH units and increased diatom-inferred ANC of about 5 to 40 µeq/L. Most of these inferred increases in pH and ANC coincided with watershed logging. For all study lakes, recovery to pre-logging acid-base lake chemistry conditions was followed by continued decline in pH by 0.05 to 0.44 pH units and ANC by up to 26 µeq/L, probably because of acidic deposition. The 12–lake mean inferred decreases in pH and ANC in response to acidic deposition were 0.24 pH units and 14 µeq/L, respectively (Davis et al., 1994).

Modeling Studies

The most extensive regional modeling study that provides estimates of past acidification of Adirondack lakes is that of Sullivan et al. (2006b). They modeled past changes in the acid-base chemistry of 70 Adirondack lake watersheds, including 44 that were statistically selected to be representative of the approximately 1,320 lake watersheds in the Adirondacks that have lakes larger than 1 ha and deeper than 1 m and that have ANC ≥ 200 µeq/L. Model hindcasts were constructed using both the MAGIC and PnET-BGC models.

Based on MAGIC model outputs extrapolated to the regional Adirondack lake population, maximum past acidification occurred by about 1980 or 1990, with median ANC of the population under investigation of about 61 µeq/L (reduced from a median of 92 µeq/L estimated for the pre-industrial

period). By 1990, 10% of the population target lakes had decreased in ANC to below −16 µeq/L and 25% had ANC <28 µeq/L. Percentile values in 2000 illustrated limited chemical recovery (3 to 5 µeq/L) compared with simulated values in 1980 and 1990.

The MAGIC model simulations suggest that none of the target lakes were chronically acidic (had ANC <0 µeq/L) under pre-industrial conditions, but that by 1980 there were about 204 acidic Adirondack lakes. That number decreased by an estimated 14% between 1980 and 2000. Similarly, the MAGIC model simulations suggested that there were no Adirondack lakes having ANC <20 µeq/L in 1850, but by 1990 there were 263 such lakes. Many lakes (N = 191) were estimated to have had pre-industrial ANC below 50 µeq/L, and this estimate increased threefold by 1990, followed by a decrease to 399 lakes in 2000.

PnET-BGC model simulations generated output generally similar to results provided by MAGIC model simulations. PnET-BGC simulations suggested that lakewater SO_4^{2-}, NO_3^-, and base cation concentrations under pre-industrial conditions were much lower than current values. In 1850, simulated SO_4^{2-} concentrations in all study lakes were less than 25 µeq/L, and the median value was about 15 µeq/L. By 1980, the median simulated SO_4^{2-} concentration had increased more than sixfold to about 100 µeq/L. Simulated lake NO_3^- concentrations also increased markedly during that time, with the median value increasing from about 4 µeq/L in 1850 to 12 µeq/L in 1980. Simulated increases in the sum of divalent base cation concentrations were less than for SO_4^{2-} concentrations, with the median value increasing from 93 µeq/L in 1850 to 140 µeq/L in 1980. This large change in $SO_4^{2-} + NO_3^-$ relative to the change in the sum of base cation concentrations was the major mechanism driving the decreases in ANC and pH associated with historical increases in acidic deposition.

Simulated lakewater ANC and pH and soil base saturation decreased from pre-industrial conditions to recent times. Results from PnET-BGC suggested that the median Adirondack lake, from among the estimated 1,320 lakes in the population larger than 1 ha that had measured recent ANC <200 µeq/L, had pre-industrial ANC near 80 µeq/L; an estimated 10% of the lake population had pre-industrial ANC <41 µeq/L; and one-fourth had pre-industrial ANC <64 µeq/L. Percentiles for the year 2000 suggest decreases in SO_4^{2-}, NO_3^-, and sum of base cations, and small increases in ANC since 1990 for lower-ANC lakes.

Results from PnET-BGC suggest that none of the lakes in the Adirondack population had pre-industrial ANC below 20 µeq/L. By 1990, there were 289 lakes having ANC <20 µeq/L and 217 chronically acidic (ANC ≥ 0 µeq/L) lakes according to PnET-BGC simulations. There were 202 lakes in the population simulated to have had pre-industrial ANC below 50 µeq/L, and this number increased 2.8 times by 1980 under the PnET-BGC simulations.

PnET-BGC has also been used to characterize past conditions at streams within the HBEF. Gbondo-Tugbawa et al. (2002) used relationships between current emissions and deposition, and estimates of past emissions to reconstruct historical deposition conditions. Their analysis also considered land disturbances such as logging in 1918–1920 and hurricane damage in 1938. Using this approach, they estimated that past soil base saturation in the mineral soil (circa 1850) was approximately 20%, stream SO_4^{2-} concentration was approximately 10 µeq/L, stream ANC was about 40 µeq/L, stream pH was approximately 6.3, and stream Al_i concentration was below 1 µmol/L (Driscoll et al., 2001b).

Recent Trends

Sulfur deposition has contributed to chronic soil and surface water acidification in the eastern U.S. to a much greater extent than has N deposition. Nitrate concentrations in acid-sensitive drainage waters in the eastern U.S. are generally much lower than SO_4^{2-} concentrations.

The concentration of SO_4^{2-} in precipitation has declined for about the past three decades throughout the northeastern U.S., in response to decreased atmospheric emissions and deposition. EPA's LTM Program has been collecting monitoring data since the early 1980s for many lakes and streams in acid-sensitive areas of the U.S., including the Northeast. These data allow evaluation of trends and variability in key components of lake and streamwater chemistry before, during, and subsequent to Title IV implementation. Throughout the northeastern U.S., the concentration of SO_4^{2-} in surface waters has

decreased substantially (Figure B-4) in response to decreased emissions and atmospheric deposition of S. Decreased concentrations of SO_4^{2-} in lakes and streams of a third, or more, have been commonly observed.

Lakewater SO_4^{2-} concentrations have decreased steadily in Adirondack lakes, at least since 1978 (Driscoll et al., 1995; Stoddard et al., 2003). Initially, there was not a systematic increase in lakewater pH or ANC in response to the decreased SO_4^{2-} concentrations. Rather, the decline in lakewater SO_4^{2-} during the 1980s was charge-balanced by a nearly equivalent decrease in concentrations of base cations in many of the low-ANC lakes (Driscoll et al., 1995). Similar findings were reported by Stoddard and Kellog (1993) for lakes in Vermont. F-factors for the nine ALTM lakes that showed significant declines in both the sum of base cations (SBC) and $(SO_4^{2-} + NO_3^-)$ concentration ranged from 0.55 to greater than 1.0, with a mean of 0.93 (Driscoll et al., 1995). These high F-factor values for chemical recovery from acidification were similar to results of historical acidification obtained by Sullivan et al. (1990), based on diatom reconstructions of historical change for 33 Adirondack lakes.

Trend analysis results for the period 1982 to 1994 were reported by Stoddard et al. (1998) for 36 lakes in the northeastern U.S. having ANC ≥ 100 µeq/L. Trend statistics among sites were combined through a meta-analytical technique to determine whether the combined results from multiple sites had more significance than the individual Seasonal Kendall Test statistics. All lakes showed significant declining trends in SO_4^{2-} concentration ($\Delta SO_4^{2-} = -1.7$ µeq/L/yr; $p \geq 0.001$). Lakewater ANC responses were regionally variable. Lakes in New England showed evidence of ANC recovery ($\Delta ANC = 0.8$ µeq/L/yr; $p \geq 0.001$), whereas Adirondack lakes exhibited either no trend or further acidification, largely because of declines in base cation concentrations.

The observed changes in the concentration of NO_3^- in some surface waters have likely been due to a variety of factors, including climate. During the 1980s, NO_3^- concentration increased in many surface waters in the Adirondack and Catskill Mountains in New York (Driscoll and Van Dreason, 1993; Murdoch and Stoddard, 1993). There was concern that northeastern forests were becoming N-saturated, leading to increased NO_3^- leaching from forest soils throughout the region. Such a response could negate the benefits of decreased SO_4^{2-} concentrations in lake and stream waters. However, this trend was reversed in about 1990, and the reversal could not be attributed to a change in N deposition. Nitrate leaching through soils to drainage waters is the result of a complex set of biological and hydrological processes. Key components include N uptake by plants and microbes, transformations between the various forms of inorganic and organic N, and local precipitation patterns. Most of the major processes are influenced by climatic factors, including temperature, moisture, and snowpack development. Therefore, NO_3^- concentrations in surface waters respond to many factors in addition to N deposition and can be difficult to predict. It is likely that monitoring programs of several decades or longer will be needed to separate trends in NO_3^- leaching from climatic variability in forested watersheds (Driscoll et al, 1995).

Monitoring data collected during the 1990s in the LTM and TIME projects illustrated that most regions included in the monitoring efforts showed large declines in SO_4^{2-} concentrations in surface waters over the 10 years of monitoring, with rates of change ranging from 1.5 to 3 µeq/L/yr (Figure B-5). These declines in lake and stream SO_4^{2-} concentration were considered consistent with observed declines in S wet deposition. Surface water NO_3^- concentrations also decreased, but only in the two regions that had the highest ambient surface water NO_3^- concentrations (Adirondacks and Northern Appalachian Plateau), but were relatively unchanged in regions with lower concentrations. DOC increased in each region over time. This finding suggests an increase in the contribution of natural organic acidity, which would partially offset the expected chemical recovery from decreased acidic deposition.

Sulfate concentration in Lake and Stream Water (µeq/L)
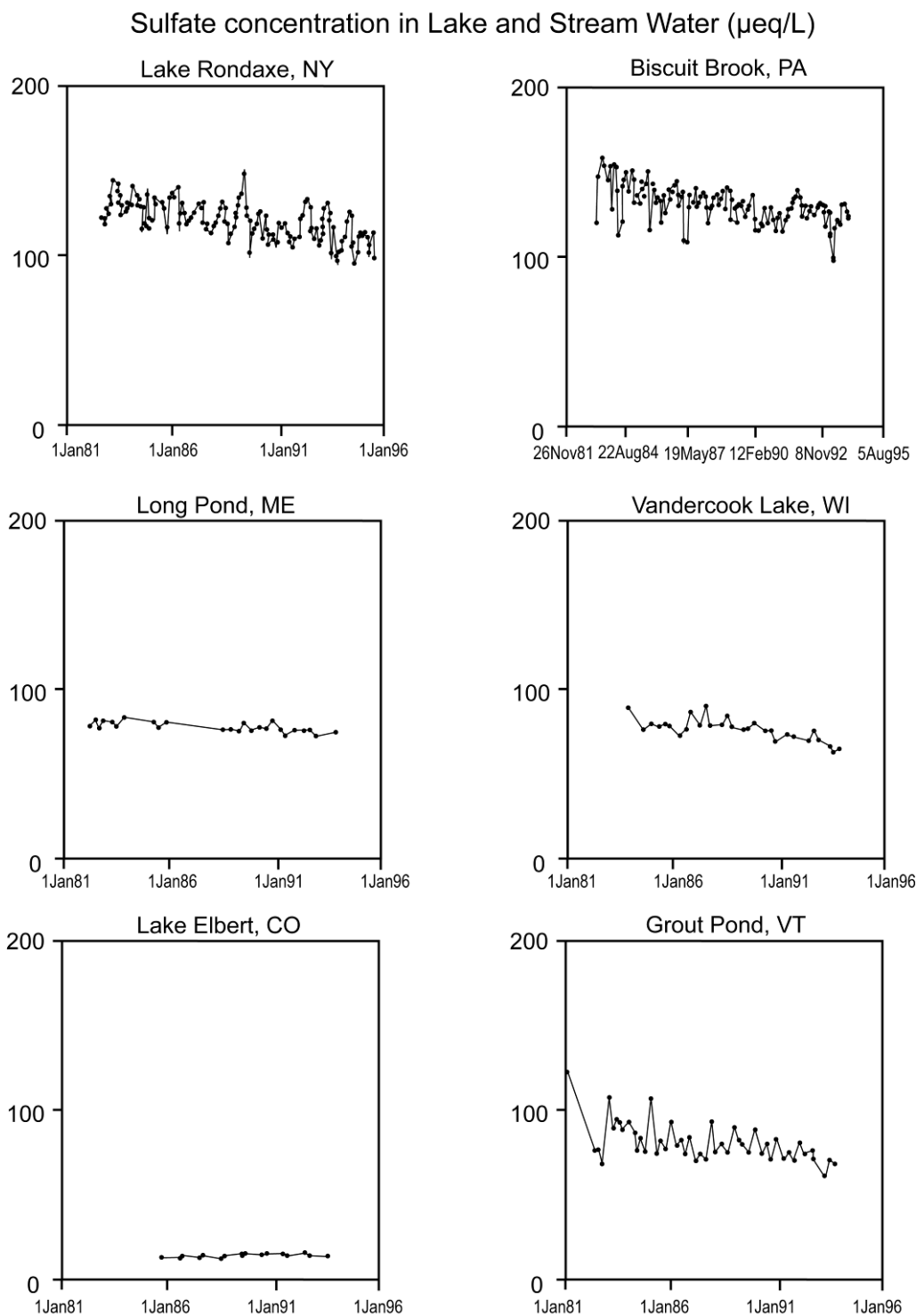
Figure B-4. **Measured concentration of SO$_4^{2-}$ in selected representative lakes and streams in six regions of the U.S. during the past approximately 15 years. Data were taken from EPA's Long-Term Monitoring (LTM) program.**

ANC increased in the Adirondacks at a rate of about +1 µeq/L/yr, despite a decline in surface water base cation concentrations (Ca^{2+} + Mg^{2+}. The decline in base cations offset some of the decline in SO$_4^{2-}$,

and thus limited the increase in ANC or pH that occurred in response to lower SO_4^{2-} concentrations. Surface water ANC and pH increased significantly in the 1990s; Al_i concentrations declined slightly. Regional surface water ANC did not change significantly in New England (Stoddard et al., 2003).

Moderate increases in surface water ANC during the 1990s reduced the estimated number of acidic lakes and stream segments in the northeastern U.S. Stoddard et al. (2003) estimated that there were 150 Adirondack lakes in the year 2000 that had ANC less than 0 (8.1% of the lake population), compared to 13% (240 lakes) in the early 1990s.

Lakewater SO_4^{2-} concentrations in the most acid-sensitive Maine lakes declined by about 12% to 22% during the period 1982 to 1998 (Kahl, 1999). Only in the seepage lakes, however, was there evidence of a small decline in lakewater acidity during that period (Table B-7).
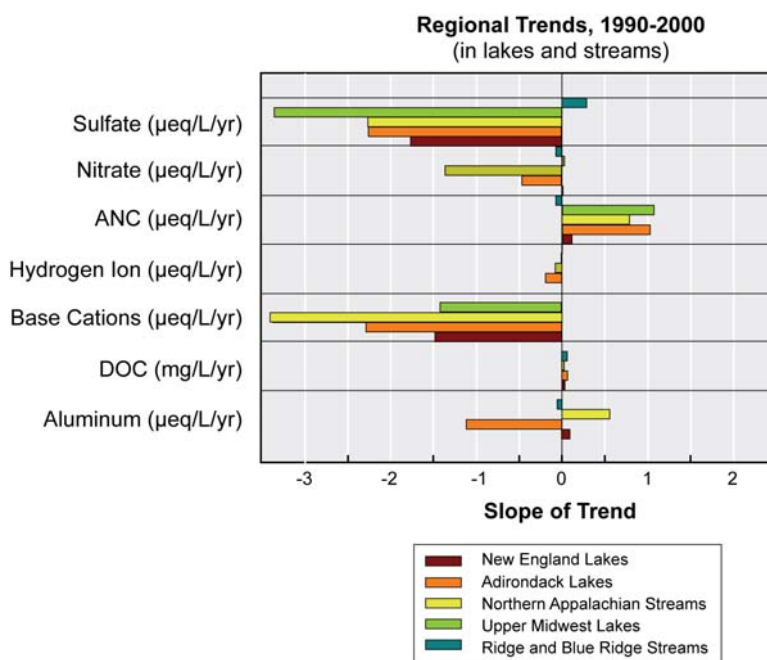
Source: Stoddard et al. (2003).

Figure B-5.   Summary of regional trends in surface water chemistry from 1990 through 2000 in regions covered by the Stoddard et al. (2003) report.

However, evidence for reductions in lakewater ANC in seepage lakes from the mid-1980s to 1998 were based on a comparison of only two sampling points, which may have been influenced by climatic variation. Therefore, the conclusion of decreasing acidity of seepage lakes is considered preliminary. The seepage lakes are generally hydrologically isolated from their surrounding soil environment. They therefore did not show a clear decreasing trend in base cation concentrations, as has been found in drainage lakes throughout the Northeast. The high-elevation lakes, in contrast, showed small declines in lakewater acidity during the 1980s, but that trend slowed or reversed in the 1990s (Kahl, 1999). Both the seepage and high elevation lakes showed increased DOC concentrations of 10% to 20%, generally by about 0.5 to 1.0 mg/L. The increase in dissolved organic matter would be expected to limit the extent of ANC and pH recovery that would otherwise accompany the observed decreases in SO_4^{2-} concentration. Whereas NO_3^- concentrations decreased during the 1990s in many lake chemistry datasets (Stoddard et al., 2003), the high-elevation lakes in Maine continued to show high concentrations.

The reference stream of the Bear Brook Watershed Study (East Bear Brook) has the longest continuous, high-frequency data record of stream chemistry in Maine. Sulfate and NO_3^- concentration have both declined substantially since 1987. Base cations declined by an almost equivalent amount, and the increase in ANC has been limited (Kahl, 1999).

Long-term stream water data from the HBEF reveal a number of changes that are consistent with trends in lakes and streams across Europe and eastern North America (Evans and Monteith, 2002; Stoddard et al., 2003, 1999). Stream water draining the HBEF reference watershed (Watershed 6) had a 32% decline in annual volume-weighted concentrations of SO_4^{2-} (−1.1 µeq/L) between 1963 and 2000 (Driscoll et al., 2007a). This decrease in stream SO_4^{2-} concentration corresponds to both decreases in atmospheric emissions of SO_2 and to bulk precipitation concentrations of SO_4^{2-} (Likens et al., 2001). In addition, there has been a long-term decrease in stream concentrations of NO_3^- that is not correlated with a commensurate change in emissions of NO_X or in bulk deposition of NO_3^-. The long-term declines in stream concentrations of strong acids ($SO_4^2 + NO_3^-$; −1.9 µeq/L/yr) have resulted in small but significant increases in pH, from 4.8 to 5.0 (Driscoll et al., 2007a). Streams at HBEF remain acidic compared to background conditions, when stream pH was estimated to be approximately 6.0 (Driscoll et al., 2007). The increase in stream pH has been limited because of marked concurrent decreases in the sum of base cations (−1.6 µeq/L/yr; Driscoll et al., 2001b).

Future Projections

MAGIC model simulations were conducted for the NAPAP IA to forecast the response of lakes and streams in the eastern U.S. to S deposition. Results were reported by NAPAP (1991), Sullivan et al. (1992), and Turner et al. (1992). The projected median change in lakewater or streamwater ANC during 50–year simulations was similar among regions, except in the Southern Blue Ridge and Mid-Atlantic Highlands, where acidification was delayed due to S adsorption on watershed soils. MAGIC projected relatively small future loss of ANC in most northeastern watersheds under continued constant deposition. These modeled changes were due to a simulated slight depletion of the supply of base cations from soils (Turner et al., 1992).

On average, each kg/ha/yr change in S deposition was projected by MAGIC to cause a 3 to 4 µeq/L median change in surface water ANC. Such projected changes in ANC, while considerably smaller than was generally thought to occur in the 1980s, nevertheless suggested widespread sensitivity of surface water ANC to changes in S deposition throughout the northeastern U.S. (Sullivan, 2000).

Since 1990, adjustments have been made to the MAGIC model and its application method in response to model testing using paleolimnological data (Sullivan et al., 1992, 1996a) and the results of acidification and deacidification experiments (Cosby et al., 1995, 1996; Norton et al., 1982) and empirical studies (Sullivan and Cosby, 1998). The net effect has been that the model projects somewhat less sensitivity of Adirondack lakes to change in S deposition as compared with the version of MAGIC applied in 1990 (Sullivan and Cosby, 1998).

Model projections of future acid-base chemistry under three scenarios of future atmospheric emissions controls were presented by Sullivan et al. (2006a) and Zhai et al. (2008) for lakes in the Adirondack Mountains to evaluate the extent to which lakes might be expected to continue to increase in ANC in the future. Estimated levels of S deposition at one representative watershed are shown in Figure B-6 for the hindcast period and in the future under the three emissions control scenarios. Model simulations for 44 statistically selected Adirondack lakes using the MAGIC and PnET-BGC models were extrapolated to the regional lake population. Cumulative distribution frequencies of ANC response projected by MAGIC are shown in Figure B-7 for the past (1850), peak acidification period (1990), and future (2100). Results for the future are given for each of the scenarios.

Results suggested that the ongoing trend of increasing lakewater ANC for the most acid-sensitive lakes would not continue under future emissions and deposition levels anticipated as of 2003 (Base Case Scenario). The numbers of Adirondack lakes having ANC below 20 and below 50 µeq/L were projected to increase between 2000 and 2100 under that scenario, and the number of chronically acidic Adirondack

lakes (i.e., ANC less than 0) was projected to stabilize at the level reached in 2000. This projected reversal of chemical recovery of acid-sensitive lakes was due to a continuing decline in the simulated pool of exchangeable base cations in watershed soils.

Simulations suggested that re-acidification might be prevented with further reductions in emissions and deposition.

Chen and Driscoll (2005b) applied the PnET-BGC model to 44 EMAP lake watersheds in the Adirondacks. PnET-BGC was used to predict the acid-base chemistry of soils and surface waters, and to assess the fisheries status during pre-industrial conditions (~1850) and under three future acidic deposition scenarios.
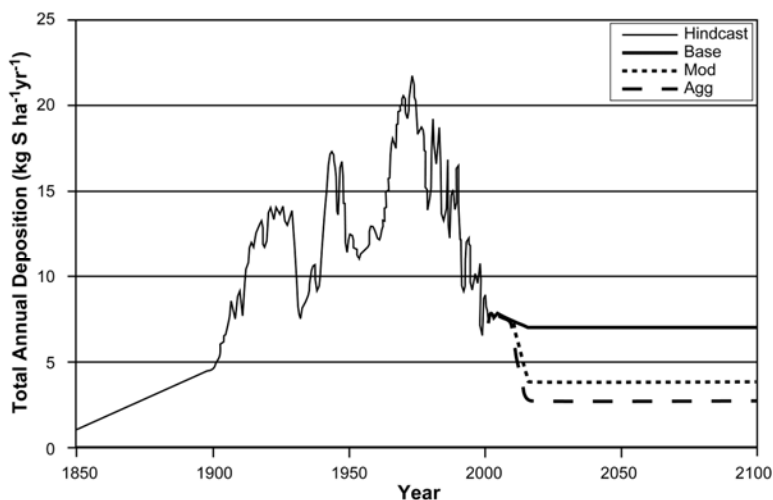
Source: Sullivan et al. (2006b).

Figure B-6.   **Estimated time series of S deposition at one example watershed in the SW Adirondack Mountains used by Sullivan et al. (2006b) as input to the MAGIC model for projecting past and future changes in lakewater chemistry attributable to acidic deposition. Future deposition estimates were based on three emissions control scenarios (Base Case, Moderate Additional Controls, Aggressive Additional Controls).**

MAGIC Model Estimates of ANC Distribution
Adirondack Lakes with ANC < 200 µeq/L
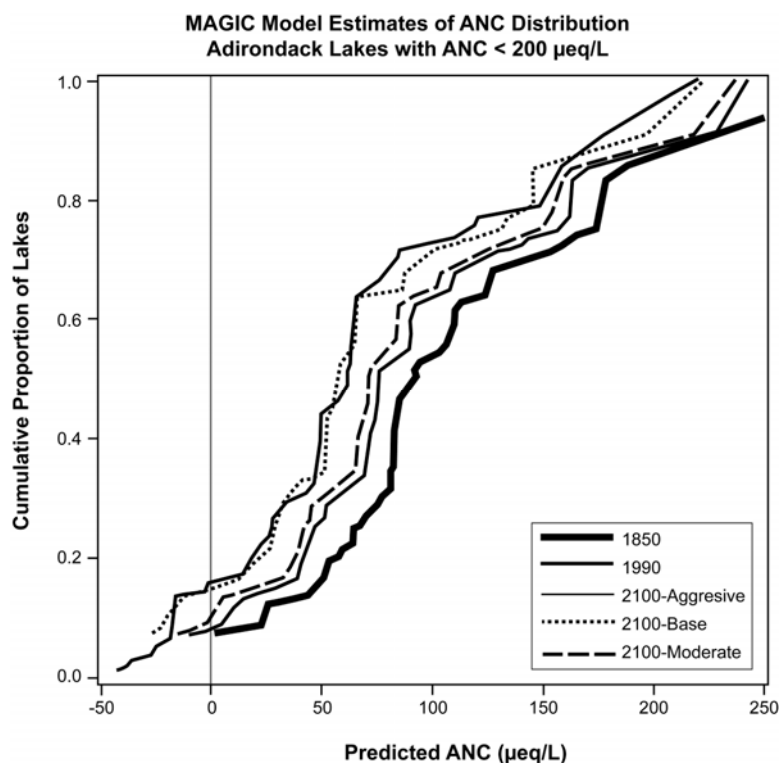
Figure B-7. Simulated cumulative frequency distributions of lakewater ANC at three points in time for the population of Adirondack lakes.

Model hindcasts using PnET-BGC indicated that acidic deposition has greatly altered surface waters and soils in the Adirondacks over the past 150 years, and that some ecosystems are continuing to acidify despite decreases in S deposition. The model was applied to three future emissions scenarios: base case, moderate emissions reductions, and aggressive emissions reductions. A case study for Indian Lake in the Adirondacks illustrated that larger reductions in deposition caused greater decreases in SO_4^{2-} and base cation concentrations in stream water and greater recovery in pH and ANC. Within the full population of lake-watersheds, some showed decreasing ANC and pH values from 1990 to 2050 even under the moderate and aggressive reduction scenarios. By 2050 to 2100, however, nearly all lakes experienced increasing ANC and pH. The rate of soil base saturation regeneration increased very slowly over the modeled time period, compared to changes in surface water chemistry. For 95% of the lake-watersheds studied, simulated soil base saturation remained below 20% in 2100 under all emissions scenarios.

There are few streams in the northeastern U.S. for which future acid-base chemistry status has been modeled. One notable exception is the modeling conducted for streams at the HBEF and in the Catskill Mountains. Calculations performed by Driscoll et al. (2003a) using the PnET-BGC model suggested that "aggressive reductions in N emissions alone will not result in marked improvements in the acid-base status of forest streams." For example, in response to an aggressive utility emissions control scenario (hypothesized 75% reduction in utility N emissions beyond the CAAA), the ANC values of Watershed 6 at HBEF in New Hampshire and Biscuit Brook in the Catskill Mountains in New York were only projected to increase by 1 and 2 µeq/L, respectively, by the year 2050 (Driscoll et al., 2003a). Projected changes in water chemistry in response to differing levels of N deposition were small in comparison with model projections of variations resulting from climatic factors (Aber, 1997; Driscoll et al., 2003a).

B.3.4.2. Southeastern Surface Waters

The two regions in the Southeast that were identified by Charles (1991) as containing low-ANC surface waters are the Appalachian Mountains and Northern Florida. The Appalachian Mountain region contains many streams that have low ANC, and it receives one of the highest rates of acidic deposition in the U.S. (Herlihy et al., 1993). Streamwater acid-base chemistry has been extensively studied in this region (Church et al., 1992; Herlihy et al., 1993; Sullivan et al., 2002, 2003; Van Sickle and Church, 1995).

Northern Florida contains the highest percentage of acidic lakes of any lake population in the U.S. (Linthurst et al., 1986a, b). Most lakes in Florida are located in marine sands overlying carbonate bedrock and the Floridan aquifer, a series of limestone and dolomite formations that underlies most of Florida. Most of the acidic and low-ANC lakes are located in the Panhandle and north central lake districts.

The current status, past acidification and recent trends in surface waters chemistry for both the Appalachian Mountains and northern Florida are discussed below.

Appalachian Mountains

Current Status

One of the most important processes affecting watershed acid-neutralization throughout much of the Southeast is S-adsorption on soil. If S adsorption on soil is high, relatively high levels of S deposition have little or no effect on stream acid-base chemistry, at least in the short-term. However, this S-adsorption capacity can become depleted over time under continued S deposition, and this causes a delayed acidification response.

Sulfur-adsorption varies by physiographic province. It is highest in the soils of the Southern Blue Ridge, where typically about half of the incoming S is retained. Adsorption is lower in the Valley and Ridge watersheds and especially in the Appalachian Plateau (Herlihy et al., 1993). In general, S adsorption is higher in the southern portions of the Appalachian Mountain region.

The Mid-Atlantic Highlands consists of the portions of the Blue Ridge Mountains, Ridge and Valley, and Appalachian Plateau ecoregions between the Virginia-North Carolina border and the Catskill Mountains in southeastern New York. Acid mine drainage (AMD) is a major source of acidity to streams in the Mid-Atlantic Highlands but in many cases is easy to identify due to the high concentrations of SO_4^{2-} in the streams that are influenced by AMD (Herlihy et al., 1991). Acidic and low-ANC streams affected by AMD were removed before analyses of acid-base chemistry population statistics.

Streams in the Appalachian Mountain portion of the mid-Atlantic region receive some of the largest acidic deposition loadings of any region of the U.S. A compilation of survey data from the mid-Appalachians yields a consistent picture of the acid-base status of streams. Acidic streams, and streams with very low ANC, are almost all located in small (watershed area <20 km^2), upland, forested catchments in areas of base-poor bedrock. Acidic surface waters in this region are nearly always found in forested watersheds because the thin soils and steep slopes that make these watersheds unsuitable for agriculture and other development also contribute to their sensitivity to acidic deposition (Baker et al., 1991b).

In the subpopulation of upland forested streams, which comprises about half of the total stream population in the mid-Appalachian area, data from various local surveys showed that 5% to 20% of the streams were acidic, and about 25 to 50% had ANC <50 μeq/L (Herlihy et al., 1993). NSS estimates for the whole region showed that there were 2330 km of acidic streams and 7500 km of streams with ANC <50 μeq/L. In these forested reaches, 12% of the upstream reach ends were acidic and 17% had pH ≥ 5.5 (Table B-4). Sulfate from atmospheric deposition was the dominant source of acid anions in acidic mid-Appalachian streams. In these acidic streams, the low pH (median 4.9) and high levels of Al_i (median

129 µg/L) leached through soils by acidic deposition were considered to be sufficiently high to cause damage to aquatic biota. Acidic streams in this subpopulation typically had low DOC (mean 1.5 mg/L).

Localized studies have clearly shown that streamwater ANC is closely related to bedrock mineralogy (Herlihy et al., 1993). Sullivan et al. (2007a) delimited a high-interest area for streamwater acidification sensitivity within the Southern Appalachian Mountain region (Virginia/West Virginia to Georgia) based on geological classification and elevation. It covered only 28% of the region, and yet included almost all known acidic and low ANC (<20 µeq/L) streams, based on evaluation of about 1,000 streams for which water chemistry data were available. They found that the vast majority of low ANC sample streams were underlain by the siliceous geologic sensitivity class, which is represented by such lithologies as sandstone and quartzite. Low ANC streamwater throughout the region was also found to be associated with a number of watershed features in addition to lithology and elevation, including ecoregion, physiographic province, soil type, forest type and watershed area.

Sulfate mass balance analyses indicated that, because of watershed SO_4^{2-} retention, soils and surface waters of the region have not yet realized the full effects of elevated S deposition. On average, based on NSS data, sites in the Blue Ridge Mountains retain 35% of incoming SO_4^{2-} from atmospheric deposition. The amount of SO_4^{2-} retention was strongly related to ecoregion in the order, Piedmont >Blue Ridge and Ridge & Valley >Appalachian Plateau.

Herlihy et al. (1993) believed that the observed differences were due to the effects of cumulative loadings from atmospheric S deposition and not due to inherent ecoregional differences in the soils. They also concluded that S retention will likely continue to decrease in the future, resulting in further losses of stream ANC.

Both mineral acids and organic acids play important roles in the acid-base status of streams in the Mid-Atlantic Coastal Plain (Baker et al., 1991b). Acidic streams in the New Jersey Pine Barrens (Table B-2) are largely inorganically dominated, but most likely they were naturally organically acidic in the past. It is uncertain what effect the addition of inorganic acids from acidic deposition has had on these low ionic strength colored systems. Over half the streams in the Pine Barrens included in the NSS were acidic, and virtually all (96%) had ANC less than 50 µeq/L. Human disturbances in the Pine Barrens often result in the alkalinization of streams (increases in pH and ANC) that alter the natural Pine Barrens aquatic biota. Outside of the Pine Barrens in the NSS, the remainder of the acidic streams in the Coastal Plain were all high DOC organically dominated systems. Low DOC (<4 mg/L), acidic streams have been observed, however, in other Mid-Atlantic Coastal Plain surveys.

The Virginia Trout Stream Sensitivity Study (VTSSS) surveyed streamwater chemistry for 344 (~80%) of the native brook trout (*Salvelinus fontinalis*) streams in western Virginia. About half of the streams included in the VTSSS had ANC <50 µeq/L. In contrast, the NSS (Kaufmann et al., 1988) data for western Virginia suggested that only about 15% of the streams in the NSS target population had ANC <50 µeq/L. These differences may reflect the smaller watershed size, more mountainous topography, and generally more inert bedrock of the VTSSS watersheds, as compared with the overall NSS stream population.

In the Appalachian Plateau of West Virginia there are two wilderness areas located in close proximity in an area of base-poor bedrock — Dolly Sods and Otter Creek Wilderness Areas. Most streams draining these wilderness areas are acidic or low in ANC.

In the Great Smoky Mountains National Park in North Carolina and Tennessee, Cook et al. (1994) reported high NO_3^- concentrations (~100 µeq/L) in upland streams which were correlated with elevation and forest stand age. The old growth sites at higher elevation showed the highest NO_3^- concentrations. This pattern could have been due to the higher rates of N deposition and flashier hydrology at high elevation, and also decreased N uptake by trees in older forest stands. High N deposition at these sites has likely contributed to both chronic and episodic acidification of streamwater (Flum and Nodvin, 1995; Nodvin et al., 1995).

Recent Trends

Population estimates from TIME surveys of streams in the Northern Appalachian Plateau region suggested that 5014 km of streams (11.8% of the stream length) were acidic in 1993−94, but that only 3600 km of streams (8.5% of the stream population) remained acidic in this region in 2000. The approximate rate of estimated change in Gran ANC in the region (Table B-5) was +0.79 µeq/L/yr. On this basis, Stoddard et al. (2003) estimated that roughly 3600 km of stream (8.5%) remained acidic 10 years later. This represents about a 28% decrease in acidic stream length over the preceding decade.

Future Projections

Model projections of future changes in acid-base chemistry of streams in the southeastern U.S. were presented by Sullivan et al. (2002, 2003, 2005). In the eight-state Southern Appalachian Mountains region, Sullivan et al. (2005) modeled future effects of atmospheric S and N deposition on aquatic resources. Modeling was conducted with the MAGIC model for 40 to 50 sites within each of three physiographic provinces, stratified by stream water ANC class. Simulations were based on assumed constant future atmospheric deposition at 1995 levels and on three regional strategies of emissions controls provided by the Southern Appalachian Mountains Initiative (SAMI), based on the Urban to Regional Multiscale One-Atmosphere model (Odman et al., 2002).

The NSS statistical frame (Kaufmann et al., 1991) was used to estimate the number and percentage of stream reaches in the region that were projected to change their chemistry in response to the emissions control strategies. There was a small decline in the estimated length of projected acidic (ANC ≥ 0) streams in 2040 from the least to the most restrictive emissions control strategy, but there was little difference in projected stream length in the other ANC classes as a consequence of adopting one or another strategy. However, projections of continued future acidification were substantially larger under a scenario in which S and N deposition were held constant into the future at 1995 levels. Turner et al. (1992) also reported MAGIC model simulation results that suggested substantial acidification (~20 µeq/L) of aquatic systems would occur in the southeastern U.S. if deposition remained constant at 1985 levels. Those model analyses were conducted as part of the National Acid Precipitation Assessment Program (NAPAP, 1991).

The SAMI emissions control strategies used in the modeling represented air regulatory requirements being implemented at the time of SAMI's formation, expected reductions under recent federal regulatory actions, and additional emissions controls applied to all emissions sectors in the eight SAMI states. The spatial variability of these emissions controls resulted in varying estimated future changes in S and N deposition at different locations within the SAMI region. The SAMI strategies were designated A2, B1, and B3. A2 is the reference strategy that represented SAMI's best estimates for air emission controls under regulations for which implementation strategies were relatively certain at the time of the study (about the year 2000). Emissions reductions under the A2 strategy included the acid rain controls under Title IV of the 1990 Amendments to the CAAA, the 1-h O_3 standard, NO_X reductions required under EPA's call for revised State Implementation Plans (SIPs), and several highway vehicle and fuel reductions. The A2 strategy was applied for all eastern states and focused on the utility and highway vehicle sectors. The B1 and B3 strategies assumed progressively larger emissions reductions, targeted only to the eight SAMI states but covering all emissions sectors.

Streams exhibited a broad range of response to the cumulative S deposition loadings received to date and the large simulated decreases in S deposition in the future under the emissions control strategies (Figure B-8). Some streams showed modeled stream water SO_4^{2-} concentrations increasing in the future, even while S deposition was reduced by more than two-thirds. These were mostly sites that had relatively low SO_4^{2-} concentrations in 1995 (≥ about 50 µeq/L) because of S adsorption on soils. They generally showed simulated future acidification, which was most pronounced for the A2 strategy. Other streams were simulated to show relatively large decreases in future stream water SO_4^{2-} concentrations and concurrent increases in ANC in response to the strategies, with progressively larger changes from the A2 to the B3 strategy. These tended to be streams that had relatively high concentrations of SO_4^{2-}

(>50 µeq/L) in 1995, suggesting that they were closer to steady state with respect to S inputs and outputs. Some streams were projected to exhibit future decreases in both SO_4^{2-} and NO_3^- concentrations but nevertheless to continue to acidify. This response was attributed by Sullivan et al. (2004) to large simulated decreases in base cation concentrations at these sites due to soil base cation depletion.
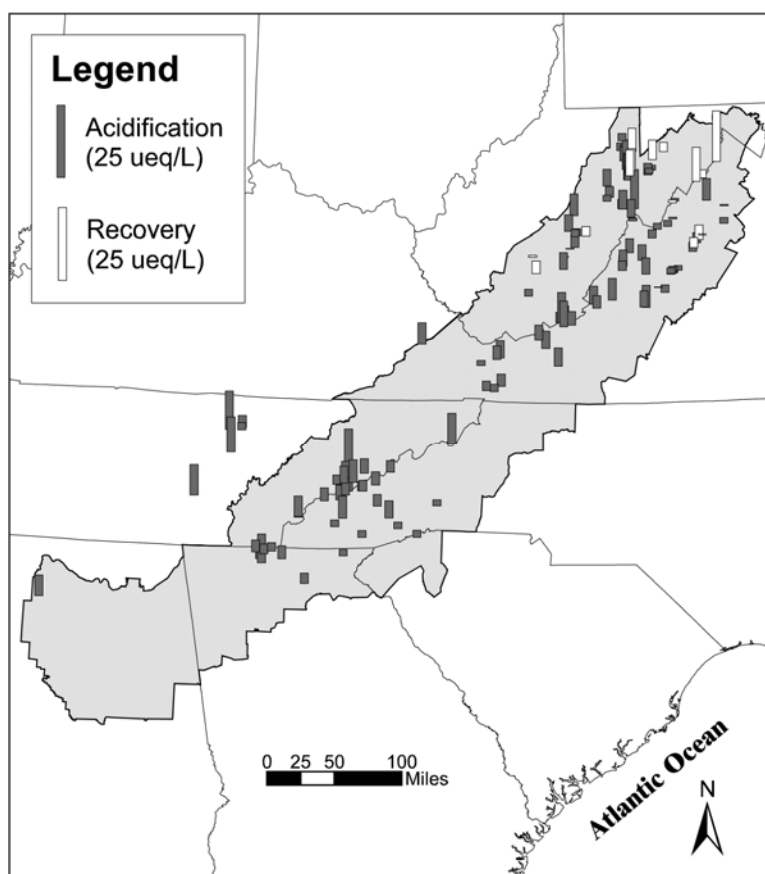
Source: Sullivan et al. (2004)

Figure B-8.   Map showing simulated changes in streamwater ANC from 1995 to 2040 in response to the SAMI A2 emmissions control strategy, representing existing emissions control regulations.

Most simulated changes in stream water ANC from 1995 to 2040 were rather modest (Table B-8), given the very large estimates of decreased S deposition. Few modeled streams showed projected change in ANC of more than about 20 µeq/L. Some of the largest changes were simulated for some of the streams that were most acidic in 1995. For such streams, however, even relatively large increases in ANC would still result in negative ANC stream water, and therefore little biological benefit would be expected from the simulated improvement in chemistry. The model results suggested, however, that benefits would continue to accrue well beyond 2040 for all strategies, even if deposition was held constant at 2040 levels into the future.

Florida Surface Waters

Current Status

According to the ELS survey conducted in 1984, 75% of the Florida Panhandle lakes were acidic at that time, as were 26% of the lakes in the northern peninsula. Most of the acidic lakes were clearwater (DOC <400 µmol) seepage lakes in which the dominant acid anions were Cl^- and SO_4^{2-}. Most of the acidic and low-ANC lakes are located in the Panhandle and north central lake districts. In these areas, the Floridan aquifer is separated from overlying sand deposits by a confining layer called the Hawthorne formation. The major lake districts are located in karst terrain, where lakes formed through dissolution of the underlying limestone followed by movement of surficial deposits into solution cavities (Arrington and Lindquist, 1987).

Flow of water from most of the lakes is downward, recharging the Floridan aquifer. Lake stage varies in response to long-term trends in precipitation, and perhaps in response to groundwater withdrawals. ANC generation in most lakes that have been studied appears to be due primarily to in-lake SO_4^{2-} and NO_3^- reduction (Baker et al, 1988; Pollman and Canfield, 1991). Retention of SO_4^{2-} by watershed soils may also be important. Lakes can be highly alkaline where groundwater interacts with the deeper aquifer. Lakes with hydrologic contributions from shallow aquifers in highly weathered sands can be quite acidic and may be sensitive to acidic deposition.

DOC concentrations are high in many Florida lakes, but organic anions are less important than SO_4^{2-} in most low-ANC and acidic lakes (Pollman and Canfield, 1991). Aluminum concentrations tend to be very low in Florida lakes despite the high lakewater acidity because most of the Al^{n+} is removed from soil solution by precipitation and ion exchange reactions within 75 cm depths (Graetz et al., 1985), and relatively little Al^{n+} is transported in groundwater to lake waters.

Baker et al. (1988) reported that retention of inorganic N is nearly 100% in most Florida lakes. ANC generation from SO_4^{2-} retention may approach 100 µeq/L in some Florida lakes (Pollman and Canfield, 1991). These in-lake processes are important for generating ANC. Base cation deposition and NH_4^+ assimilation can also influence the acid-base status of lakes in Florida.

The Northern Florida Highlands high interest area identified by Baker et al. (1991a) consists of the northern portion (north of 29°N latitude) of the Central Lake District and the Florida Panhandle (Figure B-3). Acidic streams were located in the Florida Panhandle and were mildly acidic (mean pH 5.0) and extremely dilute, with very low sea salt-corrected SBC (mean 21 µeq/L) and sea salt corrected SO_4^{2-} concentrations (mean 16 µeq/L). One-fourth of these acidic Panhandle streams were organic-dominated but the remaining sites all had DOC <2 mg/L and were inorganically dominated. Inorganic monomeric Al concentrations in these acidic streams were very low (mean 11 µg/L). In these low DOC, low ANC Panhandle streams, it was suggested that the degree of SO_4^{2-} and NO_3^- retention was an important control on streamwater ANC (Baker et al., 1991a).

Past Acidification

Considerable research has been conducted on past acidification in Florida lakes. Historical analyses of lake chemistry (Battoe and Lowe, 1992), inferred historical deposition (Hendry and Brezonik, 1984; Husar and Sullivan, 1991), and paleolimnological reconstructions of lake pH (Sweets, 1992; Sweets et al., 1990) suggest evidence that some Florida lakes have acidified in response to acidic deposition. However, the role of acid deposition in lakewater acidification is not entirely clear (Pollman and Canfield, 1991), and the interpretation is complicated by regional and local changes in land use and hydrology (Sullivan, 2000).

An alternative explanation for the apparent acidification of some lakes is the regional decline in the potentiometric surface of the groundwater (Sweets et al., 1990). Large groundwater withdrawals of the Floridan aquifer for residential and agricultural purposes may have reduced groundwater inflow of base cations into seepage lakes, and therefore caused less buffering of acidity. Other land use changes may

have increased lake pH by providing inputs of fertilizer, which would increase lake productivity. Paleolimnological evidence of this effect was provided by Brenner and Binford (1988) and Deevey et al. (1986).

It is likely that lake chemistry in Florida has been heavily effected by land use changes. More than half of the Florida lakes included in the ELS showed evidence of disturbance based on deviations from expected geochemistry (Pollman and Canfield, 1991). Such effects complicate efforts to determine the role of acidic deposition in controlling lakewater acid-base chemistry.

Diatom-inferred pH reconstructions of lakewater chemistry of six seepage lakes in Florida were calculated as part of the PIRLA-I project and reported by Sweets et al. (1990). An additional 10 seepage lakes were cored as part of PIRLA-II, and results of those analyses were reported by Sweets (1992). Paleolimnological study lakes are located in the Panhandle, the Trail Ridge Lake District, and Ocala National Forest, generally in terraces of highly weathered loose sand that were deposited on top of the clay-confining layer.

Of the six lakes analyzed in PIRLA-I, two (Barco and Suggs) were inferred to have acidified since 1950 (Sweets et al., 1990). The timing of the onset of inferred acidification correlated with increases in SO_2 emissions and S deposition, which increased consistently between about 1945 and 1985 (Husar and Sullivan, 1991).

Of the 16 Florida seepage lakes studied in the PIRLA-II projects, 5 were located in or near the Trail Ridge Lake District, and all showed diatom-inferred acidification of at least 0.2 pH units (Sweets, 1992). Lakes located in the Panhandle region and Ocala National Forest generally did not show evidence of recent acidification. The exception was Lake Five-O, which was inferred to have decreased by 2 pH units. However, the diatom data suggested that this pH decline was associated with a sudden change in chemistry, probably caused by a catastrophic disturbance such as sinkhole development, rather than by acidification from atmospheric deposition (Pollman and Sweets, 1990; Sweets, 1992).

B.3.4.3. Upper Midwest

The Upper Midwest contains numerous lakes created by glaciation. The region has little topographic relief and with its deep glacial overburden, it also has little or no exposed bedrock. Acid-sensitive surface waters in the Upper Midwest are mainly seepage lakes (Eilers, 1983). Most drainage lakes and some of the seepage lakes in the Upper Midwest region receive substantial inflow from groundwater, which is generally high in base cation concentrations from dissolution of carbonate and silicate minerals. Relatively high concentrations of base cations in these lakes make them insensitive to acidification from acidic deposition. The seepage lakes that have low base cation concentrations, and that are therefore more acid-sensitive, generally receive most of their water input from precipitation directly on the lake surface (Baker et al., 1991b).

Current Status

Based on the ELS survey, the Upper Midwest has a large population of low ANC lakes, but relatively few chronically acidic (ANC $\geq$ 0) lakes (Linthurst et al., 1986a; 1986b). Acidic lakes in the Upper Midwest are primarily small, shallow, seepage lakes that have low concentrations of base cations and Al and moderate SO_4^{2-} concentrations. Organic anions, estimated by both the Oliver et al. (1983) method and the anion deficit, tend to be less than half the measured SO_4^{2-} concentrations in the acidic lakes (Eilers et al., 1988), but much higher in many of the drainage lakes that are less sensitive to acidification from acidic deposition.

Groundwater flow-through lakes in the Upper Midwest can be identified on the basis of having Si concentration greater than about 1 mg/L (Baker et al., 1991b). They generally have high pH and ANC, due to groundwater inputs of base cations (e.g., (Baker et al., 1991b). Based on results from the ELS survey, only 6% of these lakes had ANC $\geq$ 50 μeq/L and none were acidic. Groundwater recharge lakes

(those having Si concentration less than 1 mg/L) constituted 71% of the seepage lakes in the Upper Midwest, and were more frequently low pH and ANC. Five percent were acidic and 9% had pH ≥ 5.5. Nearly 90% of Upper Midwestern lakes that had ANC ≥ 50 µeq/L were in this category (Baker et al., 1991b). Such lakes tend to be susceptible to acidification from acidic deposition.

Sullivan (2000) summarized patterns in lakewater chemistry across the Upper Midwest from the ELS survey. Lakewater pH, ANC, base cations, and DOC all decreased from west to east across the region. Lakewater SO_4^{2-} concentrations did not show a comparable change, despite a substantial increase in wet SO_4^{2-} deposition from Wisconsin to Michigan. Cook and Jager (1991) attributed the absence of a more pronounced gradient in lakewater SO_4^{2-} concentration across the region to watershed sources of S in Minnesota and high anion retention in seepage lakes, which predominate in the eastern portion of the region. The retention of SO_4^{2-} by dissimilatory reduction is generally high for seepage lakes because of their long hydraulic retention times (τw). For example, an Upper Midwestern seepage lake with mean depth of 3 m and hydraulic retention time of 7.5 years would be expected to lose about 50 µeq/L of SO_4^{2-} from the water column by this process (Cook and Jager, 1991).

Lakewater concentrations of inorganic N reported by the ELS were low throughout the Upper Midwest. In addition, snowmelt would not be expected to provide any significant NO_3^- influx to lakes in the Upper Midwest because most snowmelt infiltrates the soil before reaching the drainage lakes, and because snowmelt input of N into seepage lakes would be limited mainly to the snow on the lake surface and immediate near-shore environment. Aluminum concentrations are far lower in the Upper Midwest than in lakes of similar pH in the Northeast.

Wetlands are common throughout the Upper Midwest. They contribute to high production of organic matter which is reflected in high DOC concentrations in many lakes. Despite the abundant wetlands, SO_4^{2-} is the dominant anion in the low-ANC (≥ 50 µeq/L) groundwater recharge seepage lakes.

Base cation production is the dominant ion-enrichment process in most Upper Midwestern lakes. Even in low-ANC groundwater-recharge seepage lakes, base cation production accounts for 72% to 86% of total ANC production (Cook and Jager, 1991).

Past Acidification

Space-for-time substitution analysis was used to infer the general levels of past change in lake water acid-base chemistry in the Upper Midwest. Such an analysis assumes that study lakes were generally similar in acid-base chemistry before the onset of acidic deposition and that the only substantial driver of recent change in acid-base chemistry has been the level of acidic deposition. Across an increasing S depositional gradient from eastern Minnesota eastward to eastern Michigan, ANC expressed as (HCO_3^- - H^+) decreased and the ratio SO_4^{2-} to SBC increased in the groundwater recharge seepage lakes. In Michigan and Wisconsin, many lakes had SO_4^{2-} >SBC, indicating that the acidity was due to high SO_4^{2-} relative to SBC concentration. There were also many lakes that had high concentrations of DOC, and organic acidity probably accounted for many of these lakes having ANC <0. The spatial pattern in (HCO_3^- - H^+) could not be attributed to DOC, which generally showed a decreasing trend with increasing acidic deposition.

The concentration of lakewater (Ca^{2+} + Mg^{2+}) also decreased with increasing acidic deposition, probably due to lower levels of base cation deposition and greater amounts of precipitation in the eastern portion of the region. Atmospheric deposition is an important source of base cations for groundwater recharge seepage lakes because of minimal groundwater inputs. In the eastern portion of the region, such lakes are more sensitive to pH and ANC depression in response to either elevated SO_4^{2-} or DOC. The spatial patterns for low ANC groundwater recharge lakes in the Upper Midwest are consistent with the following hypotheses (Sullivan et al, 1990a; Sullivan, 1990, 2000a):

1. Sensitivity to mineral and organic acidity increased from west to east because of decreasing lakewater base cation concentrations, and this may have been due, in part, to changes in base cation deposition and precipitation volume along this gradient.

2. High concentrations of DOC were responsible for the acidic conditions in some of the lakes, and DOC may have decreased in response to acidic deposition.

3. Many of the lakes in eastern Michigan, and some in Wisconsin, were acidic because of high SO_4^{2-} relative to base cation concentration, and had probably been acidified by acidic deposition.

Diatom-inferred pH reconstructions were completed for 15 lakes in the Upper Midwest region, and summarized by Kingston et al. (1990) and Cook and Jager (1991). Four lakes, all of which had measured pH <5.7, showed a diatom-inferred pH decline of 0.2 to 0.5 pH units during the preceding 50 to 100 years. Diatom-inferred pH increased in one lake by 0.2 pH units. No change was inferred for the other 10 lakes, including 4 lakes with pH >6.0. No major, recent, regional acidification was indicated by the diatom-inferred pH reconstructions. Inferred changes in most lakes were small, and were no greater during the industrial period than during the pre-industrial period (Sullivan, 2000a).

Although diatom data suggested that some Upper Midwestern lakes may have acidified since pre-industrial times, there is little paleolimnological evidence indicating substantial widespread acidification in this region (Cook and Jager, 1991; Kingston and Birks, 1990). Land use changes and other human disturbances of Upper Midwestern lakes and their watersheds have probably exerted more influence on the acid-base chemistry of lakes than has acidic deposition (Kingston and Birks, 1990; Sullivan et al, 1990a; Sullivan, 1990, 2000a). The portion of the region most likely to have experienced acidification from acidic deposition is the Upper Peninsula of Michigan, where acidic seepage lakes are particularly numerous (Baker et al., 1991b); acidic deposition is highest for the region, and the $[SO_4^{2-}]/[SBC]$ ratio is commonly >1.0. The percentage of acidic lakes in the eastern portion of the Upper Peninsula of Michigan (east of longitude 87°) was estimated to be 18% to 19% in 1984 (Eilers et al., 1988; Schnoor et al., 1986).

Recent Trends

Regional trend values for long-term monitoring lakes during the period 1990 to 2000 suggested that SO_4^{2-} declined in lakewater by 3.63 µeq/L/yr, whereas lakewater NO_3^- concentrations were relatively constant. The large decrease in SO_4^{2-} concentration was mainly balanced by a large decrease in base cation concentrations (−1.42 µeq/L/yr) and an increase in ANC (+1.07 µeq/L/yr). All of these trends were significant at p <0.01 (Stoddard et al., 2003). In the Upper Midwest, an estimated 80 of 251 lakes that were acidic in the mid-1980s were no longer acidic in 2000. This change may be due to reduced levels of S deposition (Stoddard et al., 2003).

B.3.4.4. West

Portions of the mountainous West contain large areas of exposed bedrock, with little soil or vegetative cover to neutralize acidic inputs. This is particularly true of alpine regions of the Sierra Nevada, northern Washington Cascades, the Idaho batholith, and portions of the Rocky Mountains in Wyoming and Colorado. However, the percentage of exposed bedrock in a watershed does not always indicate acid-sensitivity. If the bedrock contains even small deposits of calcareous minerals or if physical weathering such as that caused by glaciers causes a high production of base cations within the watershed (Drever and Hurcomb, 1986), surface waters may be alkaline, and are not sensitive to acidification from acidic deposition.

The areas that are sensitive to adverse effects from acidic deposition in the western U.S. form two nearly continuous ranges, the Sierra Nevada, which extends through most of the length of California, and the Cascade Mountains, which extend from northern California to northern Washington (see Figure B-9.). The sensitivity of the Rocky Mountains varies widely because the ranges are discontinuous with highly variable geological composition. For that reason, assessments of the sensitivity of Rocky Mountain aquatic resources to acidification should be specific to individual ranges (Turk and Spahr, 1991).
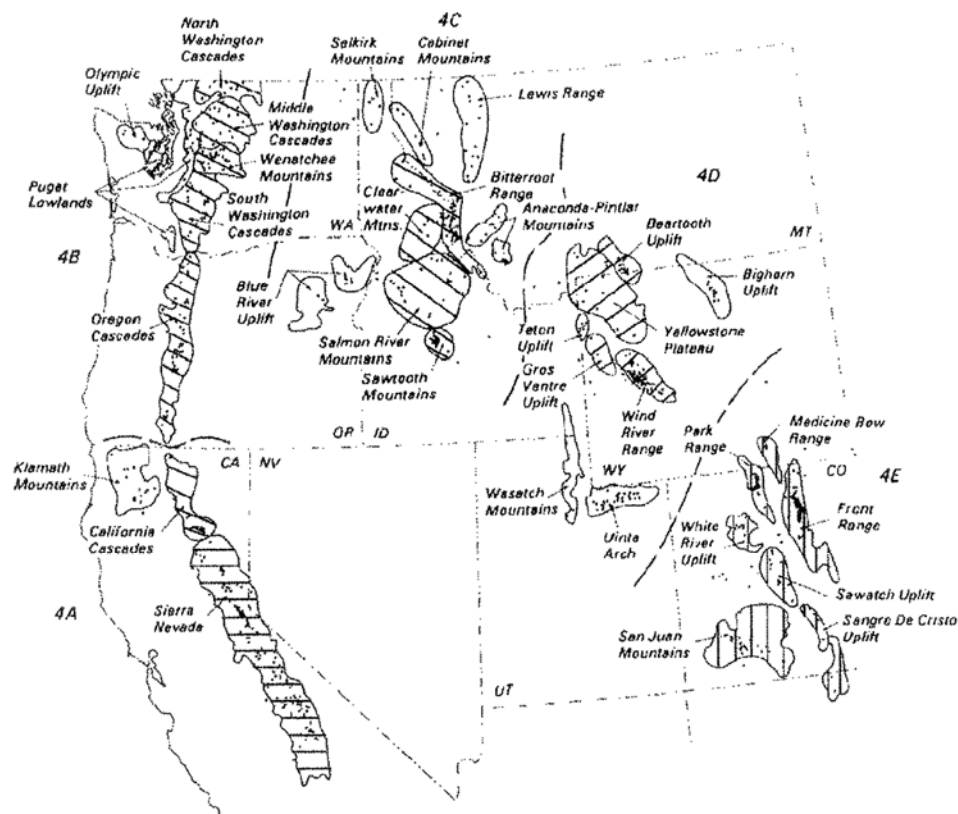
Source: Landers et al. (1987).

Figure B-9.   Major geomorphic units and locations of lakes sampled in the Western Lake Survey. Those areas known to contain sensitive lake resources are shaded with cross-hatching.

The NAPAP SOS/T Reports and the IA (NAPAP, 1991) provided only a cursory treatment of aquatic effects issues in the West, largely because it was well known that atmospheric deposition of S and N were generally low compared to highly affected areas in the East (Sullivan, 2000a) and because results from the WLS (Landers et al., 1987) indicated that there were virtually no acidic (ANC $\geq$ 0) lakes in the West. NAPAP (1991) indicated, however, that high-elevation areas of the West contained many of the watersheds most sensitive to the potential effects of acidic deposition.

Because of the proximity of western urban and industrial pollution sources to individual mountain ranges, it is important to consider emissions in the immediate vicinity of sensitive resources as well as regional emissions. Atmospheric deposition in the far western ranges (i.e., Sierra Nevada, Cascade Mountains) is largely influenced by local emissions, particularly emission sources to the west (upwind) of sensitive resources. In the Rocky Mountains, deposition chemistry is often influenced by a more complex collection of emission sources. For example, in the Mt. Zirkel Wilderness of northwestern Colorado, SO_4^{2-} and NO_3^- in the snow appeared to originate largely from sources in the Yampa Valley, about 75 km to the west (Turk, 1992). Rocky Mountain National Park is affected by emissions from the Front Range to the southeast.
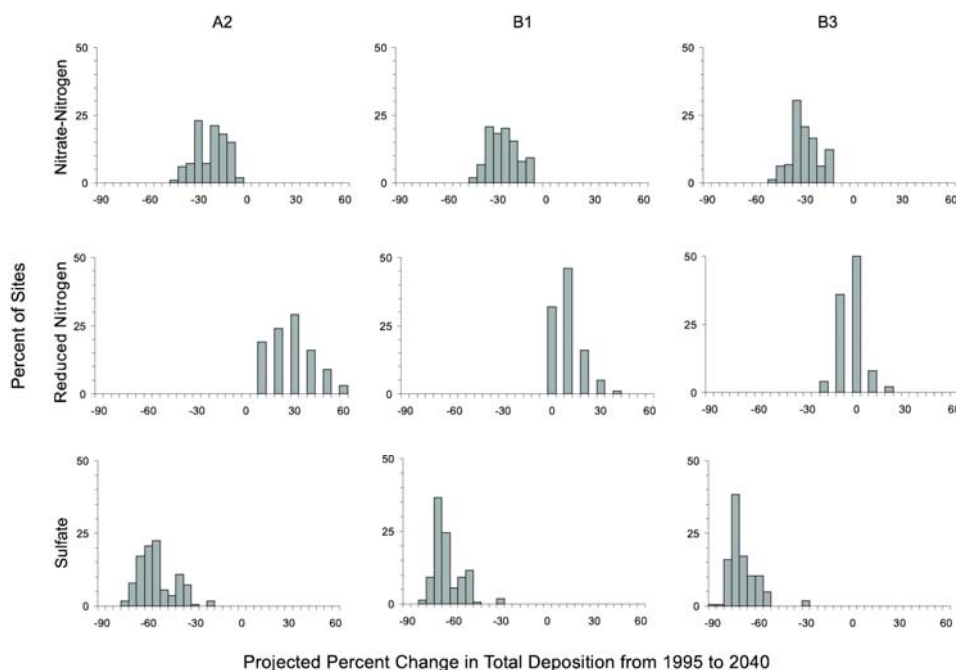
Figure B-10. Estimated percent changes in the total deposition of sulfur, reduced nitrogen, and nitrate-nitrogen at MAGIC modeling sites from 1995 to 2040 under each of the emissions control strategies

The acid base chemistry of lake and stream waters in Rocky Mountain National Park appears to be primarily a function of the interactions among several key parameters and associated processes: atmospheric deposition, bedrock geology, the depth and composition of surficial deposits and associated hydrologic flowpaths, and the occurrence of soils, tundra, and forest vegetation (Sullivan, 2000a). Potential biological effects of acidic deposition on lakes in the Rocky Mountains are primarily attributable to acidification from high NO_3^- concentration. In general, such effects tend to be episodic, rather than chronic. Highest NO_3^- concentrations in both precipitation and surface waters are found above timberline in Colorado, where biological activity, and therefore NO_3^- uptake, by terrestrial and aquatic biota is lowest.

Current Status

The available information on acid-base chemistry of surface waters in the West is based mostly on synoptic data from the WLS (Landers et al., 1987) and some more localized studies. Acid anion concentrations in most western lakes are low during fall, but can be higher during snowmelt (Williams and Melack, 1991). Available data from intensive study sites in the West (e.g., Loch Vale, CO, Emerald Lake Basin, CA, and the Glacier Lakes Watershed, WY) suggest that episodic depression of stream pH may be more pronounced than for lakes. However, there are no available systematic regional stream chemistry data with which to assess regional sensitivity of streams to acidic deposition.

In most western lakes concentrations of SO_4^{2-} are low, although watershed sources of S are substantial in some cases (Table B-9). Turk and Spahr (1991) presented a conceptual model for expected SO_4^{2-} distributions in lakewaters in the West that can be used as an aid in identifying the proportion of watersheds with significant watershed sources of S. Considering that atmospheric sources can account for generally <30 µeq/L of SO_4^{2-} in the West, it appears that many lakes, particularly in Colorado, receive variable amounts of watershed S (Sullivan, 2000a) (Figure B-10).

Nitrate concentrations in most WLS lakes were near 0 during fall (Landers et al., 1987), although fall NO_3^- concentrations were high in some cases (Table B-10). For example, nearly one fourth of the lakes in northwest Wyoming had NO_3^- >5 µeq/L and almost 10% had NO_3^- >10 µeq/L (Table B-10). In both the Sierra Nevada and Colorado Rockies subregions, about 10% of the lakes had fall NO_3^- concentrations above 5 µeq/L (Table B-10).

It is important to note that even low to moderate concentrations of NO_3^- in western lakes might be significant in view of: the low base cation concentrations in many lakes; potential for continuing N deposition to eventually exhaust natural assimilative capabilities; and the fact that these distributions are based on fall data. Time-intensive discharge and chemical data for two alpine streams in Loch Vale watershed identified strong seasonal control on streamwater NO_3^- concentrations (Campbell et al., 1995). In spite of the paucity of soil cover, the chemical composition of streams is regulated much as in typical forested watersheds. Soils and other shallow groundwater matrices such as boulder fields are more important in controlling surface water chemistry than their abundance would indicate. Spring streamwater NO_3^- concentrations ranged to 40 µeq/L, compared with summer minimum values near 10 µeq/L. Elution of acidic waters from snowpack along with dilution of base cations originating in shallow groundwater caused episodes of decreased ANC in alpine streams (Campbell et al., 1995). A subalpine stream in the same watershed similarly displayed decreased ANC and elevated monomeric Al concentrations during snowmelt over 2 years of intensive sampling, related to elevated concentrations of SO_4^{2-}, NO_3^-, and DOC (Denning et al., 1991). Limited data collected during snowmelt suggest that spring concentrations could be several times higher than samples collected during the fall (e.g., Reuss et al., 1995).

The surface water chemistry data for the West indicate that the Sierra Nevada and Cascade Mountains constitute the mountain ranges with the greatest number of sensitive resources (Table B-9 and Table B-10). Lakes in the Sierra Nevada are especially sensitive to effects from acidic deposition because of the predominance of granitic bedrock, thin acidic soils, large amounts of precipitation, coniferous vegetation, and dilute nature of the lakes (Melack et al., 1985; Melack and Stoddard, 1991). Surface waters in this region are among the poorly buffered surface waters in the U.S. (Landers et al., 1987; Melack and Stoddard, 1991). The hydrologic cycle is dominated by the annual accumulation and melting of a dilute, mildly acidic (pH about 5.5) snowpack.

During the 1980s, an Integrated Watershed Study (IWS) was conducted at seven lakes in the Sierra Nevada, including Emerald Lake and surrounding watersheds (~3,000 m elevation) to determine the effects of acidification on surface waters (Tonnessen, 1991). Three lakes (Lost, Pear, and Emerald) had volume-weighted mean ANC in the range of 15 to 30 µeq/L. Moderate ANC waters (Topaz, Spuller, and Marble Fork) exhibited mean ANC in the range of 30 to 50 µeq/L. Crystal and Ruby Lakes had mean annual ANC >50 µeq/L.

Many Cascade and Rocky Mountain lakes are also highly sensitive to potential acidic deposition effects (Nelson, 1991; Turk and Spahr, 1991). It does not appear that chronic acidification has occurred to any significant degree, although episodic acidification has been reported for lakes in the Colorado Front Range (Williams and Tonnessen, 2000). The data that would be needed for determining the extent and magnitude of episodic acidification have not been collected to a sufficient degree in acid-sensitive areas of the West to support regional assessment of episodic acidification (Sullivan, 2000a).

Along the eastern edge of the Continental Divide in Colorado and southeastern Wyoming, Musselman et al. (1996) conducted a synoptic survey of surface water chemistry in the mountainous areas that are exposed to relatively high (by western standards) deposition of N. A total of 267 high-elevation lakes situated in watersheds having a high percentage of exposed bedrock or glaciated landscape were selected for sampling. None of the lakes were chronically acidic (ANC <0), although several had ANC <10 µeq/L, and more than 10% of the lakes had ANC <50 µeq/L. The WLS data for lakes in Colorado and Wyoming demonstrate that surface waters in this area had fall concentrations of NO_3^- in the range of 10 to 30 µeq/L, and likely had substantially higher NO_3^- concentrations during spring.

The weight of evidence suggests many high-elevation lakes in the West receive N deposition sufficiently high to cause chronic NO_3^- leaching, and likely some degree of associated chronic and

episodic acidification. However, existing data are insufficient to make a conclusive determination (Sullivan, 2000a).

Past Acidification

The limited paleolimnological data available for lakes in the western U.S. suggest that widespread chronic acidification probably has not occurred. Some lakes may have experienced recent pH declines, but the magnitude of such changes has likely been small (Sullivan, 2000a).

In the Sierra Nevada, paleolimnological reconstructions of lakewater pH and ANC were calculated by Holmes et al. (1989) at 24 depth intervals at Emerald Lake, for the period 1825 to the present. Significant trends were not found for either pH or ANC, and the authors concluded that Emerald Lake had not been acidified by acidic deposition. Whiting et al. (1989) completed paleolimnological analyses of three additional lakes in the Sierra Nevada. Eastern Book Lake (pH = 7.06) showed evidence of both long-term alkalization (~0.3 pH units over the past 200 years) and pH fluctuations since 1970. Lake 45 (pH = 5.16) may have acidified slightly (~0.2 pH units) over the last 60 years. Lake Harriet (pH = 6.52) showed no significant change.

In Rocky Mountain National Park, Colorado, Baron et al. (1994) investigated metal stratigraphy, diatom stratigraphy, and inferred pH profiles of four subalpine lakes. They found no evidence of historical influence on pH attributable to atmospheric deposition. Other paleolimnological studies of Rocky Mountain lakes report similar results: metals (primarily lead) exhibit temporal dynamics related to the increase and decline of precious metal mining in the region, but these are asynchronous with other metal or biological indicators of acidification (Wolfe et al., 2003). Both the study by Wolfe et al. (2003) and a study by Saros et al. (2003) showed no evidence of acidification of lake waters over time, but increasing evidence of eutrophication from atmospheric N deposition (see Annex C).

DayCent-Chem, a model that simulates the daily dynamics of plant production, soil organic matter, cation exchange, mineral weathering, elution, stream discharge, and stream solute concentrations, was able to recreate daily stream chemistry dynamics over 13 years for an alpine watershed in the Colorado Front Range (Hartman et al., 2007). Using the model to hindcast stream chemical dynamics back to 1900 revealed changes in simulated pH coincident with maximum SO_2 emissions in the late 1960s and early 1970s. Model simulations suggested annual mean pH values decreased to 5.6 to 5.8 during the years of maximum regional SO_2 emissions, and have since recovered to circumneutral values. Simulated ANC responded to both SO_2 and NO_X emissions, decreasing to annual values of 20 to 25 µeq/L during years of highest SO_2 or NO_X emissions compared with current mean annual ANC values near 50 µeq/L Hartman.

Recent Trends

Limited monitoring data are available on recent trends in surface water chemistry in the western regions and are mostly limited to the recent past and a number of reconnaissance studies (Melack and Stoddard, 1991; Nelson, 1991; Turk and Spahr, 1991). Existing information on recent trends in surface water chemistry since the 1980s suggests that conditions vary widely across the West. Parts of Colorado, Wyoming and the western Cascades showed decreased ANC, while Emerald Lake experienced reduced NO_3^- concentrations.

Turk et al. (1993) reported the results of 5 years of monitoring for ten lakes in the Mt. Zirkel and Weminuche Wilderness areas in Colorado. Based on lake concentrations of SO_4^{2-} and Cl^- and on wet deposition concentrations of SO_4^{2-}, NO_3^-, and H^+, Turk and Spahr (1991) concluded that low-ANC lakes had lost no more than 5 µeq/L ANC in the Bitterroot Range of the Northern Rocky Mountains, 12 µeq/L ANC in the Wind River Range of Wyoming, and 10 µeq/L ANC in the Front Range of Colorado. It is likely that the actual ANC losses had been much less than these estimates (Sullivan, 2000a).

Future Projections

The DayCent-Chem model was used to project a timeline to acidification for an alpine watershed of Rocky Mountain National Park (Hartman et al., 2007). At current levels of N deposition of 4 to 6 kg N/ha/yr, acidification does not occur over 48 years of simulation, but increasing deposition amounts lead to first episodic acidification over time at deposition of 7.0 to 7.5 kg N/ha/yr. MAGIC model simulation results suggested that a sustained N deposition load of 12.2 kg N/ha/yr would be required over a period of 50 years to cause chronic acidification of the Andrews Creek watershed in Rocky Mountain National Park (Sullivan et al., 2005).

B.3.4.5. Temporal Variability in Water Chemistry

Water chemistry changes on both intra-annual and inter-annual time scales in response to changes in environmental conditions. Because of this variability, many years of data are required to establish the existence of trends in surface water chemistry. Assignment of causality to changes that are found to occur is even more difficult.

Temporal variability in surface water and soil solution chemistry, and patterns in nutrient uptake by terrestrial and aquatic biota, influence acidification processes and pathways. Thus, conditions are constantly changing in response to episodic, seasonal, and inter-annual cycles and processes. In particular, climatic fluctuations that govern the amount and timing of precipitation inputs, snowmelt, vegetative growth, depth to groundwater tables, and evapoconcentration of solutes influence soil and surface water chemistry and the interactions between pollution stress and sensitive aquatic and terrestrial biological receptors.

Decreases in pH with increases in flow are nearly ubiquitous in drainage waters throughout the U.S. (Wigington et al., 1991). Chemical changes during episodes are controlled in part by acidic deposition and in part by natural processes, including dilution of base cation concentrations, nitrification, flushing of organic acids from terrestrial to aquatic systems, and the neutral salt effect. Episodic acidification pulses may last for hours to weeks, and sometimes result in depletion of ANC in acid-sensitive streams and lakes to negative values and concomitant increases in Al_i in solution to toxic levels.

During episodes, which are driven by rainstorms and/or snowmelt events, both discharge (streamflow volume per unit time) and water chemistry change, sometimes dramatically. This is important because streams may in some cases exhibit chronic chemistry that is still suitable for aquatic biota, but nevertheless experience occasional episodic acidification with lethal consequences (Wigington et al., 1993).

The most important factor governing watershed sensitivity to episodic acidification is the pathways followed by snowmelt water and stormflow water through the watershed. These pathways determine the extent of acid neutralization provided by the soils and bedrock in that watershed. High-elevation watersheds with steep topography, extensive areas of exposed bedrock, deep snowpack accumulation, and shallow, base-poor soils tend to be most sensitive to episodic acidification.

Rainfall and snowmelt typically pass through the soil profile before reach a stream channel. The typical soil profile in acid-sensitive watersheds has lowest pH in upper organic soil horizons, increasing down the profile to higher pH at depth. Drainage water chemistry during baseflow conditions is generally reflective of conditions in the lower soil horizons and the subsoil. During high flows during snowmelt or rainfall events, however, flow-routing favors water flowpaths through upper horizons. During such events, drainage water chemistry, therefore, typically reflects the lower pH, higher organic content, and lower ANC of these upper soil horizons (Sullivan, 2000a). As such, storm flow and snowmelt are often associated with episodes of extreme surface water acidity due to an increase in the proportion of flow derived from water that has moved laterally through the surface soil without infiltration to deeper soil horizons (Wigington et al., 1991).

The routing of water as it flows through a watershed determines the degree of contact with acidifying or neutralizing materials and therefore influences (along with soils and bedrock characteristics) the amount of episodic acidification that occurs. In any given watershed, surface water ANC may vary in time depending upon the proportion of the flow that has contact with deep versus shallow soil horizons; the more subsurface contact, the higher the surface water ANC (Turner et al., 1991). This can be attributed in part to higher base saturation and (in some watersheds) greater SO_4^{2-} adsorption capacity in subsurface soils. It may also relate to the accumulation in the upper soil horizons of acidic material derived from atmospheric deposition and decay processes (Lynch and Corbett, 1989; Turner et al., 1991). Episodic acidification is often the limiting condition for aquatic organisms in streams that can be suitable for aquatic life under baseflow conditions.

Episodes are generally accompanied by changes in at least two or more of the following chemical parameters: ANC, pH, base cations, SO_4^{2-}, NO_3^-, Al^{n+}, organic acid anions, and DOC (Sullivan, 2000a). The U.S. EPA Episodic Response Project (ERP) confirmed the chemical and biological effects of episodic pH depressions in lakes and streams in parts of the U.S. (Wigington et al., 1993). The ERP illustrated that episodic processes are mostly natural, that SO_4^{2-} and especially NO_3^- attributable to atmospheric deposition play important roles in the episodic acidification of some surface waters, and that the chemical response that has the greatest effect on biota is increased Al_i concentration. Similar findings had been reported elsewhere, especially in Europe, but the ERP helped to clarify the extent, causes, and magnitude of episodic acidification in portions of the U.S. (Sullivan, 2000a).

Water chemistry trends documented by long-term monitoring programs and reported here represent recovery from chronic acidification. Most surface waters exhibit seasonally lower ANC and pH values than would be captured by trend analysis that considers only chronic chemistry data. In many cases, sites that are relatively low in ANC, but not chronically acidic, undergo short-term episodic acidification to negative ANC values during spring snowmelt, or during intense rain events. Lawrence (2002) found that 16% of total stream reaches in the West Branch Neversink River, in the Catskill Mountains of New York, were chronically acidic, whereas 66% of total stream reaches has a high likelihood of becoming acidic during high flows.

Most research on episodic processes has been conducted on stream systems, which tend to be more susceptible to such effects than lakes. Spatial variability can be considerable in lakes, and this complicates efforts to quantify the magnitude of episodic effects (Gubala et al., 1991). Moreover, synoptic lake surveys are typically conducted during the autumn "index period," during which time lakewater chemistry exhibits low temporal variability. Although autumn is an ideal time for surveying lakewater chemistry in terms of minimizing variability, lakewater samples collected during autumn provide little relevant data on episodic processes, and in particular on the dynamics or importance of N as an agent of acidification. Nitrate concentrations in lakewater are elevated during the autumn season only in lakes having watersheds that exhibit fairly advanced symptoms of N saturation (Stoddard, 1994).

Mixing zones have received little attention despite the fact that they can be acutely toxic to aquatic biota. Whether an area of acidic water that comes in contact with non-acidic water is a safe haven or a toxic zone depends on many parameters, one of the most important of which is the amount and form of Al species produced at the boundaries. For example, Al hydroxide ($Al(OH)_3$)) can precipitate out of solution if pH is suddenly increased within a mixing zone. This form of Al is acutely toxic to fish.

The mechanisms that produce acidic episodes can include dilution of base cations and flushing of NO_3^-, SO_4^{2-} and/or organic acids from forest soils to drainage water (Kahl et al., 1992; Lawrence, 2002; Wigington et al., 1996; Wigington, 1999). Acidic deposition can contribute to episodic acidification of surface water both by supplying N which can produce pulses of NO_3^- during high flow periods, contributing hydrologically mobile SO_4^{2-} through dry deposition, and by lowering baseline pH and ANC, so that episodes are sufficient to produce biologically harmful conditions (Stoddard et al., 2003).

Episodic acidification due to atmospheric deposition is most commonly associated with N deposition, and effects tend to be most pronounced during snowmelt. However, snowmelt can flush into surface waters N that was deposited from the atmosphere to the snowpack and also N that was mineralized within the soil under the snowpack during winter. A substantial component of the NO_3^- flux

may have been derived from mineralization of organic N (Ley et al., 2004). Much of the N released from the snowpack during the melting period is retained in underlying soils and only a component of that is flushed to surface waters. Where soils are sparse, as in alpine regions of the western U.S., most snowpack N is flushed to surface waters, and even though there is evidence through use of isotopic tracers that much of the N was cycled microbially, snowpack N has been reported to caused temporary acidification of alpine streams (Campbell et al., 2002; Williams and Tonnessen, 2000).

Episodic pH and ANC depressions during snowmelt are largely driven by base cation dilution and NO_3^- enrichment in most areas (Campbell et al., 1995; Stoddard, 1995; Wigington et al., 1991, 1993), although Denning et al. (1991) found a significant decline of both pH and ANC associated with DOC flushing from forest soils. Pulses of increased SO_4^{2-} during hydrological episodes are usually attributable to S storage and release in soils (for example, in the southeastern U.S.) or wetlands. More commonly, lake and streamwater concentrations of SO_4^{2-} decrease or remain stable during snowmelt. This is probably because most stream flow during episodes is derived from water previously stored in watershed soils that is then forced into streams and lakes by the piston effect.

In the Northeast, the most severe acidification of surface waters generally occurs during spring snowmelt (Charles, 1991). Stoddard et al. (2003) found that on average, spring ANC values in New England, the Adirondacks, and the Northern Appalachian Plateau were about 30 μeq/L lower than summer values during the period 1990 to 2000 (Figure B-11). This implies that lakes and streams in these regions would need to recover to chronic Gran ANC values above about 30 μeq/L before they could be expected to not experience acidic episodes (Stoddard et al., 2003). However, the estimate of 30 μeq/L is certain to be low because the comparison was made with non-episodic sampling in spring.

In the West, episodic acidification is an especially important issue for surface waters throughout high-elevation areas. A number of factors pre-dispose western systems to potential episodic effects (Peterson et al., 1998; Sullivan, 2000a), including:

- the abundance of dilute to ultradilute lakes which exhibit very low concentrations of base cations, and therefore ANC, throughout the year;

- large snowpack accumulations at the high-elevation sites, thus causing substantial episodic acidification via the natural process of base cation dilution; and

- short hydraulic retention times for many of the high-elevation drainage lakes, thus enabling snowmelt to rapidly flush lake basins with highly dilute meltwater.

Based on measurements of microbial biomass, CO_2 flux through the snowpack, and soil N pools, Williams et al. (1996a) concluded N cycling under the snowpack in Colorado during the winter and spring was sufficient to supply the NO_3^- measured in stream waters. Brooks et al. (1996) investigated soil N dynamics throughout the snow-covered season on Niwot Ridge, CO. Sites with consistent snow cover had a 3 to 8 cm layer of thawed soil under the snowpack for several months before snowmelt began. Nitrogen mineralization in this thawed layer contributed to N_r pools that were significantly larger than the pool of N stored in the snowpack. As snowmelt began, soil inorganic N pools decreased sharply, concurrent with a large increase in microbial biomass N. As snowmelt continued, both microbial N and soil inorganic N decreased, presumably due to increased demand by growing vegetation (Brooks et al., 1996).
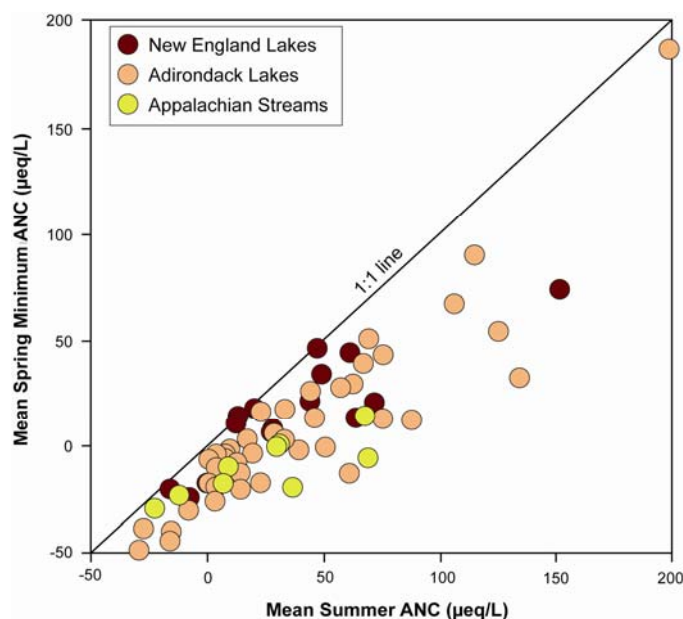
Figure B-11.   Relationship between mean summer and spring ANC values at LTM sites in New England, the Adirondacks, and the Northern Appalachian Plateau.

In the Sierra Nevada, the hydrology of alpine and subalpine ecosystems is dominated by snowfall and snowmelt, with over 90% of the annual precipitation falling as snow. The relatively small loads of acidic deposition can supply relatively high concentrations of SO_4^{2-} and NO_3^- to lakes and streams during the early phase of snowmelt (Stoddard, 1995) through the process of preferential elution (Johannessen and Henriksen, 1978).

Lakewater pH and ANC in the Sierra Nevada generally decrease with increasing runoff, reaching minima near peak snowmelt discharge. Most other solutes exhibit temporal patterns that indicate dilution or a pulse of increased concentration followed by either dilution or biological uptake. Williams and Melack (1991) and Williams et al. (1995) documented ionic pulses (2 to 10 days in duration) in meltwater concentrations in the Emerald Lake watershed twofold to twelvefold greater than the snowpack average. Sulfate and NO_3^- concentrations in meltwater decreased to below the initial bulk concentrations after about 30% of the snowpack had melted. The initial meltwater draining from the snowpack had concentrations of NO_3^- and NH_4^+ as high as 28 µeq/L, compared to bulk snowpack concentrations <5 µeq/L (Williams et al., 1995). Streamwater NO_3^- concentrations peaked during the early snowmelt period, with maximum streamwater concentrations of 18 µeq/L. During summer, streamwater NO_3^- concentrations were always near or below detection limit.

Stoddard (1995) reported results for two lakes in the Sierra Episodes Study, one of which (Treasure Lake) typified the response of most high elevation lakes in the study and one whose response was most extreme (High Lake). At Treasure Lake, ANC began to decline at the onset of snowmelt and reached a minimum at peak runoff, corresponding with minimum base cation, NO_3^-, and SO_4^{2-} concentrations. The lakewater did not become acidic. High Lake watershed contained a deeper snowpack, and began melting later in the season. ANC fell to 0 and below twice during the first 10 days of snowmelt. The ANC minimum corresponded with maximum concentrations of base cations, NO_3^- and Al. Nitrate concentrations increased to values greater than 40 µeq/L, exceeding concurrent increases in base cations and causing the lake to become acidic for brief periods. Stoddard (1995) concluded that High Lake appeared to be representative of the most extreme conditions of episodic acid-sensitivity in the Sierra Nevada.
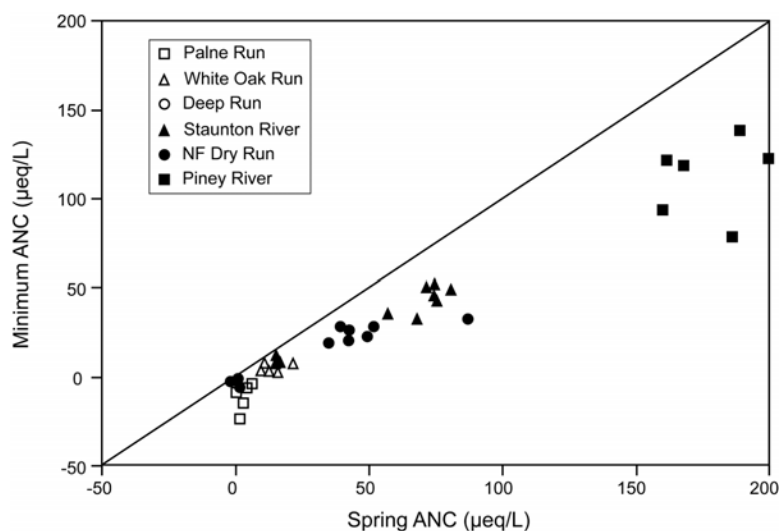
Figure B-12. Minimum streamwater ANC sampled at each site during each year versus median spring ANC for all samples collected at that site during that spring season. Data are provided for all intensively studied streams within Shenandoah National Park during the period 1993−1999. A 1:1 line is provided for reference. The vertical distance from each sample point upwards to the 1:1 line indicates the ANC difference between the median spring value and the lowest sample value for each site and year.

Data regarding episodic variability in streamwater ANC for six intensively studied sites within Shenandoah National Park for the period 1993 to 1999 are presented in Figure B-12 (Sullivan et al, 2003). The minimum measured ANC each year at each site (which generally is recorded during a large rain or snowmelt episode) is plotted against the median spring ANC for that year at that site. Sites that exhibited median spring ANC below about 20 µeq/L (Paine Run, White Oak Run, Deep Run) generally had minimum measured ANC about 10 µeq/L lower than median spring ANC.

In contrast, at the high-ANC Piney River site (median spring ANC >150 µeq/L), the minimum measured ANC was generally more than about 40 µeq/L lower than the respective median spring ANC. At sites having intermediate ANC values, with median spring ANC in the range of about 30 to 90 µeq/L, the minimum ANC measured each year was generally about 20 to 30 µeq/L lower than the respective median spring ANC. Thus, there is a rather clear pattern of larger episodic ANC depressions in streams having higher median ANC and smaller episodic ANC depressions in streams having lower median ANC. The two sites that had median spring ANC between about 0 and 10 µeq/L consistently showed minimum measured values below 0. Streams having low chronic ANC can be expected to experience relatively small episodic ANC depressions. However, those depressions can result in minimum ANC values that are associated with toxicity to aquatic biota.

A recent study by Deviney et al. (2006) Deviney used hourly ANC predictions over short time periods to compute recurrence intervals of annual water-year minimum ANC values for periods of 6, 24, 72, and 168 h. They extrapolated the results to the rest of the Shenandoah National Park catchments using catchment geology and topography. On the basis of the models, they conclude that large number of Shenandoah National Park streams have 6- to 168-h periods of low ANC values, which may stress resident fish populations (Deviney et al., 2006). Specifically, on the basis of a 4–year recurrence interval, approximately 23% of the land area (44% of the catchments) can be expected to have conditions that are indeterminate (ANC 20 to 50), episodically acidic (ANC 0 to 20) or chronically acidic (ANC less than 0) for 72 continuous hours. Many catchments are predicted to have successive years of low-ANC values potentially sufficient to extirpate some species (Deviney et al., 2006). The authors of the study reported

that smaller catchments are more vulnerable to episodic acidification than large catchments underlain by the same bedrock. Catchments with similar topography and size are more vulnerable if underlain by less basaltic and carbonate bedrock.

There are several different mechanisms of episodic acidification in operation in the streams in Shenandoah National Park, depending at least in part on the bedrock geology of the stream. The most acidic conditions in Shenandoah National Park streams occur during high-flow periods, in conjunction with storm or snowmelt runoff. The general relationship between flow level and ANC is evident in Figure B-13, which plots ANC measurements against flow for three intensively studied streams representing the major bedrock types in the park. The response of all three streams is similar in that most of the lower ANC values occur in the upper range of flow levels.

Consistent with observations by Eshleman (1988), the minimum ANC values that occur in response to high flow are related to baseflow ANC values. Paine Run (siliciclastic bedrock) had a mean weekly ANC value of about 6 μeq/L and often had high-flow ANC values that were less than 0 μeq/L. Staunton River (granitic bedrock) had a mean weekly ANC value of about 82 μeq/L and had only a few high-flow ANC values less than 50 μeq/L. Piney River (basaltic bedrock) had a mean weekly ANC value of 217 μeq/L and no values as low as 50 μeq/L.

Eshleman and Hyer (2000) estimated the contribution of each major ion to observed episodic ANC depressions in Paine Run, Staunton River, and Piney River during a 3−year period. During the study, 33 discrete storm events were sampled and water chemistry values were compared between antecedent baseflow and the point of minimum measured ANC (near peak discharge). The relative contribution of each ion to the ANC depressions was estimated using the method of Molot et al. (1989), which normalized the change in ion concentration by the overall change in ANC during the episode. At the low-ANC (~0) Paine Run site on siliciclastic bedrock, increases in NO_3^- and SO_4^{2-}, and to a lesser extent organic acid anions, were the primary causes of episodic acidification. Base cations tended to compensate for most of the increases in acid anion concentration. ANC declined by 3 to 21 μeq/L (median 7 μeq/L) during the episodes studied.
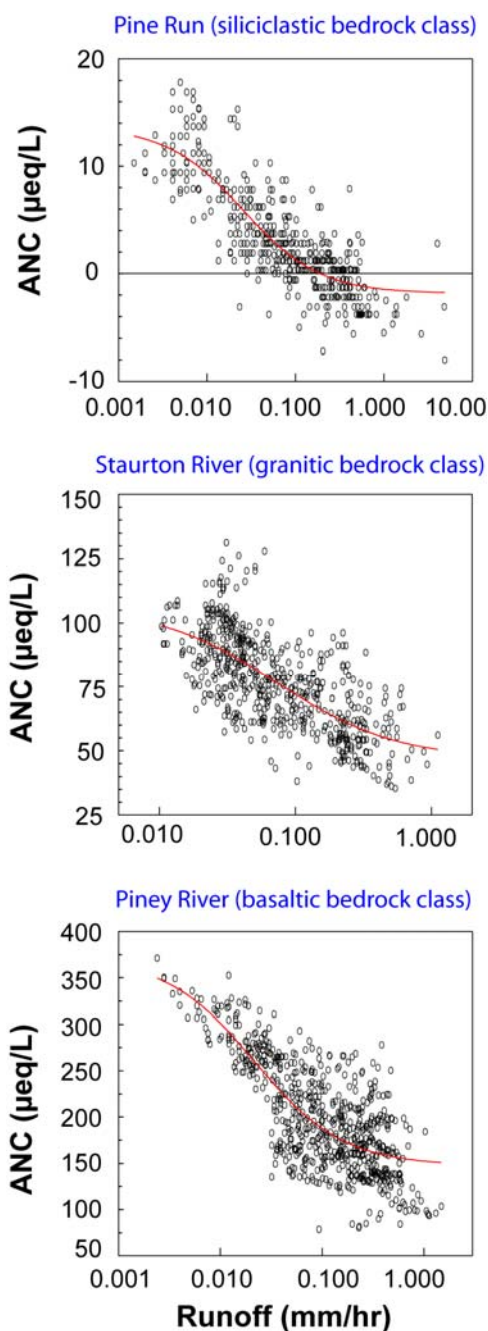
Source: Sullivan et al. (2003).

Figure B-13   Relationship between ANC and runoff for streamwater samples collected at intensively studied sites in Shenandoah National Park. The data represent samples collected during the 1992–1997 period.

At the intermediate-ANC (~60 to 120 µeq/L) Staunton River site on granitic bedrock, increases in SO_4^{2-} and organic acid anions, and to a lesser extent NO_3^-, were the primary causes of episodic acidification. Base cation increases compensated these changes to a large degree, and ANC declined by 2 to 68 µeq/L during the episodes (median decrease in ANC was 21 µeq/L).

At the high-ANC (~150 to 200 µeq/L) Piney River site on basaltic (69%) and granitic (31%) bedrock, base cation concentrations declined during episodes (in contrast with the other two sites where base cation concentrations increased). Sulfate and NO_3^- usually increased. The change in ANC during the episodes studied ranged from 9 to 163 µeq/L (median 57 µeq/L; Eshleman and Hyer, 2000).

Previous studies have shown that mobilization of dissolved Al during episodic acidification is a primary cause of fish mortality in streams that have low ANC under baseflow conditions (Wigington et al., 1993). Streams with higher ANC during baseflow are less likely to become sufficiently acidic during episodes to bring much Al into solution.

Figure B-14 provides an example of changes in ANC, pH, and total monomeric Al that occurred in Paine Run, Staunton River, and Piney River during a high-flow episode in January 1995. Under baseflow conditions, ANC at the Paine Run site was above 0 µeq/L, pH was above 5.5, and Al concentration was less than about 1 µM. Discharge levels increased dramatically during the episode, resulting in depression of ANC to less than 0 µeq/L, pH values less than 5.5, and an increase in Al concentration to near 3 µM, above the threshold for adverse effects on some species of aquatic biota.
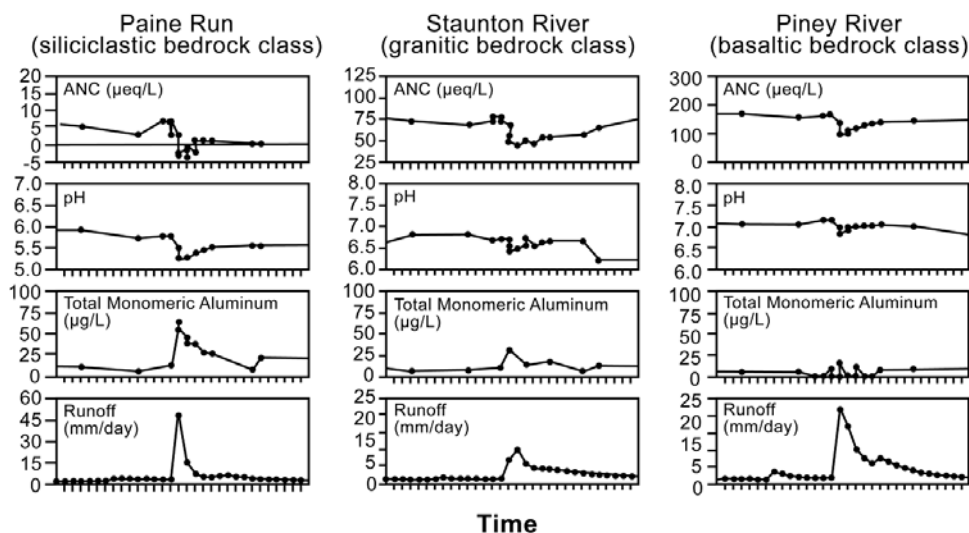
Source: Sullivan et al. (2003).

Figure B-14. Decrease in ANC and pH and increase in dissolved aluminum in response to a sharp increase in streamflow in three watersheds within Shenandoah National Park during a hydrological episode in 1995. The watersheds were selected to be representative of the three geologic sensitivity classes within the park. Data are shown for the month of January 1995.

The same episode also resulted in substantial declines in ANC in the granitic (Staunton River) and basaltic (Piney River) watersheds. However, ANC values at these two sites were relatively high before the episode (about 75 and 175 µeq/L, respectively) and did not decline to below about 50 µeq/L during the episode at either site, and pH values remained above 6.0 and 6.5, respectively.

In general, pre-episode ANC is a good predictor of minimum episodic ANC and also a reasonable predictor of episodic ΔANC. Higher values of pre-episode ANC lead to larger ΔANC values, but minimum ANC values of such streams are generally not especially low. Lowest minimum ANC values are reached in streams that have low pre-episode ANC, but the ΔANC values for such streams are generally small.

Webb et al. (1994) developed an approach to calibration of an episodic acidification model for VTSSS long-term monitoring streams in western Virginia that was based on the regression method

described by Eshleman (1988). Median, spring quarter ANC concentrations for the period 1988 to 1993 were used to represent chronic ANC, from which episodic ANC was predicted. Regression results were very similar for the four lowest ANC watershed classes, and they were therefore combined to yield a single regression model to predict the minimum measured ANC from the chronic ANC. Extreme ANC values were about 20% lower than chronic values, based on the regression equation:

$$ANC_{min} = 0.79\ ANC_{chronic} - 5.88\ (r^2 = 0.97;\ se\ of\ slope = 0.02,\ p = 0.001)$$

Because the model was based on estimation of the minimum ANC measured in the quarterly sampling program, it is probable that the true minimum ANC values were actually somewhat lower than 20% below the measured chronic ANC. Nevertheless, regression approaches for estimation of the minimum episodic ANC of surface waters, such as was employed by Webb et al. (1994) for western Virginia, provide a basis for predicting future episodic acidification. It must be recognized, however, that future episodic behavior might vary from current behavior if chronic conditions change dramatically.

The relative importance of the major processes that contribute to episodic acidification varies among the streams within Shenandoah National Park, in part as a function of bedrock geology and baseflow streamwater ANC. Sulfur-driven acidification was an important contributor to episodic loss of ANC at all three study sites, probably because S adsorption by soils occurs to a lesser extent during high-flow periods. This is due, at least in part, to diminished contact between drainage water and potentially adsorbing soils surfaces. Dilution of base cation concentrations was most important at the high-ANC site.

The documented importance of NO_3^- to episodic acidification was a relatively recent development, attributed to the effects of gypsy moth (*Lymantria dispar*) infestation in many watersheds within Shenandoah National Park (Webb et al., 1995). Consumption of foliage by the moth larvae converted foliar N, which is normally tied up in long-term N cycling processes, into more labile N forms on the forest floor.

Thus, episodic acidification of streams in Shenandoah National Park can be attributed to a number of causes, including dilution of base cations and increased concentrations of sulfuric, nitric, and organic acids (Eshleman et al., 1995; Hyer et al., 1995). For streams having low pre-episodic ANC, episodic decreases in pH and ANC and increases in toxic Al concentrations can have adverse effects on fish populations. Not all of the causes of episodic acidification are related to acidic deposition. Base-cation dilution and increase in organic acid anions during high-flow conditions are natural processes. The contribution of nitric acid, indicated by increased NO_3^- concentrations, has evidently been (at least for streams in the park) related to forest defoliation by the gypsy moth (Eshleman et al., 1998; Webb et al., 1995). However, significant contributions of sulfuric acid, indicated by increased SO_4^{2-} concentrations during episodes in some streams, is an effect of atmospheric deposition and the dynamics of S adsorption on soils (Eshleman and Hyer, 2000).

B.4. Effects on Biota

Soil and surface water acidification involve changes in a number of chemical parameters, each of which has the potential to influence the health and vigor of biological communities and the species that comprise them. In most cases where biological effects of acidification have been documented, the most important chemical parameters involved in those effects have been pH, Al_i, and Ca^{2+}. Less commonly, one or more base cations other than Ca^{2+} (e.g., Mg^{2+}, K^+) or C are also involved. This is true for both aquatic and terrestrial effects.

A number of authors have examined the complex interactions between pH, Al, and Ca^{2+} that must be considered when attempting to determine the effects of acidification on both aquatic and terrestrial biota (e.g., Mount et al., 1988; Wood et al., 1990). Calcium concentration significantly affects the distribution of species and their ability to survive in acidified environments. Aluminum, leached by acid

precipitation from soils in the watershed, complicates the response considerably because some forms of Al are highly toxic to both aquatic and terrestrial species. Aluminum and hydrogen ions interact both synergistically and antagonistically depending on conditions (Havas, 1985; Rosseland and Staurnes, 1994). In the presence of naturally occurring organic acids, Al toxicity can be reduced or eliminated. A number of authors have examined the complex interactions between pH, Al, and Ca2+ that must be considered when attempting to determine the effects of acidification on both aquatic and terrestrial biota (e.g., Ingersoll et al., 1990a; Mount et al., 1988; Wood et al., 1990).

B.4.1. Types of Effects of Acidification on Biota

Ecological effects occur at four levels of biological organization: the individual; the population, comprised of many individuals; the biological community, composed of many species, (Billings, 1978); and the ecosystem. Several metrics have been developed to describe the effects of acidification at each of these levels of organization. For the individual, effects are assessed in terms of sublethal effects on condition. At the population level, effects are measured by changes in the population of a certain species. At the community level, species richness and community structure can be used to evaluate effects, and at the ecosystem level, changes in nutrient cycling and ecosystem processes are assessed. Most of these indices have been applied primarily to aquatic ecosystems. Each is discussed below.

Baker et al. (1990b) conducted a rigorous review of the effects of acidification on aquatic biota for the 1990 NAPAP State of Science/Technology reports. They evaluated hundreds of laboratory, in situ bioassay, field surveys, whole-system field experiments, and smaller mesocosm studies on the effects of acidification on aquatic biota. Their 381–page report is the most exhaustive source summarizing the aquatic biological effects of acidification from acidic deposition. The summaries provided here in Sections B.4 and B.6 rely heavily on this source.

In Shenandoah National Park, a statistically robust relationship between acid-base status of streams and fish species richness was documented. The 3 year Fish in Sensitive Habitats (FISH) study of stream acidification in Shenandoah National Park demonstrated negative effects on fish from both chronic and episodic acidification (Bulger et al., 1999). Biological differences in low- versus high-ANC streams included species richness, population density, condition factor, age, size, and field bioassay survival. Of particular note was that both episodic and chronic mortality occurred in young brook trout exposed in a low-ANC stream, but not in a high-ANC stream (MacAvoy and Bulger, 1995), and that blacknose dace (*Rhinichthys atratulus*) in low-ANC streams were in poor condition relative to blacknose dace in higher-ANC streams (Dennis et al., 1995; Dennis and Bulger, 1995).

B.4.1.1. Individual Condition Factor

Relatively little is known about changes in the condition of fish or other aquatic biota resulting from acidification. It is expected that sublethal effects will occur in acid-sensitive species well before the species is eliminated from a particular lake, stream, or terrestrial habitat. For that reason, loss of an acid-sensitive species is not necessarily an ideal indicator of acid stress. Clearly, stress begins to occur before species elimination. Sublethal effects are more difficult to quantify, but are nevertheless important.

Condition factor is one measure of sublethal effect that has been used to quantify effects of acidification on fish. Condition factor is an index to describe the relationship between fish weight and length. Expressed as fish weight/length[3], multiplied by a scaling constant, this index reflects potential depletion of stored energy reserves (Dennis et al., 1995; Everhart and Youngs, 1981; Goede and Barton, 1990). Condition factor is interpreted as depletion of energy resources such as stored liver glycogen and body fat (Goede and Barton, 1990). Fish with higher condition factor are more robust than fish having low condition factor.

$$y = 1.194x + 1.519, r^2 = .777$$
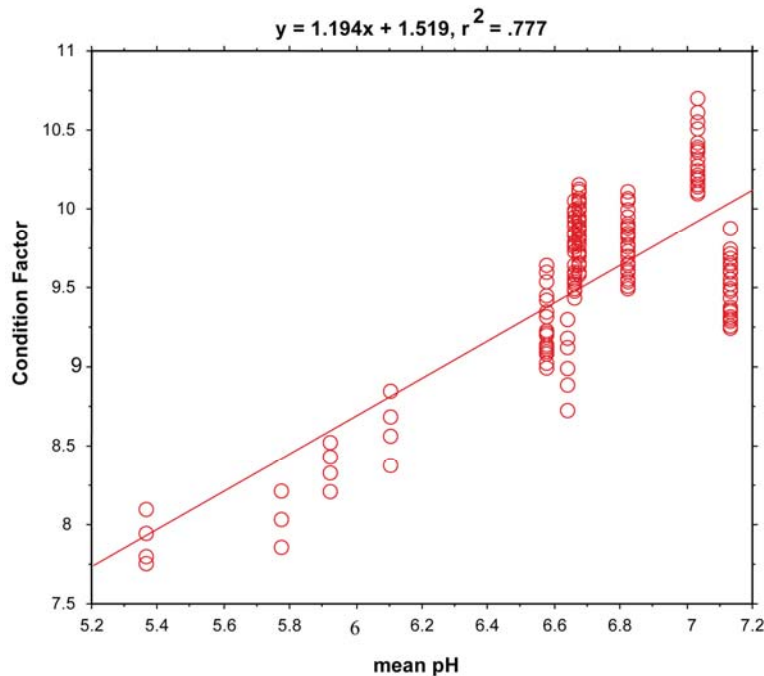
Figure B-15. **Length-adjusted condition factor (K), a measure of body size in blacknose dace (*Rhinichthys atratulus*) compared with mean stream pH among 11 populations (n = 442) in Shenandoah National Park. Values of pH are means based on quarterly measurements, 1991–94; K was measured in 1994. The regression analysis showed a highly significant relationship (p <0.001) between mean stream pH and body size, such that fish from acidified streams were less robust than fish from circumneutral streams.**

Field studies have shown lower condition factor in fish found in more acidic streams (Dennis et al., 1995). Condition factor has been developed and applied mainly for blacknose dace. This species is widely distributed in Appalachian Mountain streams and is moderately tolerant of low pH and ANC, relative to other fish species in the region. However, the concept is probably applicable to other species as well. Condition factor may be a useful metric for many species in aquatic ecosystems that are only marginally affected by acidification.

Bulger et al. (1999) observed a positive relationship between condition factor and pH in streams in Shenandoah National Park. Dennis and Bulger (1995) found a reduction in the condition factor for blacknose dace in waters near pH 6.0. The four populations shown in Figure B-15 with the lowest condition factor have mean habitat pH values within or below the range of critical pH values at which Baker and Christensen (1991) estimated that negative population effects for blacknose dace are likely for the species. The mean length-adjusted condition factor of fish from the study stream with the lowest ANC was about 20% lower than that of the fish in best condition. Comparisons with the work of Schofield and Driscoll (1987) and Kretser et al. (1989) suggest that pH in the low-pH Shenandoah National Park streams is near or below the limit of occurrence for blacknose dace populations in the Adirondack region of New York (Sullivan et al., 2003).

Chronic sublethal stress caused by pH below about 6.0 may have serious effects on a variety of wild fish populations. There is an energy cost in maintaining physiological homeostasis; the calories used to respond to stress are a part of the fish's total energy budget and are unavailable for other functions, such as growth and reproduction (Schreck, 1981, 1982; Wedemeyer et al., 1990)

Observed differences in condition factor may occur because maintenance of internal chemistry in the more acidic streams would require energy that otherwise would be available for growth and weight gain (Dennis and Bulger, 1999; Sullivan et al., 2003). The energy costs to fish for active iono-osmoregulation can be substantial (Bulger, 1986; Farmer and Beamish, 1969). Because of the steep gradient in Na^+ and Cl^- concentrations between fish blood and freshwater, there is constant diffusional loss of these ions, that must be replaced by energy-requiring active transport. Low pH increases the rate of passive loss of blood electrolytes (especially Na^+ and Cl^-), and Al elevates losses of Na^+ and Cl^- above the levels that occur due to acid stress alone (Wood, 1989).

It is also possible that the loss of sensitive individuals or early life stages within species may reduce competition for food among the survivors, resulting in better growth rates, survival, or condition. Similarly, competitive release (increase in growth or abundance subsequent to removal of a competitor) may result from the loss of a sensitive species, with positive effects on the density, growth, or survival of competitor population(s) of other species (Baker et al., 1990b). However, in some cases where acidification continued, transient positive effects on size of surviving fish were shortly followed by extirpation (Bulger et al., 1993).

Acid stress is at least partly responsible for the lower condition of blacknose dace populations in Shenandoah National Park, though reduced access to food or lower food quality (Baker et al., 1990b), either resulting from the nature of soft water streams or exacerbated by acidification, cannot be ruled out. Primary productivity is low in headwater streams and lower still in soft water headwaters, which are more likely to be acidified. Production of invertebrates is likely to be low in such streams as well (Wallace et al., 1992). Thus, lower food availability cannot be discounted as a potential contributor to lowered condition in Shenandoah National Park blacknose dace populations in low-pH streams. Nevertheless, reduced growth rates have been attributed to acid stress in a number of other fish species, including Atlantic salmon (*Salmo salar*), Chinook salmon (*Oncorhynchus tshawytscha*), lake trout (*Salvelinus namaycush*), rainbow trout (*Oncorhynchus mykiss*), brook trout, brown trout (*Salmo trutta*), and Arctic char (*Salvelinus alpines*).

B.4.1.2. Species Composition

Species composition refers to the mix of species that are represented in a particular ecosystem. Acidification alters species composition in aquatic ecosystems. There are a number of species common to many oligotrophic waters that are sensitive to acidic deposition and that cannot survive, compete, or reproduce in acidic waters. In response to small to moderate changes in acidity, acid-sensitive species are often replaced by other more acid-tolerant species, resulting in changes in community composition, but little or no change in total community abundance or biomass. The effects of acidification are continuous, with more species being affected at higher degrees of acidification. Therefore, the degree of alteration of surface water biological community composition increases as surface waters become more acidic. There is a consistent pattern of lower community diversity with increased acidification.

B.4.1.3. Taxonomic Richness

Taxonomic richness is a metric that is commonly used to quantify the effects of an environmental stress such as acidification or eutrophication. The richness metric can be applied at various taxonomic levels. For example, the number of fish species can be used as an index of acidification (Bulger et al., 1999). Similarly, acidification effects on aquatic insects can be evaluated on the basis of the number of families or genera of mayflies (order Ephemeroptera) (Sullivan et al., 2003).

Acidification results in the loss of acid-sensitive species, with more species lost with higher degrees of acidification. A direct outcome of population loss caused by acidification is a decline in species

richness (the total number of species in a stream or lake). This is a highly predictable outcome of regional acidification, although the pattern and rate of species loss varies from region to region.

Decreases in ANC and pH and increases in Al_i concentration contribute to declines in species richness and abundance of zooplankton, macroinvertebrates, and fish (Keller and Gunn, 1995; Schindler et al., 1985). Species richness is positively correlated with pH and ANC (Kretser et al., 1989; Rago and Wiener, 1986) because of the elimination of acid-sensitive species (Schindler et al., 1985). Knowledge of the spatial distribution of pH and other water quality variables is necessary to explain the presence or absence of species within heterogeneous environments. Organisms that are mobile and can sense the pH of their environment can move to areas (called refugia) that have more favorable water chemistry. Although some species are favored by increased acidity, species diversity generally decreases as surface water acidity increases.

Decreases in species richness have been observed for all major trophic groups of aquatic organisms (Baker et al., 1990b). Baker et al. (1990b) discussed 10 selected studies that documented this phenomenon, with sample sizes ranging from 12 to nearly 3,000 lakes and streams analyzed per study.

Lake and stream size can be an important complicating factor in interpreting species richness data. Larger lakes and streams in larger watersheds would generally be expected to contain more species than smaller lakes or streams in smaller watersheds, irrespective of acid-base chemistry. Nevertheless, when adjusted for lake size, lakes with pH less than approximately 6.0 contain significantly fewer species than lakes with pH above 6.0 (Figure B-17) (Frenette et al., 1986; Matuszek and Beggs, 1988; Rago and Wiener, 1986; Schofield and Driscoll, 1987).

Studies in the Adirondack Mountains demonstrated the effect of acidification on species richness; of the 53 fish species recorded in Adirondack lakes by the ALSC, about half (26 species) were absent from lakes with pH below 6.0. Those 26 species included important recreational species, such as Atlantic salmon, tiger trout (*Salmo trutta* X *Salvelinus fontinalis*), redbreast sunfish (*Lepomis auritus*), bluegill (*Lepomis macrochirus*), tiger musky (*ESO$_X$ masquinongy* X *lucius*), walleye (*Sander vitreus*), alewife (*Alosa pseudoharengus*), and kokanee (*Oncorhynchus nerka*) (Kretser et al., 1989), plus ecologically important minnows that serve as forage for sport fish. Fully 346 of 1,469 lakes surveyed by the ALSC supported no fish at all at the time of the survey. These lakes were significantly lower in pH, dissolved Ca^{2+}, and ANC, and had higher concentrations of Al_i than lakes hosting one or more species of fish (Gallagher and Baker, 1990). Among lakes with fish, there was an unambiguous relationship between the number of fish species and lake pH, ranging from about one species per lake for lakes having pH less than 4.5 to about six species per lake for lakes having pH >6.5 (Kretser et al., 1989; Driscoll et al., 2001). Figure B-17 shows the mean number of fish species for pH classes from 4.0 to 8.0 in lakes in the Adirondacks. It is important to note, however, that there are many possible causes of fish absence in addition to acidification. These include lack of suitable habitat (especially for spawning), winter kill, blocked access, etc.
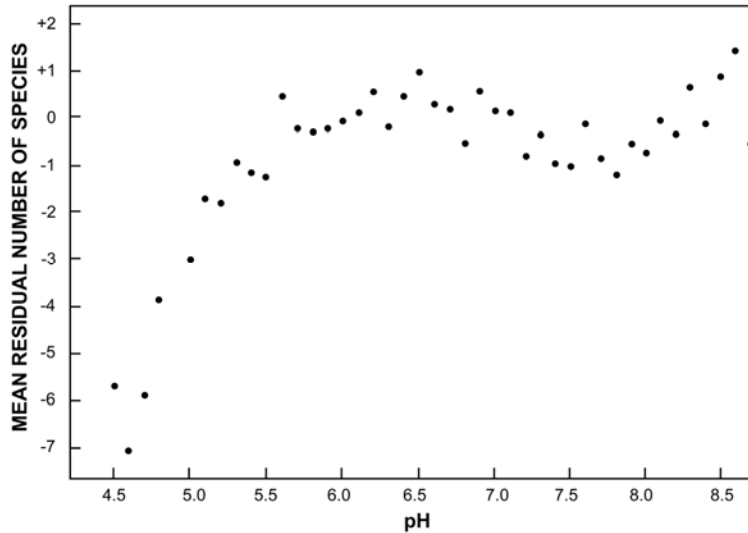
Figure B-16. **Mean residual number of species per lake for lakes in Ontario, by pH interval. The residual number of species for a lake is the deviation of the observed number from the number predicted by lake area.**

Sullivan et al. (2006b) developed a relationship between fish species richness and ANC class for Adirondack lakes. Fish species richness observations, as a function of ANC (μeq/L) class, were fit to a logistic relationship by a non-linear regression analysis. Under chronically acidic conditions (summer index or annual average ANC <0 μeq/L), Adirondack lakes are generally fishless. There was a marked increase in mean species richness with increases in ANC up to values of approximately 100 μeq/L. The asymptote for the fish species equation was 5.7 species. This analysis suggests that there could be loss of fish species with decreases in ANC below approximately 100 μeq/L. It does not account, however, for the possibility that lakes having higher ANC are often larger, and therefore support more fish species because of increased habitat diversity and complexity.

As an element of the FISH project (Bulger et al., 1999), numbers of fish species were compared among 13 Shenandoah National Park streams spanning a range of pH and ANC conditions. There was a highly significant (p <0.0001) relationship between stream acid-base status (during the 7–year period of record) and fish species richness among the 13 streams. The streams with the lowest ANC hosted the fewest species (see Figure B-18).
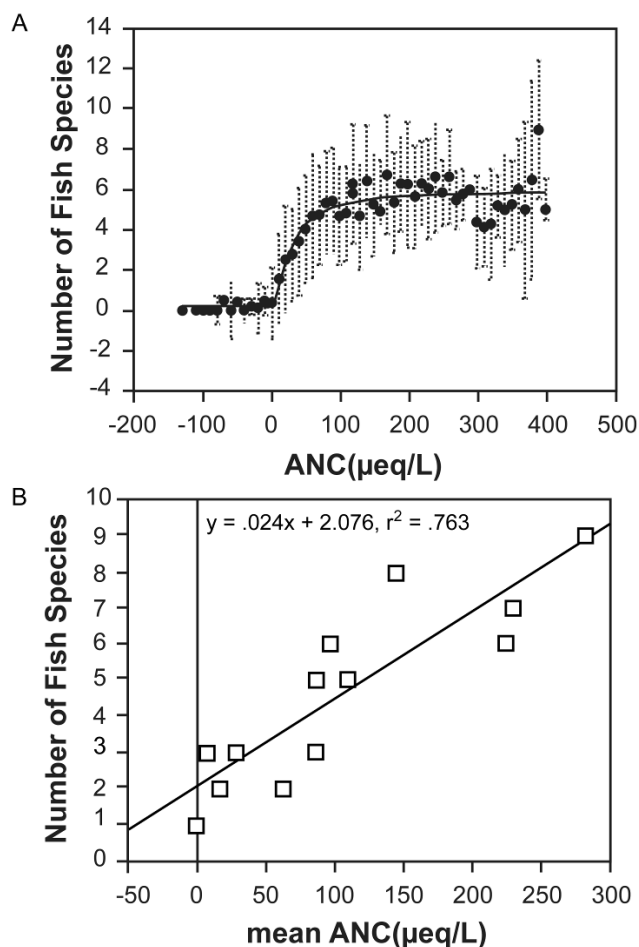
Figure B-17. Number of fish species per lake or stream versus acidity statues, expressed either as pH or ANC. (A) Adirondack lakes (Sullivan et al., 2006b); (B) streams in Shenandoah National Park (Bulger et al., 1999). The data for the Adirondacks are presented as mean and range of species richness within 10 μeq/L ANC categories, based on data collected by the Adirondack Lakes Survey Corporation.

Median stream ANC values and watershed areas are shown in Table B-11 for the 14 streams used by Bulger et al. (1999) to develop the relationship between ANC and fish species richness shown in Figure B-18. Despite the overall similarities, these study streams vary in watershed area by a factor of 10. The streams that have larger watershed areas generally have more fish species than the streams having smaller watershed areas. All of the "rivers" have watersheds larger than 10 km^2 and ANC higher than 75 μeq/L. In contrast, the majority (but not all) of the "runs" have watershed area smaller than 10 km^2 and ANC less than 20 μeq/L. All of the streams that have watershed areas smaller than 10 km^2 have three or fewer known species of fish present. All of the streams having larger watersheds (>10 km^2) have three or more known fish species; seven of nine have five or more species; and the average number of fish species is six. There is no clear distinction between river and run, but it is clear that as small streams in Shenandoah National Park combine and flow into larger streams and eventually to rivers, two things happen: acid-sensitivity generally declines, and habitat generally becomes suitable for additional fish species (Sullivan et al., 2003).
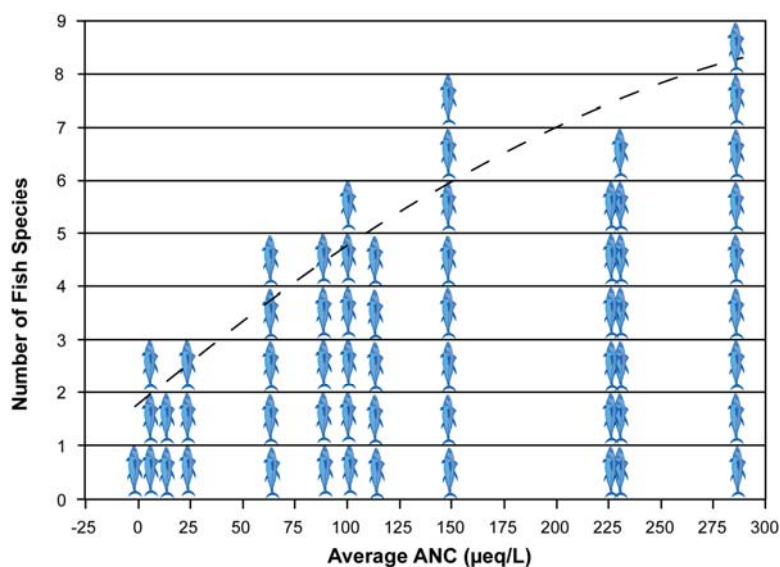
Source: Redrawn from Bulger et al. (1999).

Figure B-18. **Number of fish species among 13 streams in Shenandoah National Park. Values of ANC are means based on quarterly measurements, 1987–94. The regression analysis shoed a highly significant relationship (p <0.0001) between mean stream ANC and number of fish species. Streams having ANC consistently <75 µeq/L had three or fewer species.**

South of Shenandoah National Park the effects of surface water acidification on fish species richness have been studied in some detail in the St. Marys River in Virginia. Fish species richness was closely associated with surface water acid-base chemistry. Bugas et al. (1999) conducted electrofishing in the St. Marys River in 1976, and every 2 years from 1986 through 1998. Systemic stream acidification occurred during the study period. Sampling occurred at six sites between the downstream end of the St. Marys Wilderness and the headwaters over a distance of about 8 km. The number of fish species in the St. Marys River within the wilderness declined from 12 in 1976 to 4 in 1998. Three of the four species present in 1998 (brook trout, blacknose dace, fantail darter [*Etheostoma flabellare*]) are tolerant of low pH and are typically the only fish species present in streams having similar levels of acidity in Shenandoah National Park, which is also located in Virginia (Bulger et al., 1999). Bugas et al. (1999) reported that successful brook trout reproduction in the St. Marys River occurred only 1 year out of 4 during the period 1995 through 1998. Eight of the fish species recorded in one or more early years have not been observed in more recent years. Several, including blacknose dace, rainbow trout, and torrent sucker (*Thoburnia rhothoeca*), showed a pattern of being progressively restricted over time to lower river reaches, which generally have higher ANC. The number of fish species decreased with decreasing minimum ANC, from nine species at ANC of about 160 µeq/L to one to three species at ANC near 0. The best fit regression line suggested, on average, a loss of one species for every 21 µeq/L decline in annual minimum recorded ANC value.

Dynamic water chemistry model projections have been combined with biological dose-response relationships to estimate declines in fish species richness with acidification. A relationship derived from the data in Figure B-18 was used by Sullivan et al. (2003) with stream ANC values predicted by the MAGIC model to provide estimates of the expected number of fish species in each of the modeled streams for the past, present, and future chemical conditions simulated for each stream. The coupled geochemical and biological model predictions were evaluated by comparing the predicted species richness in each of the 13 streams with the observed number of species that occur in each stream. The agreement between predicted and observed species numbers was good, with a root mean squared error (RMSE) in predicted number of species across the 13 streams of 1.2 species. The average error was 0.3

species, indicating that the coupled models were unbiased in their predictions. Model reconstructions of past species richness in the streams suggested that historical loss of species had been greatest in the streams located on the most sensitive geological class (siliciclastic). The average number of species lost from streams on the three bedrock types examined were estimated as: 1.6 species on siliciclastic bedrock; 0.4 species on granitic bedrock; and 0.4 species on basaltic bedrock. In the case of the siliciclastic streams, the projected past changes were much larger than the average error and RMSE of the coupled models, suggesting that the projections were reasonably robust.

It appears that fish species richness is controlled by multiple factors, of which both acidification and watershed area can be important. Watershed area might be important in this context because smaller watersheds may contain smaller streams having less diversity of habitat, more pronounced effects on fish from high-flow periods, or lower food availability. Such issues interact with other stresses, including acidification, to determine overall habitat suitability.

For Shenandoah National Park, Bulger et al. (1999) concluded that the most important cause of the observed decline in species richness with decreasing ANC was acid stress associated with acidification. However, an additional causal factor may have been the decrease in the number of available aquatic niches when moving from downstream locations (which are seldom low in pH and ANC) to upstream locations (which are often low in pH and ANC in this region; (Sullivan et al., 2003). The relative importance of this latter factor, compared with the importance of acid stress, in determining this relationship is unknown.

In the Adirondack region, Driscoll et al. (2001b) concluded that high-elevation lakes are more likely to be fishless than larger lakes at low elevation (Gallagher and Baker, 1990) because they have poor access for fish immigration, poor fish spawning substrate, or low pH, or they may be susceptible to periodic winter kills. Nevertheless, small, high-elevation Adirondack lakes with fish also had significantly higher pH compared with fishless lakes; acidity is likely to play an important role in the absences of fish from such lakes (Driscoll et al., 2001b).

B.4.1.4. Community Structure

Ecosystem response to pollutant deposition is a direct function of the ecosystem's ability to ameliorate resulting changes in individual species (Strickland et al., 1993). To determine ecosystem response and the possible effects on community structure, species responses must be scaled in both time and space and be propagated from the individual to the more complex levels of community interaction within an ecosystem.

Individuals within a population vary in their ability to withstand a stress. The response of each individual is based on its genetic constitution (genotype), its stage of growth at time of exposure to the stress, and the microhabitat in which it lives (Levin, 1998). The range within which individuals in the population can exist and function determines the ability of the population to survive when exposed to a chronic stress. Those individuals that are able to cope with the stress survive and reproduce. The same kinds of pressures act on populations of different species. Competition among species results in community change over time and eventually produces ecosystems composed of populations of species that have the capability to tolerate the stress (Guderian et al., 1985; Rapport and Whitford, 1999; U.S. EPA, 2004).

Work conducted on the biological effects of acidification has largely been focused on the response of fish, especially salmonids (trout and salmon). This focus tends to be driven by the value people place on fish and fishing, rather than any ecological consideration. Other vertebrate, invertebrate, plant, and algal communities are also sensitive to acidification. In general, higher order trophic groups are more susceptible to acidification. Thus, in terms of changes in community structure in response to aquatic acidification, the general progression of sensitivity is as follows: fish >invertebrates (benthic and zooplankton) >algae >microbes (Baker et al., 1990b). Population-level fish response to acidification is primarily through recruitment failure, a result of increased mortality of early life stages or indirect effects

through the food chain (loss of prey species). Al_i, pH, and Ca^{2+} have been identified as the variables most likely to have the greatest influence on fish community structure.

B.4.1.5. Indices of Ecological Effects

The most widely used index of acidification effect is the Acid Stress Index (ASI) developed by Baker et al. (1990b). This index uses fish bioassay survival data fitted to a maximum likelihood logistic regression model as a function of exposure to pH, Al, and Ca^{2+} to predict the probability of fish survival expressed as a percent mortality. This approach can aid in determination of effects on species composition by predicting the probability of occurrence of species of varying acid sensitivity. Separate ASI models were developed for tolerant, intermediate, and sensitive fish species. Approximate ASI reference levels were established for various species based on logistic regression of fish presence as a function of the sensitive, intermediate, and tolerant ASI values for brown bullhead (*Ameiurus nebulosus*), brook trout, lake trout, and common shiner (*Luxilus cornutus*). They are presented in Table B-12.

The ASI was deemed a useful index of stress by Baker et al. (1990b), even though the relationships between ASIs and fish population status could not be quantified precisely because of confounding factors. Such factors included the abundance and types of food species, competitors and predators present, variations in habitat quality, and density-dependent effects on fecundity.

B.4.2. Timing of Effects

B.4.2.1. Life Stage Differences in Sensitivity

Episodic and chronic changes in the chemistry of surface waters can have different effects on aquatic organisms and populations depending on species and the life history stages present. More is known about the sensitivity to acidification of the life stages of fish than is known for other aquatic organisms. In general, early life stages are more sensitive to acidic conditions than the young-of-the-year, yearlings, and adults (Baker and Schofield, 1985; Baker et al., 1990b; Johnson et al., 1987). Also, small fish, especially swim-up fry, are probably less mobile and less able to avoid exposure to adverse chemical conditions than the relatively larger adults (Baker et al., 1996).

There are a number of issues of acidification timing that are important to determination of the extent and magnitude of effects. One important issue concerns the timing of acidity exposure relative to life stage. For example, adult fish are generally more tolerant of acidity than early life stages such as eggs, fry and juveniles. There could be substantial differences in effect based on small differences in age or timing of exposure to acidity. No definite pattern was observed by Baker et al. (1990b) across all studies or species. This may reflect either differences in the test conditions or actual differences among species.

The presence of early life stages of brook trout, which are most sensitive to adverse effects from acidification (Bulger et al., 2000), varies with season. For example, the most acid-sensitive stages of brook trout development are present in Virginia streams throughout the cold season in general, and the winter in particular (Figure B-19).

Acid-Sensitive Life Stages of the Brook Trout
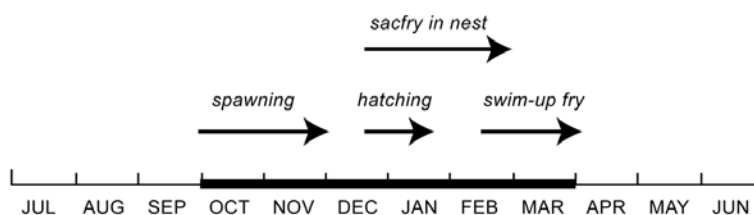
Source: Sullivan et al. (2003).

Figure B-19.   Life stages of brook trout.

The processes of oogenesis and fertilization in fish and aquatic invertebrates are especially sensitive to low pH (Havas et al., 1995; Muniz, 1991). In fish, this sensitivity is most likely due to adverse effects on the female spawner. For instance, Beamish et al. (1976) reported that reduced serum and plasma Ca^{2+} in female fish in acidified Canadian lakes lead to a higher probability for failure in producing viable eggs. A depletion of Ca^{2+} from bone and increased numbers of females with unshed eggs have also been linked to sensitivity at this life stage (cf. Muniz, 1991; Rosseland, 1986).

After fertilization, the embryo seems to be susceptible to acidic waters throughout the whole period of development. The periods shortly after fertilization and before hatching seem to be most critical (Rosseland, 1986). The susceptibility of the embryo can be the result of direct exposure to elevated H^+ concentrations and also to the toxic effects of Al_i at intermediate pH-values. Low pH in the surrounding water also results in pH-depression inside the egg, leading to either a prolongation of the hatching or to a reduced hatching success (Rosseland, 1986). Eggs lying in gravel on stream and lake beds are to some extent protected from exposure to rapid changes in pH (Gunn and Keller, 1984b; Lacroix, 1985). Nevertheless they can experience high mortality during periods of acid runoff, such as snowmelt (Gunn and Keller, 1984a).

In fish, emergent alevins show susceptibility to the adverse effects of Al_i and H^+ that increases with age (Baker and Schofield, 1982; Wood and McDonald, 1982). Rosseland (1986) indicated that this increasing sensitivity results from changes that take place in the respiratory system. Shortly after hatch, alevins still respire through their skin but gradually gills become the primary organ of gas and ion exchange. Gills are the locus for interference of H^+ and Al_i with iono-regulatory exchange. Woodward et al. (1989) exposed cutthroat trout (*Oncorhynchus clarki*) from the Snake River in Wyoming to pH depressions from pH 4.5 to 6.5 in the laboratory. Fertilized egg, eyed embryo, alevin, and swim-up larval stages were exposed to low pH for a period of seven days. Each life stage was monitored for mortality, growth, and development for 40 days after hatching. Reductions in pH from 6.5 to 6.0 in low-Ca^{2+} water (70 µeq/L) did not affect survival, but reduced growth of swim-up larvae. The eggs, alevin, and swim-up larval stages showed significantly higher mortality at pH 4.5 than at pH 6.5. Mortality was also higher at pH 5.0 than at pH 6.5, but only statistically higher for eggs.

Woodward (1991) exposed greenback cutthroat trout (*Oncorhynchus clarki stomias*) in the laboratory to 7–day pH depressions. Low-Ca^{2+} (65 µeq/L) water at pH 6.5 was experimentally reduced to pH values of 6.0, 5.5, 5.0, and 4.5. Four life stages were exposed: freshly fertilized egg, eyed embryo, alevin, and swim-up larva. Alevin survival was reduced at pH 5.0, whereas survival of eggs, embryos, and swim-up larvae was reduced at pH 4.5. Swim-up larvae showed feeding inhibitions at pH 4.5. The authors concluded that the threshold for effects of acidity on greenback cutthroat trout in the absence of Al was pH 5.0 (Woodward, 1991).

Yellowstone cutthroat trout (*O. c. bouveri*) were exposed to 7–day pH depressions by Farag et al. (1993). Of the four life stages studied, eggs were most sensitive to low pH. Eggs exposed for seven days to pH 5.0 test water showed a statistically significant reduction in survival compared with eggs exposed for seven days to pH 6.5 water. Survival of alevin and swim-up larvae were significantly reduced from near 100% at pH 6.5 to near 0% at pH 4.5. Intermediate pH values (6.0, 5.5) in all cases showed reduced survival compared with the control (6.5) but not by statistically significant amounts. Eyed embryos were not sensitive to any of the exposures.

According to Bulger et al. (1999), adult brook trout in Shenandoah National Park streams are more tolerant of acidity than are adult blacknose dace. For both species, the early life stages are more sensitive than the adults, and brook trout young are actually more sensitive than blacknose dace adults (Bulger et al., 1999). Blacknose dace spawn during summer and the eggs and very young fry are therefore somewhat protected from the most acidic episodes, which typically occur during cold-season, high-flow conditions.

B.4.2.2. Biological Effects of Episodes

Episodic decreases in pH and ANC can produce chemical conditions in lakes, and especially in streams, that are as harmful to biota as chronic acidification (Baker et al., 1996). Adverse effects on biota occur particularly when changes involve pH, Al_i, or Ca^{2+} (Baker et al., 1990b). Aquatic biota vary greatly in their sensitivity to episodic decreases in pH and increases in Al_i in waters having low Ca^{2+} concentration. However, Baker et al. (1990b) concluded that episodes are most likely to affect biota if the episode occurs in waters with pre-episode pH above 5.5 and minimum pH during the episode of less than 5.0.

Results from the ERP demonstrated that episodic acidification can have long-term adverse effects on fish populations. Streams with suitable chemistry during low flow, but low pH and high Al_i levels during high flow, had substantially lower numbers and biomass of brook trout than in non-acidic streams (Wigington et al., 1996). Streams having acidic episodes showed significant mortality of fish.

Some brook trout avoided exposure to stressful chemical conditions during episodes by moving downstream or into areas with higher pH and lower Al_i. This movement of brook trout only partially mitigated the adverse effects of episodic acidification, however, and was not sufficient to sustain fish biomass or species composition at levels that would be expected in the absence of acidic episodes. Just as spatially heterogeneous environments or refugia enable some species to survive in otherwise unfavorable conditions, temporal heterogeneity often has the opposite effect. These findings suggest that stream assessments based solely on chemical measurements during low-flow conditions will not accurately predict the status of fish populations and communities in small mountain streams unless some adjustment is made for episodic processes (Baker et al., 1996a, 1990b; Sullivan, 2000a; Wigington et al., 1996).

In Shenandoah National Park, MacAvoy and Bulger (1995) used multiple bioassays over 3 years in one of the low-ANC streams as part of the FISH project to determine the effect of stream baseflow and acid episode stream chemistry on the survival of brook trout eggs and fry. Simultaneous bioassays took place in mid- and higher-ANC reference streams. Acid episodes (with associated low pH and elevated Al_i concentrations, and high streamwater discharge) induced rapid mortality in the low-ANC stream, while the test fish in the higher-ANC stream survived (Bulger et al., 1999).

In the West, it has also been shown that native trout are sensitive to short-term increases in acidity. For example, Woodward et al. (1989) exposed native western cutthroat trout to pH depressions (pH 4.5 to 6.5) in the laboratory. Reductions in pH from 6.5 to 6.0 in low-Ca^{2+} water (70 μeq/L) did not affect survival, but did reduce growth of swim-up larvae. Eggs, alevins, and swim-up larvae showed significantly higher mortality at pH 4.5 as compared to pH 6.5. Mortality was also somewhat higher at pH 5.0, but only statistically higher for eggs. Some species of aquatic biota in western aquatic ecosystems have been shown to be somewhat more sensitive to pH and ANC change than are cutthroat trout (Baker et al., 1990b).

Multiple logistic regression models were used by Van Sickle et al. (1996) to relate fish bioassay mortality rates to summary statistics of time-varying stream chemistry over the 20–day bioassay periods. Higher mortality of all three test fish species (brook trout, dace, sculpin [*Cottus* spp.]) during the in situ bioassays was clearly associated with increased Al_i. In addition, individual bioassays conducted during chronically or episodically acidified conditions had higher median mortality than did those during non acidic conditions, but no mortality differences were detected between chronically acidic and episodically acidic conditions. Time-weighted median Al_i was the best single predictor of 20–day mortality for both brook trout and sculpin, whereas the number of days with Al_i >200 µg/L provided the best prediction of blacknose dace mortality.

In the Northeast, Baker et al. (1996) studied the effects of episodic acidification on fish in 13 small streams in the Adirondack and Catskill Mountains of New York and the Northern Appalachian Plateau in Pennsylvania. They conducted in situ bioassays with brook trout and blacknose dace, mottled sculpin (*Cottus bairdi*) or slimy sculpin (*Cottus cognatus*) depending on the region, to measure direct toxicity. Movements of brook trout individuals in relation to stream chemistry were tracked using radiotelemetry. Electrofishing surveys assessed fish community status and the abundance and biomass of brook trout in each stream. Streams with suitable conditions during low flow, but moderate-to-severe episodic acidification during high flow, had higher fish mortality in bioassays, higher net downstream movement of brook trout during events, and lower brook abundance and biomass compared to nonacidic streams. These streams lacked the more acid-sensitive fish species (blacknose dace and sculpin). Movement of trout into refugia (areas with higher pH and lower Al) during episodes partially mitigated the adverse effects of episodes.

Chemical measurements by ERP during high flow correlated with fish community status. In general, reduced trout abundance occurred in ERP streams with median high flow pH <5.0 and Al_i >100 to 200 µg/L. Acid -sensitive fish species were absent from streams with median high flow pH <5.2 and Al_i >100 µg/L. More recently, Baldigo et al. (2007) found that mortality of brook trout young of the year occurred at concentrations as low as 54 µg/L .Al_i was the single best predictor of fish mortality in ERP bioassays (Van Sickle et al., 1996) and has been identified as an important toxic factor in other bioassays and field studies (Ingersoll et al., 1990b; Mount et al., 1988; Rosseland et al., 1990). The relationships between pH and Al_i or ANC and Al_i vary among streams (Wigington et al., 1996), and therefore predictions of potential effects on fish based solely on pH or ANC may be misleading. High Al_i concentrations during episodes are probably the dominant cause of adverse effects on fish during episodic acidity events.

Biological Effects of Chronic Acidification

Changes in surface water acid-base chemistry, including pH, ANC, Al_i, and Ca^{2+}, can affect in-stream and in-lake biota. Adverse biological effects may be seen at pH less than about 6.0 to 6.5 and Al_i greater than about 30 to 50 µg/L (1 to 2 µM). It tends to increase with decreasing pH, and reaches potentially toxic concentrations (>~2 µM) in surface drainage waters having pH less than about 5.5. Effects vary substantially by organism, life stage, and the concentration of DOC. Inorganic Al in solution is also toxic to plants.

Calcium can ameliorate the toxic effects of acidity and Al on biota. Most organisms can tolerate lower pH and higher Al_i at higher Ca^{2+} concentrations, but in natural environments, elevated concentrations of Al_i are only found in Ca^{2+}-depleted systems. This effect is most important at low Ca^{2+} levels. Overall biological effects noted with decreasing pH are described in Table B-13 (Baker et al., 1990b). The organisms most likely to respond to such changes in water chemistry include fish, aquatic insects, zooplankton, and diatoms. In some cases, amphibians are also important sensitive biological receptors. Most available data are for fish response.

In most stream or lake survey areas, direct quantification of biological responses to surface water acidification is not possible, given the scarcity or absence of biological long-term monitoring and dose-

response data. Few biological long-term monitoring studies have been conducted. Much of the available in situ dose-response data have been generated from studies of streams in Virginia and Pennsylvania and lakes in New York. Data with which to evaluate acidification relationships have been scarce in most other regions.

Lakes

Fish status assessments for the eastern and upper midwestern U.S. were conducted by Baker et al. (1990b), by region, using a variety of assessment methods. For the northeast region, two water chemistry models were linked to fish response models: the Integrated Lake-Watershed Acidification Study (ILWAS) model and MAGIC. For the Adirondack subregion, three process models were used: ILWAS, MAGIC, and Regional MAGIC. For other areas in the eastern U.S. and for the Upper Midwest, analysis of fish status was limited to application of the sensitive, intermediate, and tolerant toxicity models.

Assessment results reported by Baker et al. (1990b) for the Adirondack region are presented in Table B-14 showing results based on the ASI. Table B-15 shows the estimated percentage of Adirondack lakes with acid-base chemistry unsuitable for fish population survival according to various assessment models based on responses for brook trout, lake trout, and common shiner. Assessment results for the Northeast region are presented in Tables B-16 and B-17.

In acid-sensitive lakes in the western U.S., the focus is often mainly on native cutthroat trout. It is important to note, however, that many high-elevation western lakes and streams were historically fishless. The top predators in such aquatic ecosystems were often amphibians or crustaceans. Thus, even though cutthroat trout might be considered native to the region, they are not necessarily native to a particular lake or stream.

Streams

In streams, the major organisms of concern with respect to water acidification are fish, amphibians, benthic macroinvertebrates, and periphyton (attached algae). All of these groups have shown adverse effects in response to acidification (see Annex B-6). Most available data are for fish and aquatic insects, mainly in the southeastern U.S. Streams affected by acidic deposition tend to occur at high elevation. They are often high-gradient and flow through base-poor geology.

Baker et al. (1990b) presented assessment results for the mid-Appalachian region as the distribution (percent) of NSS lower node, upper node, and total streams classified in various ASI values (Baker et al., 1990b). Most of the streams were classified in the lowest ASI category (Table B-18). Assessment results for the interior Southeast region were similar (Table B-19).

Some fish response research has also been conducted for streams in the Catskill Mountains. Baker and Christensen (1991) estimated that the fish species found in the Neversink River Basin in the Catskill Mountains are typically lost when pH decreases to the range of 4.7 to 5.2 (brook trout), 5.5 to 5.9 (slimy sculpin), 4.7 to 5.7 (brown trout), 5.6 to 6.2 (blacknose dace), and 4.9 to 5.3 (Atlantic salmon).

The Shenandoah National Park FISH Project evaluated the effects of streamwater acidification on fish populations and communities in streams in Shenandoah National Park. Fish species richness, population density, condition factor, age distribution, size, and bioassay survival were all lower in streams having low-ANC compared to intermediate-ANC and high-ANC streams (Bulger et al., 1995; Dennis et al., 1995; Dennis and Bulger, 1995; MacAvoy and Bulger, 1995).

Bulger et al. (2000) developed model-based projections using the MAGIC model to evaluate the potential effect of reductions in S deposition of 40% and 70% from 1991 levels using data from VTSSS and SWAS. Projections were based on four brook trout stream categories: Suitable , ANC >50 µeq/L; Indeterminate, ANC 20 to 50 µeq/L; Marginal, ANC 0 to 20 µeq/L; and Unsuitable, ANC <0 µeq/L. Three scenarios of future acidic deposition were modeled: constant deposition at 1991 levels, 40% reduction from 1991 deposition levels, and 70% reduction from 1991 deposition levels. Based on observed 1991 ANC values, approximately 30% of all trout streams in Virginia were marginal or unsuitable for brook trout because they were either episodically (24%) or chronically (6%) acidic. In

addition, another 20% of the streams were classified as indeterminate, and brook trout in these streams may or may not have been affected. Based on the model simulations, 82% of these streams would not have been acidic before the onset of acidic deposition and would likely have been suitable for brook trout.

The model projections suggested that neither the 40% nor the 70% reductions in acidic deposition would be expected to increase the number of streams that were suitable for brook trout above the ambient 50%. In fact, the results suggested that a 70% reduction in deposition would be needed in the long-term just to maintain the number of streams that were considered suitable for brook trout. Because of the length of time required to restore buffering capacity in watershed soils, most of the marginal or unsuitable streams were expected to remain marginal or unsuitable for the foreseeable future.

To develop projections of probable past and future responses of aquatic biota to changing S deposition in Shenandoah National Park, the MAGIC model was coupled by Sullivan et al. (2003) with several empirical models that linked biological response to past and future model projections of water quality. Unlike MAGIC, which is a geochemical, process-based model, the biological effects estimates were based on observed empirical relationships rooted in correlation and expressed as linear relationships. Correlation does not necessarily imply cause, but an observed pattern of co-variation between variables does provide a context for analysis of a possible relationship. In this case, the projections did not require extrapolation and are, therefore, statistically robust. To the extent that the observed empirical relationships used in the coupled models do in fact reflect the effects of acid stress on aquatic biota, the projections were also biologically robust.

The geochemical and biological response models also differ in that MAGIC is a dynamic model and explicitly predicts the time course of changing water quality, whereas the empirical relationships used for estimating biological response were static. These relationships reflected a point in time (when the observations were made) and provided no information concerning the dynamics of biological response. That is, the empirical models predicted a new biological status for a new water chemistry, but gave no indication of the time required to achieve the biological status once the water quality change had occurred.

There are thus two considerations that must be kept in mind when interpreting the biological responses predicted using a combination of process-based and empirical modeling approaches: the causality of the relationship between water quality and response, and the dynamics of biological response. With respect to the issue of causality, acidification is a disturbance and disturbance usually lowers species richness. In turn, loss of species usually lowers ecosystem stability. Biodiversity loss is a predictable and proven consequence of acidification, and there are abundant examples of this in North America and Europe (Bulger et al., 2000). With respect to the timing of biological response, it can be variable and difficult to predict.

B.4.2.3. Timing of Recovery from Acidification

Lakes and streams show spatial and temporal variability in response to a host of biotic and abiotic factors. Against this background of variability, it is difficult to detect changes in biological communities in response to changes in an individual environmental stressor without long-term biological data (Schindler, 1990; Lancaster et al., 1996). Long-term data sets are rare, and there are few well-documented instances of temporal changes in biological communities in response to changes in water chemistry. Regardless, it is known that surface water acidification affects virtually all trophic levels (e.g., Flower and Battarbee, 1983; Lancaster et al., 1996; Økland and Økland, 1986; Ormerod and Tyler, 1991; Rundle and Hildrew, 1990; St. Louis et al., 1990; Siminon et al., 1993; Sullivan, 2000a).

Biological recovery can occur only if chemical recovery is sufficient to allow survival and reproduction of acid-sensitive plants and animals. The time required for biological recovery is uncertain. For terrestrial ecosystems, it may be decades after soil chemistry is restored because of the long life of many plant species and the complex interactions of soil, roots, microbes, and soil biota. For aquatic systems, research suggests that stream macroinvertebrate populations may recover relatively rapidly

(within approximately 3 years), whereas lake populations of zooplankton recover more slowly (Gunn and Mills, 1998).

The timing of fish recovery is highly uncertain, and probably will depend heavily on dispersal opportunities. Stocking could accelerate fish population recovery (Driscoll et al., 2001b). Fish populations have recovered in acidified lakes when the pH and ANC have been raised through liming or reduction of acidic deposition (Hultberg and Andersson, 1982; Beggs and Gunn, 1986; Dillon et al., 1986; Keller and Pitblado, 1986; Raddum et al., 1986; Gunn et al., 1988; Kelso and Jeffries, 1988).

Studies in Canada have improved understanding of the feasibility and complexity of biological recovery in response to chemical recovery from acidification. Biological recovery of previously acidified lakes is expected to be a slower process than chemical recovery. Sometimes there are other environmental stresses in addition to acidity, such as metal contamination (Gundersen and Rasmussen, 1995; Havas et al., 1995; Jackson and Harvey, 1995; McNicol et al., 1995; Yan et al., 1996b). Barriers can be imposed by water drainage patterns between lakes that hinder re-colonization by some fish species (Jackson and Harvey, 1995). Predation by non-acid-sensitive fish species can affect the recovery of zooplankton and macroinvertebrate communities (McNicol et al., 1995). Finally, tributary-spawned fish can be preyed upon when they move downstream into lakes inhabited by predatory fish and birds (Schofield and Keleher, 1996).

Changes in surface water chemistry as a direct response to changes in S and N deposition are difficult to predict. Both chemical and biological effects of changing deposition can lag as the ecosystem comes into equilibrium with the modified deposition inputs. Soils or wetlands may continue to release S at a high rate for many years subsequent to a decrease in S deposition. As a result, surface water SO_4^{2-} concentrations may decrease in the future as a consequence of deposition changes that have already occurred. If soil base cations have become depleted, base cation concentrations in some surface waters could decrease in the future irrespective of any further changes in SO_4^{2-} concentrations. This would be expected to contribute to additional acidification.

Studies in the U.S., Canada, and Europe have illustrated the feasibility and complexity of biological recovery in response to decreased surface water acidity. There is currently no theoretical basis on which to predict the paths of biological recovery. At some scale, each stream or river is unique. The null hypothesis is that recovery will proceed in the same fashion as acidification, only backwards. Thus, for example, the last species lost (the most acid-tolerant) would be the first to return. However, time lags are expected to differ widely among species and among water bodies. Biological recovery of previously acidified lakes or streams can lag behind chemical recovery because of such factors as (a) limits on dispersal and recolonization; (b) barriers imposed by water drainage patterns (Jackson and Harvey, 1995); (c) the influence of predation (McNicol et al., 1995); and (d) other environmental stresses (Gunn et al., 1995; Havas et al., 1995; Jackson and Harvey, 1995; McNicol et al., 1995; Yan et al., 1996a,1996b).

Limitations on dispersal and recolonization can hamper biological recovery from chronic and episodic acidification. If fish move into refugia areas during low pH and then return, behavioral avoidance would reduce the overall effect of acidification on fish populations. However, if fish move out of the stream system in response to sublethal episodes, as suggested by Baker et al. (1996), and do not return or return in smaller numbers, then the population level effects of episodic acidification would be greater than predicted based on mortality tests alone.

Stream macroinvertebrate communities are often dominated by immature life stages of flying insects, such as mayflies, dragonflies, and stoneflies. Such species have rather rapid colonization times, such that a functional stream macroinvertebrate community may return in only a few years in response to improved chemistry. However, fish community recovery is expected to be quite variable, depending on sources of colonists. In streams, fish could be introduced as soon as the water quality becomes suitable or the macroinvertebrate community becomes established. In streams that had simple fish communities in the past, a fish community might become rapidly established. It might take decades for complex communities without species introductions.

The Sudbury region of Ontario, Canada has been important for studying the chemical and biological effects of S deposition. Mining and smelting of copper-nickel ore began in the 1880s. By the

1950s and 1960s, SO_2 emissions from the mining and smelting operations peaked at over 5,000 tons/day and extensive acidification of nearby surface waters was documented (Beamish and Harvey, 1972). Emissions of SO_2 then decreased during the 1970s to less than one-third of the peak values. This region has been the focus of extensive chemical and biological effects work since the 1980s (Keller, 1992). Sulfur emission reductions resulted in improved water quality in many lakes (Keller and Pitblado, 1986; Keller et al., 1986), and some fisheries recovery was also documented (Gunn and Keller, 1990; Keller and Yan, 1991). Griffiths and Keller (1992) found changes in the occurrence and abundance of benthic invertebrates that were consistent with a direct effect of reduced lakewater acidity. A more recent assessment of recovery of ecosystems in Canada provided further evidence of biological recovery, but also showed that the spatial extent of recovery was limited to lakes that had been severely acidified by the Sudbury smelter (Jeffries et al., 2003).

Whitepine Lake, located 90 km north of Sudbury, had low pH (5.4) and ANC (1 µeq/L) in 1980 and its fish populations displayed symptoms of acid stress. Acid-tolerant yellow perch (*Perca flavescens*) were abundant, but the more acid-sensitive species lake trout and white sucker (*Catostomus commersoni*) were rare and not reproducing. Fish populations were studied by Gunn and Keller (1990) from 1978 through 1987, and zooplankton were sampled at least monthly during the open-water periods of 1980 through 1988. During the period between 1980 and 1988, pH increased to 5.9 and ANC increased to 11 µeq/L. Young lake trout first reappeared in 1982 and became increasingly abundant throughout the study. The number of benthic invertebrate taxa increased from 39 in 1982/83 to 72 in 1988, and the relative abundance of many of the invertebrates found in 1982 changed along with the changes in water chemistry (Gunn and Keller, 1990). Research at Sudbury clearly documented that chemical recovery of lakes was possible upon reduced emissions and deposition of S, and also that biological recovery, involving multiple trophic levels, would soon follow.

Baker et al. (1990b) used field-based models to test the potential for biological recovery. The models were calibrated from the observed among-lake or among-stream associations between fish status and the chemical and physical characteristics measured in the surface water. The models were generally calibrated using chemistry data collected in conjunction with surveys of fish status. It was assumed that the systems surveyed were at steady state and that the observed status of the fish community was determined by the observed chemical and physical conditions in the lake or stream. For each species considered, the current presence or absence of the species was analyzed as a function of the water quality variables associated with acidification (e.g., pH, Al, Ca^{2+}, ANC, and DOC) using maximum likelihood logistic regression (Reckhow et al., 1987). Models developed from data from the ELS and the ALSC were calibrated against data from Ontario lakes.

The results from the various models were compared to their prediction of the change in the number of Adirondack lakes with unsuitable acid-base chemistry, given a 50% decrease or a 30% increase in S deposition relative to the existing conditions. All the models provided similar results (Figure B-20) with the exception of those that relied on the pCa/pH term to predict fish status. Those models seemed to overestimate the effect of Ca^{2+}, and thus underestimate predicted fish response to changes in acidic deposition.
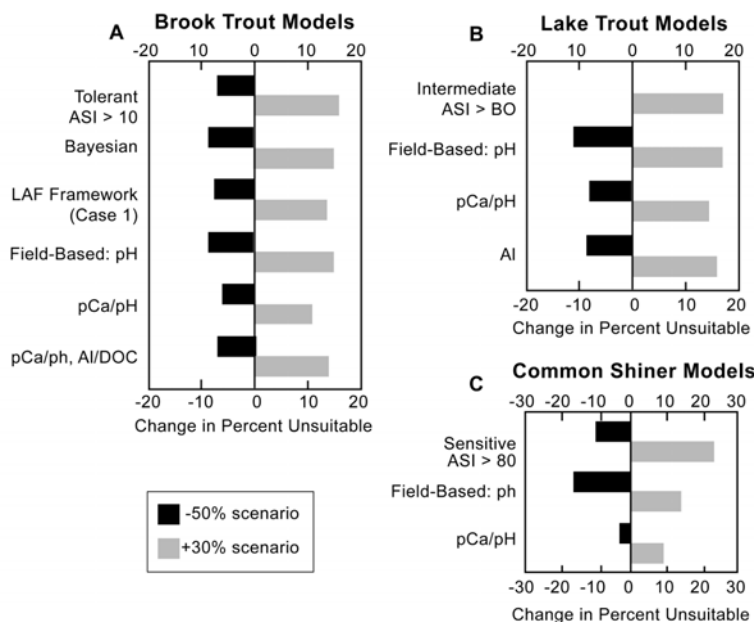
Source: Baker et al. (1990b).

Figure B-20. Example model application. Projected changes in the percentage of Adirondack lakes (Direct/Delayed Response project target population) with acid-base chemistry unsuitable for the survival of fish populations in the year 2034, versus current simulated conditions, based on projected changes in water chemistry from the Model of Acidification of Groundwater in Catchments (MAGIC) and using alternative models of fish response, given a 50% decrease in deposition or a 30% increase in deposition. (a) brook trout, (b) lake trout, (c) common shiner.

An important consideration for measuring the success of S and N emissions controls is the development of appropriate expectations for the magnitude of potential chemical recovery. Most lakes inferred to have been measurably acidified by atmospheric deposition were already marginally acidic, typically with pH less than about 6, before anthropogenic atmospheric pollution began before 1900. Therefore, full recovery of currently acidic lakes would not be expected to yield neutral pH. Nevertheless, increases in ANC may allow recovery of fish populations even if pH remains relatively low (Stoddard et al., 2003).

B.4.3. Effects by Ecosystem Type

B.4.3.1. Terrestrial Ecosystems

Due to a strong dependency on atmospheric deposition and exposure to gaseous compounds as the major sources of nutrients, lichens are affected by changes in these conditions. Vulnerability of lichens to increased N input is generally greater than that of vascular plants (Fremstad et al., 2005). Even in the Pacific Northwest, which receives uniformly low levels of N deposition, changes from acid-sensitive and N-sensitive to pollution-tolerant and nitrophilic lichen taxa are occurring in some areas (Fenn, 2003). In eastern North America and central Europe, areas experiencing relatively high levels of acidic deposition have experienced noticeable reductions in cyanolichen abundance on both coniferous and deciduous trees (Richardson and Cameron, 2004). Effects on lichen species biodiversity are also likely (McCune, 1988; van Haluwyn and van Herk, 2002).

Fenn et al. (2007) speculated that large, pollution-sensitive macrolichens, including epiphytic cyanolichens, will be replaced by N-tolerant species in areas where development expands in western Oregon and Washington into N-limited Coast Range forests. Currently, in the Pacific Northwest, nitrophilic lichen species are common in and around Seattle, Portland, Spokane, the Tri-cities, Salem, Oregon's agricultural lands in the northeast and southwest, and the Willamette Valley (Fenn et al., 2007). The USDA Forest Service website contains information about lichen species pollution tolerance, diversity, and preferred habitat in relation to exposure to N (http://www.nacse.org/lichenair).

In London, epiphyte diversity, including a majority of the lichen taxa, declined in areas where NO_2 surpassed 40 μg/m^3 and NO_X surpassed 70 μg/m^3. Lichens remaining in areas affected by these levels of exposure contained almost exclusively families *Candelariaceae*, *Physciaceae* and *Teloschistaceae* (Davies et al., 2007).

Progressive decline in ectomycorrhizal fungal (EMF) community structure and species richness was observed at five Alaskan coniferous forest sites (white spruce [*Picea glauca*] dominant) along an N deposition gradient (1 to 20 kg N/ha/yr) downwind from a large industrial complex on the Kenai Peninsula. The effects were attributed to both acidification and fertilization processes (Lilleskov et al., 2002). EMF communities are important in tree nutrition and C balance, and EMF trees tend to be dominant in N-limited forest ecosystems. A shift in EMF community structure could result in changes in tree species.

Westman et al. (1985) summarized the literature of negative effects of SO_2 on native plants, including decreased pollen germination and tube elongation in both angiosperms and gymnosperms. It is often difficult to separate the effects of SO_2 exposure on plants from the effects of S deposition. This is because areas that experience high SO_2 exposure generally also receive high S deposition. Kozlowski (1985) summarized relative susceptibility of different trees, lichens, and bryophytes to SO_2.

Available information is not sufficient to draw conclusions regarding the increased likelihood of future effects on the condition of hardwood forests in the Southern Appalachian Mountain region (Sullivan et al., 2002). Certainly, such effects are less likely for hardwood forests than for spruce-fir forests. Red oak seedlings grown in a greenhouse in deciduous forest soils exhibited no response to acidified soil (pH 4.0 from 9:1 H_2SO_4:HNO_3) or to high or low SO_4^{2-} inputs (12.8 to 24.8 mg/L). The lack of response suggested that red oak seedlings are not sensitive indicators of acidification effects from S deposition (McClenahen, 1987).

Grasslands and Alpine Tundra

Alpine communities are considered very sensitive to changes in N deposition, but documented effects in the scientific literature have been attributed to nutrient enrichment, rather than acidification (Seastedt et al., 2004; Bowman et al., 2006). Lower-elevation grasslands, especially those in semi-arid environments, would be expected to be even less sensitive to acidification because of low water leaching potential and the common presence of base-rich Mollisol and Aridisol soils. However, some effects of acidification may be manifested in mesic grasslands.

In a review of SO_2 effects on grasses in the United Kingdom, Bell (1985) suggested that damage can occur at levels as low as 150 μg/m^3. However, he asserted that any ubiquitous critical load value must be modified to include variations due to environmental conditions and combined effects with other pollutants. He also suggested that many grass species exhibit a tolerance to SO_2, resulting from more intraspecific competition in agricultural grasslands. Westman et al. (1985) also provided evidence of the evolution of a tolerant grass species, Bromus rubens, in southern California coastal sage scrub, influenced by an average of 3.7 μmol/m^3 of SO_2 over 25 years.

Studies of SO_2 effects on timothy grass (*Phleum pratense*) showed diminished leaf production and increased leaf senescence in seedlings exposed to 0.120 ppm SO_2 for 35 days (Mansfield and Jones, 1985). In another experiment, Mansfield and Jones (1985) reported that exposure to 0.120 ppm SO_2 in seedlings over 40 days resulted in a 62% reduction in the dry weight of roots and 51% reduction in the

dry weight of shoots, as well as a significant decline in leaf-area ratio (LAR) and specific leaf area (SLA) by the end of the experiment. They suggested that decreased growth and shifts in LAR and SLA could lead to decreased hardiness and increased susceptibility to water stress.

In a 5–year exposure of native mixed prairie grassland in Montana, Lauenroth and Milchunas (1985) exposed grasses to a control (~20 µg/m^3) and three elevated levels of SO_2 (~60, 106, 184 µg/m^3). Year-to-year S accumulation did not appear to occur over the 5–year course of the treatment, though progressive increases in root and rhizome S concentrations were observed seasonally. No significant negative effects on either above-ground net primary productivity or below-ground biomass dynamics in grasses were observed, except a decrease in biomass for *Bromus japonicus*. However, lichen cover declined after 1–year of exposure at the low treatment level. Though no biomass or cover effects were observed at the community level, there were minor population changes. These results are consistent with the nature of semi-arid grasslands that typically adjust well to perturbations (Lauenroth and Milchunas, 1985).

Arid Lands

At the time of the previous AQCD, it was believed that arid and semi-arid ecosystems were not as susceptible to soil acidification and high NO_3^- leaching as are forested ecosystems. This is because of a scarcity of water for NO_3^- leaching, except on an episodic basis, and because arid soils tend to be more alkaline than soils in more humid environments. No new research has altered that conclusion. Arid lands in the U.S. generally receive low levels of S deposition. However, N deposition can be quite high, especially in southern California in the vicinity of the Los Angeles Basin. Little work has been done on the effects of acidification on arid land ecosystems. As reviewed by Fenn et al. (2003), acidification effects have not been demonstrated at the Central Arizona-Phoenix LTER site, despite the almost 30 kg N/ha/yr of deposition received. Nevertheless, N deposition has the potential to increase plant growth and denitrification and alter community composition in arid environments (Egerton-Warburton and Allen, 2000; Allen et al., 2005). Such changes could alter key ecosystem processes and, as such, merit consideration. There has been little research to examine these issues and, therefore, the state of knowledge is similar to what it was in 1993.

B.4.3.2. Aquatic Ecosystem

Chronic Effects

Sulfate

The study of Clow and Mast (1999) is unique in that SO_4^{2-} trends were evaluated with both raw data and data adjusted for existing trends in flow. From 1967 to 1983, Clow and Mast (1999) showed a decreasing trend in SO_4^{2-} concentrations in a Catskill river, no trend in three rivers in Maine, Pennsylvania, and Virginia, and an increasing trend in a river in Ohio. The Maine river did show a decreasing trend before flow adjustment of the data. From 1984 to 1996, however, Clow and Mast (1999) found decreasing trends in SO_4^{2-} concentrations in all five rivers, both with and without flow adjustment. The rivers in Pennsylvania, Ohio, and Virginia were south of the maximum southern extent of glaciation, and therefore were more likely to be subject to the effects of SO_4^{2-} adsorption in soils of their watersheds. In such streams, decreasing S-adsorption on soils would be expected to counteract the effects of decreasing S deposition in terms of effects on stream SO_4^{2-} concentration.

Surface waters in other unglaciated regions exhibited decreasing trends in SO_4^{2-} by the 1980s. Concentrations of SO_4^{2-} in 130 northeastern lakes in 1984 were compared to those in the same lakes in 2001 (Warby et al., 2005). Median concentrations in each subregion were lower in 2001 than 1984, and in the region as a whole, the overall median decrease was 1.53 µeq/L/yr. A decrease in SO_4^{2-} concentrations

that averaged 2.16 µeq/L/yr was also observed in 47 of 48 Adirondack lakes from 1992 to 2004, and a similar decrease of 2.09 µeq/L/yr was observed in a subset of these lakes from 1982 to 2004 (Driscoll et al., 2007a).

The pattern of increasing concentrations of SO_4^{2-} in surface waters before the year of peak S emissions in 1973, followed by widespread decreasing trends in SO_4^{2-} concentrations after the peak (with the only exception being the Blue Ridge Mountain region in Virginia), provides convincing evidence of the link between S emissions and SO_4^{2-} concentrations in surface waters. A similar link has been shown in Europe (Stoddard et al., 1999). On this basis, continued decreases in S emissions would be expected to result in further decreases in SO_4^{2-} concentrations in surface waters, although the rate of response is uncertain due to an incomplete knowledge of S retention mechanisms in terrestrial systems. Also, in a detailed analysis of flow effects on SO_4^{2-} trends, Murdoch and Shanley (Murdoch and Shanley, 2006) found SO_4^{2-} that higher concentrations of SO_4^{2-} occurred at corresponding high, medium and low flows in 2000 to 2002 than in 1997 to 1999 in two of the rivers studied by Clow and Mast (1999), and at high and medium flows in a third river. Continued monitoring of surface waters will be needed to verify a future link between emissions and SO_4^{2-} concentrations in surface waters.

Nitrate

Driscoll et al. (1985) found that NO_3^- concentrations in 20 lakes in the early 1980s in the Adirondack region of New York averaged 12% of SO_4^{2-} concentrations, whereas Lovett et al. (2000) found that baseflow NO_3^- concentrations in 1994–97 were an average of 37% of SO_4^{2-} concentrations in 39 streams in the Catskill region of New York. Average concentrations of NO_3^- in most southeastern streams also tend to be considerably less than SO_4^{2-} concentrations (Webb et al., 2004).

High-frequency sampling in the study of Murdoch and Stoddard (1993) demonstrated the importance of NO_3^- during high-flow conditions in Catskill streams in which concentrations periodically equaled or exceeded SO_4^{2-} concentrations. This study also reported increasing trends in NO_3^- concentrations during the period of 1970 to 1990 in all 16 Catskill streams for which data were available. A similar increase in NO_3^- concentrations was reported for Adirondack lakes in the 1980s (Stoddard et al., 1999). These increasing trends in NO_3^- concentrations were attributed to N saturation in response to atmospheric deposition (Aber et al., 1998).

The relationship between N deposition and surface water NO_3^- concentrations up through the 1980s suggested that continued N deposition would further the accumulation of N in terrestrial ecosystems and drive continued increases in surface water NO_3^- concentrations. However, more recent information on NO_3^- concentrations have been less consistent with the concept of N saturation. Goodale et al. (2003) resampled New Hampshire streams in 1996–97 that had been previously sampled in 1973−74 and found substantially lower NO_3^- concentrations in the more recent sampling, despite two decades of relatively stable levels of deposition to otherwise undisturbed forests. The lower NO_3^- concentrations could not be accounted for by differences in flow or forest succession, but interannual climate variation was proposed as a possible cause. The long-term record of dissolved inorganic N (which is largely NO_3^-) concentrations at the HBEF showed a similar pattern; high concentrations in the late 1960s and 1970s, followed by decreases to minimum values in the mid-1990s (Aber et al., 2002). These authors attributed this pattern to a combination of environmental factors, but did not identify a single most important control variable. A reversal from increasing trends in NO_3^- concentrations in the 1980s to decreasing trends in the 1990s was also observed in Adirondack lakes (Driscoll et al., 2003a). A small decrease in atmospheric deposition of N also occurred in this region through the 1990s, but was not considered sufficient by these authors to explain the decreasing trend in lakewater NO_3^- concentrations. Rather, they proposed that increased concentrations of atmospheric CO_2 may have resulted in a fertilization effect that increased N assimilation (Driscoll et al., 2007a).

In general, trends in surface water NO_3^- concentrations during the 1990s were much smaller than trends in SO_4^{2-}, with the only ecologically significant changes occurring in the two regions with the highest ambient NO_3^- concentrations. Lakes in the Adirondacks and streams in the Northern Appalachian

Plateau both exhibited small but significant downward trends in NO_3^- in the 1990s (Table B-6). Both of these regions are central to the debate over whether N saturation is a legitimate threat to the health of forests and surface waters (Aber et al., 1998; Stoddard, 1994). While declining NO_3^- concentrations in these regions is a positive development for these ecosystems, it is not known if these trends will continue, especially because they do not appear to reflect changes in N emissions or deposition. The presence of strong upward trends in NO_3^- in these same regions in the 1980s (Murdoch and Stoddard, 1992; Stoddard, 1994) suggests that trends measured on the scale of a single decade may reflect variability in long-term patterns of changing NO_3^- leakage from forested watersheds. Such patterns are controlled by factors that may take many years of additional research to determine. While great uncertainty exists and the time scales of N saturation may be longer than previously considered (e.g., centuries rather than decades), the long-term retention of N deposition in forested regions is unlikely to continue indefinitely (Aber et al., 2003).

In New England and the Upper Midwest, where ambient NO_3^- concentrations are much lower than in the Adirondacks and Northern Appalachian Plateau, NO_3^- concentrations in surface waters were unchanged during the 1990s. The Ridge/Blue Ridge province registered a small, but significant, decrease in NO_3^- during the 1990s, but interpretation of trends for NO_3^- in this region is complicated by an outbreak of gypsy moths that also occurred during this period. Forest defoliation by gypsy moths was the most likely cause of a pulse in NO_3^- export from many streams in this region in the mid-1990s (Eshleman et al., 1998).

Some evidence of climate effects on long-term trends in NO_3^- concentrations in surface waters was provided by studies of Mitchell et al. (1996) and Murdoch et al. (1998). A synchronous pattern in NO_3^- concentrations was observed from 1983 to 1993 in four small watersheds in New York, New Hampshire, and Maine, which included anomalously high concentrations during the snowmelt period of 1990. The region-wide spike in NO_3^- concentrations followed an unusually cold December that may have disrupted soil N cycling processes (Mitchell et al., 1996). Murdoch et al. (1998) also found that mean annual air temperatures were strongly related to average annual NO_3^- concentrations in most years in a Catskill watershed with elevated NO_3^- concentrations in stream water. Those relationships were explained by microbial control of N release in watersheds that were considered to be N-saturated.

Efforts to explain the decreasing trends in NO_3^- concentrations under conditions of reasonably stable atmospheric N deposition have focused on terrestrial N cycling and N-saturation theory. However, processes within lakes may have also played a role in the trends in Adirondack lakes. In a study of 30 of the 48 lakes studied by Driscoll et al. (2003a; 2007a), Momen et al. (2006) found that concentrations of NO_3^- were inversely correlated with concentrations of Chl a in 11 lakes, and that Chl a was increasing in concentration in 9 lakes. The increase in pH observed in most of these lakes may have stimulated productivity so that N assimilation by plankton increased (Momen et al., 2006).

Thus, there is little or no apparent relationship between recent trends in N deposition and trends of NO_3^- concentrations in surface waters, in sharp contrast to S deposition and SO_4^{2-} concentrations. Rather than disprove the concept of N-saturation; however, these studies more likely reflect the complexities of N utilization within terrestrial and aquatic ecosystems. These complexities create considerable uncertainty with regard to how future trends in NO_3^- concentrations in surface waters will respond to changing levels of deposition.
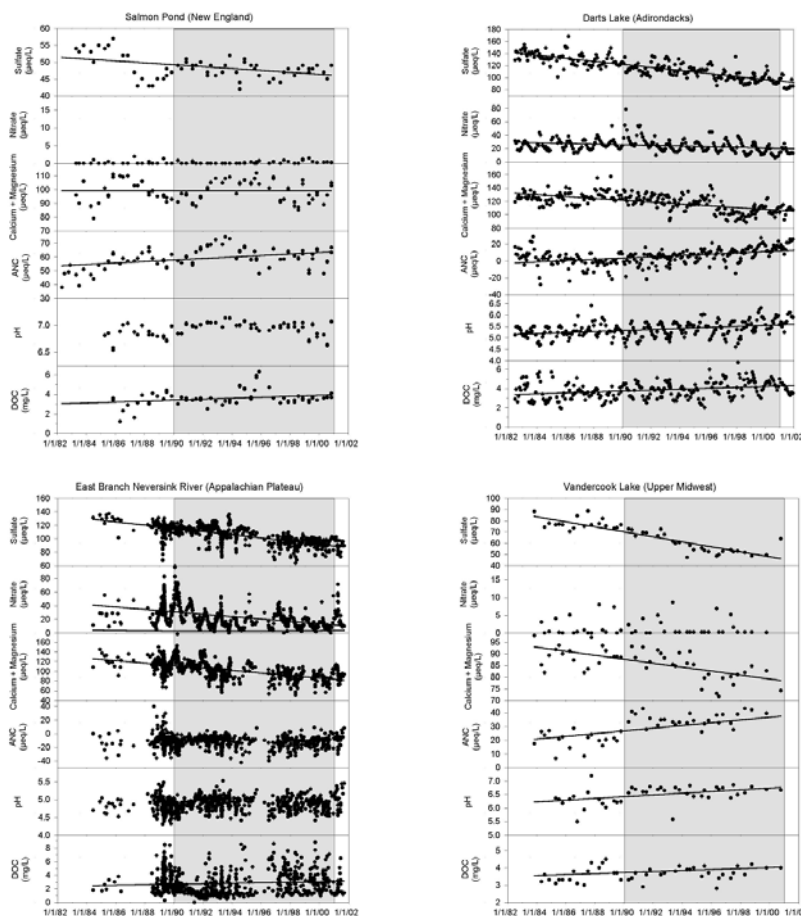
Figure B-21. Time series data for SO₄²⁻, NO₃⁻, base cations [Ca²⁺ + Mg²⁺], Gran ANC, pH, and DOC in example Long Term Monitoring Lakes and streams that have relatively low ANC. The example surface waters include Salmon Pond, Maine (New England region); Darts Lake, NY (Adirondack region); East Branch Neversink River (Appalachian Plateau region); and Vandercook Lake, Wisconsin (Upper Midwest region). Significant trends are indicated by trend lines. Shaded box indicates time period of analyses reported by Stoddard et al. (2003).

Base Cations

The earliest trends of base cation concentrations in acid-sensitive surface waters of the U.S. were presented by Stoddard (1991) for 12 streams in the Catskill region. In 5 of 12 streams, concentrations of $(Ca^{2+} + Mg^{2+})$ increased from 1915–22 to 1945, but decreased from 1945–46 to 1990. In the remaining seven streams, concentrations increased during both periods, but at a lower rate in the more recent period in five of the seven streams. In streams that showed an increase in concentrations during both periods, the average rate of increase from 1915 to 1922 was 2.8 µeq/L, whereas the average rate of increase from 1945 to 1990 was 1.2 µeq/L. Data on SO_4^{2-} trends were not available for the early period, but the trends in $(Ca^{2+} + Mg^{2+})$ concentrations were consistent with the expected pattern of high rates of cation leaching during the early stages of acidification from S deposition.

Clow and Mast (1999) observed trends in $(Ca^{2+} + Mg^{2+})$ concentrations that were generally consistent with SO_4^{2-} trends in five eastern rivers from 1968 to 1983. Decreasing trends in concentrations of $(Ca^{2+} + Mg^{2+})$ and SO_4^{2-} concentrations were observed in a Maine river, and increasing trends in $(Ca^{2+}$

+ Mg^{2+}) and SO_4^{2-} concentrations were observed in an Ohio river. None of the three other rivers showed a decrease in concentrations of (Ca^{2+} + Mg^{2+}), and only one showed a decreasing trend in SO_4^{2-} concentrations. For the period 1984 to 1996, the trend in SO_4^{2-} concentrations was negative in the Ohio River and the concentrations of (Ca^{2+} + Mg^{2+}) showed no trend. Also, a negative trend in (Ca^{2+} + Mg^{2+}) concentrations in a Virginia river was coupled with a negative trend in SO_4^{2-} concentrations. Relations for the other three rivers were similar to the earlier period of 1984 to 1996.

The study of Likens et al. (1996) evaluated trends in base cations in relation to trends in (SO_4^{2-} + NO_3^-) in the long-term record for the HBEF. This record showed an approximately linear, increasing relationship between concentrations of base cations and (SO_4^{2-} + NO_3^-) from 1964 to 1969, then a reversal in 1970 to a decreasing trend up to 1994. The slope of the phase with increasing anion concentrations was steeper than the slope for the phase with decreasing anion concentrations. This indicates lower base cation leaching per equivalent of mobile anion, and therefore suggests depletion of base cations stored in soil. The study of Lawrence et al. (1999b) showed decreased concentrations of base cations at a rate that exceeded decreases in (SO_4^{2-} + NO_3^-) in Catskill streams from 1984 to 1997. In streams within western Virginia and in Shenandoah National Park, concentrations of base cations did not exhibit significant trends from 1988 to 2001, perhaps due to the influence of S adsorption on streamwater SO_4^{2-} concentrations.

Regional declines in base cation concentrations were measured in the LTM Program from 1990 to 2000 in New England lakes, Adirondack lakes, Appalachian streams, and upper Midwest lakes (Stoddard et al., 2003). These results were consistent with decreased Ca^{2+} concentrations measured by Warby et al. (2005) in 130 acid-sensitive lakes in the Northeast between 1984 and 2001. The rate of decrease identified by Warby et al. (2005) for base cations (1.73 μeq/L) was somewhat less than the rate of decrease in SO_4^{2-} concentrations (1.53 μeq/L). Driscoll et al. (2007), also documented decreasing trends in base cation concentrations in 16 Adirondack Lakes from 1982 to 2004, and similar rates of decrease in 48 lakes (including the 16) from 1992 to 2004.

In summary, decreases in base cation concentrations over the past two to three decades are ubiquitous and closely tied to trends in SO_4^{2-} concentrations in acid-sensitive regions of the U.S. Reports of increases in concentrations of base cations in acid-sensitive regions were not found in the literature. In most regions, rates of decrease for base cations have been similar to those for SO_4^{2-} and NO_3^-, with the exception of streams in Shenandoah National Park. Decreasing trends of base cation concentrations do not necessarily indicate further acidification or recovery of surface waters, but do indicate lower leaching rates in soils, a prerequisite for recovery of soil base saturation. However, decreased concentrations of base cations, particularly Ca^{2+}, would also be expected to lower productivity in oligotrophic surface waters.

Acid Cations

Measurements of pH (sometimes expressed as H^+) have been routinely collected in surface waters in the U.S. where effects of acidic deposition have been monitored, but a long-standing reliance on titrated ANC rather than pH as the primary chemical measurement has limited the amount of pH data published. The longest continuous record of pH in surface waters dates back to 1963 at the HBEF (Driscoll et al., 2001b). This record shows an overall increasing trend from 1963 to 1994, although most of the increase occurred after 1980. In Adirondack lakes, 12 of 16 monitored from 1982 to 2004 showed an increase in pH, but the rates of change among lakes were highly variable, and one lake showed a decrease in pH (Driscoll et al., 2007a). When expressed as H^+ concentration, the average increase for the 12 lakes was 0.18 μeq/L/yr. In this same region, pH also increased in 31 of 48 lakes (including the 16 lakes monitored from 1982) from 1992 to 2004. Two lakes showed increases in pH over the 12 years.

Comparison of pH measurements of 130 lakes in 1984 and in 2001, in the northeastern U.S., showed an overall average increase in pH of 0.002 units (Warby et al., 2005). However, in this assessment, lakes in the Adirondack region did not show a significant increase, nor did lakes in central New England, or Maine. The Catskill/Poconos region of New York and Pennsylvania showed an average

increase of 0.008 pH units per year, and southern New England showed an average increase of 0.002 pH units per year. Through continuous monitoring from 1990 to 2000, Stoddard et al. (2003) found a decrease in H^+ (0.19 μeq/L/yr) similar to that observed in the same Adirondack lakes by Driscoll et al. (200a7) from 1992 to 2004 (0.18 μeq/L), and an increase in Appalachian streams (0.08 μeq/L/yr) and Midwest lakes (0.01 μeq/L/yr). No trends were found in New England lakes or Blue Ridge streams in Virginia in this study. Stream monitoring in the Adirondack region from 1991 to 2001 showed an increase in H^+ in one stream, no trend in a second stream, and also an increase in a third stream near the outlet of a lake (Lawrence et al., 2004). In summary, decreasing trends in pH in surface waters are common through the 1990s up to 2004, but many exceptions occur, and overall, the rates of change have been small.

The discovery that Al_i was toxic to aquatic life resulted in a considerable amount of data on Al concentrations in surface waters in the 1980s, but most of this sampling was done either once or for a limited period of time (Johnson et al., 1981; Driscoll and Newton, 1985; Driscoll et al., 1987; Lawrence et al., 1987; Cronan et al., 1990). Monitoring of Al_i concentrations was begun in 16 Adirondack lakes in 1982 and expanded to 48 lakes in 1990. From 1982 to 2004, 5 of the original 16 Adirondack monitoring lakes showed decreasing trends in Al_i concentrations at rates that ranged from 0.02 μM/yr to 0.18 μM/yr (Driscoll et al., 2007a). From 1992 to 2004, 24 of the 48 lakes showed decreasing trends in Al_i concentrations (Driscoll et al., 2007a). The analysis of Stoddard et al. (2003) also observed an average decrease in Al_i concentrations from 1990 to 2000 in the same group of Adirondack lakes reported on by Driscoll et al. (2007a), but observed no trend for this period in New England lakes, Appalachian streams, or Midwest lakes.

Monthly stream chemistry monitoring at the HBEF showed decreases in Al_i concentrations at four locations along the reference stream for the experimental forest from 1982 to 2000, but no trends at two other locations along this stream (Palmer et al., 2004). These data also showed a surprising decrease in pH at two of the locations where Al_i decreased, and no pH trend at the other two locations where Al_i decreased (Palmer et al., 2004). Comparison of total Al concentrations in 130 lakes in the northeastern U.S. in 1984 with those measured in 2001 showed lower average concentrations in 2001 in the Adirondack region, the Catskill/Pocono region, central New England, southern New England, and Maine (Warby et al., 2005). Because these measurements are of total Al, they are not directly comparable to Al_i. Most recently, Lawrence et al. (in review) found that 49 of 195 streams (25%) during August base flow in the western Adirondack region had Al_i concentrations above 2.0 μM, the level above which toxic effects on biota have been shown (Driscoll et al., 2001b; Baldigo et al., 2007).

Acid Neutralizing Capacity

In response to reduced levels of acidic deposition required by the CAA and other emissions control legislation, Stoddard et al. (2003) found trends during the 1990s toward increasing Gran ANC (Figure B-21) in all of the glaciated regions of the eastern U.S. (i.e., New England, Adirondacks, Northern Appalachian Plateau) and Upper Midwest, and decreasing Gran ANC in the Ridge/Blue Ridge province. Changes were relatively modest compared with observed reductions in SO_4^{2-} concentrations. Only the regional increases in the Adirondacks, Northern Appalachian Plateau, and Upper Midwest were statistically significant (Figure B-21). Median increases of about +1 μeq/L/yr in the Northern Appalachian Plateau, Adirondacks and Upper Midwest represent significant movement towards ecological recovery from acidification (Stoddard et al., 2003).

It has been hypothesized that decreases in acidic deposition will yield the most chemical recovery in lakes and streams that have experienced the most severe acidification. Using data from all of the sites in regions where decreases in surface water SO_4^{2-} and NO_3^- have occurred, Stoddard et al. (2003) found that acidic lakes and streams exhibited a highly significant median increase in Gran ANC of +1.3 μeq/L/yr during the 1990s. Low-ANC sites (0 to 25 μeq/L) showed a smaller significant median ANC increase of +0.8 μeq/L/yr. Moderate ANC sites, those with mean ANC values greater than 25 μeq/L, showed no significant change in Gran ANC (Figure B-21).

All of the glaciated regions in the eastern U.S. showed declines in base cation ($Ca^{2+} + Mg^{2+}$) concentrations during the 1990s, with the average changes in the range of −1.5 to −3.4 µeq/L/yr. All of the regional trends were highly significant (Figure B-21). Across the eastern U.S., surface water SO_4^{2-} has decreased at a rate of about −2.5 µeq/L/yr (the mean of regional median slopes), and NO_3^- at a rate of −0.5 µeq/L/yr, in surface waters on glaciated terrain during the 1990s. These rates of change set an upper limit to our expectation of ANC recovery of +3 µeq/L/yr (i.e., the sum of SO_4^{2-} and NO_3^- trend magnitudes). The Gran ANC increase reported by Stoddard et al. (2003) was actually about one-third of this maximum, +1 µeq/L/yr. The difference between the observed Gran ANC trend and the maximum trend estimated from rates of acid anion change can largely be explained by the average regional median decline in ($Ca^{2+} + Mg^{2+}$ concentrations, which was about −2.0 µeq/L/yr (Stoddard et al., 2003).

Episodic Effects

Episodic acidification can result naturally from the mobilization of organic acids and from dilution of base cation concentrations, but decreases in pH and ANC associated with increases in SO_4^{2-} and NO_3^- are largely attributable to acidic deposition (Wigington et al., 1996). Episodic acidification is most common in the early spring and late fall as a result of snowmelt and rainstorms, and is least common in summer, when high flows tend to be infrequent. Seasonal variations in stream flow also result in seasonal patterns of surface water chemistry at base flow. Lakes and streams at base flow tend to be more acidic in early spring than at other times of the year and low flows in late summer tend to be least acidic (Lawrence et al., 2007).

The transient nature of high flows makes episodic acidification difficult to measure. Therefore, assessments have generally estimated the number of lakes and streams prone to episodic acidification by combining episode information from a few sites with base flow values of ANC determined in large surveys (Eshleman et al., 1995; Bulger et al., 2000; Driscoll et al., 2001b). Inclusion of episodically acidified water bodies in regional assessments substantially increases estimates of the extent of surface water acidification. For example, baseflow samples collected from 1991 to 1994 through the U.S. EPA TIME Program indicated that 10% of the 1,812 lakes (>1 ha surface area) in the Adirondack region of New York could be considered chronically acidic on the basis of ANC values less than 0 µeq/L, but that an additional 31% of these lakes had baseflow ANC values less than 50 µeq/L and were, therefore, estimated to be susceptible to episodic acidification (Driscoll et al., 2001b). Lawrence (2002) also estimated the extent of episodically acidified stream reaches in a Catskill, NY watershed (area = 85 km²) through the use of an index site at the base of the watershed that became episodically acidified at high flows. Upstream sites with a lower base flow ANC than the index site at the same date and time were found to have a high likelihood of becoming episodically acidified. Base flow sampling of 122 upstream sites indicated that approximately 16% of the total upstream reaches were chronically acidified (ANC <10 µeq/L), but that 66% of the stream reaches became episodically acidified.

Stoddard et al. (2003) compared seasonal data from New England lakes, Adirondack lakes and Northern Appalachian streams, collected monthly to quarterly, to evaluate the difference between the chemistry of surface waters in the summer and in the spring. Results indicated that spring values of ANC were an average of 30 µeq/L lower than summer ANC. This study referred to samples collected in spring as "episodic samples," although sampling was done independent of flow. Therefore, the 30 µeq/L difference should be considered a seasonal effect rather than an episodic effect.

The most thorough characterization of episodic variations in stream chemistry was conducted through the ERP, in which 13 low-order streams (watershed areas less than 24 km²) in the Adirondack and Catskill regions of New York, and the Appalachian Plateau in Pennsylvania were monitored from 1988 to 1990 (Wigington et al., 1996). Acid episodes with chemical concentrations within the 90th percentile involved decreases in ANC of up to 200 µeq/L, decreases in pH of up to one unit, and increases in concentrations of Al_i of up to 15 µM (Wigington et al., 1996). Results also showed that acid episodes reduced the size of fish populations and eliminated acid-sensitive species if median high-flow pH was less than 5.2 and Al_i concentrations exceeded 3.7 µM, despite the relatively short duration of episodes (Baker

et al., 1996). Baker et al. (1996) concluded that effect on biota from episodic acidification were likely to be similar to those from chronic acidification. Elimination of an annual age class can result from an episode that occurred in the presence of a sensitive life stage. Largely on the basis of this study, the EPA concluded that reversal of effects from episodic acidification could be used as a key ecological endpoint for an acid deposition standard for protection of the environment (U.S. EPA, 1995a).

Despite the significance of the findings of ERP, little assessment or monitoring of episodes was done in the 1990s. One exception was the work of Hyer et al. (1995) in three watersheds of differing geology in Shenandoah National Park. Results suggested that episodic acidification was occurring throughout the park on all bedrock types, although acidification was not sufficient to cause elevated Al concentrations. Lawrence (2002) also documented severe episodic acidification in August 1998 in a tributary of an ERP stream, where Al_i concentrations increased from 1.6 to 7.3 μM in 6.5 h.

In the first large-scale study designed to sample streams during high-flow conditions, Lawrence et al. (2007) found that 124 out of 188 (66%) western Adirondack streams were prone to acidification to the level at which Al_i becomes mobilized. Only streams accessible with less than a 60–min hike were sampled in this study. The March, 2004 survey was chosen to represent episodic conditions, and a survey conducted August 16–18, 2004 was chosen to represent base flow conditions. Based on this comparison, 35% of the streams were chronically acidified, 30% of the streams were episodically acidified, and 34% were not acidified. Survey results were also used to estimate that 718 km of stream reaches were prone to acidification, although 3085 km of stream reaches within the study region could not be assessed because of inaccessibility.

There have been no studies in the U.S. that determine if either the severity or frequency of episodic acidification has lessened. In a study of two streams in Nova Scotia (Laudon et al, 2002), trends in ANC in four phases of storm hydrographs from 1983 to 1998, were not detected other than in the peak-flow phase of one stream (an increase of 0.87 μeq/L). In Sweden, the anthropogenic contribution to episodic decreases in ANC were estimated to range from 40 to 80% in five streams from 1990 to 1999 (Laudon et al, 2002).

B.5. Effects on Watersheds and Landscapes

B.5.1. Interactions among Terrestrial, Transitional, and Aquatic Ecosystems

Acidification has pronounced effects on nutrient cycling in terrestrial, transitional, and aquatic ecosystems. Of particular importance in this regard is the role of N deposition in influencing N cycling. This topic is discussed in detail in Section 5. Also important are the influences of acidification on the availability of Ca^{2+} and other nutrient base cations (Mg^{2+}, K^+).

In general, decomposition, nutrient cycling, productivity, and other system-level processes in surface waters are not as sensitive as species composition and richness to relatively small amounts of acidification. Such effects only seem to occur at high levels of acidification (e.g., pH <5). This is because acid-sensitive species are often replaced by more acid-tolerant species that perform the same function until acidification becomes severe. For example, whereas changes in microbial composition and abundance have been observed with acidification, they appear to have minimal effect on overall microbial respiration and nutrient cycling. At extreme levels of acidity, however, these system-level functions may also decrease. Thus, system-level functions are not generally good indicators of light to moderate levels of acidification.

Integrating the effects of atmospheric deposition across spatial scales is difficult. The response of a single plant, or small group of plants, cannot be easily scaled up to examine effects on plant communities, ecosystems, watersheds, or geographic regions. Integration typically requires a combination of approaches, including ecosystem modeling, experimental manipulation studies, surveys across pollution deposition gradients, and long-term monitoring studies. Similarly, aquatic effects at the population level can be readily quantified, but extrapolation to the community or aquatic ecosystem level is problematic. Linking research results across scales will be an important component of future research. Measurements that correlate with ecosystem processes, such as foliar N concentration, leaf area index, or spectral reflectance, can in some cases be remotely sensed. They offer great promise for future assessment of terrestrial effects across spatial scales.

Effects of atmospheric deposition of acidifying substances on soil, vegetation, and surface water are manifested in specific processes, affecting energy, water and nutrient flow, intra- and inter-species competitive interactions, and ecosystem primary production. Therefore, effects on sensitive species (only some of which have been documented) have the potential to cascade throughout the ecosystem and become manifested at a variety of scales. Such ecosystem- to landscape-scale effects from atmospheric deposition of acidifying substances are known to occur, but the results of these interacting processes have not been conclusively demonstrated.

It is also evident that acidification from natural and human-caused disturbances, including climatic stressors (temperature, moisture availability, wind), insect infestation, disease, fire, and timber harvest, can affect the severity of effect of atmospheric deposition of SO_X and NO_Y. Although it is clear that such interactions can occur, there are no studies that have clearly documented that acidic deposition at levels that commonly occur across broad landscapes in the U.S. has conclusively altered ecosystem structure or function. Similarly, although it is widely believed that acidic atmospheric deposition can make plants more susceptible to the adverse effects of other natural and human-caused stressors, such effects have not been conclusively demonstrated in more than a few cases. The data demonstrating and quantifying the extent to which SO_X and NO_Y deposition are altering natural terrestrial ecosystems via acidification pathways are sparse. In particular, effects of soil and soil water acidification on soil ecosystem processes and nutrient cycling are poorly known. Even less is known about effects on soil microorganisms and food webs, or how such effects interact with the above-ground vegetation community.

B.5.2. Interactions with Land Use and Disturbance

The prevailing scientific consensus during the 1980s held that most lakes in eastern North America that had pH less than about 5.5 to 6.0 had been acidified by acidic deposition. Reports that acidic lakes and streams were rare or absent in similar areas not receiving acidic deposition were used as evidence of acidification by acidic deposition in many regions (e.g., Baker et al., 1991b; Murdoch and Stoddard, 1992; Neary and Dillon, 1988; Sullivan et al., 1988). An alternative hypothesis had been advanced by Rosenquist (1978), Krug (1989, 1991), and Krug and Frink (1983) that land use changes could explain recent lake acidification in southern Norway and the northeastern U.S. According to this hypothesis, natural soil processes and changes in vegetation can generate more acidity than is received from atmospheric deposition. For example, an increase in acidic humus formation in response to decreased upland agriculture was suggested as being responsible for regional acidification in southern Norway, rather than acidic deposition (Rosenqvist, 1978). Subsequent acidic deposition effects research in some cases seemed to be designed to refute this hypothesis rather than to explore the relationships between land use and acid-base chemistry (cf. Havas et al., 1984; Birks et al., 1990). Research intended to discriminate between acidic deposition and land use as the major cause of acidification generally concluded that acidic deposition was the principal cause of regional acidification in certain areas of North America and Europe. Perhaps more appropriate research questions might have focused on quantifying the relative importance of land use activities or landscape change in exacerbating or ameliorating acidic deposition effects. The

importance of acidic deposition as an agent of acidification does not preclude the importance of land use and landscape changes which, in some cases, may actually be more important than acidic deposition (Sullivan et al., 1996b).

There has not been a regional evaluation of land use changes in areas of the U.S. susceptible to surface water acidification from acidic deposition. It has therefore not been possible to quantify the extent or magnitude of land use effects on acidification. It is clear, however, that such changes can have important effects on acid-base status (Sullivan, 2000a), especially as influenced by N deposition (Goodale and Aber, 2001).

Changes in human land use activity, and associated changes in vegetative structure, influence ecosystem response to external stressors such as acidic deposition, exposure to O_3, natural disturbance factors such as wind and fire, and climatic changes. Some activities contribute to the acidification of soil and surface waters; other activities decrease acidity (Sullivan et al., 1996b) (Table B-21).

Forest management practices, especially those that have occurred over many generations of trees, can have important effects on soil erosion, nutrient supplies, and organic material. Such effects can influence the availability of base cations for acid neutralization and/or aspects of N cycling.

Forests are efficient at scavenging S and N from the atmosphere. Differences in forest canopy, particularly between deciduous and coniferous trees, can cause large differences in dry deposition, and therefore total deposition of S and N. In regions that receive high levels of acidic deposition, the presence of forest vegetation, especially coniferous trees, enhances total deposition of acid-forming precursors (Rustad et al., 1994). In addition to the enhanced deposition caused by the presence of large trees, there are also differences in nutrient uptake. In particular, younger trees take up larger quantities of N and other nutrients than do trees in older forests. Therefore, changes in the occurrence and age or species composition of the forest can influence the rates of atmospheric deposition to the site as well as the fate of atmospherically deposited substances.

Landscape processes and watershed disturbance can influence soil and water acidification in many ways. Land use practices and vegetation patterns have been changing in various parts of the U.S. for decades to centuries. These changes in human activity can influence the response of forested ecosystems to external stressors, including atmospheric deposition of S or N, natural disturbance factors such as wind and fire, and climatic changes. Some processes contribute to the acidification of soil and surface waters or reduce the base saturation of the soils thereby increasing their sensitivity to acidic deposition. Other processes cause decreased acidity (Sullivan et al., 1996b; Sullivan, 2000a).

Watershed disturbance from logging, blowdown, and fire disrupts the normal flow of water and can cause increased contact between runoff water and soil surfaces, leading to increased base cation concentration and ANC in drainage water. Recovery from disturbance can cause a decrease in drainage water ANC as the system returns to pre-disturbance conditions. In particular, soil loss through erosion can reduce the base cation pool size, thereby limiting the capacity of soils to neutralize atmospheric acidity. In addition, forest harvesting has an important effect on forest N-demand, thereby reducing the likelihood of future N-saturation in response to high N deposition. Forest management practices, especially those that have occurred over many generations, have had important effects on soil chemistry, nutrient supplies, and organic material.

Watershed disturbances, including road building, agriculture, mining, urbanization, logging, blowdown, and fire can alter various aspects of ecosystems biogeochemistry. Such disturbances can influence the water budget, base cation mobilization, routing of drainage water, nutrient input, and S and N cycling in ways that affect the acid-base chemistry and nutrient dynamics of soils and drainage waters (Sullivan et al., 1996b). The effects of such disturbances can greatly modify the response of a given watershed to atmospheric inputs of S and N.

B.5.2.1. Timber Harvest

Removal of the forest affects drainage water quality in several ways. Deposition of S and N are reduced; leaching of NO_3^- increases and, in some cases, causes a pulse of surface water acidification. Base cations tied up in wood are lost when wood is transported off-site. Regrowth of the forest may further affect drainage water quality through vegetative uptake of N and base cations. Trees accumulate base cations to a greater degree than anions. To balance the charge discrepancy, roots release an equivalent amount of protons and acidify the soil. Base cation accumulation by trees is age-dependent. Young forests grow faster and are therefore more acidifying than older forests (Nilsson et al., 1982; Nilsson, 1993). They also retain greater amounts of N.

Most forests in the northeastern U.S. are recovering from extensive human disturbance that occurred over a period of about 200 years. Landscapes were mainly forested during pre-colonial times, logged or cleared for agriculture in the mid to late 19th century, and are now largely early to mid-seral stage regenerating forests (Niering, 1998).

In some areas that experience relatively high levels of acidic deposition, there is growing concern about sustainable timber productivity (Adams, 1999). Harvest-induced leaching losses have been estimated to range from 6 to 60 kg/ha/yr of N, 28 to 48 kg/ha/yr of Ca^{2+}, and 7 to 16 kg/ha/yr of Mg^{2+} (Federer et al., 1989). Timber harvesting also increases leaching losses from the site because of the reduction in transpirational water loss. The increased water flux after tree removal increases the opportunity to leach base cations from the soil.

If base cations sequestered in tree wood are removed from the site by tree harvesting, the result is a decrease in the available base cation pool on the site. Physical disturbances to forest soils during logging operations and increased soil temperature that results from exposure of the forest floor to sunlight may also cause a short-term increase in the rates of N mineralization and nitrification (Joslin et al., 1992). The resulting increase in NO_3^- production and leaching further depletes base cations from the soil pool.

Johnson et al. (1991a) measured short-term (3 years) effects of logging at HBEF in New Hampshire on soil acid-base chemistry. Base saturation of the mineral soil Bh horizon decreased from 14 to 11% and pH decreased by 0.24 pH units.

Likens et al. (2002) reported results of a 34–year study of the biogeochemistry of forest ecosystems at HBEF. Part of the study evaluated the effects of tree removal on S cycling and related biogeochemical processes. Vegetation removal resulted in increased decomposition of organic matter and nitrification. These changes, in turn, lowered soil water pH, enhanced SO_4^{2-} adsorption on mineral soil, and therefore decreased the flux of SO_4^{2-} in stream water. With subsequent vegetation regrowth, the adsorbed SO_4^{2-} was released from the soil to drainage water, and streamwater SO_4^{2-} concentrations increased.

Baldigo et al. (2005) compared the effects of clear-cut and timber-stand improvement (TSI) harvests on water chemistry and mortality of caged brook trout in three Catskill Mountain streams. Harvests removed 73% of tree basal area from a clearcut subbasin, 5% basal area from a TSI subbasin, and 14% basal area at a site below the confluence of both streams (the combined effect of the two harvest methods). Water quality and trout mortality were affected only in the clearcut stream. Acidity and concentrations of NO_3^- and Al_i increased sharply during high flows after the first growing season (1997). Acid-Al_i episodes were severe during this period and decreased steadily in magnitude and duration thereafter. All trout at the clearcut site died within 7 days during spring 1998, and 85% died during spring 1999. Only background mortality was observed in other years at this site and at the other three sites during all tests. The effects of tree harvests on fish communities are of concern because they might interact with effects of acidic deposition and produce more substantial effects on biota than either stress factor on its own.

B.5.2.2. Insect Infestation

Effects of insect-caused defoliation on the N cycle can be pronounced. The foliar N consumed by insects is deposited on the forest floor as insect feces (frass), greenfall, and insect biomass. Some of this deposited N is subsequently taken up by tree roots and soil microbes, with little effect on the nutritional condition of the trees or the site. Where a sizable component of this N is leached in drainage water, the nutritional consequences can be more significant. There are also various feedback mechanisms. For example, low N supply can slow the population growth of defoliating insects (Mason, 1992) and enhance the tree's chemical defenses against insects (Hunter and Schultz, 1995). The amount of N leaching loss is generally small, relative to atmospheric deposition inputs and relative to the amount of N transferred to the forest floor with the defoliation (Lovett and Ruesink, 1995; Lovett et al., 2002). Nevertheless, it can be high enough to contribute to base cation depletion of soils and effects on downstream receiving waters. The extent of NO_3^- leaching may be partly related to the extent of defoliation and tree mortality that occurs and also the amount of precipitation that occurs immediately after the defoliation (Lovett et al., 2002).

Forest insect infestation can have profound effects on the acid-base and nutrient chemistry of soils and drainage waters. Effects of a gypsy moth infestation in Shenandoah National Park provide a good example. Between the mid-1980s and the early 1990s, the southward expanding range of the European gypsy moth traversed Shenandoah National Park and affected all of the University of Virginia's SWAS study watersheds (Webb, 1999). Some areas of the park were heavily defoliated 2 to 3 years in a row. The White Oak Run watershed, for example, was more than 90% defoliated in both 1991 and 1992. This insect infestation of forest ecosystems in Shenandoah National Park resulted in substantial effects on streamwater chemistry. The most notable effects of the defoliation on park streams were dramatic increases in the concentration and export of N and base cations in streamwater. Following defoliation, NO_3^- export increased to previously unobserved levels and remained high for over 6 years before returning to predefoliation levels. The very low levels of pre-disturbance NO_3^- export in park streams were consistent with expectations for N-limited, regenerating forests (Aber et al., 1989; Stoddard, 1994). Release of NO_3^- to surface waters following defoliation was likewise consistent with previous observations of increased N export due to forest disturbance (Likens et al., 1970; Swank, 1988). The exact mechanisms have not been determined, but it is evident that the repeated consumption and processing of foliage by the gypsy moth larva disrupted the ordinarily tight cycling of N in Shenandoah National Park forests.

Although N is thought to play an important role in the chronic acidification of surface waters in some areas (Sullivan et al., 1997), the elevated concentrations of NO_3^- in Shenandoah National Park streams following defoliation did not appear to contribute to baseflow acidification in White Oak Run. This was due to a concurrent increase in concentrations of base cations in streamwater (Webb et al., 1995). Both NO_3^- and base cation concentrations increased during high-runoff conditions, although the increase in base cations did not fully compensate for the episodic increase in NO_3^-. Episodic acidification following defoliation thus became more frequent and more extreme in terms of observed minimum ANC (Webb et al., 1995).

The full effect of the gypsy moth on aquatic resources in Shenandoah National Park is not well understood. One consequence may be a reduction in the supply of available soil base cations and associated effects on streamwater ANC. Repeated periods of defoliation would probably increase the effect of episodic acidification on sensitive aquatic fauna and may determine the conditions under which some species are lost. Ultimately such effects may depend upon both the severity of future gypsy moth or other insect outbreaks and possibly on the amount of atmospheric N deposition. Gypsy moth populations typically display a pattern of periodic outbreaks and collapse (Cambell, 1981). It remains to be seen what the long-term pattern will be (Sullivan et al., 2003).

Webb et al. (1994) compared pre- and post-defoliation streamwater chemistry for 23 VTSSS watersheds. Nitrate concentrations, measured quarterly, increased in most of the streams in response to defoliation, typically by 10 to 20 µeq/L or more. The increased streamwater NO_3^- concentration was

probably derived from the N content of the foliage that had been consumed by the gypsy moth larvae and converted to feces on the forest floor. Sulfate concentrations and ANC also decreased in streamwater. Although the mechanism for decreased SO_4^{2-} was not totally clear, Webb et al. (1994) hypothesized that increased nitrification in response to the increased soil N pool may have caused soil acidification, which would be expected to have increased soil S adsorption (Johnson and Cole, 1980). Decreased S deposition during the comparison period may also have contributed to the SO_4^{2-} response.

Eshleman et al. (1998) reported NO_3^- outputs from five small (<15 km^2) forested watersheds in Virginia and Maryland from 1988 to 1995. The study watersheds varied in geology, vegetation, and acid sensitivity, with baseflow ANC typically in the range of 0 to 10 μeq/L in Paine Run to the range of 150 to 350 μeq/L in Piney River. Oak species (*Quercus* spp.), which are a preferred food source of gypsy moth larvae, occupied about 60% to 100% of the study watersheds. Nitrate concentrations increased in at least three of the watersheds in association with intense defoliation by the gypsy moth larva during the late 1980s to early 1990s, to peak annual average NO_3^- concentrations of about 30 to 55 μeq/L. Most of the increased NO_3^- leaching occurred during storm flow conditions.

A number of other studies have been conducted that examined the effects of gypsy moth, or other forest insect pests, on watershed biogeochemistry. Defoliation of poplars (*Populus* sp.) by gypsy moth larvae in southwestern Michigan did not result in appreciable NO_3^- leaching (Russell et al., 2004).

Other pest species can have similar effects. For example, spruce-fir forests throughout the southern Appalachian Mountains have been subjected to significant disturbance, especially from the balsam wooly adelgid, a European pest which has infested Fraser fir since about the 1960s. Severe fir mortality has occurred in many areas. This disturbance factor has the potential to interact with acidic deposition and other ecosystem stresses, and contribute to multiple-stress tree mortality and to changes in biogeochemical cycling.

Defoliation by the elm spanworm (*Ennomos subsignarius* Hübner) larvae in old-growth hemlock-hardwood forests on the Allegheny High Plateau of northwestern Pennsylvania increased streamwater NO_3^- concentrations from pre-defoliation levels of about 29 μeq/L to peak values the summer after defoliation of about 100 μeq/L (Lewis and Likens, 2007).

B.5.3. Wind or Ice Storm Damage

Forest blowdown might affect surface water acid-base chemistry by changing the pathway followed by drainage water through watershed soils (Dobson et al., 1990). Pipes formed in the soil by decaying tree roots can alter hydrologic flow so that less water enters the soil matrix, where neutralization processes buffer the acidity of rainwater and snowmelt. Pipes tend to occur most commonly in near-surface soil horizons where most tree rooting occurs. Contact between drainage water and mineral soil is reduced when runoff is routed through them. If enhanced pipeflow, resulting from sudden extensive tree mortality, affects a large portion of a watershed, runoff water may have less opportunity for acid neutralization than would be the case in the absence of such pipeflow.

Severe canopy damage occurred in 1998 in response to an ice storm at HBEF and surrounding areas in the White Mountains. Houlton et al. (2003) reported effects of this disturbance on N cycling and leaching losses. Subsequent to the ice storm, drainage water NO_3^- concentrations increased sevenfold to tenfold. Peak streamwater NO_3^- concentrations during spring months reached or exceeded 50 μeq/L at many sites. There were no significant differences, however, in N mineralization, nitrification, or denitrification rates between damaged and undamaged areas. Houlton et al. (2003) interpreted these results as an indication that increased NO_3^- leaching was probably due to decreased root uptake rather than accelerated N cycling by soil microbes. The amount of NO_3^- leaching loss was estimated to be more than half of the entire year's worth of atmospheric N deposition.

B.5.3.1. Fire

Fire can increase concentrations of NO_3^- and SO_4^{2-} in soils and drainage water (cf. Chorover et al., 1994; Riggan et al., 1994). Fenn and Poth (1998) hypothesized that successful fire suppression efforts may have contributed to the development of N-saturation in fire-adapted ecosystems in southern California by allowing N to accumulate in soil and in the forest floor, and by maintaining dense mature stands with reduced N demand.

The effects of fire on NO_3^- leaching in chaparral stands in the San Gabriel Mountains, CA that received high atmospheric N deposition were investigated by Riggan et al. (1994). Study watersheds were burned with fires of different intensity and, after rainfall, NO_3^- and NH_4^+ were measured in watershed streams. Nitrogen release was up to 40 times greater in burned watersheds than in unburned watersheds, and the amount and concentration of N release were found to be related to fire intensity.

Chorover et al. (1994) evaluated the effects of fire on soil and stream water chemistry in Sequoia National Park, CA. Burning increased concentrations of NO_3^- and SO_4^{2-} in soil water and stream water. Sulfate concentrations increased 100 fold. Nitrate concentrations also increased and remained higher in soils and stream water for about 3 years. These results suggest that successful fire suppression may have contributed to the development of N saturation in fire-adapted ecosystems in southern California by allowing N to accumulate in the soil and forest floor, and by maintaining dense mature stands with reduced N demand (Fenn and Poth, 1998).

B.5.3.2. Multiple Stress Response

Acidification-related effects of S and N deposition do not occur in isolation; they interact with disturbances of various types, both natural and human-caused. They also influence a range of biogeochemical processes that may be difficult to predict. Overall, the interactions between disturbance and ecosystem acidification as a consequence of acidic deposition are not well understood.

It is believed that high rates of N deposition cause increased susceptibility of forests to other stressors, including reducing the resistance of some tree species to frost, insect damage, or drought. The effects of acidic deposition can interact with a variety of stressors, both natural and human-caused. The end result might include adverse effects that would not occur solely in response to acidic deposition, or in response to any one of the other stressors.

Watershed disturbance might also effect Hg cycling and its relationship to S deposition. For example, Garcia and Carignan (2000), in a study of 20 watersheds in Quebec, Canada, found that the average Hg concentration in 560–mm northern pike (ESO_X *lucius*) was significantly higher in lakes whose watersheds had recently (1995) been logged (3.4 µg/g), as compared with reference lake watersheds (1.9 µg/g), that had remained undisturbed for at least 40 years. Fish tissue Hg concentration also increased with increasing DOC and lakewater SO_4^{2-} concentration, and with decreasing pH.

B.6. Ecological indicators of acidification

B.6.1. Biological Indicators

Surface water acidification from acidic deposition causes effects on organisms at all trophic levels. Early studies focused on the loss of fish populations, especially salmonids. Later studies also reported that many species of phytoplankton, zooplankton, insect larvae, crayfish, snails, and freshwater mussels are sensitive and are often reduced or absent from acidified lakes and streams (Havas, 1986; Baker et al.,

1990b). Similarly, many species of microrhizal fungi and lichens have been reported to be particularly sensitive to acidic deposition in terrestrial ecosystems.

Effects of acidification on aquatic biota have been demonstrated in laboratory and field bioassays (e.g., Baker et al., 1996), whole-ecosystem acidification experiments (e.g., Schindler et al., 1985), and field surveys (e.g., Baker and Schofield, 1982; Gallagher and Baker, 1990). Many of the species that commonly occur in acid-sensitive surface waters susceptible to acidic deposition cannot reproduce or survive if the water is acidic. Some sensitive species of fish, invertebrates, and algae cannot survive at moderate levels of acidity. For example, some zooplankton predators, sensitive mayfly species, and sensitive fish species are affected at pH values below the range of 5.6 to 6.0 (Baker and Christensen, 1991). Such pH values generally equate to ANC below about 25 to 50 µeq/L.

There are few published examples of long-term monitoring data for biological assemblages in acid-sensitive surface waters, and none in the U.S. Therefore, conclusions about the effect of acidic deposition on the distribution of sensitive species are based on other kinds of data (Stoddard et al., 2003). For example, the number of fish species increases with increasing pH and ANC when evaluated for multiple water bodies across the landscape. This result has been shown for streams in Virginia, lakes in the Adirondacks, and both high-elevation and seepage lakes in Maine (Figure B-17).

Given the available data, it is clear that acidification from acidic deposition limits the distribution of acid-sensitive fish, benthic invertebrate, phytoplankton, and zooplankton species, but a lack of adequate data makes it difficult to quantify the magnitude of change in biota from historical condition or in response to recent (past two to three decades) decreases in acidic deposition in individual lakes or streams. Studies in Canada and Europe have illustrated the feasibility and complexity of biological recovery in response to decreased acidity.

Threshold pH levels for adverse biological effects have been summarized for a variety of aquatic organisms (Haines and Baker, 1986; Baker et al., 1990b). The effects of low pH are specific to the organism, and perhaps region, under consideration and depend also upon the concentrations of other chemical constituents in the water, notably Al_i and Ca^{2+}. In general, populations of salmonid fish are not found at pH levels less than 5.0, and smallmouth bass (*Micropterus dolomieu*) populations are usually not found at pH values less than 5.2 to 5.5 (Haines and Baker, 1986). A number of synoptic surveys indicate loss of species diversity and absence of many other fish species in the pH range of 5.0 to 5.5 (Haines and Baker, 1986). Levels of pH less than 6.0 to 6.5 have been associated with adverse effects on populations of dace, minnows, and shiners (family Cyprinidae), and bioassays suggest that given sufficient Al concentrations, pH less than 6.5 can lead to increased egg and larval mortality in blueback herring (*Alosa aestivalis*) and striped bass (*Morone saxatilis*) (Hall, 1987; Klauda et al., 1987).

Mycorrhizal fungi have been suggested as possible biological indicators of atmospheric deposition effects by Løkke et al. (1996) because they are intimately associated with tree roots, depend on plant assimilates, and play essential roles in plant nutrient uptake. Thus, mycorrhizal fungi can influence the ability of their host plants to tolerate different anthropogenically generated stresses. Mycorrhizae and associated fine roots have short lifespans and their turnover appears to be controlled by environmental factors. Changes in mycorrhizal species composition, or the loss of dominant mycorrhizal species in areas where diversity is already low, may cause increased susceptibility of plants to stress (Løkke et al., 1996).

Mycorrhizal fungi are dependent for their nutrition on the supply of assimilates from the host plant. Stresses that shift the allocation of C reserves to the production of new leaves at the expense of supporting tissues will be reflected rapidly in decreased fine root and mycorrhizal biomass (Winner and Atkinson, 1986). Decreased C allocation to roots could also affect soil carbon and rhizosphere organisms. For example, earthworms are believed to decrease in abundance, and in species number, in acidified soils (Løkke et al., 1996). Soil dwelling animals, including earthworms, are important for decomposition, soil aeration, and nutrient redistribution in the soil. They contribute to decomposition and nutrient availability, mainly by increasing the accessibility of dead plant material to microorganisms.

B.6.1.1. Phytoplankton

Phytoplankton are the small microscopic plants or plant-like organisms that live suspended in the water column of lakes and large rivers. Acidification results in decreased species richness and diversity of phytoplankton communities. There is also a shift in the composition of dominant taxa, but species composition shifts cannot be accurately predicted (though it is clear that community restructuring occurs with acidification). This effect is most prevalent in the pH 5 to 6 range (Baker et al., 1990b). Acidification has also been found to cause decreases in food web complexity (indicated by the number of trophic links or species) in the Adirondack Mountains (Havens and Carlson, 1998). Both Al toxicity and P limitation may also be responsible for shifts in phytoplankton community composition. Neither grazing pressure nor changes in water clarity associated with acidification seem to have a major effect on phytoplankton community structure. There is no consistent pattern of acidification effects on phytoplankton biomass. Various lakes have shown increases, decreases, or no change in phytoplankton biomass with acidification (Baker et al., 1990b). Leavitt et al. (1999) suggested that the complex interactions between pH, DOC, and light explain the high variability in the algal biomass-acidification relationship. In most lakes, acidification has a negligible effect on primary productivity.

Diatoms, which comprise an important component of the phytoplankton, are excellent indicators of environmental change in aquatic ecosystems, including acidity, nutrient status, salinity, and climatic features (Stoermer and Smol, 1999; Sullivan and Charles, 1994). There are thousands of different species, many of which have rather narrow ecological tolerance ranges. Diatoms have been widely used as indicators of past lake acidification. Inference based on diatom fossil remains preserved in lake sediments is an excellent approach for quantifying historical chemical change (Charles and Norton, 1986).

Paleolimnological reconstructions of past lakewater chemistry are based on transfer functions derived from relationships between current lakewater chemistry and diatom (or, in some cases, chrysophyte) algal remains in surface sediments. Predictive relationships are developed using regional lake datasets, and are then applied to diatom assemblage data collected from horizontal slices of lake sediment cores to infer past lakewater conditions (Charles et al., 1990a; Husar and Sullivan, 1991).

Periphyton are the small microscopic plants (or plant-like organisms) that live on submerged substrates in aquatic systems (e.g., stream or lake bottoms). As seen in phytoplankton communities, acidification results in decreased species richness, community alteration, and emergence of new dominant species in periphyton communities. Many diatom and blue-green bacterial periphyton species cannot tolerate acidic conditions. On the other hand, green algae, particularly the filamentous Zygnemataceae, increase in relative abundance at lower pH (Baker et al., 1990b). Unlike for phytoplankton, there is evidence that the biomass of attached periphyton increases at lower pH.

Studies of phytoplankton recovery from acidification indicate that there is an increase in phytoplankton species richness and diversity as pH increases. In the Experimental Lakes area of Ontario, previously acidified lakes have been experimentally de-acidified. In Lake 223, there was little increase in phytoplankton diversity as pH changed from 5.0 to 5.8 but a strong recovery of diversity at pH above 6 (Findlay and Kasian, 1996). In Lake 302S, profound change began at pH 5.5; phytoplankton assemblages at pH below 5.5 resembled acidified lakes. Cyanobacteria were among the first to recover at pH 5.5 to 5.8 (Findlay et al., 1999). In the Killarney Park area of Ontario, Findlay (2003) reported that lakes that were previously low in pH (5.0 to 5.5) and are now above pH 6 have shifted towards phytoplankton assemblages typical of circumneutral environments.

B.6.1.2. Zooplankton

Field survey and experimental lake studies both indicate that acidification reduces zooplankton species richness. Effects of acidification on community biomass and abundance, however, were not definitive. Some studies indicated a lower biomass under low pH conditions, whereas other studies showed no consistent pattern in the biomass-pH relationship. Limited data indicated that acidification

does not alter zooplankton community grazing rates. Zooplankton species that have been shown to be sensitive to low pH include *Diaptomus sicilis, Epischura lacustris, Tropocyclops parsinus mexicanus, Daphnia galeata mendotae, Daphnia rosea, Diaphanosoma birgei, Leptodora kindtii, Asplanchna priodonta,* and *Conochilus unicornis*. In North America, species reported to have increased dominance in acidic lakes (acid-tolerants) include *Keratella taurocephala, Bosmina longirostris,* and *Diaptomus minutus*. Possible mechanisms for zooplankton sensitivity to low pH include ion regulation failure, reduced O_2 uptake, inability to reproduce, and Al toxicity. Indirect effects of acidification on zooplankton communities are also possible due to pH-induced shifts in higher trophic level zooplankton predators. This mechanism is probably of less importance than the direct effects of low pH. It is also probable that under acidic conditions, zooplankton communities are less able to ameliorate nutrient additions or control algal densities (Baker et al., 1990b).

Reported pH thresholds for zooplankton community alteration range from 5 to 6. Holt and Yan (2003) reported a threshold of community change at pH 6 for lakes in southern Ontario. Locke and Sprules (1994) reported that acidification below pH 5 in the 1970s overcame the resistance stability of the zooplankton community in Ontario Precambrian Shield lakes. The subset of study lakes that showed pH recovery from acidification 20 years later in 1990 also showed recovery in the stability of the zooplankton community. Holt and Yan (2003) also noted recovery in zooplankton community composition (based on similarity to neutral lakes) in the subset of Killarney Park (Ontario) lakes in which the pH increased to over 6 during the 1971 to 2000 study period. They did not, however, note any time trend of increasing species richness between recovering lakes and non-recovering lakes.

Recovery in experimentally acidified Lake 223 back to pH 6.1 was studied by Malley and Chang (Malley and Chang, 1995). They reported that the zooplankton community was still in a state of flux. Species diversity that had been reduced during the acidification phase had partially returned to preacidification levels. Rotifers had recovered less than crustaceans. One decade after cessation of the experimental acidification of Little Rock Lake in Wisconsin, recovery of the zooplankton community was complete (Frost et al., 2006). Recovery did not follow the same trajectory as the initial acidification, however, indicating a substantial hysteresis in zooplankton community recovery. About 40% of the zooplankton species in the lake exhibited a lag of 1 to 6 years to recover to levels noted in the neutral reference basin.

In situ enclosure studies were conducted for 35 days at Emerald Lake in the Sierra Nevada by Barmuta et al. (1990). The lake sediments were included within the experimental enclosures. This allowed the investigators to document the response of zoobenthos as well as zooplankton. Treatments included a control (pH 6.3) and acid addition to reach pH levels of 5.8, 5.4, 5.3, 5.0, and 4.7. Results indicated that zooplankton were sensitive to acidification but zoobenthos were unaffected by the experimental treatment. *Daphnia rosea* and *Diaptomus signicauda* decreased in abundance below the range of pH 5.5 to 5.8 and were eliminated below about pH 5.0. *Bosnia longirostris* and *Keratella taurocephala* generally became more abundant with decreasing pH. Barmuta et al. (1990) concluded that even slight acidification of high-elevation lakes in the Sierra Nevada might alter the structure of the zooplankton community.

Sullivan et al. (2006a) found that zooplankton taxonomic richness varied with ANC in Adirondack lakes (Table B-22). Taxonomic richness expressed as number of species of crustaceans, rotifers, and total zooplankton, increased with increasing ANC. In general, lakewater ANC explained nearly half of the variation in total zooplankton and crustacean taxonomic richness, but less for rotifer richness. These results (Table B-22) provided the basis for estimating changes in zooplankton richness in response to past or future changes in lakewater ANC. Several zooplankton species found in lakes in the Sierra Nevada are also known to be sensitive to acidity status (Gerritsen et al., 1998).

B.6.1.3. Benthic Invertebrates

Within stream systems, macroinvertebrate communities are among the most sensitive life forms to disturbances, including those associated with atmospheric deposition (Cairns and Pratt, 1993). In

addition, they are relatively easy to sample in the field (Plafkin et al., 1989; Resh et al., 1995; Karr and Chu, 1999).

Acidification results in the loss of acid-sensitive benthic invertebrates and decreases in pH of one unit or more typically result in species loss. Invertebrate taxa that are most sensitive to acidification are mayflies, amphipods, snails, and clams. At low levels of acidification (pH 5.5 to 6.0), acid-sensitive species are replaced by more acid-tolerant species, yielding little or no change in total community species richness, diversity, density, or biomass. If pH decreases are larger, more species will be lost without replacement, resulting in decreased richness and diversity. Many sites also note decreases in invertebrate biomass and productivity (more so in streams than lakes). High levels of acidification (pH <5) were found to virtually eliminate all mayflies, crustaceans and mollusks from French streams (Guerold et al., 2000). Examples of sensitive benthic invertebrate species include *Baetis rhodani, Gammarus lacustris, Hyalella azteca, Asellus aquaticus, Orconectes rusticus*, and *O. propinquous*. Stoneflies are generally more acid-tolerant than mayflies and caddisflies.

Possible mechanisms for acidification effects on invertebrates include direct toxicity of H^+ and Al, disruption of ion regulation, and reproductive failure. Indirect effects due to acidification-induced changes to invertebrate predator populations are also possible (Baker et al., 1990b). Acidic episodes in streams can cause increased downstream drift of acid-sensitive species, particularly *Baetis* (Kratz et al., 1994; Smock and Gazzera, 1996).

It has been well documented that low streamwater pH can be associated with reductions in invertebrate species richness or diversity (Townsend et al., 1983; Raddum and Fjellheim, 1984; Burton et al., 1985; Kimmel et al., 1985; Hall and Ide, 1987; Peterson and Van Eechhaute, 1992; Rosemond et al., 1992; Sullivan et al., 2003), and sometimes density (Hall et al., 1980; Townsend et al., 1983; Burton et al., 1985; Kimmel et al., 1985). Effects on invertebrate density are not universal; a number of studies have found no density effects (Harriman and Morrison, 1982; Simpson et al., 1985; Ormerod and Tyler, 1987; Winterbourn and Collier, 1987). However, a decrease in species richness with decreasing pH has been found in almost all such studies (Rosemond et al., 1992), and this finding has been especially pronounced in streams for order Ephemeroptera (mayflies).

The Ephemeroptera-Plecoptera-Tricoptera (EPT) Index is a common measure of stream macroinvertebrate community integrity. The EPT metric is the total number of families present in those three insect orders (mayflies, stoneflies, and caddisflies, respectively). The total number of families is generally lower at acidified sites because species within those families tend to exhibit varying acid sensitivity (USDA, 1996). Mayflies tend to be most sensitive of the three, and stoneflies tend to be least sensitive (Peterson and Van Eechhaute, 1992).

There has been some recovery in benthic invertebrate communities in surface waters exhibiting chemical recovery from acidification. In Scotland, Soulsby et al. (1995) reported an increase in acid-sensitive mayflies in some streams that showed recent ANC increases. However, no increases in invertebrates were observed in the most acidic streams despite observed increases in ANC. They suggested that further acidic deposition reductions and sufficient time for reversal of soil acidification may be required before biotic recovery can occur. Tipping et al. (2002) noted increases of invertebrate richness and diversity in the English Lake District in their study streams that had pH increases of 0.3 to 0.5 units since about 1970.

Responses of aquatic macroinvertebrates to acidification were evaluated by Kratz et al. (1994) in 12 streamside channels in Sequoia National Park, CA. Replicated treatments included a control (pH 6.5 to 6.7) and experimental exposure at pH levels of 5.1 to 5.2 and 4.4 to 4.6. Invertebrate drift was monitored continuously and benthic densities were determined before and after acidification. Single 8-h acid pulses increased the drift of sensitive taxa, and benthic densities were reduced. *Baetis* showed reduced density post-treatment to less than 25% of control densities in both pH reduction treatments (5.2, 4.6) and two different experimental exposures. Densities of *Paraleptophlebia* appeared to be reduced by the acidification, but most treatment effects were not statistically significant. Kratz et al. (1994) suggested that the effects of acid inputs on benthic species densities depended on microhabitat preferences. *Baetis* nymphs are epibenthic and active. They are often found on the upper surfaces of rocks where they are

directly exposed to acidified water. This may have been responsible for their greater response to acidification.

B.6.1.4. Fish

By 1990 it was well established that pH in the range of 4.0–6.5 could cause significant adverse biological effects on fish. Low pH was one of the most important factors resulting in adverse effects. The toxicity of pH was, in most cases, the result of impaired body salt regulation. Decreased pH in the water inhibited the active uptake of Na^+ and Cl^- and stimulated the passive loss of these ions (Baker et al., 1990b).

The response to acidification was not uniform, however. Some species and life stages experienced significant mortality in bioassays at relatively high pH (e.g., pH 6.0–6.5 for eggs and fry of striped bass and fathead minnow) (Buckler et al., 1987; McCormick et al., 1989), whereas others were able to persist at quite low pH without adverse effect (Mudminnow; [Umbra spp.] at pH 4.0 and Umbra pygmaea at pH 3.5) (Dederen, 1987). Many minnows and dace (Cyprinidae) are sensitive to acidity (threshold effects at pH <5.5 to 6.0), but some common game species such as brook trout, largemouth bass, and small mouth bass are relatively insensitive (threshold effects at pH <5.0 to 5.5). A summary of studies that demonstrated the difference among species is shown in Table B-23. Table B-24 summarizes the results from a variety of studies that determined the threshold values of pH for various taxa and kinds of effects.

The effect of acidification on aquatic organisms, especially fish, is due in large part to the toxic effect of Al_i that is released from watershed soils. A number of studies reviewed by Baker et al. (1990b) reported threshold values of Al_i for various species and effects. Those results are presented in Table B-25. The effects of low pH and high Al_i can be ameliorated to an extent in the presence of increased Ca^{2+} concentration. A summary of the effect of increasing Ca^{2+} concentration is presented in Table B-26.

Fish populations in acidified streams and lakes of Europe and North America have declined, and some have become extinct as a result of atmospheric deposition of acids and the resulting changes in water quality (Baker et al., 1990b). A variety of factors, including Al_i, DOC, and Ca^{2+}, along with the timing and magnitude of episodic fluctuations in toxic acid and Al_i concentrations, are related to the degree to which surface water acidification influences fish survival in natural systems (Baker et al., 1990b; Baldigo and Murdoch, 1997; Gagen et al., 1993; Siminon et al., 1993; Van Sickle et al., 1996). Aluminum fractionation and Al_i concentration are directly dependent upon pH levels (Driscoll et al., 1985).

Fish communities of acid-sensitive streams and lakes may contain a variety of species, but are often dominated by trout. Across the eastern U.S., brook trout is often selected as an indicator of acidification effects on aquatic biota because it is native to many eastern streams and lakes and because residents place great recreational and aesthetic value on this species. It must be emphasized, however, that brook trout is a relatively acid-tolerant species. Many other fish species, including rainbow and brown trout, as well as a variety of other fish species, are more acid-sensitive than brook trout. In many Appalachian Mountain streams that have been acidified by acidic deposition, brook trout is the last species to disappear; it is generally lost at pH near 5.0 (MacAvoy and Bulger, 1995), which usually corresponds in these streams with ANC near 0 (Sullivan et al., 2003).

Although there are known differences in acid sensitivity among fish species, experimentally determined acid sensitivities are available for only a minority of freshwater fish species. Baker and Christensen (1991) reported critical pH values for 25 species of fish. They defined critical pH as the threshold for significant adverse effects on fish populations. The reported range of pH values represents the authors' estimate of the uncertainty of this threshold. The range of response within species depends on differences in sensitivity among life stages, and on different exposure concentrations of Ca^{2+} and Al. To cite a few examples, blacknose dace is regarded as very sensitive to acid stress, because population loss due to acidification has been documented in this species at pH values as high as 6.1; in field bioassays,

embryo mortality has been attributed to acid stress at pH values as high as 5.9. Embryo mortality has occurred in common shiner at pH values as high as 6.0. Although the critical pH range for rainbow trout is designated as 4.9–5.6, adult and juvenile mortality have occurred at pH values as high as 5.9. Brown trout population loss has occurred over the pH range of 4.8–6.0, and brook trout fry mortality has occurred over the range of 4.8–5.9 (Baker and Christensen, 1991). Relative sensitivities can be suggested by regional surveys as well, although interpretation of such data is complicated by factors that correlate with elevation. Such factors, including habitat complexity and refugia from high-flow conditions, often vary with elevation in parallel with acid sensitivity. It is noteworthy, however that about half of the 53 fish species found in Adirondack Mountain waters in New York never occur at pH values below 6.0 (Kretser et al., 1989; Driscoll et al., 2001b); for those species whose acid tolerances are unknown, it is probable that acid sensitivity is responsible for at least some of these absences. It is the difference in acid tolerance among species that produces a gradual decline in species richness as acidification progresses, with the most sensitive species lost first.

Effects on biota can be assessed as effects on a particular sensitive species or species perceived to be important, or as effects on the richness or diversity of fish or other potentially sensitive life form. For example, Bulger et al. (2000) developed ANC thresholds for brook trout in Virginia, which are presented in (Table B-27). These values were based on annual average stream water chemistry, and therefore represent chronic exposure conditions. The likelihood of additional episodic stress is incorporated into the response categories in the manner in which they are interpreted. For example, the episodically acidic response category, which has chronic ANC in the range of 0 to 20 µeq/L, represents streams that are expected to acidify to ANC near or below 0 during rainfall or snowmelt episodes. In such streams, sublethal and/or lethal effects on brook trout are possible (Bulger et al., 2000; Sullivan et al., 2003).

Fish species richness, population density, condition factor, age distribution, size, and bioassay survival have all been shown to be reduced in low-ANC streams as compared to intermediate-ANC and high-ANC streams (Bulger et al., 1995; Dennis et al., 1995; Dennis and Bulger, 1995; MacAvoy and Bulger, 1995). Fish species richness is a good indicator of acidification response. Lakes or streams having pH below about 5.0 or ANC below about 0 generally do not support fish. Depending on the region, waters having pH above about 6.5 and ANC above about 50 µeq/L support large, but variable, numbers of species. There is often a positive relationship between pH and number of fish species, at least for pH values between about 5.0 and 6.5, or ANC values between about 0 and 50 to 100 µeq/L (Bulger et al., 1999; Sullivan et al., 2006a). Such observed relationships are complicated, however, by the tendency for smaller lakes and streams, having smaller watersheds, to also support fewer fish species, irrespective of acid-base chemistry. This pattern may be due to a decrease in the number of available niches as stream or lake size decreases. Nevertheless, fish species richness is one of the most useful indicators of biological effects of surface water acidification.

Acidification and the associated elevated concentrations of Al_i in surface waters have adversely affected fish populations and communities in parts of the Adirondack Mountains of northern New York (Baker and Schofield, 1982; Johnson et al., 1987; Kretser et al., 1989; Schofield and Driscoll, 1987; Siminon et al., 1993) and in acid-sensitive streams of the Catskill Mountains of southeastern New York (Stoddard and Murdoch, 1991) and the Appalachian Mountains from Pennsylvania to Tennessee and South Carolina (USDA, 1996; Bulger et al., 1999, 2000).

Adverse effects of low pH and high Al_i concentration on fish include increased mortality, decreased growth, decreased reproductive potential, and ionoregulatory impairment. A partial list of studies demonstrating such effects is provided in Table B-28 from Baker et al. (1990b). It has been shown, however, that there is marked variability among species and among life stages within species in the specific levels of pH and Al_i that produce measurable responses.

Surface-water acidification can affect fish populations by a number of mechanisms ranging from increased morality and emigration to decreased food supplies (Baker et al., 1990b). The primary reason for population decline and extinction, however, is usually the failure of a species to successfully recruit young-of-the-year fish (Mills et al., 1987; Brezonik et al., 1993). The response of aquatic communities to

acidification, therefore, should appear first as changes in age distribution and decreased health of individual fish (growth and condition), then as decreased biomass and density in populations of acid-intolerant fish species, and finally as elimination of sensitive species (Baker et al., 1990b).

The primary mechanism for the toxic effects of low pH and elevated Al on fish involves disruption of normal ion regulation at the gill surface resulting in increased rates of ion loss and inhibition of ion uptake (McWilliams and Potts, 1978; Leivestad, 1982; Wood and McDonald, 1987; Bergman et al., 1988). Additional effects might include disruption of Ca^{2+} metabolism (Peterson and Martin-Robichaud, 1986; Gunn and Noakes, 1987; Reader et al., 1988), and decreased hatching success (Runn et al., 1977; Peterson et al., 1980; Haya and Waiwood, 1981; Waiwood and Haya, 1983).

Prominent physiological disturbance for fish exposed to acid waters are iono- and osmoregulatory failure, acid-base regulatory failure, and respiratory and circulatory failure. Most of these effects can be directly attributed to effects on gill function or structure. The acute toxicity of low pH in acidic waters results in the loss of Ca^{2+} from important binding sites in the gill epithelium, which reduces the ability of the gill to control membrane permeability (McDonald, 1983; Havas, 1986; Exley and Phillips, 1988).

The energy costs to fish for active iono-osmoregulation can be substantial (Farmer and Beamish, 1969; Bulger, 1986). The concentrations of serum electrolytes (such as Na^+ and Cl^-) are many times higher (often 100–fold higher) in fish blood than in the fresh waters in which they live. The active uptake of these ions occurs at the gills. Because of the steep gradient in Na^+ and Cl^- concentrations between the blood and fresh water, there is constant diffusional loss of these ions, which must be replaced by energy-requiring active transport. Low pH increases the rate of passive loss of blood electrolytes (especially Na^+ and Cl^-); and Al elevates losses of Na^+ and Cl^- above the levels due to acid stress alone (Wood, 1989). For example, dace in an acidified stream maintain whole-body Na^+ at levels similar to dace in a high-ANC stream (Dennis, 1995), despite probable higher gill losses of electrolytes due to acid/Al stress. Therefore, the homeostatic mechanisms at the gill responsible for maintaining blood electrolyte levels must work harder and use more energy to maintain these levels for dace in the acidified stream.

Whole lake experiments and artificial stream channel experiments have shown that acidification can lead to loss of fish species. A summary of the work on Lake 223 in the Experimental Lakes Area in Canada is provided in Table B-29. Work at Little Rock Lake in Wisconsin suggested that rock bass suffered recruitment failure at pH 5.6 or below. Artificial channel studies showed poor survival and reproductive success for fathead minnow at pH 5.9 to 6.0.

ANC criteria have been used for evaluation of potential acidification effects on fish communities. The utility of these criteria lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, Ca^{2+}, and Al. Bulger et al. (2000) developed ANC thresholds for brook trout response to acidification in forested headwater catchments in western Virginia (See Table B-27). Note that because brook trout are comparatively acid tolerant, adverse effects on many other fish species should be expected at relatively higher ANC values.

Streams with chronic ANC greater than about 50 µeq/L are generally considered suitable for brook trout in southeastern U.S. streams because they have a large enough buffering capacity that persistent acidification poses no threat to this species, and there is little likelihood of storm-induced acidic episodes lethal to brook trout. In such streams, reproducing brook trout populations are expected if the habitat is otherwise suitable (Bulger et al., 2000), although some streams may periodically experience episodic chemistry that affects species more sensitive than brook trout. Streams having annual average ANC from 20 to 50 µeq/L may or may not experience episodic acidification during storms that can be lethal to juvenile brook trout, as well as other fish. Streams that are designated as episodically acidic (chronic ANC from 0 to 20 µeq/L) are considered marginal for brook trout because acidic episodes are likely (Hyer et al., 1995), although the frequency and magnitude of episodes vary. Streams that are chronically acidic (chronic ANC less than 0 µeq/L) are not expected to support healthy brook trout populations (Bulger et al., 2000).

Field surveys provided a regional context for fish response to acidification. Although there were some variations, the results of field surveys generally confirmed the results of bioassays, field

experiments, and other intensive field studies. The results of many field surveys were summarized in Baker et al. (1990b) and are compiled in (Table B-30).

It is important to note, however, that the absence of fish from a given lake or stream in an area that experiences surface water acidification does not necessarily imply that acidification is responsible for the absence of fish. For example, results of fisheries research in the Adirondacks has indicated that many Adirondack lakes always had marginal spawning habitat for brook trout (Schofield, 1993), and some of the currently fishless acidic lakes probably never supported fish.

Many of the data for the assessment of fish status in the Adirondack region of New York come from the reports by Kretser et al. (1989) and Baker et al. (1990a). The status of fish and of the presence of individual species were related to a variety of lake characteristics. Of the lakes without fish, 42% had high organic acid content that may have caused the observed low pH, 13% were bog lakes of high acidity and naturally poor fish habitat, 9% had pH >5.5 suggesting other factors were likely responsible for the lack of fish, and 3% were small high-elevation lakes that were unlikely to have fish regardless of acid-base chemistry. However, 34% of the lakes surveyed (112 lakes) that had no fish at the time of survey had low pH that was most likely the result of acid deposition and no other obvious explanation for the lack of fish.

Multivariate regression of the presence/absence of brook trout in Adirondack waters produced a ranking of factors that appeared to influence the presence of brook trout when biological factors were excluded from the analysis (stocking, presence of associated species, presence of competitors). Among contributing factors, including SiO_2, ANC, DOC, substrate, and distance to the nearest road, pH ranked first as a predictor of brook trout presence (Christensen et al., 1990). The results of this analysis supported the hypothesis that 1990 levels of pH and related variables restricted the distribution of some fish in Adirondack waters.

Fish toxicity models have been developed as mathematical regression functions fit to observations of fish mortality when exposed to constant levels of pH, Al_i, and Ca^{2+} in laboratory toxicity tests. These models had the advantage that they dealt directly with the interaction effects of pH, Al, and Ca^{2+}, but they did not account for the effects of variations in other aspects of surface water quality, and they could not be directly interpreted in terms of population-level response.

The many bioassays conducted of pH effects were screened by Baker et al. (1990b) to provide data most suitable for model development. Bioassays selected for inclusion were those that measured the mortality of early life stages, those that incorporated different combinations of pH, Al, and Ca^{2+}, and those that used fish of varying sensitivity (Bergman et al., 1988).

Acidity and Al toxicity are not the only stress factors that influence the distribution of fish in acid-sensitive streams. Other habitat characteristics, including water temperature and stream channel morphology, can be important (Sullivan et al., 2003). In addition, it is probable that some trout populations have been affected by competition with other introduced species (Larson and Moore, 1985).

B.6.1.5. Amphibians

Some species of amphibians are considered to be highly sensitive to changes in environmental conditions and some species have probably been adversely affected by acidic deposition in some areas. Furthermore, several species of amphibian have exhibited marked declines in abundance throughout the western U.S. in recent decades and there has been much speculation concerning the cause(s) of these declines in abundance.

Populations of many species of amphibians have declined or become eradicated throughout the world in recent decades (Barinaga, 1990; Wake, 1991). The causes have not been evident and some of the declines have occurred in remote pristine areas. For example, in the Sierra Nevada, at least two of five species of aquatic-breeding amphibians, *Rana muscosa* (mountain yellow-legged frog) and *Bufo canorus* (Yosemite toad) have been declining (Phillips, 1990). A number of hypotheses have been proposed for amphibian decline, including acidic deposition. In the western U.S., however, acidic deposition has been discounted as the primary cause of the decline of *R. muscosa* and *B. canorus* in the Sierra Nevada and of

R. pipiens and *B. boreas* in the Rocky Mountains (Corn et al., 1989; Bradford et al., 1992). Grant et al. (2005) reported little relationship between streamwater ANC and the adjacent salamander community in Shenandoah National Park.

In some cases, population fragmentation as a consequence of fish predation may be a more likely cause (Bradford et al., 1993). It is generally recognized that *R. muscosa* was eliminated by introduced fish early in the 20th century in many lakes and streams in Sequoia and Kings Canyon National Parks. The amphibians have been eliminated from nearly all waters inhabited by fish, presumably by predation on tadpoles. Before 1870, virtually all of the high-elevation (>2500 m) lakes in the Sierra Nevada were barren of fish, but have since been stocked with fish. Fish introductions may have contributed to recent amphibian declines because amphibian populations are now more isolated from each other than formerly. The role of atmospheric deposition as an additional stressor is not clear.

The acidification sensitivity of temporary ponds, where many amphibians live or reproduce, have not been well studied. These ponds tend to fill directly from rain or snowmelt and thus can be more acidic than surrounding lakes and streams. There is a correlation between pond acidity and amphibian abundance.

There are both acid-sensitive and acid-tolerant amphibians. Examples of acid-sensitive amphibians include the spotted salamander (Ambystoma maculatum) and Jefferson salamander (*Ambystoma jeffersonianum*). Embryos of acid-sensitive species are killed by water with pH less than about 4.5. Acid-tolerant embryos may survive at a pH of 3.7. Toxicity is not solely a matter of pH, but is also influenced by Ca^{2+}, Al_i, and DOC concentrations. It is also dependent on the life stages present and water temperature (Baker et al., 1990b). Large-scale amphibian extinctions in any geographic region due to acidic deposition have not been detected.

Although acidic deposition may play a role in some areas, there is no evidence to suggest that it is a primary factor. Other issues, including fish introductions, are probably more important as stressors on amphibian populations across broad regional to national scales.

B.6.1.6. Fish-Eating Birds

Relative to other trophic groups, there are few studies assessing acidification effects on fish-eating birds. Limited data suggest that fish-eating birds are adversely affected by acidification. Acidification effects on birds may be indirect, related to changes in the quantity and quality of food. Other potential causal pathways include delayed egg laying, lighter/thinner egg shells, and reduced chick growth in acidic waters (Tyler and Ormerod, 1992). There is also concern about increased metal and Hg concentrations in fish-eating birds associated with bioaccumulation from contaminated fish in known areas of acidification (Baker et al., 1990b).

Fish-eating birds can serve as biological indicators of lakes affected by acidic deposition (McNicol, 2002). Lack of prey resources, decreased food quality, and elevated lake water methylmercury (MeHg) concentrations that could be associated with acidification may negatively effect foraging, breeding, and/or reproduction for the common loon (*Gavia immer*), common merganser (*Mergus merganser*), belted kingfisher (*Ceryle alcyon*), osprey (*Pandion haliatus*), American black duck (*Anas rubripes*), ring-necked duck (*Aythya collaris*), eastern kingbird (*Tyrannus tyrannus*), and tree swallow (*Tachycineta bicolor*) (Table B-31) (Longcore and Gill, 1993). Breeding distribution for the common goldeneye (*Bucephala clangula*), an insectivorous bird, may be positively effected by acidic deposition (Longcore and Gill, 1993). Reduced prey diversity and quantity have been observed to create feeding problems for nesting pairs of loons on low-pH lakes in the Adirondacks (Parker, 1988).

Since the mid 1980s, a statistically significant increase in fish-eating birds has been observed in the Sudbury region of Ontario, Canada, which has corresponded with a decreasing abundance of common goldeneye (McNicol, 2002). This interaction has been attributed to an increase in prey for pisciverous birds and a decrease in available prey for insectivorous birds as a result of stricter S emissions controls in the U.S. and Canada (McNicol, 2002). Logistic regression modeling with measured pH and species

occurrence data for acid-sensitive lakes in the Algoma region of Ontario showed that the occurrence of fish, common loons, and common mergansers is positively related to lake water pH (McNicol, 2002). Predictions of common loon and merganser recovery for this area were made using the Waterfowl Acidification Response Modeling System (WARMS) under varying S emissions control scenarios targeted for 2010 (McNicol, 2002). The modeled emissions scenarios include:

- S1: sulfate emissions equal to those in the early 1980s (base case)

- S2: sulfate emissions equal to that in 1994 (full Canadian emissions reductions based on the 1991 Canada/U.S. Air Quality Agreement)

- S3: expected sulfate emissions in 2010 (full implementation of U.S. emissions reductions based on the 1991 agreement)

- S4: a hypothetical 50% reduction in expected 2010 sulfate emissions

- S5: a hypothetical 75% reduction in expected 2010 sulfate emissions

The number of lakes projected to be suitable for supporting breeding pairs and broods increased with lake pH and stricter emissions controls (Table B-32) (McNicol, 2002).

Marginal improvements to fish-eating bird habitat were predicted to occur by 2010 (S3), with more significant improvements expected under hypothetical S emissions reductions of 50% and 75% (S4 and S5) for lakes with pH below 6.5 (McNicol, 2002). Fundamental to the predicted improvement of these fish-eating bird populations is the expected increase in food availability with lake pH recovery.

Elevated MeHg accumulation in fish-eating birds in Wisconsin and the northeastern U.S. has been linked to lake acidification (Meyer et al., 1995; (Hrabik and Watras, 2002)Evers et al., 2007). This form of Hg is toxic, bioavailable, and accumulates in top predators to levels of concern for both human health and the environment (Table B-33) (Evers et al., 2007).

Acidic deposition might contribute to Hg toxicity in fish-eating birds because SO_4^{2-} addition to wetland environments could stimulate the production of MeHg, thereby increasing lake water concentrations of MeHg (Jeremiason et al., 2006). Kramar et al. (2005) determined that the extent of wetland located in close proximity (less than150 m) to loon territory was positively correlated with Hg concentrations in loon blood. Wetland MeHg production is discussed in greater detail in Section 6.3.

Accumulation of MeHg in fish-eating birds can result in damage to nervous, excretory, and reproductive systems (Wolfe et al., 1998). Table B-34 lists several studies indicating effects related to mercury bioaccumulation in avian eggs and tissues. Reproduction is considered one of the most sensitive endpoints to chronic low-level MeHg exposure for fish-eating birds (Wolfe et al., 1998). Reduced clutch size, increased number of eggs laid outside the nest, eggshell thinning, and increased embryo mortality have all been documented (Wolfe et al., 1998).

Table B-1.   N-saturated forests in North America, including estimated N inputs and outputs.

Location	Forest Type	Elevation (m)	N Input (kg/ha/yr)	N Output (kg/ha/yr)	Reference
Adirondack Mts., northeastern New York	Northern hardwoods or hardwood/conifer mix	396–661	9.3a	Stage 1 N lossb	Driscoll and Van Dreason (1993)
Catskill Mts., southeastern New York	Mainly hardwood; some eastern hemlock	335–675	10.2a	Stage 1 and 2 N lossb	Stoddard (1994)
Turkey Lakes Watershed, Ontario, Canada	Sugar maple and yellow birch	350–400	7.0–7.7 (as throughfall)	17.9–23.6	Foster et al. (1989); Johnson and Lindberg (1992)

Whitetop Mt., southwestern, Virginia	Red spruce	1,650	32c	47c	Joslin and Wolfe (1992); Joslin et al. (1992)
Fernow, West Virginia	Mixed hardwood	735–870	15–20	6.1	Gilliam et al. ; Peterjohn et al. (1996)
Great Smoky Mts. National Park, Tennessee	American beech	1,600	3.1d	2.9	Johnson and Lindberg (1992)
Great Smoky Mts. National Park, Becking Site, North Carolina	Red spruce	1,800	10.3d	19.2	Johnson et al. (1991c)
Great Smoky Mts. National Park, Tower Site, North Carolina	Red spruce	1,740	26.6	20.3	Johnson et al. (1991c)
Front Range, Colorado	Alpine tundra, subalpine conifer	3,000–4,000	7.5–8.0	7.5	Williams et al. (1996a)
San Dimas, San Gabriel Mts., southern California	Chaparral and grasslands	580–1,080	23.3e	0.04–19.4	Riggan et al. (1985)
Camp Paivika, San Bernardino Mts., southern California	Mixed conifer	1,600	30	7–26	Fenn et al. (1996)
Klamath Mts., northern California	Western coniferous	NA	Mainly geologicg	NAg	Dahlgren (1994)
Thompson Forest, Cascade Mts., Washington	Red alder	220	4.7 plus >100 as N_2 fixation	38.9	Johnson and Lindberg (1992)

[a] Estimated total N deposition from wet deposition data is from Driscoll et al. (1991) for the Adirondacks, and from Stoddard and Murdoch (1991) for the Catskills. Total deposition was estimated based on the wet deposition: total N deposition ratio (0.56) at Huntington Forest in the Adirondacks (Johnson, 1992). N deposition can be higher in some areas, especially at high-elevation sites such as Whiteface Mountain (15.9 kg N/ha/yr); (Johnson, 1992). [b] Stage 1 and 2 of N loss according to the watershed conceptual model of Stoddard (1994). N discharge (kg N/ha/yr) data are not available, only stream water NO_3^- concentration trend data were collected. [c] Values appear high compared to other sites, especially N leaching losses. Joslin and Wolfe (1992) concede that "there is considerable uncertainty associated with the estimates of atmospheric deposition and leaching fluxes." However, elevated NO_3^- concentrations in soil solution and lack of a growth response to N fertilization ratio (Joslin and Wolfe, 1994) support the hypothesis that the forest at Whitetop Mountain is N -saturated. [d] Estimated total N deposition from throughfall data. Total deposition was estimated based on the throughfall/total N deposition ratio from the nearby Smokes Tower site (Johnson, 1992). [e] Annual throughfall deposition to the chaparral ecosystem. [f] N output is from unpublished stream water data (Fenn and Poth, 1999). The low value represents a year of average precipitation, and the high value is for 1995, when precipitation was nearly double the long-term average. N output includes N export in stream water and to groundwater. [g] Annual input and output data are not known, although N deposition in this forest is probably typical for much of the rural western U.S. (2–3 kg N/ha/yr; Young et al., 1988). Excess N is from weathering of ammonium in mica schist bedrock. The ammonium was rapidly nitrified, leading to high NO_3^- concentrations in soil solution (Dahlgren, 1994).

Table B-2 **Summary of measured ANC, pH, and Al concentrations compared with reference values in the six high-interest areas.**

Area	n*	N*	Percent of Population with		
			ANC ≥ 0	pH ≥ 5.5	Al_i >100 µg/L
ADIRONDACKS					
Southwest lakes	52	450	38	51	36
Other lakes	84	707	0	3	0

NEW ENGLAND					
Seaboard Lowlands lakes	94	848	8	11	0
Highland lakes	354	3,574	2	5	2
MID-ATLANTIC HIGHLANDS					
Forested lakes	91	433	10	9	1
Other lakes	52	791	0	0	0
Forested streams	78	11,631	12	17	8
Other streams	69	10,172	0	2	0
ATLANTIC COASTAL PLAIN					
Northeast lakes	22	187	11	15	7
Pine Barrens streams	12	675	56	92	56
Other streams	31	7,452	10	24	15
FLORIDA					
Northern Highland lakes	32	522	63	53	10
Northern Highland streams	18	669	28	55	0
EASTERN UPPER MIDWEST					
Low silica lakes	155	1,254	16	19	1
High silica lakes	125	1,673	3	4	2

* n = sample size, N = estimated number of lakes or upstream reach ends in population.
Source: Baker et al. (1990b).

Table B-3   **Sources of data and sample sizes for datasets analyzed by Stoddard et al. (2003), along with estimates of the condition of surface waters in each region in the 1980s.**

Source of Data and Region	No. of Sites[1]	Size of Population[2]	Percent Acidic in 1980s[3]
STATISTICAL SURVEYS			
New England Lakes[4]	30	4,327 lakes	5%
Adirondack Lakes[4]	43	1,290 lakes	14%
Appalachian Plateau Streams	31	72,000 stream miles	6%
SENSITIVE SURFACE WATERS			
New England Lakes	24	N.A.	5%
Adirondack Lakes	48	N.A.	14%
Northern Appalachian Streams	9	N.A.	6%
Upper Midwest Lakes	38	N.A.	3%

Ridge/Blue Ridge Streams	69	N.A.	5%

Table B-4 **Estimates of change in number and proportion of acidic surface waters in acid-sensitive regions of the North and East, based on applying current rates of change in Gran ANC to past estimates of population characteristics from probability surveys.**

	Results of Regional Survey				Results of Monitoring during 1990s			
Region	Population Size	Number Acidic[1]	% Acidic[2]	Time Period of Estimate	Rate of ANC change[3]	Estimated Number Acidic in 2000	% Acidic in 2000	% Change in Number of Acidic Systems
New England	6,834 lakes	386 lakes	5.6%	1991–94	+0.3	374 lakes	5.5%	−2%
Adirondacks.	1830 lakes	238 lakes	13.0%	1991–94	+0.8	149 lakes	8.1%	−38%
No. Appalachians	42,426 km	5014 km	11.8%	1993−94	+0.7	3600 km	8.5%	−28%
Ridge/Blue Ridge	32,687 km	1634 km	5.0%	1987	−0.0	1634 km	5.0%	0%
Upper Midwest	8,574 lakes	251 lakes	2.9%	1984	+1.0	80 lakes	0.9%	−68%

Source: Stoddard et al. (2003)

Table B-5 **Regional trend results for long-term monitoring sites for the period 1990 through 2000.**

Region	SO_4^{2-} (µeq/L/yr)	NO_3^- (µeq/L/yr)	Base Cations $[Ca^{2+} + Mg^{2+}]$ (µeq/L/yr)	Gran ANC (µeq/L/yr)	Hydrogen (µeq/L/yr)	DOC (mg/L/yr)	Aluminum (µg/L/yr)
New England Lakes	−1.77**	+0.01ns	−1.48**	+0.11ns	−0.01ns	+0.03*	+0.09ns
Adirondack Lakes	−2.26**	−0.47**	−2.29**	+1.03**	−0.19**	+0.06**	−1.12**
Appalachian Streams	−2.27*	−1.37**	−3.40**	+0.79*	−0.08*	+0.03ns	+0.56ns
Upper Midwest Lakes	−3.36**	+0.02ns	−1.42**	+1.07**	−0.01*	+0.06**	−0.06ns
Ridge/Blue Ridge Streams	+0.29**	−0.07**	−0.01ns	−0.07ns	+0.01ns	NA	NA

ns regional trend not significant (p >0.05). * p <0.05. ** p <0.01. NA insufficient data. Note: Values are median slopes for the group of sites in each region. Source: Stoddard et al. (2003)

Table B-6 Slopes of trends in Gran ANC in acidic, low, and moderate ANC lakes and streams, 1990–2000.

ANC Class	Number of Sites	Change in Gran ANC (µeq/L/yr)
Acidic (ANC <0 µeq/L)	26	+1.29**
Low ANC (0 <ANC <25 µeq/L)	51	+0.84**
Moderate ANC (25 <ANC <200 µeq/L)	43	+0.32 ns

ns trend not significant (p >0.05). ** p <0.01. Note: Analysis includes all sites in New England, Adirondacks, Appalachian Plateau, and Upper Midwest; Ridge and Blue Ridge sites excluded. Source: Stoddard et al. (2003)

Table B-7 Changes in key chemical characteristics during periods of record in Maine aquatic systems.

	Years	Change in (all in µeq/L)					
		Sulfate	Nitrate	Base Cations	Calculated ANC[a]	ANC	DOC[b]
Acadia NP lakes (22)	17	−10	0	−17	−7	0	−2
LTM lakes @ Tunk Mtn (6) − spring	17	−9	0	−10	−1	1	1
LTM lakes @ Tunk Mtn (6) − fall	17	−7	0	−9	−2	−2	1
LTM lakes since 1990 − fall only	8	−9	0	−10	−1	−1	0
High elevation lakes (90)	12	−16	1	−23	−8	−2	4
Seepage lakes (120)	12	−9	1	−1	7	7	4
East Bear Brook at BBWM	11	−22	−16	−44	−6	−4	1
RLTM lakes (16)	7	−6	1	−17	−12	−4	2

[a] Calculated ANC = [change in base cations] minus [change in (sulfate + nitrate)]. [b] DOC (µeq/L) = DOC in mg/l * 4 (e.g., Kahl et al., 1999). Source: Kahl et al. (1999)

Table B-8 Projected changes (µeq/L) in median values of streamwater chemistry at the regional modeling sites from 1995 to 2040 in each of the three emissions control strategies, stratified into two segments of the SAMI region (northeast and southwest) and by physiographic province.

Physiographic Province	Number of Sites	Δ Sulfate	Δ Nitrate	Δ SBC	ΔANC
A2 STRATEGY[1]					
VIRGINIA AND WEST VIRGINIA					
Blue Ridge	16	1.8	0.03	−2.2	−4.0
Valley and Ridge	41	−0.45	0.02	−6.8	−6.6
Appalachian Plateau	34	−31.2	−3.5	−33.8	−4.4

NORTH CAROLINA, TENNESSEE, SOUTH CAROLINA, GEORGIA, AND ALABAMA					
Blue Ridge	33	8.8	0.15	1.0	−8.0
Appalachian Plateau	6	15.3	0.15	−1.2	−15.9
VIRGINIA AND WEST VIRGINIA					
Blue Ridge	16	−2.7	−0.04	−3.0	−1.0
Valley and Ridge	41	−5.6	−0.37	−8.2	−4.7
Appalachian Plateau	34	−36.3	−4.9	−38.4	−1.4
NORTH CAROLINA, TENNESSEE, SOUTH CAROLINA, GEORGIA, AND ALABAMA					
Blue Ridge	33	5.6	−0.48	−0.60	−5.4
Appalachian Plateau	6	11.6	−0.23	−1.9	−13.3
B3 STRATEGY[1]					
VIRGINIA AND WEST VIRGINIA					
Blue Ridge	16	−7.4	−0.09	−5.1	2.9
Valley and Ridge	41	−13.8	−0.36	−10.3	−0.83
Appalachian Plateau	34	−40.4	−5.8	−39.3	2.6
NORTH CAROLINA, TENNESSEE, SOUTH CAROLINA, GEORGIA, AND ALABAMA					
Blue Ridge	33	3.2	−1.0	−2.3	−3.2
Appalachian Plateau	6	7.2	−0.53	−3.1	−10.4

[1] Emissions control strategies were based on existing regulations (A2), moderate additional controls (B1), and more aggressive additional controls (B3)

Source: Sullivan et al. (2004)

Table B-9. **Population estimates of water chemistry percentiles for selected lake populations in the western U.S.[a]**

Population	n	N	pH		ANC (µeq/L)		SBC (µeq/L)		SO_4^{2-} (µeq/L)		NO_3^- (µeq/L)		DOC (mg/L)	
			P1	P5	P1	P5	P1	P5	P95	P99	P95	P99	P50	P99
Sierra Nevada	114	2,119	5.84	6.31	15	16	21	26	90	386	8	10	0.8	2.7
Cascades	146	1,473	5.95	6.25	11	18	20	31	60	97	3	6	1.3	2.6
Idaho Batholith	88	937	6.34	6.42	21	33	30	45	30	43	3	4	1.2	2.4
NW Wyoming	38	648	6.56	6.56	38	38	64	66	41	2,909	13	32	1.0	4.8
Colorado Rockies	121	1,173	6.02	6.65	25	42	58	80	915	2,212	10	13	1.3	5.7

[a]Data from Landers et al. (1987). [b]Excluding Fern Lake (4D3−017) which is naturally acidic. Note: The 1st and 5th percentiles (P1, P5) are presented for pH, ANC (µeq/L), and SBC (µeq/L) and the 95th and 99th (P95, P99) percentiles are shown for SO_4^{2-} (µeq/L) and NO_3^- (µeq/L). The median (P50) and 90th percentiles are shown for DOC (mg/L).

Table B-10. Population estimates of the percentage of lakes in selected subregions of the West with ANC and NO_3^- within defined ranges.

	ANC (µeq/L)			NO_3^- (µeq/L)	
	<0	**<25**	**<50**	**>5**	**>10**
Sierra Nevada	0	8.7	39.3	10.6	1.5
Cascades	0	10.2	22.4	1.5	0.0
Idaho Batholith	0	2.0	23.6	4.6	3.9
NY Wyominga	0	2.3	12.8	22.8	8.9
Colorado Rockies	0	0.9	5.5	9.8	1.8

a Excluding Fern Lake (4D3−017) which is a naturally acidic lake. Source: Landers et al. (1987)

Table B-11. Median streamwater ANC and watershed area of streams in Shenandoah National Park that have water chemistry and fish species richness data.

Site ID	Watershed Area (km²)	Median ANC (µeq/L)	# Fish Species
SMALLER WATERSHEDS (<10 KM²)			
North Fork Dry Run	2.3	48.7	2
Deep Run	3.6	0.3	N.D.a
White Oak Run	4.9	16.2	3
Two Mile Run	5.4	10.0	2
Meadow Run	8.8	−3.1	1
LARGER WATERSHEDS (>10 KM²)			
Brokenback Run	10.1	74.4	3
Staunton River	10.6	76.8	5
Piney River	12.4	191.9	7
Paine Run	12.7	3.7	3
Hazel River	13.2	86.8	6
White Oak Canyon	14.0	119.3	7
N. Fork Thornton River	18.9	249.1	9
Jeremy's Run	22.0	158.5	6
Rose River	23.6	133.6	8

a No data were available regarding the number of fish species in Deep Run. Source: Sullivan (2003)

Table B-12. Reference levels for the Acidic Stress Index based on logistic regression of fish presence as a function of the sensitive intermediate and tolerant ASI values for brown bullhead, brook trout, lake trout, and common shiner.

Reference Acid Stress Index		Fish Response
Lakes	**Streams**	
Tolerant ASI >30	Intermediate ASI >30	Loss of all fish species
Tolerant ASI >10	Sensitive ASI >30	Loss of brook trout
Intermediate ASI >80		Loss of other sport fish, such as smallmouth bass and lake trout
Sensitive ASI >80	Sensitive ASI >10	Loss of acid-sensitive species, such as minnows.

Source: Baker et al. (1990b).

Table B-13. General summary of biological changes anticipated with surface water acidification, expressed as a decrease in surface water pH.

pH Decrease	General Biological Effects
6.5 to 6.0	Small decrease in species richness of plankton and benthic invertebrate communities resulting from the loss of a few highly acid-sensitive species, but no measurable change in total community abundance or production.
	Some adverse effects (decreased reproductive success) may occur for highly acid-sensitive fish species (e.g., fathead minnow, striped bass).
6.0 to 5.5	Loss of sensitive species of minnows and dace, such as fathead minnow and blacknose dace; in some waters, decreased reproductive success of lake trout and walleye, which are important sport fish species in some areas.
	Visual accumulation of filamentous green algae in the near-shore zone of many lakes and in some streams.
	Distinct decrease in species richness and change in species composition of plankton and benthic invertebrate communities, although little if any change in total community abundance or production.
	Loss of some common invertebrate species from zooplankton and benthic communities, including many species of snails, clams, mayflies, and amphipods, and some crayfish.
5.5 to 5.0	Loss of several important sport fish species, including lake trout, walleye, rainbow trout, and smallmouth bass, as well as additional nongame species such as creek chub.
	Further increase in the extent and abundance of filamentous green algae in lake near-shore areas and streams.
	Continued shift in species composition and decline in species richness of plankton, periphyton, and benthic invertebrate communities; decreases in total abundance and biomass of benthic invertebrates and zooplankton may occur in some waters.
	Loss of several additional invertebrate species common in surface waters, including all snails, most species of clams, and many species of mayflies, stoneflies, and other benthic invertebrates.
	Inhibition of nitrification.
5.0 to 4.5	Loss of most fish species, including most important sport fish species such as brook trout and Atlantic salmon. A few fish species are able to survive and reproduce in water below pH 4.5 (e.g., central mudminnow, yellow perch, and in some waters, largemouth bass).

Measurable decline in the whole-system rates of decomposition of some forms of organic matter, potentially resulting in decreased rates of nutrient cycling.	
Substantial decrease in number of species of plankton and benthic invertebrates and further decline in species richness of plankton and periphyton communities; measurable decrease in total community biomass of plankton and benthic invertebrates of most waters.	
Loss of additional species of plankton and benthic invertebrate species, including all clams and many insects and crustaceans.	
Reproductive failure of some acid-sensitive species of amphibians, such as spotted salamanders, Jefferson salamanders, and the leopard frog.	

Source: Baker et al. (1990b).

Table B-14. **Estimated percentage of Adirondack lakes with and Acidic Stress Index exceeding the reference levels for effects on fish populations, based on diatom-inferred historical (pre-industrial) chemistry and present-day measured and inferred acid-base chemistry.**

ASI Reference Level	DDRP Target Population				ELS/NSWS Target Population Measured
	Diatom Inferred			Measured	
	Historical	Current	Net Change		
Tolerant ASI >30	0.0	3.6	+3.6	1.8	2.2
Tolerant ASI >10	0.0	9.1	+9.1	10.9	6.5
Intermediate ASI >80	7.3	21.8	+14.5	21.8	15.2
Sensitive ASI >80	28.5	41.2	+12.7	32.7	20.0

Source: Baker et al. (1990b).

Table B-15. **Estimated percentage of Adirondack lakes with acid-base chemistry unsuitable for fish population survival, based on diatom-inferred historical (pre-industrial) chemistry and present-day measured and inferred acid-base chemistry.**

Fish Species Model[a]	DDRP Target Population[b]				ELS/NWS Target Population[b]	ALSC
	Diatom-Inferred[c]					
	Historical	Current	Net Change	Measured	Measured	Measured
BROOK TROUT						
Bayesian	2.7	13.0	+10.3	14.2	10.1	21.8
LAF framework	-	-	-	-	15.8	24.6
pH	2.3	11.3	+9.0	12.8	9.3	22.2
pCa/pH	16.0	13.3	−2.6	14.5	10.3	23.0
pCa/pH, Al/DO[C]	16.6	15.6	−1.0	19.2	13.9	23.5
LAKE TROUT						

| Fish Species Model[a] | DDRP Target Population[b] | | | | ELS/NWS Target Population[b] | ALSC |
| | Diatom-Inferred[c] | | | | | |
	Historical	Current	Net Change	Measured	Measured	Measured
pH	6.4	18.1	+11.2	21.4	14.4	30.9
pCa/pH	31.7	25.1	−6.6	29.0	18.9	-
Inorg. Al	23.9	38.6	+14.7	26.2	17.1	-
COMMON SHINER						
pH	19.2	29.6	+10.5	33.5	21.3	42.3
pCa/pH	45.8	37.7	−8.1	40.2	29.1	-

[a] All models, except the brook trout Bayesian model (Section 3.5) and LAF framework (Section 3.4), are field-based acidification response models as defined in Section 3.3.3. [b] ELS/NSWS target population in Subregion 1A, defined in Section 3.1 (N = 1,290 lakes); a subset of these lakes was considered for the DDRP and sediment diatom analyses, for example, excluding lakes with ANC >400 µeq/L and with site depths <1.5 m (N = 675 lakes). See Sullivan (1990) for further details. [c] Estimates of acid-base chemistry inferred from sediment diatom analysis; methods and water chemistry described in Sullivan (1990). - Analysis not conducted. Source: Baker et al. (1990b).

Table B-16. **Estimated percentage of the lakes in the Northeast and Upper Midwest, ELS/NSWS target population with an Acidic Stress Index exceeding the reference levels for fish populations defined in Table C-12.**

ASI Reference Level	Subregion 1A	Northeast Region	Upper Midwest Region
Tolerant ASI >30	2.2	1.0	0.5
Tolerant ASI >10	6.5	2.4	1.0
Intermediate ASI >80	15.2	5.7	2.0
Sensitive ASI >80	20.0	8.6	3.1

Source: Baker et al. (1990b).

Table B-17. **Estimated percentage of lakes in the Northeast, ELS/NSWS target populations with acid-base chemistry unsuitable for fish population survival.**

Fish Species/Model	Subregion 1A	Entire Northeast
BROOK TROUT		
Bayesian	10.1	3.7
LAF Framework	15.8	8.9
pH	9.3	3.5
pCa/pH	10.3	4.4
pCa/pH, Al/DOC	13.9	7.0
LAKE TROUT		

Fish Species/Model	Subregion 1A	Entire Northeast
pH	14.4	5.8
pCa/pH	18.9	8.9
Inorganic Al	17.1	6.3
COMMON SHINER		
pH	21.3	9.5
pCa/pH	29.1	19.7

Source: Baker et al. (1990b)

Table B-18. **Distribution of acidic stress index values among the NSS-1 Target populations for the mid-Appalachian region.**

	Number (%)		Total Length (%)
	Lower Node	Upper Node	
SENSITIVE ASI			
≥ 10	84.6	66.7	76.1
10–30	10.1	18.9	14.0
30–50	1.4	1.9	1.9
50–80	1.8	2.6	1.6
>80	2.0	9.8	6.4
INTERMEDIATE ASI			
≥ 10	97.8	89.3	88.9
10–30	0.2	2.5	0.7
30–50	0.6	1.3	0.4
50–80	0.1	1.4	0.4
>80	1.3	5.4	1.9
TOLERANT ASI			
≥ 10	99.4	97.1	98.1
10–30	0.6	1.4	0.9
30–50	0.0	0.6	0.3
50–80	0.0	0.9	0.7
>80	0.0	0.0	0.0

Source: Baker et al. (1990b).

Table B-19. Distribution of acidic stress index values among the NSS-1 target populations for the interior Southeast region.

	Number (%)		Total Length (%)
	Lower Node	Upper Node	
SENSITIVE ASI			
≥ 10	79.4	70.1	75.9
10–30	18.8	21.1	18.8
30–50	0.0	1.7	2.0
50–80	1.7	5.2	2.5
>80	0.0	1.7	0.7
INTERMEDIATE ASI			
≥ 10	100.0	98.3	99.3
10–30	0.0	0.0	0.0
30–50	0.0	0.0	0.0
50–80	0.0	0.0	0.0
>80	0.0	1.7	0.7
TOLERANT ASI			
≥ 10	100.0	100.0	100.0
10–30	0.0	0.0	0.0
30–50	0.0	0.0	0.0
50–80	0.0	0.0	0.0
>80	0.0	0.0	0.0

Source: Baker et al. (1990b).

Table B-20. Comparison of solution and tissue chemistries at threshold treatment levels where significant impacts on tree growth or nutrient content were first observed. In many cases, adverse impacts were observed at the lowest Al treatment level. Hence, the actual threshold Ca/Al ratio may be higher than reported. Results are from a variety of studies reported in the literature.

Study	Solution Al (µmol/L)	Solution Ca/Al (M)	Foliar Ca (mg/km)	Foliar Al (mg/km)	Foliar Ca/Al (M)	Root Ca (mg/km)	Root Al (mg/kg)	Root Ca/Al(M)	Type of Study or Experiment[a]	Response Variable[b]	Al Analysis Used in Ratio[c]
NORWAY SPRUCE											
Godbold et al. (1988)	100	1.3							H	N	Ali
Matzner et al. (1989)	100+	0.3 to 1.8							F	N	Alt
Stienen and Bauch (1988)	1500	0.66	1470	32	31	770	1890	0.28	H	N,B	Alt
Schroder et al. (1988)	2000	1							H	N	Ali
RED SPRUCE											
Thornton et al. (1987)	250	1	1100	65	11.4	650	6000	0.07	H	B	Ali
Hutchinson et al. (1986)	185	2.2							S	B	Alt
Joslin and Wolfe (1988)	200	nd	~3000		~2000				S	B	Ali
Schier (1985)	1850	1.35			12.9			0.43	H	B,N	Ali
Ohno et al. (1988)	250	0.8			14				S	N	Ala in soil paste
Joslin and Wolfe (1992)		0.45							F	B	Alt
WHITE SPRUCE											
Nosko et al. (1988)	50	0.2							H	B	Alt
RED OAK											
Joslin and Wolfe (1989)	300	4.05			11.9			0.06	S	B	Alt in SrCl2
DeWald et al. (1990)	115	4.48	3630	75	32.4	3630	6415	0.38	S	B	Alt

Study	Solution Al (µmol/L)	Solution Ca/Al (M)	Foliar Ca (mg/km)	Foliar Al (mg/km)	Foliar Ca/Al (M)	Root Ca (mg/km)	Root Al (mg/kg)	Root Ca/Al(M)	Type of Study or Experiment[a]	Response Variable[b]	Al Analysis Used in Ratio[c]
McCormick and Steiner (1978)	7405	0.54							H	B	Alt
HONEYLOCUST											
Thornton et al. (1986b ;1986c)	50	1.1			8.4			0.21 to 0.32	H	B	Ali
Sucoff et al. (1990)	100	1.4						0.35	S	B	Ali
Wolfe and Joslin (1989)	100	4.3						0.71	S	B	Ali
SUGAR MAPLE											
Thornton et al. (1986a)	100–600	0.42 to 2.5	~2000	~190	9.9	~1500	~2700	0.4	H	B,N	Ali
LOBLOLLY PINE											
Cronan et al. (1989) Thornton (unpubl.)	500–3000	0.5	900	260	2.3	3700	7770	0.32	H	N	Ali
AMERICAN BEECH											
Cronan et al. (1989)	500–3000	0.5	2670	69	26.1	1140	7930	0.1	H	N	Ali
EUROPEAN BEECH											
Asp and Berggren (1990)	300	0.35			3.8			0.2	H	N	Ali
Cronan et al. (1989)	500	0.5							H	N	Ali
PEACH											
Edwards and Horton (1977)	222				10.8			0.008	H	N	Ali
SCOTCH PINE											
Ilvesniemi (1992)	185	nd	400	300	0.9		2300		S	N,B	Alt
McCormick and Steiner (1978)	2960	1.35							H	B	Alt

Study	Solution Al (µmol/L)	Solution Ca/Al (M)	Foliar Ca (mg/km)	Foliar Al (mg/km)	Foliar Ca/Al (M)	Root Ca (mg/km)	Root Al (mg/kg)	Root Ca/Al(M)	Type of Study or Experiment[a]	Response Variable[b]	Al Analysis Used in Ratio[c]
VIRGINIA PINE											
McCormick and Steiner (1978)	2960	1.35							H	B	Alt
PITCH PINE											
McCormick and Steiner (1978)	2960	1.35							H	B	Alt
Cumming and Weinstein (1990)	50	20							S	N,B	Alt
BIRCHES: GRAY, PAPER AND YELLOW											
McCormick and Steiner (1978)	4444	0.9							H	B	Alt
EUROPEAN BIRCH											
Goransson and Eldhuset (1987)	1000	0.02						0.17	H	N	Ali
RADIATA PINE											
Truman et al. (1986)	17	10.5	2120	800	1.8	1320	1850	0.48	H	N	Alt
DOUGLAS-FIR											
Keltjens and Van Loenen (1989)	370	0.54	2300	300	5.2				H	B	Alt
LARCH											
Keltjens and Van Loenen (1989)	555	0.36	1800	250	4.9				H	B	Alt

a Types of study include hydroponic (H), soil or sand culture (S), or existing forest (F). b Response variables include biomass (B), or nutrient content (N).
c Aluminum measurements include Ali (Ali), monomeric Al (Ala), and total Al (Alt). Since most of the lab studies were conducted under conditions of low pH and minimal DOC, measurements of total Al, Ali, and labile Al are very comparable. Source: Cronan and Grigal (1995)

Table B-21. **Overview of selected major processes by which landscape change can alter drainage water acid-base chemistry**

Landscape Change	Effect on Acid-Base Chemistry
Logging, blowdown	Dilution
	Lower deposition, less acidity
	Pulse of NO_3^- acidity initially
	Less base cation neutralization, more acidity
	Less water contact with mineral soils, less neutralization of acidic deposition inputs
Road building and construction	More base cation neutralization, less acidity initially
	Depletion of base cation reserves in soils, more acidity long-term
Drainage of wetlands	Re-oxidation of stored S, pulses of acidity with increased discharge
Drought	Reduced groundwater inputs to seepage lakes with consequent increased acidity
	Increased relative baseflow to drainage waters with consequent decreased acidity
Lake shore development	Decreased acidity
Insect damage	Pulse of NO_3^- acidity initially

Source: Sullivan (2000)

Table B-22. **Observed relationships between zooplankton species richness (R) and lakewater ANC.**

Taxonomic Group	Equation	r^2	p
Total Zooplankton	R = 15.65 + 0.089ANC	0.46	0.001
Crustaceans	R = 6.35 + 0.028ANC	0.47	0.001
Rotifers	R = 9.04 + 0.053ANC	0.30	0.001

Source: Sullivan et al. (2006a). Reprinted with permission.

Table B-23. Threshold response of increased mortality of fish to low pH listed from least sensitive to most sensitive.

Study	Species	Increased Mortality Threshold, pH	Study Conditions
Johnson et al. (1987)	Blacknose dace, creek chub	5.9 - 6.0	In situ bioassay with early life stages in Adirondack surface waters
	Brook trout	4.8 - 5.1	
Holtze and Hutchinson (1989)	Common shiner	5.4 - 6.0	Laboratory exposure of early life stages to pH and Al.
	Lake whitefish, white sucker, walleye	5.1 - 5.2	
	Smallmouth bass	4.8	
Johansson et al. (1977)	Atlantic salmon	5.0	Laboratory tests with eggs exposed to low pH, no Al.
	Brown trout	4.5 - 5.0	
	Brook Trout	4.5	
Swenson et al. (1989)	Black crappie	5.5	Laboratory tests with early life stages exposed to pH and Al.
	Rock bass	5.0	
	Yellow perch, largemouth bass	4.5	
Mills et al. (1987)	Fathead minnow	5.9	Whole-lake treatment (fish population recruitment failure)
	Slimy sculpin	5.6 - 5.9	
	Lake Trout	5.6	
	Pearl dace	5.1	
	White sucker	5.0 - 5.1	

Source: Baker et al. (1990b).

Table B-24.   Threshold values of pH for various taxa and effects.

Reference	Type of Study	Taxa	pH	Observed Effects
Buckler et al. (1987)	Lab bioassay	Striped bass	6.5	>50% larval mortality
McCormick et al. (1989)	Lab bioassay	Fathead minnow	6.0	Significant decrease in embryo survival
Mills et al. (1987)	Whole-lake experiment	Fathead minnow	5.9	Population recruitment failure
Klauda et al. (1987)	Lab bioassay	Blueback herring	5.7	>50% mortality of larvae
Holtze and Hutchinson (1989)	Lab bioassay	Common shiner	5.4	>50% embryo mortality
Baker and Schofield (1980)	Lab bioassay	White sucker	5.2	Substantial reduction in embryo survival
Kane and Rabeni (1987)	Lab bioassay	Smallmouth bass	5.1	>50% mortality of larvae after 30–day exposure
Leino et al. (1987)	Whole-Lake experiment	Adult fathead minnow	5.2–5.8	Increased numbers of chloride (ionoregulatory) cells on the gills
Lacroix (1985a)	Field survey	Atlantic salmon parr (age 1+)	4.9–5.3	Significantly lower blood Cl levels; high K levels
McDonald and Milligan (1988)	Lab bioassay	Adult brook trout	5.2	Reduced Na transport activity
McWilliams and Potts (1978)	Lab bioassay	Adult brown trout	5.0	Net Na loss; major shift in the gill tansepithelial potential
Tietge et al. (1988)	Lab bioassay	Adult brook trout	4.9	Increased volume density of lamellar chloride cells on gills
Booth et al. (1988)	Lab bioassay	Adult brook trout	4.8	Net loss of Na and Cl
Audet and Wood (1988)	Lab bioassay	Adult rainbow trout	4.8	Decreased plasma Na and Cl levels
Peterson and Martin-Robichaud (1986)	Lab experiment	Atlantic salmon larvae	4.5	Reduced accumulation of Na, K, and Ca
Powell and McKeown (1986)	Lab bioassay	Coho salmon parr and smolts	4.4	Net decrease in plasma Na

Source: Baker et al. (1990b).

Table B-25. Threshold values of Al for various species and effects (form of Al not specified for most studies).

Reference	Type of Study	Taxa	pH	Al (µg/L)	Observed Effect (at similar pH without added Al)
Sadler and Lynam (1988)	LB	Brown trout	5.2	30	Significant reduction in fish growth
Turnpenny et al. (1987)	Field survey	Broen trout	—	40	Fish absent or rare in streams in Wales and England
Holtze and Hutchinson (1989)	LB	Walleye	4.9	50	>50% mortality of embryos to 4–d post-hatch
Skogheim and Roseland (1986)	Field mesocosm experiment	Atlantic salmon	5.1	75	>50% mortality of smolts
Klauda and Palmer (1987)	LB	Blueback herring	5.5–5.6	100	>50% larval mortality
Rosseland and Skogheim (1984)	LB	Atlantic salmon	4.9–5.0	130	Significant increase in mortality of presmolts
Baker and Schofield (1982)	LB	White sucker	5.2	200	>50% larval mortality
Fjellheim et al. (1985)	LB	Eel	5.1	230	Significant increase in elver mortality
Brown (1983)	LB	Brown trout	4.5–5.4	250	>50% fry mortality
Schofield and Trojnar (1980)	Field study	Brook trout	4.9	286	No survival of trout stocked into lakes with higher total Al (even after accounting for pH effects).
Ormerod et al. (1987)	Whole-stream experiment	Atlantic salmon and brown trout	5.0	350	>50% mortality of young-of-the-year.

Source: Baker et al. (1990b)

Table B-26. The effects of increasing Ca^{2+} to ameliorate low pH and high Al.

Reference	Type of Study	Taxa	pH	Al Range (µg/L)	Ca^{2+} Range (µeq/L)	Observed Response to Increasing Ca^{2+}
Brown (1982, 1983)	LB	Brown trout	4.5–5.1	—	12–400	Increased embryo survival and hatch
Wright and Snekvik (1978)	Field survey	Brown trout	4.5–7.5	—	20–200	Trouot status significantly correlated with log Ca^{2+} and pH.
Brown (1983)	LB	Brown trout	4.5–5.4	0–500	12–100	Increased fry survival in low pH or high Al waters
McDonald (1983)	LB	Rainbow trout	4.3	—	69–223	Decreased adult mortality and net loss of Na and Cl
Edwards et al. (1987)	LB	Brown trout	4.2	—	100–5600	Lower loss of plasma Na and Cl ions
Freda and McDonald (1988)	LB	Common shiner, rainbow trout	4.0	—	70–1000	Significant decrease in Na loss
Mount et al. (1988)	LB	Brook trout	5.0–6.3	0–500	25–400	Increased survival and growth of adults; increased progeny survival with adult exposure to low and high Al
Sadler and Lynam (1988)	LB	Brown trout	5.2	0–80	8–800	Increased yearling survival and growth in waters with elevated Al.

Source: Baker et al. (1990b).

Table B-27. Brook trout acidification response categories developed by Bulger et al. (2000) for streams in Virginia.

Response Category	Chronic ANC Range (µeq/L)	Expected Response
Suitable	>50	Reproducing brook trout expected if other habitat features are also suitable
Indeterminate	20 to 50	Brook trout response expected to be variable
Episodically acidic	0 to 20	Sub-lethal and/or lethal effects on brook trout are possible
Chronically acidic	<0	Lethal effects on brook trout probable

Table B-28. Partial listing of bioassays demonstrating decreased fish survival in waters with low pH and (or) elevated aluminum.

Reference	Species	Life Stage	Lab/Field
Johansson and Kihlström (1975)	Northern pike	Fry	Lab
Johansson and Milbrink (1976)	Roach European perch	Egg	Lab, field
Johansson et al. (1977)	Brown trout; Brook trout	Egg and fry	Lab
Trojnar (1977)	White sucker	Egg and fry	Lab
Peterson et al. (1980)	Atlantic salmon	Egg	Lab
Schofield and Trojnar (1980)	Brook trout	Fry	Lab
Baker and Schofield (1982)	Brook trout; White sucker	Egg and fry	Lab
Brown (1983)	Brown trout	Fry	Lab
Hulsman et al. (1983)	Walleye Rainbow trout	Egg Fry	Field
Sharpe et al. (1983)	Brook trout; Brown trout Rainbow trout; Mottled sculpin	Fry and adult	Field
Jagoe et al. (1984)	Arctic char	Egg and fry	Lab
Lacroix (1985b)	Atlantic salmon	Egg and fry	Field
Ingersoll (1986)	Brook trout	Egg and fry	Lab
Buckler et al. (1987)	Striped bass	Fry	Lab
Johnson et al. (1987)	Brook trout; Lake trout Creek chub; Blacknose dace	Egg, fry, and young-of-year	Field
Klauda and Palmer (1987)	Blueback herring	Egg and fry	Lab
Lacroix and Townsend (1987)	Atlantic salmon	Juvenile	Lab
Wales and Liimatainen (1987)	Walleye	Egg	Field
Palmer et al. (1988)	Bluegill; Fathead minnow	Juvenile	Lab
Gunn (1989)	Lake trout	Egg and fry	Lab, field
Holtze and Hutchinson (1989)	Common shiner; Lake whitefish White sucker; Walleye Smallmouth bass; largemouth bass	Egg and fry	Lab
Hutchinson et al. (1989)	Lake trout Brook trout	Egg and fry	Lab

Table B-29.   Mills et al., 1987. Shows effect of various pH on fish forage fish and lake trout.

Biota	1977 pH 6.13	1978 pH 5.93	1979 pH 5.64	1980 pH 5.59	1981 pH 5.02	1982 pH 5.09	1983 pH 5.13
Forage fish		Fathead minnow experience recruitment failure	Fathead minnow near extinction; slimy sculpin decline in abundance	Increase in abundance of pearl dace, Suckers very abundant.	White sucker recruitment failure; no effect on adult growth and survival	Recruitment failure for all species	Recruitment failure for all species
Lake trout	Increase in condition i.e., "fatter"		Increased abundance of young-of-the-year	Lake trout recruitment failure; condition similar to preacidification	Recruitment failure; no effect on adult growth and survival	Lake trout condition poor; recruitment failure; reduced adult survival	Lake trout condition very poor; recruitment failure; reduced adult survival

Source: (Baker et al., 1990b).

Table B-30.   Range of minimum pH of fish species occurrence in 11 lake surveys.

Family and Species	High Minimum pH	Low Minimum pH
CYPRINIDAE		
Bluntnose minnow	6.6	5.6
Fathead minnow	6.3	5.1
Blacknose dace	6.8	5.6
Pearl dace	5.9	4.7
Northern redbelly dace	5.9	4.7
Common shiner	6.2	4.9
Golden shiner	5.5	4.5
Creek chub	5.9	4.6
SALMONIDAE		
Brook trout	5.6	4.6
Lake trout	5.2	4.9
Brown trout	5.0	4.6
Atlantic salmon	6.3	5.3
CENTRARCHIDAE		
Smallmouth bass	7.0	4.9
Largemouth bass	5.0	4.6

Family and Species	High Minimum pH	Low Minimum pH
Pumpkinseed	6.6	4.6
Bluegill	4.5	4.5
Rock bass	6.2	4.6
Black crappie	5.6	5.6
PERCIDAE		
Yellow perch	5.8	4.4
Walleye	6.9	5.2
Johnny darter	6.2	4.9
Iowa darter	6.2	4.6
ESOCIDAE		
Northern pike	5.9	4.0
CATASTOMIDAE		
White sucker	5.5	4.6
ICTALURIDAE		
Brown bullhead	5.6	4.5
UMBRIDAE		
Central mudminnow	4.5	4.2
GASTEROSTEIDAE		
Brook stickleback	5.4	4.6

Source: Baker et al. (1990b).

Table B-31. Studies[a] that either did (yes) or did not (no) yield evidence that acidic deposition affected certain species of birds

Species	Diet/ Foraging		Breeding Distribution		Reproductive Measures		Reference[a]
	Yes	No	Yes	No	Yes	No	
Common loon	x		x	x	x	x	1–3, 19,20
Common merganser			x		x		19
Belted kingfisher			x				4
Osprey	x		x		x		5,6
Black duck	x		X		x[b]		7–9
Common goldeneye			x[b]				8
Ring-necked duck	x				x		10,11
Eurasian dipper	x		x		x		12–14
Eastern kingbird				x	x		15
Tree swallow	x			x	x		16–18

[a]1= Alvo et al. (1988); 2 = Parker (1988); 3 = Wayland and McNicol (1990); 4 = Goriup (1989); 5 = Eriksson (1983); 6 = Eriksson (1986); 7 = Hunter et al. (1986); 8 = DesGranges and Darveau (1985); 9 = Rattner et al. (1987); 10,11 = McAuley and Longcore (1988a,b) 12,13 = Ormerod et al. (1985, 1986); 14 = Ormerod and Tyler (1987); 15 = Glooschenko et al. (1986); 16,17 = Blancher and McNicol (1988, 1991); 18 = St. Louis et al. (1990); 19 = Blancher and McNicol (1991); 20 = Blair (1990).. [b]The effect was beneficial
Source: Longcore and Gill (1993)

Table B-32. Predicted habitat suitability for lakes in the Algona Model Dataset

Group	Total Model Lakes	Current Suitable Lakes	Number of Lakes with Suitable Habitat Under Each Emission Scenario														
			Current pH <6					Current pH 6–6.5					Current pH >6.5				
			S1	S2	S3	S4	S5	S1	S2	S3	S4	S5	S1	S2	S3	S4	S5
Fish	526	338	29	34	40	77	100	97	100	107	124	133	196	196	197	197	197
Common loon pairs	433	100	12	14	14	16	17	22	22	23	24	24	66	66	66	67	67
Common loon broods	433	36	2	2	2	2	2	6	6	7	7	7	28	28	28	28	28
Common merganser pairs	433	52	6	12	27	68	86	14	17	20	33	44	31	31	32	34	35
Common merganser broods	433	31	6	10	18	69	89	14	15	16	21	29	12	11	10	10	10

Results are expressed as the number of lakes with suitable habitat for fish, common loons (pairs and broods) and common mergansers (pairs and broods) under each emission scenario (S1, S2, S3, S4, S5) according to current pH classes (<6, 6–6.5, >6.5). Habitat suitability is calculated by probability of presence at time t from WARMS output (# of suitable lakes at time t/total number of lakes), for fish [n = 526], and for loons and mergansers [n = 433].

Table B-33. Summary statistics of biological data layers for mercury (Hg) concentrations in fish and wildlife (µg/g) in the northeastern U.S. and southeastern Canada.

			Hg Concentrations			
Category/Species	**Sample Size**	**Data layer Designation**	**Mean ± Standard Deviation**	**Range**	**Hg Level of Concern (Tissue Type)**	**Percentage of Samples with Concentration > Level of Concern**
HUMAN HEALTH						
Yellow perch[a]	4089	Primary	0.39 ± 0.49	<0.05–5.24	0.30 (fillet)	50
Largemouth bass[b]	934	Secondary	0.54 ± 0.35	<0.05–2.66	0.30 (fillet)	75
ECOLOGICAL HEALTH						
Brook trout	319	Secondary	0.31 ± 0.28	<0.05–2.07	0.16 (whole fish)	75
Yellow perch[c]	(841)[d]	Secondary	0.23 ± 0.35	<0.05–3.18	0.16 (whole fish)	48
Common loon[e]	1546	Primary	1.74 ± 1.20	0.11–14.20	3.0 (blood)	11
Bald eagle	217	Secondary	0.52 ± 0.20	0.08–1.27	1.0 (blood)	6
Mink	126	Secondary	19.50 ± 12.1	2.80–68.50	30.0 (fur)	11
River otter	80	Secondary	20.20 ± 9.30	1.14–37.80	30.0 (fur)	15

Note: All data are in wet weight except for fur, which is on a fresh-weight basis
[a]Fillet Hg in yellow perch is based on individuals with a standardized length of 20 cm.
[b]Fillet Hg in largemouth bass is based on individuals with a standardized length of 36 cm.
[c]Whole-fish Hg in yellow perch is based on individuals with a standardized length of 13 cm. Whole-fish Hg for yellow perch was converted to fillet Hg.
[d]The sample population of 841 yellow perch examined for whole-fish Hg is included with the 4089 fillets (i.e., the total number of all biotic data layers does not double-count yellow perch).
[e]Egg Hg for the common loon was converted to the adult blood equivalent

Table B-34. Mercury concentrations in avian eggs and tissues and related effects.

Tissue	**Concen. (ppm)**	**Wet (w) or Dry (d)**	**Endpoint**	**Species**	**Reference**
Liver	1.06	w	No effect	Common tern	Gochfeld (1980)
Liver	22.2	w	Abnormal feather loss in juveniles	Common tern	Gochfeld (1980)
Liver	5	w	Conservative threshold for major toxic effects	Water birds	Zillioux et al. (1993)
Liver	7.2	w	Increased disease and emaciation	Common tern	Spalding and Forrester (1991)
Liver	9.08	w	Nesting success	Common tern	Finley and Stendall (1978)
Liver	20.7	w	Hatching success	Common tern	Finley and Stendall (1978)

Tissue	Concen. (ppm)	Wet (w) or Dry (d)	Endpoint	Species	Reference
Liver	30	W	Neurologic effects	Osprey	Heinz (1974)
Liver	35	w	Death	Common loon	Wiemeyer et al. (1987)
Liver	54.5	w	LD33[a]	European starling	Finley et al. (1979)
Liver	97.7	w	Death	Gannet	
Liver	103.6	w	LD33	European starling	Finley et al. (1979)
Liver	126.5	w	LD33	Red-winged blackbird	Finley et al. (1979)
Liver	306 total/ 20.4 MeHg	d	No adverse effects observed	Black-footed albatross	Gochfeld (1980)
Brain	4–6	w	Failure to hatch	Black duck	Hoffman and Moore (1979)
Brain	20	w	25% mortality	Zebra finch	Scheuhammer (1988)
Egg	1–5/0.2–1.0	d	Reduced productivity in one half of the population	Merlin	Newton and Hass (1988)
Egg	0.5–1.5	w	Decreased hatchability	Pheasant	Heinz (1979)
Egg	0.86	w	Aberrant nesting behavior	Common loon	Heinz (1979)
Egg	1.0	w	Successful reproduction	Common tern	Finley and Stendall (1978)
Egg	1.0–3.6	w	Residue threshold for significant toxic effects	Variety of water birds	Zillioux et al. (1993)
Egg	2–16	w	No decreased hatchability	Herring gull	Finley and Stendall (1978)
Egg	3.65	w	27% hatching, 10–12% fledging	Common tern	Finley and Stendall (1978)
Kidney	37.4 total/ 6.2 MeHg	d	No adverse effect observed	Black-footed albatross	Kim et al. (1996)
Kidney	40.4	w	LD33	Grackle	Finley et al. (1979)
Kidney	74.3	w	LD33	Red-winged blackbird	Finley et al. (1979)
Kidney	86.4	w	LD33	European starling	Finley et al. (1979)

[a]LD33 = lethal dose, 33%. Source: Wolfe et al. (1998)

Annex C. Nutrient Enrichment Effects from Nitrogen

C.1. Effects on Biogeochemical Pathways and Cycles

C.1.1. Nitrogen Cycling in Terrestrial Ecosystems

C.1.1.1. Nitrogen Deposition Effects on DON Leaching

Some N fertilization experiments suggest that increasing N deposition drives an increase in production of dissolved organic nitrogen (DON) in soil (McDowell et al., 2004; Seely and Lajtha, 1997), but there is little evidence that elevated N deposition increases the export and loss of DON from terrestrial ecosystems. Essentially all of the increase in N export across gradients of N deposition occurs as an increase in NO_3^- rather than DON export. The latter is typically less than 2 kg N/ha/yr from most northeastern-forested watersheds (Campbell et al., 2000b; Aber et al., 2003; Goodale et al., 2000; Lovett et al., 2000).

C.1.1.2. Interactions Between Snow Melt and Nitrate Leaching

Changes in other environmental parameters can also be important. Measurement of nutrient concentrations in Emerald Lake (Sierra Nevada) over a period of 19 years suggested that NO_3^- concentration declined between 1983 and 1995. This was likely caused by changes in the snow regime induced by a drought during the period 1987 to 1992 (Sickman et al., 2003). Years that had shallow and early melting snowpacks generally had lower snowmelt NO_3^- concentration. In addition, declines in NO_3^- concentration during the growing season even in the wet years of 1993 through 2000 were likely the result of increased P loading to Emerald Lake and the consequent release of phytoplankton from P limitation (Sickman et al., 2003).

C.1.1.3. Denitrification: NO and N_2O Flux

Davidson et al. (2000) described N gas loss from terrestrial ecosystems using a conceptual model called "hole-in-the-pipe." In this model, production of NO, N_2O, and N_2 gas are functions of the general rate of N cycling processes through soil (i.e., the N flux "flowing through the pipe"), combined with information on soil water content, a key determinant of the ratio of $NO:N_2O$ (relative "hole size" for NO and N_2O gas "leakage"). The model formulation has been supported by a range of field measurements in temperate and especially tropical ecosystems (Davidson et al., 2000), and suggests that processes that increase the rate of N cycling through soils should also increase the rate of N gas loss from these systems. Production of NO and N_2O tend to be lower in temperate than in tropical ecosystems, largely because of colder temperatures and slower rates of N cycling in temperate systems, and the frequency of P rather than N limitation in tropical systems. However, increased availability of N through fertilization can increase the rate of NO and N_2O gas loss from temperate forests.

Early studies of N gas emission in response to N fertilization experiments at the Harvard Forest, MA, found small increases in N_2O production in response to the highest N treatment (150 kg N/ha/yr) to a red pine (*Pinus resinosa*) stand, but N_2O losses accounted for <0.4% of N additions (Magill et al., 2000). However, later studies found that NO emission rates can be more than an order of magnitude greater than N_2O emissions, with NO emissions amounting to 3-4% to 8% (4 to 5 kg N/ha/yr) of the N additions to the fertilized pine stands (Venterea et al., 2003, 2004). Emissions of NO and N_2O increased with fertilization rate (0, 50, and 150 kg N/ha/yr) in both the red pine and a nearby red oak (*Quercus rubra*)/red maple (*Acer rubrum*) stand (Venterea et al., 2003, 2004). A study of the response of Scots pine (*Pinus sylvestris*) stands across a gradient of N deposition in Germany found a threefold to fourfold increase in the rate of NO and N_2O production as N deposition increased from 15 to 22 kg N/ha/yr. In these forests, both gases were produced in roughly equal amounts, although as N deposition increased, the rate of NO production increased more steeply than did the rate of N_2O production (Butterbach-Bahl et al., 2002).

At Höglwald, a German site receiving 20 to 30 kg N/ha/yr in throughfall, Butterbach-Bahl et al. (2002) reported higher emissions of NO than N_2O in both a spruce and a beech stand, with N oxide emissions totaling 4.5 to 6.8 kg N/ha/yr. Intensive laboratory studies suggested additional emissions of N_2 gas amounting to 7.2 and 12.4 kg N/ha/yr in the spruce and beech stands, respectively. This is the only known forest site for which a complete (NO, NO_2, N_2O, and N_2) N gas budget has been estimated, and in total, these measurements suggest that soil emissions may balance 46% to 78% of the N received in throughfall at this site. This result suggests somewhat higher rates of N gas loss than might be inferred from a series of ^{15}N tracer studies in conifer stands across Europe, which spanned a range of rates of N input from atmospheric and experimental sources of 3 to 91 kg N/ha/yr. Across all sites, total recovery of added ^{15}N in soil, vegetation, and lysimeter leachate after 9 to 21 months amounted to 65% to 105% of added ^{15}N (Tietema et al., 1998), providing a broad constraint on N gas emissions of no more than 35% of added ^{15}N. The lowest rates of ^{15}N recovery (65% to 67%) occurred at Speuld and Ysselsteyn, two sites in The Netherlands with the highest rates of chronic throughfall N input (35 to 53 kg N/ha/yr). Although much more work is needed on complete N gas budgets, several lines of evidence suggest that trace gas emissions of N may constitute an increasing pathway of N loss with increasing rates of N deposition.

C.1.1.4. Climate and N_2O Interactions

Rainfall events are an important feature controlling N_2O produced via denitrification. Rainfall increases soil moisture. This inhibits O_2 diffusion creating anoxic conditions, which increases rates of denitrification. A study of a spruce forest sites under ambient and elevated N deposition (20 and 30 kg N/ha/yr, respectively) indicated through most of the study period N_2O emission was equivalent between the sites (Mohn et al., 2000). However, after rainfall events the maximum rate of N_2O emission was much higher for the +N plots, especially when rainfall caused low soil redox potential (an indicator of anoxic conditions). Another study of mixed spruce, pine and birch forest (100 years old) under well- and poorly drained soil moisture conditions indicated poorly drained soils produced 1/3 more N_2O (118 g N_2O^- N/ha/yr) than well drained soils. In this study, N deposition was increased in the poorly drained soil from ambient (12 kg N/ha/yr) to elevated (42 kg N/ha/yr), N_2O emissions increased by a factor of more than 2 (254 kg N/ha/yr) (Klemedtsson et al., 1997).

In addition to soil moisture, temperature also influences denitrification. The PnET-N-DNDC model is designed to simulate and predict soil C and N biogeochemistry in temperate forest ecosystems and to simulate the emissions of N_2O and NO from forest soils. The model couples the PnET model (Photosynthesis-Evapotranspiartion-Model), the Denitrification-Decomposition (DNDC) model, and an N module that are further described in Li et al. (1992; 1996; 2000a), Li (2000), and Stange et al. (2000). The PnET-N-DNDC model is designed to simulate and predict soil C and N biogeochemistry in temperate forest ecosystems and to simulate the emissions of N_2O and NO from forest soils. Denitrification is described in the model as a series of sequential reductions driven by microorganisms using N oxides as electron acceptors under anaerobic conditions. As intermediates of the processes, NO and N_2O are tightly

controlled by the kinetics of each step in the sequential reactions. The capacity of this model to simulate N trace gas emissions from forest soils was tested by comparing model results with results form field measurements at 19 different field sites across Europe and 1 site in the U.S. (Kesik et al., 2005). Possible feedbacks of temperature and precipitationchange on forest soil NO and N_2O emissions in Europe were investigated using PnET-N-DNDC (Kesik et al., 2006). The model results indicated decreasing precipitation and increasing temperature in areas with light texture soils (below 15%) resulted in decreased soil moisture values; in turn, N_2O production by denitrification decreases. Under these same environmental conditions, NO production by nitrification increases. Most laboratory studies show increasing temperature increases N_2O production, however if water filled pore space (WFPS) increases to 70-80%, then N_2 rather than N_2O is the main product of denitrification and N_2O emissions go down. This illustrates how N_2O emissions increase with increasing soil moisture until soil moisture become more conducive to N_2 emission.

C.1.2. Nitrogen Cycling in Transitional Ecosystems

C.1.2.1. Denitrification: Measurement Techniques

There are a variety of methods for measuring denitrification rates in wetland, freshwater and marine sediments, including measurements of NO_3^- loss, N_2 production, N_2O accumulation in response to acetylene inhibition of N_2O reduction, isotopic methods, and N_2:argon (Ar) measurement by membrane inlet mass spectrometry (MIMS) (Smith, 2006). Most direct measurements of denitrification have measured only rates of production of N_2O, or used the "acetylene block" technique of inhibiting transformation of N_2O to N_2 and monitoring the accumulation of N_2O as a surrogate of the sum of N_2O and N_2. The acetylene block method is highly problematic, however, as it also inhibits rates of nitrification, and so denitrification rates are strongly underestimated where nitrification and denitrification processes are coupled closely in space or time (Groffman et al., 2006).

Techniques can be based on laboratory incubation of sediment cores or in situ studies. Each method has advantages and disadvantages and many studies have been conducted to compare results among the various methods (e.g., Bernot et al., 2003; Seitzinger, 1988, 1993, 2002b; Smith et al., 2006a; Groffman et al., 2006). Kana et al. (1998) described the MIMS method to measure small changes in dissolved N_2 caused by denitrification in sediments. This technique allows measurement of N_2 flux in unperturbed sediment cores with high temporal resolution (Kana et al., 1998). This is especially useful during summer conditions when NO_3^- concentration in the water is typically low, but the high temperature can support high rates of denitrification. Under such conditions, it is likely that a coupled sequence of nitrification and denitrification accounts for substantial N loss from estuarine sediments (Kemp et al., 1990). Constraints regarding field and analytical methods have seriously limited understanding of the magnitude and controls on denitrification (Groffman et al., 2006).

C.1.2.2. Nitrogen Deposition Effects on Methane

Increased N loading to transitional ecosystems can affect both methane (CH_4)-producing and CH_4-oxidizing microbial activity. The difference between the CH_4 production and oxidation determines the magnitude of CH_4 emission from soils. There is evidence to support that ammonium compounds reduce CH_4 oxidation (Gulledge et al., 1997; King and Schnell, 1994; Steudler et al., 1989), but ammonium compounds have also been observed to increase methanotropic bacterial activity (Bodelier et al., 2000). In general CH_4 emissions from saturated soils have been observed to increase with N addition (Granberg et al., 2001; Saarnio et al., 2003; Zhang et al., 2007). A hypothesis for explaining this effect is that increases in vegetative cover caused by N addition increase C availability through root exudates, which in

turn stimulates methanogenic bacteria and CH_4 emissions (Granberg et al., 2001; Saarnio et al., 2003; Zhang et al., 2007).

Saarnio et al. (2003) observed moderate increases in CH_4 emissions from boreal wetland soils with N fertilization rates of 30 kg N/ha/yr as ammonium nitrate (NH_4NO_3). Comparable N application rates and effects on CH_4 emissions were also observed by Granberg et al. (2001) in a similar ecosystem type. Zhang et al. (2007) observed elevated CH_4 emissions from freshwater wetland soils with experimental N additions of 240 kg N/ha/yr. They postulated that additional N increased abundance of *Deyeucia angustifolia* which increased CH_4 emissions by supplying methanogenic bacteria with additional substrate in the form of root exudates. Other studies have shown that N addition had little or no effect on CH_4 emissions across a variety of ecosystem types (Ambus and Robertson, 2006; Saarnio et al., 2000; Silvola et al., 2003). Note that the N enrichment rates employed in all of the above reported studies related to N effects on soil CH_4 emissions were greater (30 to 240 kg N/ha/yr) than atmospheric N inputs in most areas of the U.S. that are heavily effected by elevated atmospheric N deposition. See ISA Section 3.4 for a discussion of methane flux from terrestrial, transition and aquatic ecosystems.

C.1.3. Nitrogen Cycling in Estuarine Ecosystems

C.1.3.1. Denitrification and Anammox in Estuarine Ecosystems

Denitrification is a major factor governing the loss of N from estuarine ecosystems. Denitrification by microbes found in estuarine and marine sediments releases much of the added N inputs back into the atmosphere (Arrigo, 2005; Vitousek et al., 1997). Collection of quantitative data on this process has been hampered, however, by the complexity of environmental controls on the denitrification process and difficulties in measuring denitrification rates (Kana et al., 1998). Major environmental controls include temperature and the availability of NO_3^-, O_2, and organic materials (Rysgaard et al., 1994; Seitzinger, 1988).

Marine microbial ecology is highly complex and poorly understood. Relatively new knowledge about anammox bacteria has completely altered scientific understanding of N cycling in the oceans. Although it was previously believed that denitrification was responsible for virtually all of the transfer of Nr in the ocean to the atmosphere as N_2 gas, it now appears that anaerobic ammonium oxidation (anammox) may account for up to 50% of the N_2 production in the oceans (Dalsgaard et al., 2005; Devol, 2003; Kuypers et al., 2005; Ward, 2003). This reaction uses NO_2^- as the primary electron acceptor and is catalyzed by planctomycete bacteria of the genera Brocadia, Kuenenia, and Scalindua. That NH_4^+ could be oxidized under anoxic conditions was theorized several decades ago based on calculations of the ratios among N, P, and C in marine ecosystems. Nevertheless, the process was not experimentally documented until the 1990s (van de Graaf et al., 1995). More recently, anammox has been detected in a variety of freshwater, estuarine, and marine waters and sediments (Dalsgaard et al., 2005; Devol, 2003; Engstrom et al., 2005; Jetten et al., 2003, 2005; Kuypers et al., 2005; Op Den Camp et al., 2006; Pilcher, 2005; Rysgaard et al., 2004; Ward, 2003)

C.1.3.2. Nitrogen Budgets

The greatest uncertainty in the development of detailed N budgets for coastal ecosystems is quantifying how much of the N deposited on the watershed is transferred through the terrestrial watershed to the estuary. The difficulty stems from multiple agricultural and mobile and stationary fuel combustion emission sources in an estuary watershed; quantifying dry deposition to the estuary surface and to the watershed; measuring gaseous losses of NH_3 and NO_X compounds to the atmosphere; and complex N flow pathways through the watershed (NRC, 2000). Published estimates of the contribution of

atmospheric deposition to estuary N load exhibit wide variability. Such estimates for a specific estuary may differ. Some examples are summarized in Table C-1. Despite the variability, it appears that atmospheric sources of N loading to estuaries in the U.S. can be quantitatively important. The major sources of N to estuaries and near-coastal marine waters in the U.S., in addition to atmospheric deposition, include wastewater effluent derived mainly from food imports and consumption, fertilizer application, livestock feed imports, and N-fixing crops (Boyer et al., 2002; Driscoll et al., 2003).

Table C-1.   **Estimated percent of total N load to Delaware Bay and Hudson River/Raritan Bay contributed by atmospheric deposition.**

Reference	Percent of N Load Contributed by Atmospheric Deposition	
	Delaware Bay	Hudson River/Raritan Bay
Paerl (1985)	44	—
Hinga et al. (1991)	—	33
Scudlark and Church (1993)	15	—
Paerl (1995)	—	68
Jaworski et al. (1997)	44	68
Alexander et al. (2001)	22	26
Castro et al. (2001)	—	10
Stacey et al. (2001)		
Land-based	16	10
Sparrow model	25	27
Castro and Driscoll (2002)	20	17
Castro et al. (2003)	23	18

Boyer et al. (2002) estimated that atmospheric deposition averaged 31% of total N inputs over the combined area of the 16 northeastern river basins. Contributions from atmospheric deposition ranged from 60% of N inputs for the basins in northern Maine to 15 to 20% for the Schuylkill and Potomac River Basins, the latter of which had large agricultural N inputs. Across all basins, estimated riverine export of N amounted to 25% of total N inputs, and ranged from 11% to 40%. This result is consistent with a similar analysis by Howarth et al. (1996), who found that basins draining to the North Atlantic exported approximately 25% of anthropogenic N inputs on average.

Turner et al. (2001) found a strong correlation between population density (persons/ km^2) and the total N loading from watershed to estuary ($r^2 = 0.78$) for coastal watersheds in the U.S. This finding is likely due to the prevalence of automobiles in heavily populated areas, along with their associated N emissions and deposition, plus the myriad non-atmospheric sources of N from human activities, particularly sewage releases. They also determined that direct atmospheric deposition becomes increasingly more important as a contributor to the total N loading to an estuary as the water surface area increases relative to total watershed area (terrestrial plus water surfaces). Turner et al. (2001) found that, on average, direct atmospheric deposition of N accounted for more than an estimated 25% of the estuarine

N load when the estuary surface occupied 20% or more of the overall watershed area. Few of the estuaries in the eastern U.S. comprise such a large percentage of their watershed (Castro et al., 2001).

The estimates of the effect of direct atmospheric deposition to estuary surfaces are hampered by uncertainties in dry deposition rates. Many published studies have assumed that dry N deposition is equal to measured wet deposition (Fisher and Oppenheimer, 1991; Hinga et al., 1991; Scudlark and Church, 1993), and this is probably biased high (Baker, 1991a). However, other studies have assumed dry N deposition rates for estuarine and near coastal areas are equal to 40% of wet (Jaworski et al., 1997) or 67% of wet (Meyers et al., 2000b). Of particular importance, the rate of dry deposition to open water surfaces is much lower than the rate of dry deposition to vegetated terrestrial surfaces. Paerl et al. (2001a) estimated that dry deposition to open estuarine surfaces is three to five times lower than to vegetated surfaces. This difference is seldom considered in N-budgeting studies, and can have a substantial effect on estimates of direct atmospheric loading to estuary surfaces, which is especially important for estuaries having low watershed area to estuary surface area ratio.

A number of empirical approaches have been developed to quantify N fluxes to the coastal zone which rely on estimates of N sources within the watershed and characteristics of the landscape. Alexander et al. (2002) compared several of these empirical methods, the most accurate and least biased of which was that of Howarth et al. (1996). A modified version of the Howarth et al. (1996) methodology was published by Boyer et al. (2006). More mechanistic approaches include those of Bouwman et al. (2005), Van Drecht et al. (2003), and Green et al. (2004).

C.1.4. Timing of Chemical Change

C.1.4.1. Interannual Change: Nitrate Leaching

Interannual changes in N cycling can be reflected in changes in streamwater chemistry. NO_3^- leaching from terrestrial ecosystems throughout the 1980s was observed in many of the original lakes in EPA's Adirondack Long Term Monitoring (ALTM) program (Driscoll and Van Dreason, 1993), which was followed by a decline during the 1990s. As a consequence of this subsequent decline, Driscoll (2003) reported an overall significant ($p < 0.1$) decrease in NO_3^- concentration for the period 1982 to 2000 for 8 of the 16 original ALTM monitoring sites. Only the one mounded seepage lake in the study (Little Echo Pond) had a small, but statistically significant, increase in NO_3^- concentration (0.01 μeq/L/yr, $p < 0.06$). It is not clear why many Adirondack watershed soils leached NO_3^- to a lesser extent during the 1990s than they did during the 1980s (Driscoll et al., 2003). Decreasing stream NO_3^- concentrations during the 1990s was also observed in the Catskill Mountains (Stoddard et al., 2003) and in New Hampshire (Goodale et al., 2003). There was not a substantial change in N emissions or deposition in the Northeast region over that period. Climatic factors, insect defoliation, increases in atmospheric CO_2, and interactions with increasing availability of DOC have been proposed as possible contributing factors to regional decreases in NO_3^- leaching (Aber et al., 2002; Driscoll et al., 2003; Goodale et al., 2003; 2005; Mitchell et al., 1996), but the driver of this decadal scale pattern remains uncertain.

C.1.4.2. Episodic Change

Nutrient enrichment effects of N deposition are controlled to a large degree by biological and hydrological processes that operate on episodic (hours to days), seasonal, and interannual time scales. Nitrogen uptake and transformation reactions and processes vary greatly with season and with climatic factors. In particular, N export from terrestrial and transitional ecosystems to aquatic ecosystems is governed by seasonal fluctuations in temperature and biological uptake, and episodic fluctuations in water movement associated with rainstorms and snowmelt. The role of N in driving biotic change in stream

ecosystems due to episodic pulses of NO_3^- associated with spring snowmelt are discussed in detail in ISA Section 3.2.

C.1.4.3. Reversibility of Impacts

Although there are relatively few studies of the reversibility of the biogeochemical effects of elevated N deposition, the few to date suggest the possibility of recovery. Experimental studies in Europe suggest that some ecosystem processes and characteristics are likely to recover rapidly following a reduction in N deposition. In a study in northern Sweden, high levels of fertilization (90 kg N/ha/yr) over 20 years induced substantial soil acidification, including loss of over half of the base cations in the mineral soil, a decrease in pH, and an increase in soluble Al (Högberg et al., 2006). However, 10 years after this treatment was stopped, the pH of the mineral soil had increased, and extractable NO_3^- was no higher than in the control plot. Stem volume growth did not substantially increase relative to the acidification period. "Clean roof" experiments that prevent N deposition inputs at sites receiving >40 kg N/ha/yr ambient atmospheric N deposition in The Netherlands increased wood and root production soon after the roof was installed (Boxman et al., 1998), and NO_3^- exports below the rooting zone were reduced dramatically within 2 years (Bredemeier et al., 1998).

A study of alpine lake sediment cores in Rocky Mountain National Park, CO (Wolfe et al., 2003) suggested the possible reversibility of N enrichment effects on lake biota. Although increased dominance of mesotrophic diatom species was correlated with increased N inputs during the 20th century, it did not appear that any of the oligotrophic species had been totally lost from study lakes. Thus, reduced future N loading may allow renewed dominance by oligotrophic diatom species.

It is not necessarily true, however, that nutrient enrichment effects of N deposition will, in all cases, be easily reversible. For example, it has been suggested that vegetation conversion in the coastal sage scrub community in California has altered hydrologic function to an extent that may be difficult to reverse. The depth of rainwater percolation into soil has been reduced as a result of invasion of non-native annual grasses. This hydrologic change inhibits the growth of deep-rooting native shrubs (Wood et al., 2006).

C.1.5. Tables Supporting Cross Ecosystem Evaluation of N_2O, CH_4 and CO_2 Flux

Table C-2 summarizes key information from the experiments included in the meta-analysis presented in ISA Section 3.3.4.

Table C-2   The study site, experimental condition, ecosystem type, N form, amount of N addition and citations is presented for all studies used in NEE, EC, CH_4 uptake, CH_4 emission and N_2O emission meta analyses.

Site	Experimental Condition	Ecosystem	N Form	N Addition (kg ha/yr)	Reference
NET ECOSYSTEM CARBON EXCHANGE (NEE)					
Swiss FACE (Lolium)	field	grassland	NH_4NO_3	320	Aeschlimann et al. 2005
Swiss FACE (Trifolium)	field	grassland	NH_4NO_3	320	Aeschlimann et al. 2005
Ottawa, Canada	field	wetland	NH_4NO_3	32	Basiliko et al. 2006
Ottawa, Canada	field	wetland	NH_4NO_3	64	Basiliko et al. 2006
Ottawa, Canada	field	wetland	NH_4NO_3	16	Bubrie et al. 2007
Ottawa, Canada	field	wetland	NH_4NO_3	32	Bubrie et al. 2007
Ottawa, Canada	field	wetland	NH_4NO_3	64	Bubrie et al. 2007
Laqueuille, France	field	grassland		175	Soussana et al. 2007
Oensingen, Switzerland	field	grassland	slurry	200	Soussana et al. 2007
Toolik Lake, AK(Inlet)	field	tundra	NH_4NO_3	100	Shaver et al. 1998
Toolik Lake, AK (Outlet)	field	tundra	NH_4NO_3	100	Shaver et al. 1998
Orange county,CA	field,w/o water addition	grassland	NO_3^-	100	Harpole et al., 2007
Orange county,CA	field, with water addition	grassland	NO_3^-	100	Harpole et al., 2007
Switzerland	field	grassland		40	Diemer 1997
Finland	field	wetland	NH_4NO_3	30	Saarnio et al. 2003
Abisko, Sweden	field	tundra	NH_4NO_3	100	Christensen et al. 1997
ecosystem carbon content (ec)					
WA	field	coniferous	.	.	Canary et al. 2000
Placerville CA	field	coniferous	NH_4^+	100	Johnson et al. 2006
Placerville CA	field	coniferous	NH_4^+	200	Johnson et al. 2006

Clayey, AL	field	coniferous	DAP	45	Leggett et al. 2006
Sandy, MS	field	coniferous	DAP	45	Leggett et al. 2006
Harvard forest, MA	field	deciduous	NH_4NO_3	150	Magill et al. 2004
Harvard forest, MA	field	coniferous	NH_4NO_3	150	Magill et al. 2004
Harvard forest, MA	field, w/o S addition	deciduous	NH_4NO_3	50	Magill et al. 2004
Harvard forest, MA	field, with S additon	deciduous	NH_4NO_3	50	Magill et al. 2004
Harvard forest, MA	field, w/o S addition	coniferous	NH_4NO_3	50	Magill et al. 2004
Harvard forest, MA	field, with S addition	coniferous	NH_4NO_3	50	Magill et al. 2004
BBWM, ME	field	deciduous	NH_4^+	25.2	Parker et al. 2001; Elvir et al. 2006
MI (site A)	field	deciduous	NO_3^-	30	Pregitzer et al. 2008; Burton et al. 2000
MI (site B)	field	deciduous	NO_3^-	30	Pregitzer et al. 2008; Burton et al. 2000
MI (site C)	field	deciduous	NO_3^-	30	Pregitzer et al. 2008; Burton et al. 2000
MI (site D)	field	deciduous	NO_3^-	30	Pregitzer et al. 2008; Burton et al. 2000
FL	field	coniferous	.	.	Shan et al. 2001
CH$_4$ EMISSION					
Netherland (eutrophic site)	Incubation	wetland	NH_4^+		Aerts and Caluwe 1999
Netherland (mesotrophic site)	incubation	wetland	NH_4^+		Aerts and Caluwe 1999
Polish (mesotrophic site)	incubation	wetland	NH_4^+		Aerts and Caluwe 1999
Netherland	incubation	wetland	NH_4^+		Aerts and Caluwe 1999
Swiss FACE	field, ambient CO_2	grassland	NH_4NO_3	84	Baggs and Blum 2004
Swiss FACE	field, elevated CO_2	grassland	NH_4NO_3	84	Baggs and Blum 2004
Minnesota	Incubation	wetland	NH_4^+	20	Keller et al., 2005
Minnesota	incubation	wetland	NH_4^+	60	Keller et al., 2005
Niwot Ridge, CO	field	grassland	urea	250	Neef et al. 1994
Finland	incubation	wetland	NH_4NO_3	30	Nykanen et al. 2002
Finland	incubation	wetland	NH_4NO_3	100	Nykanen et al. 2002
Salmisuo, Finland	field, ambient CO_2	wetland	NH_4NO_3	30	Sarrnio and Silvola 1999
Salmisuo, Finland	field, elevated CO_2	wetland	NH_4NO_3	30	Sarrnio and Silvola 1999
Sanjiang mire, China	field	wetland	NH_4NO_3	240	Zhang et al. 2007

ch₄ uptake

Quebec, Canada	incubation	coniferous	NH_4^+		Adamsen and King 1993
Quebec, Canada	incubation	coniferous	NO_3^-		Adamsen and King 1993
Michigan	field	coniferous	NH_4NO_3	10	Ambus and Robertson 2006
Michigan	field	coniferous	NH_4NO_3	30	Ambus and Robertson 2006
Michigan	field	deciduous	NH_4NO_3	10	Ambus and Robertson 2006
Michigan	field	deciduous	NH_4NO_3	30	Ambus and Robertson 2006
Michigan	field	grassland	NH_4NO_3	10	Ambus and Robertson 2006
Solling, Germany	field, with clean rain roof	coniferous	NH_4NO_3	18.5	Borken et al. 2002
Solling, Germany	field, with clean rain roof	coniferous	NH_4NO_3	24.2	Borken et al. 2002
Solling, Germany	field, w/o clean rain roof	coniferous	NH_4NO_3	18.5	Borken et al. 2002
Solling, Germany	field, w/o clean rain roof	coniferous	NH_4NO_3	24.2	Borken et al. 2002
Bousson, PA	field	deciduous	NH_4NO_3	100	Bowen et al. 2000
Perridge Forest, UK	incubation	deciduous	NO_3^-	Low N	Bradford et al. 2001
Perridge Forest, UK	incubation	deciduous	NO_3^-	High N	Bradford et al. 2001
MT Ascutney, VT	field	coniferous	NH_4^+	31.4	Castro et al. 1992
Bousson, PA	field	deciduous	NH_4NO_3	100	Chan et al. 2005
Abisko, Sweden	field	tundra	NH_4NO_3	100	Christensen et al. 1997
Finland	field	wetland	NH_4^+	100	Crill et al. 1994
Finland	field	wetland	NO_3^-	100	Crill et al. 1994
Finland	field	wetland	urea	100	Crill et al. 1994
Villingen, Germany	field	coniferous	NH_4^+	150	Gulledge and Schimel 2000
LTER Alaska	field	deciduous	NH_4NO_3	66.7	Gulledge and Schimel 2000
LTER Alaska	field	coniferous	NH_4NO_3	12.3	Gulledge and Schimel 2000
LTER Alaska	field	deciduous	NH_4NO_3	171.4	Gulledge and Schimel 2000
LTER Alaska	field	coniferous	NH_4NO_3	142.9	Gulledge and Schimel 2000

Swiss FACE	field, ambient CO_2	grassland	NH_4NO_3	560	Ineson et al. 1998
Swiss FACE	field, elevated CO_2	grassland	NH_4NO_3	560	Ineson et al. 1998
Scotland	incubation	heathland	NH_4^+	40	Macdonald et al. 1997
Scotland	incubation	heathland	NH_4NO_3	40	Macdonald et al. 1997
Scotland	incubation	heathland	NO_3^-	40	Macdonald et al. 1997
Finland	field	coniferous	NH_4NO_3	200	Maljane et al. 2006
Swale, CO	field	grassland	urea	450	Mosier et al., 1991
Midslope, CO	field	grassland	urea	450	Mosier et al., 1991
Passture, CO	field	grassland	urea	450	Mosier et al., 1991
Niwot Ridge, CO	field	grassland	urea	250	Neef et al. 1994
Villingen, Germany	field	coniferous	NH_4^+	150	Papen et. al 2001
Finland	field	wetland	NH_4NO_3	30	Saarnio et al. 2003
Gjovelandsnesset, Norway	incubation	coniferous	NH_4NO_3	30	Sitaula et al. 1995
Gjovelandsnesset, Norway	incubation	coniferous	NH_4NO_3	90	Sitaula et al. 1995
Harvard forest, MA	field	coniferous	NH_4NO_3	37	Steudler et al. 1989
Harvard forest, MA	field	deciduous	NH_4NO_3	37	Steudler et al. 1989
Harvard forest, MA	field	coniferous	NH_4NO_3	120	Steudler et al. 1989
Harvard forest, MA	field	deciduous	NH_4NO_3	120	Steudler et al. 1989
Belgium (Bulrush site)	incubation	wetland	NH_4^+		VanderNat et al. 1997
Belgium (Reed site)	incubation	wetland	NH_4^+		VanderNat et al. 1997
Costa Rica (Loam site)	field	tropical forest	NH_4^+	65	Weitz et al. 1999
Costa Rica (Clay site)	field	tropical forest	NH_4^+	65	Weitz et al. 1999
N_2O EMISSION					
Michigan biological Station	Incubation, ambient CO_2	deciduous	NH_4NO_3	Low N	Ambus and Robertson 1999
Michigan biological Station	Incubation, ambient CO_2	deciduous	NH_4NO_3	High N	Ambus and Robertson 1999
Michigan biological Station	Incubation, elevated CO_2	deciduous	NH_4NO_3	Low N	Ambus and Robertson 1999
Michigan biological Station	Incubation, elevated CO_2	deciduous	NH_4NO_3	High N	Ambus and Robertson 1999
Michigan	field	coniferous	NH_4NO_3	10	Ambus and Robertson 2006

Michigan	field	deciduous	NH_4NO_3	10	Ambus and Robertson 2006
Michigan	field	grassland	NH_4NO_3	10	Ambus and Robertson 2006
Michigan	field	coniferous	NH_4NO_3	30	Ambus and Robertson 2006
Michigan	field	deciduous	NH_4NO_3	30	Ambus and Robertson 2006
Hyytiälä	incubation	coniferous	NH_4^+		Ambus et al. 2006
Speulderbos	incubation	coniferous	NH_4^+		Ambus et al. 2006
San Rossore	incubation	coniferous	NH_4^+		Ambus et al. 2006
Glencorse	incubation	coniferous	NH_4^+		Ambus et al. 2006
Nyirjes	incubation	coniferous	NH_4^+		Ambus et al. 2006
Achenkirch	incubation	coniferous	NH_4^+		Ambus et al. 2006
Höglwald	incubation	coniferous	NH_4^+		Ambus et al. 2006
Sorø	incubation	deciduous	NH_4^+		Ambus et al. 2006
Bosco negri	incubation	deciduous	NH_4^+		Ambus et al. 2006
Schottenwald	incubation	deciduous	NH_4^+		Ambus et al. 2006
Hyytiälä	incubation	coniferous	NO_3^-		Ambus et al. 2006
Speulderbos	incubation	coniferous	NO_3^-		Ambus et al. 2006
San Rossore	incubation	coniferous	NO_3^-		Ambus et al. 2006
Glencorse	incubation	coniferous	NO_3^-		Ambus et al. 2006
Nyirjes	incubation	coniferous	NO_3^-		Ambus et al. 2006
Achenkirch	incubation	coniferous	NO_3^-		Ambus et al. 2006
Höglwald	incubation	coniferous	NO_3^-		Ambus et al. 2006
Sorø	incubation	deciduous	NO_3^-		Ambus et al. 2006
Bosco negri	incubation	deciduous	NO_3^-		Ambus et al. 2006
Schottenwald	incubation	deciduous	NO_3^-		Ambus et al. 2006
Swiss FACE	field, ambient CO_2	grassland	NH_4NO_3	84	Baggs and Blum 2004
Swiss FACE	field, elevated CO_2	grassland	NH_4NO_3	84	Baggs and Blum 2004
Swiss FACE (Lolium)	field, ambient CO_2	grassland	NH_4NO_3	420	Baggs et al., 2003
Swiss FACE (Lolium/ Trifolium)	field, ambient CO_2	grassland	NH_4NO_3	420	Baggs et al., 2003
Swiss FACE (Trifolium)	field, ambient CO_2	grassland	NH_4NO_3	420	Baggs et al., 2003
Swiss FACE (Lolium)	field, elevated CO_2	grassland	NH_4NO_3	420	Baggs et al., 2003

Site	Condition	Vegetation	Species	Value	Reference
Swiss FACE (Lolium/ Trifolium)	field, elevated CO_2	grassland	NH_4NO_3	420	Baggs et al., 2003
Swiss FACE (Trifolium)	field, elevated CO_2	grassland	NH_4NO_3	420	Baggs et al., 2003
Solling, Germany	field	coniferous	NH_4NO_3	18.5	Borken et al. 2002
Solling, Germany	field	coniferous	NH_4NO_3	24.2	Borken et al. 2002
Solling, Germany	field	coniferous	NH_4NO_3	18.5	Borken et al. 2002
Solling, Germany	field	coniferous	NH_4NO_3	24.2	Borken et al. 2002
Harvard forest	field	deciduous	NH_4NO_3	37	bowden et al. 1991
Harvard forest	field	coniferous	NH_4NO_3	37	bowden et al. 1991
Harvard forest	field	deciduous	NH_4NO_3	120	bowden et al. 1991
Harvard forest	field	coniferous	NH_4NO_3	120	bowden et al. 1991
Solling, Germany	field	deciduous	NH_4^+	140	Brumme and Beese 1992
Gullane	incubation	deciduous	NH_4^+		Castaldi and Smith 1998
Gullane	incubation	deciduous	NO_3^-		Castaldi and Smith 1998
Ascutney , VI	field	coniferous	NH_4^+	31.4	Castro et al. 1993
Allt, UK (site M3)	field	heathland	NH_4NO_3	20	Curitis et al., 2006
Allt, UK (site M4)	field	heathland	NH_4NO_3	20	Curitis et al., 2006
Afon Gwy, UK (site G1)	field	grassland	NH_4NO_3	20	Curitis et al., 2006
Afon Gwy, UK (site G2)	field	grassland	NH_4NO_3	20	Curitis et al., 2006
Afon Gwy, UK (site G3)	field	grassland	NH_4NO_3	20	Curitis et al., 2006
River Etherow, UK (site E1)	field	heathland	NH_4NO_3	20	Curitis et al., 2006
River Etherow, UK (site E2)	field	heathland	NH_4NO_3	20	Curitis et al., 2006
St. James Parish, LO	field	wetland	NO_3^-	100	Delaune et al. 1998
St. James Parish, LO	field	wetland	NH_4^+	100	Delaune et al. 1998
Saratoga	field	grassland	NH_4NO_3	168	Delgado et al. 1996
Puerto Rico	field	tropical forest	urea	300	Erickson et al. 2001
Jasper Ridge , CA	incubation, ambient CO_2	grassland	urea	200	Hungate et al. 1997
Jasper Ridge , CA	incubation, elevated CO_2	grassland	urea	200	Hungate et al. 1997
Swiss FACE	field, ambient CO_2	grassland	NH_4NO_3	560	Ineson et al. 1998
Swiss FACE	field, elevated CO_2	grassland	NH_4NO_3	560	Ineson et al. 1998
Manaus, Brazil (site 1)	field	tropical forest	NO_3^-		Keller et al. 1988

Manaus, Brazil (site 2)	field	tropical forest	NO_3^-		Keller et al. 1988
Manaus, Brazil (site 3)	field	tropical forest	NO_3^-		Keller et al. 1988
Manaus, Brazil (site 4)	field	tropical forest	NO_3^-		Keller et al. 1988
Manaus, Brazil (site 1)	field	tropical forest	NH_4^+		Keller et al. 1988
Manaus, Brazil (site 2)	field	tropical forest	NH_4^+		Keller et al. 1988
Manaus, Brazil (site 3)	field	tropical forest	NH_4^+		Keller et al. 1988
Manaus, Brazil (site 4)	field	tropical forest	NH_4^+		Keller et al. 1988
gardsjon watershed	field, well drained	coniferous	NH_4NO_3	35	Klemedtsson et. al 1997
gardsjon watershed	field, wet	coniferous	NH_4NO_3	35	Klemedtsson et. al 1997
Avoyelles, LO	field	wetland	NH_4^+	100	Lindau et al. 1994
Avoyelles, LO	field	wetland	NH_4^+	300	Lindau et al. 1994
Avoyelles, LO	field	wetland	NO_3^-	100	Lindau et al. 1994
Avoyelles, LO	field	wetland	NO_3^-	300	Lindau et al. 1994
Harvard forest	field	coniferous	NH_4NO_3	113	Magill et al. 1997
Finland	field	coniferous		200	Maljane et al. 2006
Swale, CO	field	grassland	urea	450	Mosier et al., 1991
Midslope, CO	field	grassland	urea	450	Mosier et al., 1991
Passture, CO	field	grassland	urea	450	Mosier et al., 1991
Puerto Rico	field, low tide	wetland	NH_4^+	15.4	Munoz -Hincapie et al. 2002
Puerto Rico	field, low tide	wetland	NH_4^+	130.2	Munoz-Hincapie et al. 2002
Puerto Rico	field, low tide	wetland	NH_4^+	266	Munoz -Hincapie et al. 2002
Puerto Rico	field, low tide	wetland	NO_3^-	15.4	Munoz -Hincapie et al. 2002
Puerto Rico	field, low tide	wetland	NO_3^-	130.2	Munoz -Hincapie et al. 2002
Puerto Rico	field, low tide	wetland	NO_3^-	266	Munoz -Hincapie et al. 2002
Puerto Rico	field, high tide	wetland	NH_4^+	15.4	Munoz -Hincapie et al. 2002

Puerto Rico	field, high tide	wetland	NH_4^+	266	Munoz -Hincapie et al. 2002
Puerto Rico	field, high tide	wetland	NO_3^-	15.4	Munoz -Hincapie et al. 2002
Niwot Ridge, CO (wet meadow)	field	grassland	urea	250	Neef et al. 1994
Niwot Ridge, CO (dry meadow)	field	grassland	urea	250	Neef et al. 1994
Villingen	field	coniferous	NH_4^+	150	Papen et. al (2001)
Duke FACE	incubation, ambient CO_2	coniferous	NO_3^-		Phillips et al. 2001
Duke FACE	incubation, elevated CO_2	coniferous	NO_3^-		Phillips et al. 2001
Finland	field	wetland	NO_3^-	100	Regina et al. 1998
Finland	field	wetland	NH_4^+	100	Regina et al. 1998
Finland	field	wetland	urea	100	Regina et al. 1998
Mojave	incubation	desert	NO_3^-		Schaeffer et al. 2003
Gjovelandsnesset, Sweden	field, pH=3	coniferous	NH_4NO_3	30	Sitaula et al. 1995
Gjovelandsnesset, Sweden	field, pH=3	coniferous	NH_4NO_3	90	Sitaula et al. 1995
Gjovelandsnesset, Sweden	field, pH=4	coniferous	NH_4NO_3	30	Sitaula et al. 1995
Gjovelandsnesset, Sweden	field, pH=4	coniferous	NH_4NO_3	90	Sitaula et al. 1995
Gjovelandsnesset, Sweden	field, pH=5	coniferous	NH_4NO_3	30	Sitaula et al. 1995
Gjovelandsnesset, Sweden	field, pH=5	coniferous	NH_4NO_3	90	Sitaula et al. 1995
Scotland	field	coniferous	NH_4NO_3	48	Skiba et al. 1998
Deepsyke forest	field	coniferous	NH_4NO_3	48	Skiba et al. 1999
Deepsyke forest	field	coniferous	NH_4NO_3	96	Skiba et al. 1999
Costa Rica (Loam site)	field	tropical forest		65	Weitz et al. 1999
Costa Rica (Clay site)	field	tropical forest		65	Weitz et al. 1999
Sanhuabg Mire, China	field	wetland	NH_4NO_3	240	Zhang et al. 2007

C.2. Terrestrial Ecosystems

The following sections are organized by ecosystem type and combine information that is supplemental to Section 3.3 of the ISA.

C.2.1. General C Cyling

C cycling is a complex process that includes C capture from the atmosphere by autotrophic biota, the primary producers of the ecosystem, and respiration (autotrophic + heterotrophic). In general, atmospheric nutrient (e.g., N) deposition on an ecosystem that is deficient in that nutrient will often cause an increase in growth, at least initially, especially of the primary producers. If that same nutrient is deposited on an ecosystem that has an adequate supply of that nutrient, there may be no appreciable nutrient enrichment effect, at least up to a point. Nutrient input that is greatly in excess of biological demand will often cause toxicity, reduced growth, or problems other than those associated with nutrient enrichment (i.e., N-saturation, acidification, base cation depletion) (Figure C-1).
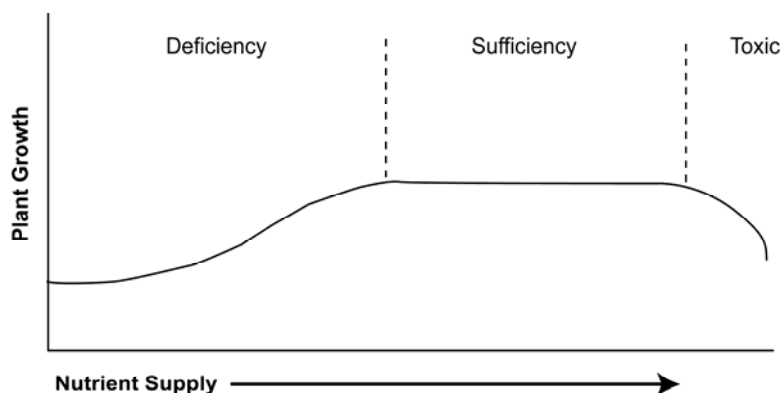
Source: U.S. EPA (1993a)

Figure C-1. **Schematic representation of the response of vegetation to nutrient addition.**

C.2.2. Forest Growth Interactions with Herbivores

Light availability, nutrient balance, and C:N:P stoichiometry are closely relate, and affect the composition of autotrophic species that will occupy a particular habitat. The resulting stoichiometric balance of C:N:P in the autotrophic community can have additional feedbacks on nutrient cycling by herbivores, detritivores, and decomposers (Sterner and Elser, 2002). Such effects also extend to herbivores, and likely other members of the food web. Forkner and Hunter (2000) altered plant growth of oak (*Quercus prinus* and *Q. rubra*) saplings through fertilizer (N, P, K) addition and then censused the densities of insect herbivore guilds and predaceous anthropods on experimental and control trees. In general, leaf chewers, phloem feeders, and leaf miners were more common on fertilized, as compared with non-fertilized, trees. Predaceous arthropods were also more abundant on fertilized trees and their densities were correlated with herbivore densities.

C.2.3. Southern California Coniferous Forest

Wet N deposition is generally low throughout the region, in the range of 1 to 3 kg N/ha/yr. However, dry deposition is highly variable, but ranges up to about 30 kg N/ha/yr or more (Bytnerowicz and Fenn, 1996; Fenn, 1997; Takemoto et al., 2001). Available data (e.g., Minnich et al., 1995) suggest progression toward less needle retention, higher shoot:root biomass ratios, increasing depth of litter, and high NO_3^- in soil solution in response to high N deposition. These changes may eventually lead to

replacement of pine species with nitrophilous and O_3-tolerant species such as fir and cedar (Takemoto et al., 2001).

Streamwater NO_3^- concentrations in montane watersheds that are downwind of the greater Los Angeles area are the highest in North America. Some streams in the San Gabriel and the San Bernardino Mountains have been documented to have levels of NO_3^- in stream water with peaks as high as 370 µeq/L (Fenn and Poth 1999), reflecting very high N deposition and N-saturation of the terrestrial ecosystem. In contrast, N leaching is low in most watersheds in the Sierra Nevada, and NO_3^- concentrations in streams are usually below 1 µeq/L. Nevertheless, some of the higher elevation watersheds in the Sierra Nevada export appreciable NO_3^- from the terrestrial environment, particularly during the early phases of snowmelt. Fenn et al. (2002) reported springtime peaks of NO_3^- concentration in lakewater up to 38 µeq/L at high elevation and for watersheds dominated by talus. At lower elevation areas, however, most of the inorganic N deposition loading is retained within the watersheds and concentrations of NO_3^- in stream and lake waters are low (Fenn et al., 2003a). Surface water NO_3^- concentrations in these areas provide an index reflecting the general levels of N deposition. For example, where surface water NO_3^- concentrations are high, N deposition to the terrestrial watershed is also high.

C.2.4. Boreal Forests

The boreal forest represents the largest terrestrial biome on Earth, and as such can have a large influence on global cycling of N and other nutrients. Plant growth in the boreal forest is limited mainly by N availability, in part because of slow mineralization of organic materials in the harsh climate (Vitousek and Howarth, 1991). Conceptual models of N cycling in the boreal forest have typically assumed that mineralization of organic N is required for plant uptake of N (Näsholm et al., 1998). However, it has been demonstrated in laboratory studies (Chapin et al., 1993) and field studies (Näsholm et al., 1998) that some boreal plants are capable of directly taking up amino acids from the soil, and therefore bypassing the need for prior mineralization. The interactions among soil abiotic processes, mycorrhizal associations, microbes, and plants are complex and poorly understood. Nevertheless, these interactions are important to global N cycling and to boreal plant species composition because organic N concentrations are typically high in the soil of boreal forests. It appears that atmospheric N deposition and climate warming have the potential to alter boreal forest plant communities by shifting nutritional processes from organic to inorganic N uptake (Näsholm et al., 1998).

C.2.5. Alpine

The western U.S. contains extensive land areas that receive low levels of atmospheric N deposition, interspersed with hot spots of relatively higher N deposition downwind of large metropolitan centers and agricultural areas (Fenn, 2003). Alpine plant communities occur in some of the areas that receive moderately elevated atmospheric N deposition such as those located in the Sierra Nevada in southern California, the Front Range in Colorado, and the Cascade Mountains in Washington (Figure C-2).
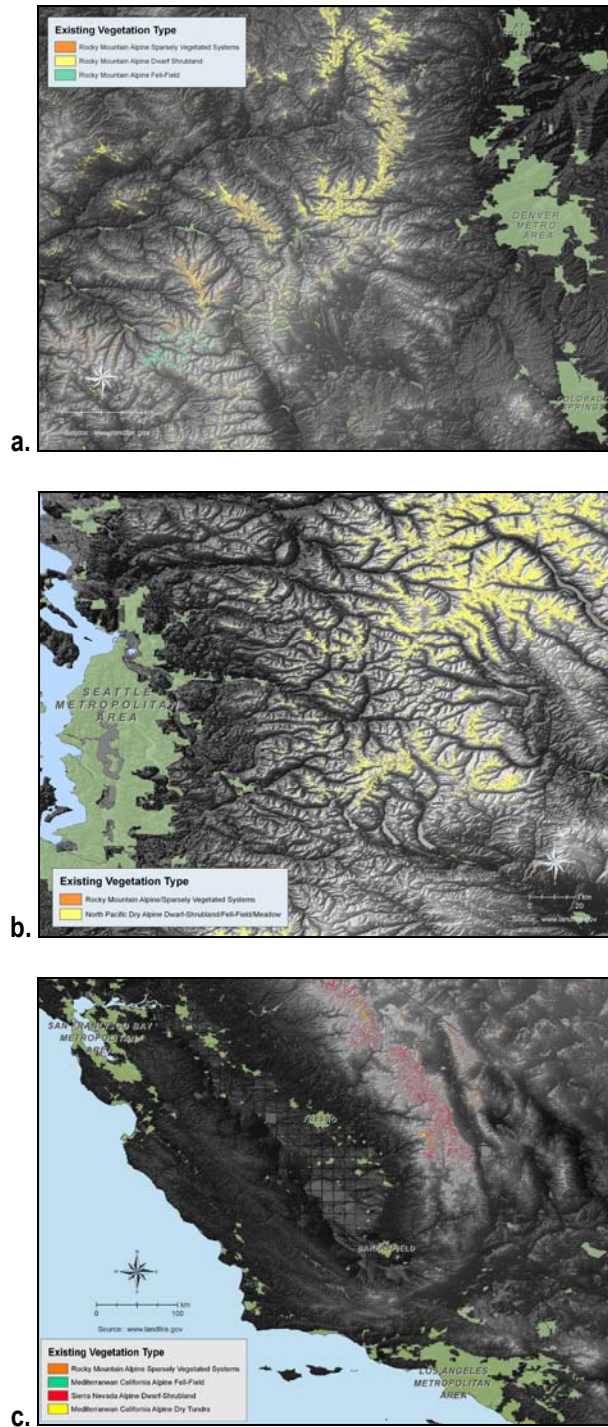
Source: Vegetative distribution data were taken from the national map LANDFIRE (September 2006) (http://gisdata.usgs.net/website/landfire/).

Figure C-2. **Distribution of alpine vegetation in three western regions that are in close proximity to urban and agricultural sources of atmospheric N emissions : a) the Denver-Fort Collins region of Colorado, b) the Seattle-Tacoma region of Washington, and c) the Fresno-Los Angeles area of California (the blue line on the map is the California/Nevada border). Alpine vegetation in these areas is sensitive to nutrient enrichment effects from atmospheric N deposition.**

Alpine plant species are typically adapted to low nutrient availability and their soil-forming processes are poorly developed, therefore they are often sensitive to effects from N enrichment (Bowman et al., 2006) including changes in species composition (Bowman et al., 1995; Seastedt and Vaccaro, 2001). Other reasons alpine tundra are sensitive to N enrichment include factors such as low rates of primary production, short growing season, low temperature, and a wide variation in moisture availability (Bowman and Fisk, 2001).

Nitrogen cycling in alpine environments is strongly tied to variations in moisture regime (Bowman et al., 1993; Bowman, 1994; Fisk et al., 1998). Blowing snow is transported across alpine landscapes by wind and tends to accumulate in certain depression areas. These areas receive much higher levels of moisture and winter season N deposition than other more wind-swept portions of the alpine environment (Bowman, 1992). Fenn et al. (2003) suggested that as much as 10 kg N/ha/yr may leach through the snow during the initial phases of snowmelt in some of the alpine areas in Colorado that accumulate substantial snowpack. It is these moist meadow areas that may be most affected by N deposition and are also the areas most likely to show changes in plant species composition and impacts on N cycling (Bowman and Steltzer, 1998).

Nitrogen deposition to the alpine tundra of Niwot Ridge in the Colorado Front Range altered N cycling and provided the potential for replacement of some native plant species by more competitive, faster-growing native species (Baron, 2000; Bowman and Steltzer, 1998; Bowman, 2000). Many plants that grow in alpine tundra, as is true of plants growing in other low resource environments (e.g., infertile soil, desert), tend to have some similar characteristics, including slow growth rate, low photosynthetic rate, low capacity for nutrient uptake, and low soil microbial activity (Bowman and Steltzer, 1998; Bowman, 2000). Such plants generally continue to grow slowly when provided with an optimal supply and balance of resources (Pearcy et al., 1987; Chapin, 1991). In addition, plants adapted to cold, moist environments grow more leaves than roots as the relative availability of N increases. These patterns of vegetative development and their response to added N affect plant capacity to respond to variation in available resources and to environmental stresses such as frost, high winds, and drought. Vegetation in the southern Rocky Mountains responds to increased N supply by increasing plant productivity for some species, but this increase in productivity is also accompanied by changes in species composition and abundance (Bowman et al., 1993). Many of the dominant plant species do not respond to additional N supply with increased production. Rather, many subdominant species, primarily grasses and some forbs, increase in abundance when the N supply is increased (Fenn et al., 2003c).

In alpine ecosystems, changes in plant species composition due to N deposition can result in increased leaching of NO_3^- from the soils because the plant species favored by higher N supply are often associated with greater rates of N mineralization and nitrification than the pre-existing species (Bowman et al., 1993, 2006; Steltzer and Bowman, 1998; Suding et al., 2006).

Total organic N pools in the soils of dry alpine meadows are large compared to pools of NH_4^+ and NO_3^- (Fisk and Schmidt, 1996). However, positive response to inorganic N fertilization has been demonstrated, and thus some plant species appear to be restricted in their ability to take up organic N from the soil and are growth-limited by the availability of inorganic N (Bowman et al., 1993, 1995; Theodose and Bowman, 1997). Miller and Bowman (2002) analyzed patterns of foliar ^{15}N, NO_3^- reductase activity, and mycorrhizal infection compared with N uptake quantified by stable isotope tracer additions in the greenhouse. ^{13}C enrichment subsequent to ^{13}C, ^{15}N-glycine addition indicated that all of the 11 genera studied were able to take-up labeled glycine to some extent. Glycine uptake ranged from about 35% to more than 100 % of NH_4^+ uptake. Only *Festuca* (fescue grass) showed glycine uptake exceeding both NH_4^+ and NO_3^- uptake (Miller and Bowman, 2002).

C.2.6. Arctic Tundra

Soluble N in tundra soil solution is dominated by organic N, including free amino acids, rather than NH_4^+ or NO_3^- (Kielland, 1995). Tundra plants appear to exhibit a range of interspecific differences that allow coexistence under conditions that reflect a single limiting element. Species differ in rooting depth, phenology, and uptake preferences for organic and inorganic forms of N (Shaver and Billings, 1975; Chapin et al., 1993; Kielland, 1994; McKane et al., 2002). McKane et al. (2002) demonstrated, based on ^{15}N field experiments, that arctic tundra plant species were differentiated in timing, depth, and chemical form of N utilization. Furthermore, the species that exhibited greatest productivity were those that efficiently used the most abundant N forms.

Ericoid mycorrhizae provide host plants with the capacity to take up N in the form of amino acids (Stribley and Read, 1980; Bajwa and Read, 1985). This is important in arctic plant communities that occur on acidic organic soils because amino acids are typically readily available in such soils, and N availability generally limits primary productivity.

Future climate warming could have important effects on N cycling in arctic tundra ecosystems. In the past, organic materials have accumulated in tundra soils, largely because decomposition has been slower than plant growth. Climate warming may increase the decomposition of soil organic matter, thereby increasing the availability of stored N (Weintraub and Schimel, 2005). The distributions of woody plant species are also increasing in response to warming, with likely feedbacks on C and N cycling. For example, the dominant shrub species in the arctic tundra in Alaska, Betula nana, is expanding its distribution in tussock vegetation communities (Weintraub and Schimel, 2005).

Poor soil aeration is caused by permafrost, resulting in poor water drainage and the development of anaerobic conditions. Vegetation composition and primary productivity vary in response to differences in soil moisture and aeration (Everett and Brown, 1982; Gebauer et al., 1995). Reduced soil O_2 can limit nutrient availability. For example, under anaerobic conditions, N mineralization and nitrification rates decrease while denitrification increases (Ponnamperuma, 1972; Gebauer et al., 1995).

C.2.7. Arid Land

From 1989 to 2004 in the Chihuahuan desert, Baez et al. (2007) observed a 43% increase in ambient N deposition, from 1.71 to 2.45 kg N/ha/yr, resulting in an additional 5.88 kg N/ha/yr deposition over that time period. They suggest that these deposition trends may result in significant plant community changes, as indicated by fertilization studies of blue gramma (*Bouteloua gracilis*) and black gramma (*B. eriopoda*). In a field addition with additions of 20 kg N/ha/yr in one season, blue gramma was favored over black gramma, the current dominant species (Baez et al., 2007).

C.2.8. Lichens

There are several potential uses of lichens for air pollution and deposition monitoring. These include measurement of tissue lichen concentrations of specific pollutants (i.e., lichens as passive monitors), determination of changes in species composition or the presence/absence of sensitive species, and identification of areas having relatively high levels of air pollution, where monitoring instrumentation could be installed to more quantitatively measure pollution levels. Assessment of long-term change in the epiphytic lichen community can be especially valuable to provide an early indication of either improving or deteriorating air quality and atmospheric deposition. Such monitoring was incorporated in 1994 into the USFS Forest Inventory and Analysis (FIA) Program (See Annex A).

Lichen communities in the Pacific Northwest show signs of air pollution damage under current air pollution levels. Symptons include decreases in the occurrences of sensitive taxa and replacement by pollution-tolerant and nitrophilous taxa (Fenn et al., 2003a; Geiser and Neitlich, 2007). Indicators of clean sites and polluted sites (Table C-3) were used by Geiser and Neitlich (2007) to create six lichen zones of air quality within the region, from worst (all sensitive species absent) to best (all sensitive species present). Air pollution was associated with effects on community composition of lichens, rather than species richness. The most widely observed effects included paucity of sensitive, endemic species, and enhancement of nitrophilous and non-native species (Geiser and Neitlich, 2007). The strongest relationship was with wet NH_4^+ deposition, consistent with findings in California (Jovan and McCune, 2005) and Europe (van Dobben et al., 2001). The zone of worst air quality was associated with absence of sensitive lichens, enhancement of nitrophyllous lichens, mean wet NH_4^+ deposition >0.06 mg N/L, lichen tissue N and S concentrations >0.6% and 0.07 %, and SO_2 levels harmful to sensitive lichens.

Jovan and McCune (2005) constructed a model based on non-metric multidimensional scaling ordination to analyze lichen species distribution from 98 FIA plots in the greater Central Valley of California. The model used epiphytic macrolichen community data to reflect air quality and climate in forested areas. Some species respond negatively to NO_X and SO_X deposition (Gauslaa, 1995; McCune, 1988; van Haluwyn and van Herk, 2002). Other species respond positively to NH_Y deposition (de Bakker, 1989; van Dobben and de Bakker, 1996; van Herk, 1999, 2001; Jovan and McCune, 2005).

Similarly, Jovan and McCune (2006) developed a model of NH_3 exposure to epiphytic macrolichens in the Sierra Nevada region. They found that lichens provide a relatively inexpensive tool for estimating fine-scale distributions of NH_3 exposure to terrestrial ecosystems. Because NH_3 has a high deposition velocity (Asman and van Jaarsveld, 1992), dry deposition of reduced N exhibits high spatial variability. Monitoring of species composition of epiphytic lichen communities can therefore help quantify spatially variable eutrophication risk to forest health in the Sierra Nevada region (Jovan and McCune, 2006).

Table C-3.   Principal Air Quality Indicator Lichen Species in Oregon and Washington

Group	Sub-Group	Indicator Species
Clean Air	Regional distribution	*Bryoria capillaris, Lobaria oregana, Sphaerophorus globosus, Usnea filipendula, Usnea scabrata*
	Sub-regional distribution	*Ahtiana pallidula, Alectoria sarmentosa, Bryoria fuscescens, Hypogymnia enteromorpha, Nephroma bellum, Nodobryoria oregana*
Polluted Air	Regional nitrophytes	*Candelaria concolor, Physcia adscendens, Xanthoria polycarpa*

* Includes only species with highest indicator value, used by Geiser and Neitlich (2007) to define air quality zones.

Source: Geiser and Neitlich (2007).

C.3. Transitional Ecosystems

The sensitivity of wetlands is particularly important given that they contain a disproportionately high number of rare plant species (Figure C-3) (Moore et al., 1989). EPA reported that, of the 130 plant species from the conterminous U.S. that were listed as threatened or endangered in 1987, 14% occurred principally in wetlands (U.S. EPA, 1993b). Bedford and Godwin (2003) indicated that a disproportionately high number of rare plant species occur in fens relative to their percent land cover (Table C-4) (Bedford and Godwin, 2003). For example, fens comprise only 0.01% of northeastern Iowa but contain 12% of the region's rare plant species and 17% of the listed endangered, threatened, and species of concern (Table C-4).
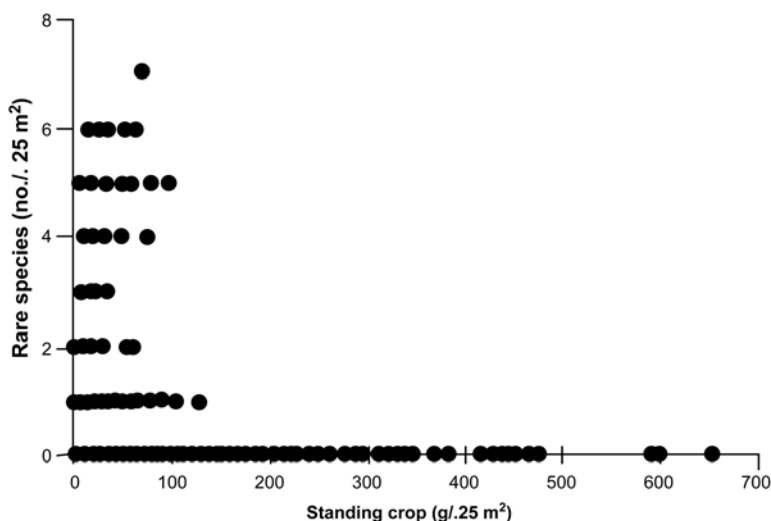
Source: Moore et al. (1989).

Figure C-3. **Number of nationally rare species versus standing crop in each of 401 quadrants from wetlands in Ontario, Quebec, and Nova Scotia.**

Table C-4. **Contribution of fens to support of plant species diversity in selected states.**

	Number of Vascular Species Found in Fens (# Native)	Percent of State Vascular Flora Found in Fens (% Native)	Non-Vascular Species Found in Fens	Number of Uncommon & Rare Species Found in Fens	Percent of State Uncommon & Rare Species Found in Fens	Percent of State Area in Fens
Colorado	~500	~14		20	3.3	0.08–0.15
Idaho	327		20	35	12.0	
Iowa	320	18		134	12.0	0.01
	(307)	(17.2)				
Montana	174		60	40		0.0015

New Hampshire	340	17.2	91	52	13.7	0.078
Calcareous fens						0.0058
Open fens						0.0726
New Jersey				96	13.5	0.00733
Calcareous fens	245			60		0.0073
Acidic seeps	169		13	36		0.00003
New York	440	13.8	77	55	7.0	0.07
	(397)	(19.0)				
North Carolina				77	11.0	0.0023

Source: Bedford and Godwin (2003).

C.4. Aquatic Ecosystems

Aquatic systems can be subdivided into major types based on hydrology. At the broadest level, freshwater aquatic ecosystems can be classified as riverine, lacustrine, and palustrine systems. Riverine systems can be identified at varying scales, including valley segment, river reach, and channel unit. Lacustrine systems include deepwater habitats associated with lakes and reservoirs. Palustrine systems include small, shallow, or intermittent water bodies, including ponds. Each type of aquatic ecosystem is potentially sensitive to nutrient enrichment effects from N deposition. Nevertheless, available data documenting such effects are limited.

The dose-response data for aquatic organisms such as those cited here are generally expressed in concentration units, as mg/L or μmol/L of N, for example. Such exposure concentration data cannot be directly related to ecosystem exposure, which is generally expressed in such units as kg/ha. This is because a given N deposition exposure can result in widely varying concentrations of N compounds (especially NO_3^-) in water. For convenience, a concentration of 1 mg/L of N (as, for example, in the case of NO_3^--N or NH_4^+-N) is equal to 71.4 μmol/L or 71.4 μeq/L of NO_3^- or NH_4^+.

C.4.1. History of Evaluating Nitrogen Enrichment in Freshwater Aquatic Ecosystems

The role of N deposition in freshwater eutrophication and acidification processes has been considered secondary to P and S, and only within the past 20 years have there been studies questioning the established science and showing N-limitation in some fresh waters, N excess in some terrestrial systems, and N-caused acidification in poorly buffered fresh waters. A number of things have conspired to prevent extensive evaluation of the effects of atmospheric N deposition on aquatic organisms via nutrient-

enrichment pathways. These include assumptions, or prevailing paradigms, that have channeled scientific thought in one direction and away from others.

First were the assumptions for many years that atmospheric deposition was caused primarily by sulfur (S) emissions and that effects on aquatic ecosystems were primarily caused by acidification processes. Only after S emissions began to decrease substantially in response to the CAAA did the role of NO_X, and still later, NH_3, emissions become recognized as potential agents of environmental change. And even then, that role was assumed to be restricted mainly to acidification from NO_3^-, a strong acid anion, not eutrophication (Reuss and Johnson, 1985). Second, because N is the nutrient most limiting to primary production in most ecosystems, it was assumed until fairly recently that N was tightly cycled in terrestrial systems, and that excess NO_3^- leaching rarely occurred in natural environments (Vitousek and Howarth, 1991). Finally, the attention of aquatic biologists has been strongly focused on the role of P in eutrophication of freshwaters for the past 40 years, largely due to the demonstrated role of P in causing large increases in algal productivity worldwide (Schindler et al., 1971; Schindler, 1974). P is an essential, and often limiting, nutrient to aquatic organisms. A large number of highly influential studies in the 1960s and 1970s exposed the role of wastewater, in particular phosphate detergents, in causing excessive algal production and anoxia in Lake Mendota (Wisconsin), Lake Washington (Washington), Lake Erie, and many other locations (Hasler, 1947; Vollenweider, 1968; Edmondson, 1969, 1991). Because of the emphasis on P as a major cause of fresh water eutrophication, Downing and McCauley (1992) wrote as recently as 1992: "opinions differ on the role of N as a limiting nutrient in lakes."

C.4.2. Interactions between Nitrogen and P loading

Results from surveys, paleolimnological reconstructions of past conditions, experimental results, and meta-analyses of hundreds of studies all consistently show N-limitation to be common in fresh waters, especially in remote areas, and there is a nearly universal eutrophication response to N-enrichment in lakes and streams that are N-limited. Surveys of lake N concentrations and trophic status along gradients of N deposition show increased inorganic N and increased productivity to be strongly related to atmospheric N deposition. Where N-enrichment has occurred, P limitation, N+P colimitation, and a few instances of Si depletion have been reported. Paleolimnological records show increases in productivity and changes in algal assemblages in the recent past (since 1950) that are correlated with increased societal use of synthetic N fertilizers and human. The paleolimnological evidence is strongest in regions with the highest N deposition, and is weaker where N deposition is lower (Wolfe et al., 2001; 2003; 2006; Saros et al., 2003). In additions to changes in productivity, algal community reorganization has been observed in the paleolimnological record, experiments, and observations of N-enriched lakes, especially those where enrichment has come from N deposition. A summary of additional studies addressing N-limitation is given in Table C-5.

It is generally believed that the Laurentian Great Lakes are P-Limited (Schelske, 1991; Downing and McCauley, 1992; Rose and Axler, 1998). Water quality in the open waters of these lakes has been improving in recent years in response to controls on point sources of P (Nicholls et al., 2001). Work by Levine et al. (1997), however, suggested a more complicated pattern of response to nutrient addition for Lake Champlain. They added nutrients to in situ enclosures and measured indicators of P status, including alkaline phosphatase activity and orthophosphate turnover time. Although P appeared to be the principal limiting nutrient during summer, N addition also resulted in algal growth stimulation. During spring, phytoplankton growth was not limited by P, N, or silica (Si), but perhaps by light or temperature (Levine et al., 1997).

Data from 28 Sierra Nevada lakes sampled in 1985 and again in 1999 suggested that NO_3^- concentrations decreased during that period and total P concentrations increased in more than 70% of the lakes sampled. Sickman et al. (2003a) concluded that lakes throughout the Sierra Nevada appear to be experiencing measurable eutrophication in response to atmospheric deposition of nutrients, but N

deposition is only part of the process. Based on the evidence of increased P loading throughout the Sierra Nevada, Sickman et al. (2003a) concluded that site-specific P sources were unlikely to be the cause of observed trends. They proposed that atmospheric deposition and accelerated internal cycling of P in response to changes in climatic factors were the most likely sources of increased P loading to the Sierra Nevada Lakes, but it is not known why atmospheric deposition of P to these lakes has increased over time. Possibilities include use of organo-phosphate pesticides and aeolian transport of soils and dust that are high in P from the San Joaquin Valley to the Sierra Nevada Mountains (Bergametti et al., 1992; Lesack and Melack, 1996; Sickman et al., 2003a).

Data from a survey of 44 lakes east and west of the Continental Divide in Colorado indicated that lakes on the western side of the Continental Divide averaged 6.6 µeq/L of NO_3^-, whereas lakes on the eastern side of the Continental Divide averaged 10.5 µeq/L of NO_3^- concentration. In the Colorado Front Range, NO_3^- concentrations in lakes above 15 µeq/L have commonly been measured, suggesting some degree of N-saturation (Baron, 1992). A meta-analysis of 42 regions in Europe and North America suggested that a majority of lakes in the northern hemisphere were limited by N in their natural state (Bergström and Jansson, 2006). While many of these lakes now receive sufficient N from deposition that they are no longer N-limited, some lakes in remote regions still maintain their original oligotrophic or ultra-oligotrophic status.

Table C-5.   Summary of additional evidence for N limitation on productivity of freshwater ecosystems.

Region	Endpoint	Observation	Ecosystem Type	Reference
Sweden	N limitation	a consistent pattern of nutrient limitation showing N limitation for deposition below approximately 2.5 kg N/ha/yr, co-limitation of N and P for deposition between ~2.5 and 5.0 kg N/ha/yr, and P limitation in areas with N deposition greater than 5.0 kg N/ha/yr.	lakes	Bergström et al. (2005)
Rocky Mountains of Colorado and Wyoming	N limitation	Review: the author concluded that the effects of atmospheric N deposition were uncertain and that a widespread shift from N to P limitation had not been clearly demonstrated.		Burns (2004)
Texas	N limitation	some instances of seasonsal N-limitation, and other instances of year-round N-limitation	rivers	Stanley et al., (1990)
Rocky Mountains of Colorado and Wyoming	N limitation	Review: Author stated that recent studies did suggest a change in diatom species dominance in the 1950s, but widespread species changes across lakes in the region and the role of N deposition in these changes needed confirmation. Thus, the available data were not clear at that time, but suggested that some changes had likely occurred in some aquatic ecosystems.	lake	Burns (2004)

C.4.3. Aquatic Species Affected

The following Section contains studies in which the amount of N added was less than 10 mg NO_3^--N/L, or 714 µM, and most studies tested the effects of 5 mg NO_3^--N/L or less. Many of these studies are summarized in Table C.6. Overall, several major effects were reported on biota treated with N enrichment: the effects on algae included growth stimulation, increased cell densities, decline or

stimulation of individual taxa, and decline in diversity; the amount of N required to stimulate growth in phytoplankton is extremely low: 3 µM or less; and animal responses included no response, decreased reproductive capability, declines in growth rate and biomass, mortality, and in one case, increased fitness because NO_3^- was detrimental to a fungal parasite.

C.4.3.1. Phytoplankton and Plants

Two species of diatom, *Asterionella formosa* and *Fragilaria crotonensis*, now dominate the flora of at least several alpine and montane Rocky Mountain lakes (Baron et al., 2000; Interlandi and Kilham, 1998; Saros et al., 2003, 2005; Wolfe et al., 2001, 2003). These species are opportunistic algae that have been observed to respond rapidly to disturbance and slight nutrient enrichment in many parts of the world. They were among the first diatoms to increase in abundance following watershed settlement and agricultural development in European lake watersheds in the 12th and 13th centuries (Anderson et al., 1995; Lotter, 1998), and North American settlements in the 18th and 19th centuries (Christie and Smol, 1993; Hall et al., 1999). In these studies, as well as in a Swedish lake influenced by acidic deposition, these two diatom species expanded following initial disturbance, and were later replaced by other species more tolerant of either acidification or eutrophication (Renberg et al., 1993; Hall et al., 1999). Moreover, the growth of *A. formosa* has been stimulated with N amendments during in situ incubations, using bioassays and mesocosms (6.4 to 1616 µM N/L; McKnight et al., 1990) (76 µM N/L; Lafrancois et al., 2004) (18 µM N/L; Saros et al., 2005).

It may seem obvious that additions of N stimulate cell growth, but not all species of diatoms or other algae are equally responsive to N supply. *A. formosa* and *F. crotonensis* have extremely low resource requirements for P, enabling them to outcompete other algae for resources and such differences in resource requirements allow some species to gain a competitive edge over others upon nutrient addition, and as a consequence, shifts in assemblages have been observed (Lafrancois et al., 2004; Saros et al., 2005; Wolfe et al., 2001; 2003). This is in keeping with findings of Interlandi and Kilham (2001), who demonstrated that maximum species diversity was maintained when N levels were extremely low (<3 µM N) in lakes in the Yellowstone National Park (Wyoming, Montana) region. The implication is that species diversity declines with increasing availability of N, and this finding complements the results of terrestrial studies that also showed a negative relationship between species diversity and N availability (Gilliam 2006; Suding et al., 2005; Stevens 2004).

P limitation and co-limitation of both N and P are reported for fresh waters in the literature, particularly during summer (Downing and McCauley, 1992; Elser 1990; Morris and Lewis 1988; Sickman et al., 2003b). Because diatoms in northern temperate freshwaters respond rapidly and favorably to N enrichment and also have relatively high Si requirements, Si can be depleted, at least seasonally, from waters that are relatively high in N and P.

Silica depletion due to nutrient enrichment has been reported for the Great Lakes (Conley et al., 1993). Increased growth of silicate-utilizing diatoms as a result of NO_3^- and phosphate (PO_4^{3-})-induced eutrophication, and subsequent removal of fixed biogenic Si via sedimentation has brought about changes in the ratios of nutrient elements Si, N, and P. In turn, such changes can cause shifts from diatoms to non-siliceous phytoplankton in large rivers and coastal marine regions (Ittekot, 2003). Reduction in dissolved Si in lakewater corresponded to phytoplankton blooms under ice and large numbers of diatoms during spring in Loch Vale Watershed, Rocky Mountain National Park (Campbell et al., 1995). This is a potential seasonal issue in water bodies underlain by aluminosilicate rocks because mineral weathering can replenish the Si supply.

C.4.3.2. Seasonal Nitrogen Input and Cyanobacteria

Some ecosystems are seasonally enhanced with N from atmospheric deposition, either from snowmelt flushing of accumulated N in winter snow, or from flushing during dormancy of terrestrial vegetation (Stoddard, 1994). While many eutrophic and hypereutrophic freshwater ecosystems have seasonal or perennial cynaobacteria that fix atmospheric N, obviating the need for an external source of N (Wetzel, 2001), only one oligotrophic lake with obligate N-fixing bacteria has been reported (Reuter et al., 1985). N-fixation is energy expensive and sometimes limited by trace metal availability, so obligate N-fixing cyanobacteria (formerly called blue-green algae) are rarely found in ultra-oligotrophic waters (McKnight et al., 1990; Vitousek and Howarth, 1991). Because of this, oligotrophic and ultraoligotrophic waters are extremely sensitive to even low inputs of N from atmospheric deposition. *Anabaena circinalis*, an obligate N-fixing cyanobacterium, was suppressed with additions of 500 µM/L N (Higley et al., 2001), and DIN levels >~200 µM/L N completely inhibited N fixation in Castle Lake, CA (Reuter et al., 1985).

C.4.3.3. Nitrate Toxicity: Invertebrates

Toxic responses to N exposure by aquatic invertebrates have been identified in a number of studies. Toxic response thresholds are typically much higher than the levels of N in surface waters that could be attributable to N deposition in the U.S. Safe Concentrations (SC), or threshold values of N, were determined by Camargo and Ward (1995) for several aquatic insects at different life stages. Early instars are generally more sensitive to N in solution than later or adult stages. The SC for late instars of *Hydropsyche occidentalis*, a caddis fly, was found to be 171 µM/L, and concentrations greater than this value induced mortality. The SC was 100 µM/L for early instars of the same species (Camargo and Ward, 1995). Another caddis fly, *Cheumatopsyche pettiti*, tolerated higher concentrations, with safe concentrations of 171 and 250 µM N/L, respectively for early and late instars (Camargo and Ward, 1995). Two species of amphipod did not survive after 120-h exposure to NO_3^- concentrations of 200 µM N/L for one species, and 314 µM N/L for the other (Camargo et al., 2005). No observable effect concentrations above which *Ceriodaphinia dubia* exhibited reduced reproductive capability ranged broadly in laboratory experiments, but some effects were seen at concentrations greater than 507 µM N/L (Scott and Crunkilton, 2000). A decline in *Daphnia spp.* was observed in mesocosm nutrient enrichment experiments where 75 µM N/L was added, but this was attributed to lower food quality of the algal assemblage that replaced the original species as a result of fertilization (Lafrancois et al., 2004). Thus, toxic responses seem to occur at N concentrations that are much higher than the concentrations required to elicit a response in competitive interactions.

A whole-ecosystem experiment at the Bear Brook watershed, ME simulated the effects of N and S deposition by means of experimental $(NH_4)_2SO_4$ addition over a period of 10 years. Researchers found that elevated N inputs had minimal effect on stream detritus processing (Chadwick and Huryn, 2003). They also found that N additions had no significant effect on stream macroinvertebrate secondary production or varying production by functional feeding groups. They concluded that climate-related variables such as flow duration and litter inputs controlled secondary production when N was not limiting (Chadwick and Huryn, 2005).

Changes to aquatic food webs have not been as thoroughly explored as changes to algal assemblages, but a few studies have shown declines in zooplankton biomass (Paul et al., 1995; Lafrancois et al., 2004) in response to N-related shifts in phytoplankton biomass toward less palatable taxa with higher C:P ratios (Elser et al., 2001). N enrichment of arctic streams not only increased periphyton biomass and productivity, but also stimulated the entire ecosystem, increasing decomposition rates, fungal biomass, and invertebrates (Benstead et al., 2005).

C.4.4. Nitrate Toxicity: Amphibians and Fish

A summary of studies on the effects of nitrate on amphibians and fish is given by Table C-6. It appears that very high NO_3^- concentrations in surface water are required to elicit a toxic response in amphibian populations. Concentrations that caused no observed effects and no observed adverse effects ranged from 357 to 714 µM N/L for frogs, salamanders, and the American toad (*Bufo americanus*) (Hecnar, 1995; Laposata and Dunson, 1998; Johansson et al., 2001; Romansic et al., 2006). In one experiment, the red-legged frog (*Rana aurora*) exhibited a decreased susceptibility to *Saprolegnia* mold when exposed to elevated NO_3^- concentrations (Romansic et al., 2006).

According to one review, adverse direct effects of N deposition on fish due to nutrient enrichment are probably minimal (Burns, 2004). N concentrations alone are not high enough to influence fish metabolism, and the extent of eutrophication is insufficient (due to induced P limitation in oligotrophic waters) to cause O_2 depletion.

Other research suggests that the eggs and fry of rainbow trout (*Oncorhyncus mykiss*; including steelhead), cutthroat trout (*O. clarki*), and chinook salmon (*O. tshawytscha*) are susceptible to elevated concentrations of NO_3^-, with rainbow trout mortality occurring after 30 day incubations in concentrations >79 µM N/L (Kincheloe et al., 1979). There were no observed effects reported below this concentration. Chinook salmon and cutthroat trout eggs and fry responded to slightly higher concentrations; no observed effects occurred below 164 µM N/L, but mortality occurred at higher concentrations (Kincheloe et al., 1979). Lake whitefish (*Coregonus clupeaformis*) and lake trout (*Salvelinus namaycush*) embryos displayed developmental delays at concentrations greater than 446 and 114 µM N/L, respectively (McGurk et al., 2006). All of these toxic threshold concentrations are much higher than the concentrations of NO_3^- in surface water that would routinely be expected to occur solely in response to atmospheric N deposition in the U.S. Nevertheless, such high concentrations of streamwater NO_3^- have been measured in the Great Smoky Mountains, NC (Cook et al., 1994) and in mixed conifer forests in southern California (Fenn and Poth, 1999).

Table C-6.   **Summary of effects of N enrichment on aquatic biota in freshwater ecosystems.**

Species	Common Name	Life Stage	N Concentration (mg NO_3^--N/L)	Observed Effects	Reference
ALGAE: PHYTOPLANKTON					
Asterionella formosa	diatoms		0.252 mg/L	stimulated growth	Saros et al. (2005)
Asterionella formosa	diatoms		6.4 µmol/L	stimulated growth	McKnight et al. (1990)
Multiple species	diatoms		1.06 mg/L	(low ambient N-deposition):increase in chlorophyll-a content and growth rate; no cell density effect	Lafrancois et al. (2004)
Asterionella formosa	diatoms		5.7×10^{-4} (>0.041 uM) (high light)	increased growth rate (measured at half the maximum growth rate)	Michel et al. (2006)
Fragilaria crotonensis	diatoms		0.252 mg/L	stimulated growth	Saros et al. (2005)
Multiple species	diatoms		1.06 mg/L	(low ambient N deposition):increase in chlorophyll-a content and growth rate; no cell density effect	Lafrancois et al. (2004)

Fragilaria crotonensis	diatoms	3.5 × 10−4 (>0.028 uM) (high light)	increased growth rate (measured at half the maximum growth rate)	Michel et al. (2006)
Fragilaria crotonensis	diatoms	8.4 × 10−6 (>0.006 uM) (med light)	increased growth rate (measured at half the maximum growth rate)	Michel et al. (2006)
Staurosirella pinnata	diatoms	8.4 × 10−6 (>0.006 uM) (med light)	increased growth rate (measured at half the maximum growth rate)	Michel et al. (2006)
Tetracyclus glans	benthic diatoms	1.7 × 10−4 (>0.012 uM) (low light)	increased growth rate (measured at half the maximum growth rate)	Michel et al. (2006)
Multiple species	phytoplankton assemblages	3.0 uM	N saturation value for maximum diversity in WY low N lakes	Interlandi et al. (1999)
not identified	phytoplankton assemblages	0.5 mg/L	NO_3^- stimulated growth seasonally, while tributary periphyton communities were P limited	Stanley et al. (1990)
not identified	phytoplankton assemblages	0.3 uM	NH_4 additions more effective at stimulating growth than NO_3^-	Levine and Whalen (2001)
not identified	phytoplankton assemblages	100 µg/L	stimulated NO_3^- uptake	Axler and Reuter (1996)
Multiple species	crysophytes	1.21 mg/L	(elevated ambient N deposition): no response to NO_3^- additions; increased chlorophyll-a and cell density when NO_3^- combined with acid and P	Lafrancois et al. (2004)
Multiple species	epilimnetic algae	0.012 mg/L	increased growth rate (measured at half the maximum growth rate)	Priscu et al. (1985)
Multiple species	hypolimnetic algae	0.050 mg/L	increased growth rate (measured at half the maximum growth rate)	Priscu et al. (1985)

PERIPHYTON

	attached benthic algae	0.5 M NaNO3 in 2% agar	biomass increased in response to N and N & P additions during period of seasonal N-limitation (July-August)	Smith and Lee (2006)
	attached benthic algae	2.5 M	NO_3^- stimulated stream algal growth during seasonal N-limitation	Bushong and Bachmann (1989)
not identified	attached benthic algae	0.5 M NaNO3 in 3% agar	NO_3^- alone stimulated stream algal growth during seasonal N-limitation, while N & P co-limited growth in other times	Wold and Hershey (1999)
not identified	attached benthic algae	0.5 M NaNO3 in 3% agar	NO_3^- alone stimulated stream algal growth during seasonal N-limitation, while N & P co-limited growth in other times	Allen and Hershey (1996)
not identified	attached benthic algae	0.036 mg/L	stimulated NO_3^- uptake	Axler and Reuter (1996)
not identified	attached benthic algae	0.5 M NaNO3 in 2% agar	no growth response	Higley et al. (2001)

not identified	epilithic		~700 µg NO$_3$–N	suppressed N$_2$-fixation	Reuter et al. (1985)
not identified	attached benthic algae		0.16 mg/L	increased summer growth rate (measured at half the maximum growth rate)	Reuter et al. (1985)
not identified	attached benthic algae		0.32 mg/L	increased winter growth rate (measured at half the maximum growth rate)	Reuter et al. (1986)
not identified	sublittoral epilithic algae		0.259 mg/L	increased growth rate (measured at half the maximum growth rate)	Reuter and Axler (1992)
not identified	eulittoral epilithic algae		0.126 mg/L	increased growth rate (measured at half the maximum growth rate)	Reuter and Axler (1992)
not identified	epipelic algae		0.713 mg/L	increased growth rate (measured at half the maximum growth rate)	Reuter and Axler (1992)
CYANOBACTERIA					
Anabaena circinalis	N fixing cyanobacteria		0.5 M NaNO$_3$ in 2% agar	decreased abundance	Higley et al. (2001)
Microcycstis sp.	non-N-fixing cyanobacteria		0.28 mg/L	increased growth rate; increased mycrocystin and anatoxin-a concentrations	Gobler et al. (2007)
INVERTEBRATES					
Hydropsyche occidentalis	caddis fly	early instaar	1.4 (SC)	mortality	Camargo and Ward (1995)
		late instaar	2.2 (SC)	mortality	Camargo and Ward (1995)
Cheumatopsyche pettiti	caddis fly	early instaar	2.4 (SC)	mortality	Camargo and Ward (1995)
		late instaar	3.5 (SC)	mortality	Camargo and Ward (1995)
Echinogammarus echinosetosus	amphipod	adult	2.8 (120 h LC0.01)	mortality	Camargo et al. (2005)
Eulimnogammarus toletanus	amphipod	adult	4.4 (120 h LC0.01)	mortality	Camargo et al. (2005)
Ceriodaphnia dubia	water flea/cladoceran	adult	7.1-56.5 (7d NOEC)	decreased reproductive ability; fewer neonates produced per female	Scott and Crunkilton (2000)
Daphnia pulex	Water flea	adult	1.06	(low ambient N-deposition): decreased biomass in response to NO$_3$–	Lafrancois et al. (2004)
Daphnia schoedleri	Water flea	adult	1.06	(low ambient N-deposition): decreased biomass in response to NO$_3$–	Lafrancois et al. (2004)
VERTEBRATES: AMPHIBIANS					
Rana temporaria	common frog	larvae	5 (70-d NOEC)	delayed development, lower growth rate and body mass at metamorphosis	Johansson et al. (2001)

Rana sylvatica	wood frog	fertilized eggs	9 (NOAEL)	no effect of NO_3^- on survivorship	Laposata and Dunson (1998)
Ambystoma jeffersonianum	Jefferson's salamander	fertilized eggs	9 (NOAEL)	no effect of NO_3^- on survivorship	Laposata and Dunson (1998)
Ambystoma maculatum	spotted salamander	fertilized eggs	9 (NOAEL)	no effect of NO_3^- on survivorship	Laposata and Dunson (1998)
Ambystoma gracile	northwestern salamander	larvae	5-20	no effect of NO_3^- on survivorship	Romansic et al. (2006)
Rana aurora	red-legged frog	larvae	5-20	no effect of NO_3^- on survivorship; NO_3^- decreased susceptibility to Saprolegnia mold	Romansic et al. (2006)
Hyla regilla	Pacific tree frog	larvae	5-20	no effect of NO_3^- on survivorship	Romansic et al. (2006)
Pseudacris triseriata	striped chorus frog	tadpole	10 (100-d LOEC)	mortality	Hecnar (1995)
Rana pipiens	northern leopard frog	tadpole	10 (100-d LOEC)	mortality	Hecnar (1995)
Bufo americanus	American toad	fertilized eggs	9.0 (NOAEL)	no effect of NO_3^- on survivorship	Laposata and Dunson (1998)
FISH					
Oncorynchus mykiss (anadromous)	steelhead	eggs	1.1 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
Oncorynchus mykiss (nonanadromous)	rainbow trout	eggs	1.1 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
Oncorynchus mykiss (nonanadromous)	rainbow trout	fry	1.1 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
Oncorynchus tshawytscha	chinook salmon	fry	2.3 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
Salmo clarki	cutthroat trout (Lahontan)	eggs	2.3 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
Salmo clarki	cutthroat trout (Lahontan)	fry	4.5 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
Coregonus clupeaformis	lake whitefish	embryo	6.25 (~120-d NOEC)	hatching and developmental delays	McGurk et al. (2006)
MISCELLANEOUS					
Saprolegnia spp.	pathogenic water mold		5-20 mg NO_3^-/L	decreased ability to infect and kill the larvae of the red-legged frog, Rana aurora	Romansic et al. (2006)

NOEC = No-observed-effect concentration; NOAEL = No-observed-adverse-effect level; SC = Safe concentration

C.5. Estuary and Coastal Ecosystems

There are a variety of factors that govern the sensitivity of estuaries and near-coastal marine waters to eutrophication from atmospheric N deposition. Of critical importance is the total N input from all sources, including both atmospheric and non-atmospheric sources. Other key elements include the dilution capacity of the watershed, which reflects the volume of water available to dilute added N, and flushing rate, which reflects the time required for inflowing water to replace estuary volume, (Bricker et al., 1999; NRC, 2000). Other potentially important factors can include the following (NRC, 2000):

- Physiography (geomorphology, dominant biological communities, biogeographic province);
- Type of primary production base (i.e., seagrasses, phytoplankton, coral, attached intertidal algae, etc.);
- Stratification and extent to which phytoplankton occupy the nutrient-rich photic zone; and
- Allochthonous inputs of organic matter.

A number of factors control the N loading rates to estuaries and the potential effects of N deposition on nutrient loading and algal blooms. Estuaries communicate with fresh water on the upstream side and with the ocean on the downstream side. The flushing of fresh river water through the system and the movement and mixing of salt water from the ocean are complicated and are always changing in response to weather and tidal cycles. The surface area, volume, and depth of the estuary are also critical factors governing the sensitivity of an estuary to N inputs. Decreases in grazer, filter-feeder, and higher trophic level populations of fish and shellfish exacerbate problems associated with nutrient over-enrichment (Jackson et al., 2001).

At the upstream end of an estuary, the water is primarily fresh much of the time. Discharge of N from the land surface, only a part of which is of atmospheric origin (mainly as deposition to the land that subsequently leached to the river water), dominates new N inputs. Further downstream within the estuary, where fresh water is more thoroughly mixed with saltwater, much of the terrestrial N load is assimilated by phytoplankton and benthic flora or removed by microbes in the process of denitrification (Paerl, 2002). The importance of atmospheric N as a contributor to the total N load beyond this zone probably increases, but there are no data to evaluate that.

The principal watershed features that control the amount of increased N flux to estuaries in the U.S. include human population, agricultural production, and the size of the estuary relative to its drainage basin (Caddy, 1993; Fisher et al., 2006; Peierls et al., 1991). Dense human populations generate large volumes of nutrient-rich wastewater. Tertiary sewage treatment can reduce effluent N concentrations to less than 35 µM, but these technologies have not been promoted as aggressively in the U.S. as elsewhere (Conley et al., 2002; U.S. EPA, 2003). Agricultural production is heavily dependent on fertilizer application to generate high yields from small areas. Fertilizer application has dramatically increased NO_3^- concentrations in ground water in many agricultural areas (Bohlke and Denver, 1995), which can leach to surface waters. Large terrestrial drainage basins that drain into small estuaries tend to have high nutrient flux if the land is heavily populated or used for agriculture.

In addition to estuaries, coastal marine ecosystems are highly susceptible to nutrient enrichment, especially from N. Land clearing, agricultural land use, sewage treatment discharge, and atmospheric deposition can all result in high loadings of N to the coastal zone. Excessive N inputs contribute to a range of impacts, including enhanced algal blooms, decreased distribution of seagrasses, and decreased dissolved oxygen (DO) concentration (Borum, 1996; Bricker et al., 1999; Nixon, 1995; Valiela et al., 1992). Because of human population growth and the great popularity of coastal areas, there is substantial potential for increased N loading to coastal ecosystems from both atmospheric and non-atmospheric sources.

C.5.1. Interacting Factors with Productivity

Results of empirical observations and short-term (3 weeks) marine mesocosm experiments suggest that there can be wide variation in the response of autotroph biomass to nutrient addition (Cloern, 2001; Olsen et al., 2006). Such variation may be attributable to the time scale of the observations, rate of water exchange, grazing pressure, and other environmental factors (Olsen et al., 2006).

C.5.2. Hydrology Interactions with Phytoplankton Biomass

River discharge has a huge influence on the hydrology and nutrient cycling of estuaries. For example, discharge from the large watershed of the Susquehanna River is important to the seasonal and interannual variability in the hydrology of Chesapeake Bay (Fisher et al., 1988; Malone et al., 1988). When discharge from the Susquehanna River is low, summer phytoplankton biomass in Chesapeake Bay tends to be low compared to spring conditions, and the phytoplankton community is dominated by small and flagellated forms (Marshall and Lacouture, 1986). Under higher river flows, summer phytoplankton biomass in the bay is higher, and has an increased prevalence of diatoms (Paerl et al., 2006).

Hydrologic variation interacts with nutrient supply to control phytoplankton seasonal patterns in Chesapeake Bay. High biomass during the spring diatom bloom leads to consequent sedimentation of organic material out of the photic zone during the transition to summer (Malone et al., 1996; Harding et al., 2002). Microbial decomposition of this material then fuels the pattern of summer anoxia in bottom waters (Paerl et al., 2006). N loading to Chesapeake Bay and its tributaries during spring high runoff periods contributes to periods of P limitation and co-limitation (Boynton et al., 1995). The ecosystem then returns to N limitation during low flow summer months (Paerl, 2002).

C.6. Watersheds, Landscapes and Disturbance

C.6.1. Interactions among Terrestrial, Transitional, and Aquatic Ecosystems

Streams, and to a lesser extent lakes, can serve as indicators of regional environmental change (Seastedt et al., 2004), partly because they integrate conditions within their watersheds including atmospheric, edaphic, geologic, and hydrologic conditions. Streams reflect the terrestrial environment most closely during high flow when much of the stream water enters the channel from the upper soil where most of the biological activity occurs. The terrestrial signal can be less clear in lakes because they have the capacity to store water and modify water chemistry through internal processes to a greater degree than streams (Lawrence et al., 2008).

Young and Sanzone (2002) provided a checklist of ecological attributes that should be considered when evaluating the effects of an environmental stressor on the integrity of ecological systems (Table C-7). The Essential Ecological Attributes (EEAs) listed in the table represent groups of related ecological characteristics (Harwell et al., 1999), including landscape condition, biotic condition, chemical and physical characteristics, ecological processes, hydrology and geomorphology, and natural disturbance regimes. The first three ecological attributes listed in Table C-7 can be classified primarily as "patterns," whereas the last three are "processes" (Bormann and Likens, 1979). They can be affected by a variety of environmental stressors (Figure C-4).

Of concern in this annex are relationships between NO_X atmospheric deposition, derived from anthropogenic sources, and one or more of the EEAs. The ranges of likely changes in ecosystem patterns and processes associated with changes in deposition are discussed in the subsections that follow.

The following discussion assesses and characterizes the overall condition or integrity of ecosystems within the U.S. that are affected by the deposition of atmospheric N and its role as a nutrient. The six EEAs – landscape condition, biotic condition, chemical/physical characteristics, ecological processes, hydrology/geomorphology, and natural disturbance regimes (Table C-7) – provide a hierarchical framework for assessing ecosystem status. Characteristics related to structure, composition, or functioning of ecological systems may be determined by the use of endpoints or ecological indicators of condition that are measureable and significant either ecologically or to society (Harwell et al., 1999).

Table C-7.   Essential ecological attributes and reporting categories.

Landscape Condition	Ecological Processes
Extent of Ecological System/Habitat Types	Energy Flow
Landscape Composition	Primary Production
Landscape Pattern and Structure	Net Ecosystem Production
Biotic Condition	Growth Efficiency
Ecosystems and Communities	Material Flow
Community Extent	Organic Carbon Cycling
Community Composition	N and P Cycling
Trophic Structure	Other Nutrient Cycling
Community Dynamics	**Hydrology and Geomorphology**
Physical Structure	Surface and Groundwater flows
Species and Populations	Pattern of Surface flows
Population Size	Hydrodynamics
Genetic Diversity	Pattern of Groundwater flows
Population Structure	Salinity Patterns
Population Dynamics	Water Storage
Habitat Suitability	Dynamic Structural Characteristics
Organism Condition	Channel/Shoreline Morphology, Complexity
Physiological Status	Extent/Distribution of Connected Floodplain
Symptoms of Disease or Trauma	Aquatic Physical Habitat Complexity
Signs of Disease	Sediment and Material Transport
Chemical and Physical Characteristics	Sediment Supply/Movement
(Water, Air, Soil, and Sediment)	Particle Size Distribution Patterns
Nutrient Concentrations	Other Material Flux

N	Natural Disturbance Regimes
P	Frequency
Other Nutrients	Intensity
Trace Inorganic and Organic Chemicals	Extent
Metals	Duration
Other Trace Elements	
Organic Compounds	
Other Chemical Parameters	
pH	
Dissolved O$_2$	
Salinity	
Organic Matter	
Other	
Physical Parameters	

Source: Young and Sanzone (2002).

The relationships among the EEAs are complex because all are interrelated. Changes in one EEA may affect, directly or indirectly, every other EEA. Ecological processes create and maintain environmental patterns, and these patterns affect how the processes are expressed (Young and Sanzone, 2002). Changes in patterns or processes can result in changes in the status and functioning of an ecosystem.

Changes in the biodiversity, composition, and structure of ecosystems relate directly to functional integrity. Changes in biodiversity are of particular significance in altering ecosystem function. The energy obtained by plants (producers) from sunlight during photosynthesis and the chemical nutrients taken up by those plants from the soil and the atmosphere are transferred to other species (consumers) within the ecosystem through food webs. The movement of chemical nutrients through an ecosystem is cyclic, as the nutrients are used or stored and eventually returned to the soil by microorganisms and fungi (decomposers). Energy is transferred among organisms through the food webs and eventually is dissipated into the environment as heat. The flows of energy and cycling of nutrients provide the interconnectedness among the elements of the ecosystem and transform the community from a random collection of numerous species into an integrated whole.

Human existence and welfare on this planet depend on life-support services provided by the interaction of the EEAs. Both ecosystem structure and function play essential roles in providing goods and services (Table C-8; Daily, 1997). Ecosystem processes provide diverse benefits including absorption and breakdown of pollutants, cycling of nutrients, binding of soil, degradation of organic waste, maintenance of a balance of gases in the air, regulation of radiation balance and climate, and fixation of solar energy (Daily, 1997; Westman, 1977; World Resources Institute, 2000). These ecological benefits, in turn, provide economic benefits and values to society (Costanza et al., 1997; Pimentel et al., 1997). Goods such as food crops, timber, livestock, fish, and drinking water have market value. The values of ecosystem services such as flood-control, wildlife habitat, cycling of nutrients, and removal of air pollutants are more difficult to measure (Goulder and Kennedy, 1997). See discussion in Annex F.

Biodiversity is an important consideration at all levels of biological organization, including species, individuals, populations, and ecosystems. Human-induced changes in biotic diversity and alterations in the structure and functioning of ecosystems are the two most dramatic ecological trends of the past

century (U.S. EPA, 2004; Vitousek et al., 1997b). The deposition of nutrient N from the atmosphere has the potential to alter ecosystem structure and function by altering nutrient cycling and changing biodiversity. It is important to understand how ecosystems respond to stress to determine the extent to which anthropogenic stresses, including N deposition, affect ecosystem services and products (Table C-8).

Particular concern has developed within the past decade regarding the consequences of decreasing biological diversity (Ayensu et al., 1999; Chapin et al., 1998; Hooper and Vitousek, 1997; Tilman, 2000; Wall, 1999). Human activities that decrease biodiversity also alter the complexity and stability of ecosystems, and change ecological processes. In response, ecosystem structure, composition and function can be affected (Figure C-5) (Chapin et al., 1998; Daily and Ehrlich, 1999; Levlin, 1998; Peterson et al., 1998b; Pimm, 1984; Tilman and Downing, 1994; Tilman, 1996; Wall, 1999).
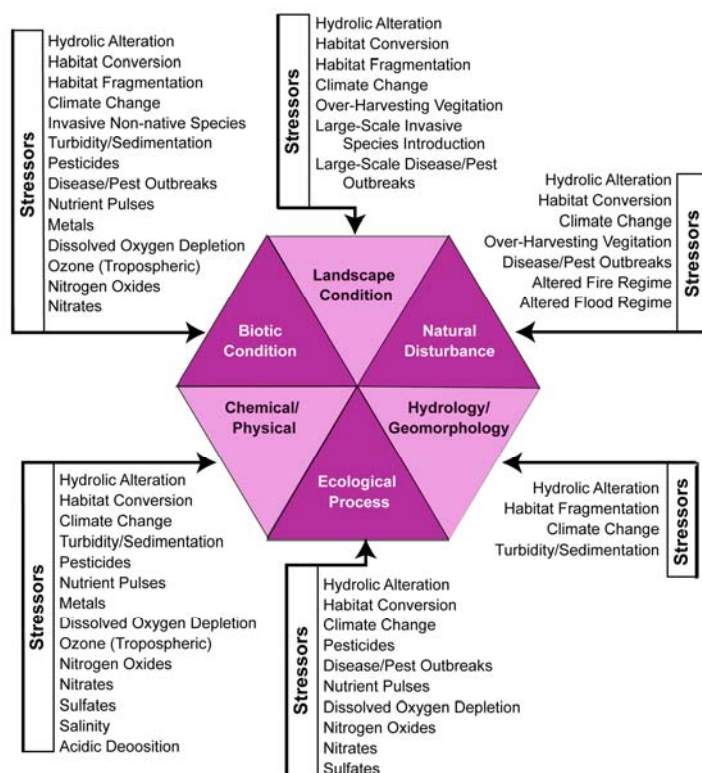
Source: Young and Sanzone (2002).

Figure C-4.   Sample stressors and the essential ecological attributes they affect.

Table C-8.   Primary goods and services provided by ecosystems.

Ecosystem	Goods	Services
Agroecosystems	Food crops	Maintain limited watershed functions (infiltration, flow control, partial soil protection)
	Fiber crops	Provide habitat for birds, pollinators, and soil organisms important to agriculture
	Crop genetic resources	Sequester atmospheric carbon
		Provide employment

Coastal Ecosystems	Fish and shellfish	Moderate storm impacts (mangroves, barrier islands)
	Fishmeat (animal feed)	Provide wildlife (marine and terrestrial (habitat and breeding areas/hatcheries/nurseries
	Seaweeds (for food and industrial use)	Maintain biodiversity
	Salt	Dilute and treat wastes
	Genetic resources	Provide harbors and transportations routes
		Provide human and wildlife habitat
		Provide employment
		Contribute aesthetic beauty and provide recreations
Forest Ecosystems	Timber	Remove air pollutants, emit O_2
	Fuelwood	Cycle nutrients
	Drinking and irrigation water	Maintain array of watershed functions (infiltration, purification, flow control, soil stabilization)
	Fodder	Maintain biodiversity
	Nontimber products (vines, bamboos, leaves, etc.)	Sequester atmospheric carbon
	Food (honey, mushrooms, fruit, and other edible plants; game)	Moderate weather extremes and impacts
		Generate soil
	Genetic resources	Provide employment
		Provide human and wildlife habitat
		Contribute aesthetic beauty and provide recreation
Freshwater	Drinking and irrigation water	Buffer water flow (control timing and volume)
	Fish	Dilute and carry away wastes
	Hydroelectricity	Cycle nutrients
	Genetic resources	Maintain biodiversity
		Provide aquatic habitat
		Provide transportation corridor
		Provide employment
		Contribute aesthetic beauty and provide recreation
Grassland Ecosystems	Livestock (food, game, hides, and fiber)	Maintain array of watershed functions (infiltration, purification, flow control, soil stabilization)
	Drinking and irrigation water	Cycle nutrients
	Genetic resources	Remove air pollutants and emit O_2
		Maintain biodiversity
		Generate soil
		Sequester Atmospheric carbon
		Provide human and wildlife habitat
		Provide employment
		Contribute aesthetic beauty and provide recreation

Source: World Resources Institute (2000).
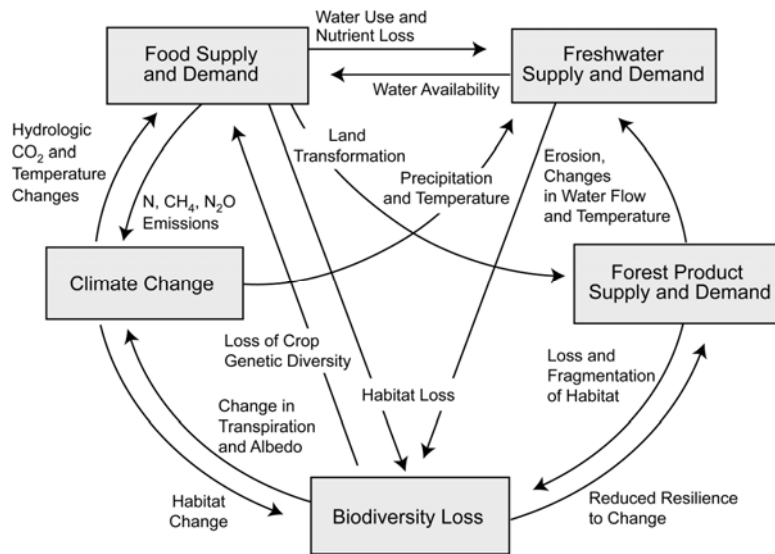
Source: Modified from Ayensu et al. (1999).

Figure C-5. Linkages among various ecosystem goods and services (food, water, biodiversity, forest products) and other driving forces (climate change).

C.6.2. Interactions with Land Use and Disturbance

Scientific understanding of N cycling in forested watersheds is complicated by ecosystem response to climatic variation, human land use, and various kinds of landscape disturbance, including insect infestation, wind storm, fire, and disease (Aber and Driscoll., 1997; Goodale et al., 2000; Mitchell et al., 2006). N dynamics in watersheds of mixed land use (i.e., agriculture, urban, forest) are even more complicated. It is clear that disturbances have major impacts on nutrient enrichment from N deposition, and that these effects can be long-lasting. Nevertheless, the scientific community is only in the early stages of learning how to quantify these interactions.

Changes in land use can affect nutrient heterogeneity in the mineral soil of forest stands. For example, Fraterrigo et al. (2005) found that patterns of variance in soil C, N, and Ca^{2+} concentration increased with the extent of intensive past land use in western North Carolina. Land use might alter the local patchiness of soil nutrients by decoupling interactions among microclimate, topography, vegetation, and soil biota. In particular, mechanical soil mixing and maintenance of agricultural monocultures can homogenize soils in cultivated systems (Robertson et al., 1993; Paz-Gonzalez and Taboada, 2000). Such effects may be important if the land use is changed to forest. Similarly, changes in species composition can alter the spatial distribution of nutrients in litter inputs (Dijkstra and Smits, 2002; Fraterrigo et al., 2005).

In the northeastern U.S., concentrations of N in streams of upland forested watersheds tend to be considerably lower than in streams draining watersheds with other land uses. In a comparison of small watersheds in eastern New York, concentrations of N were highest and most variable in a stream draining a watershed where the predominant land use was row crop production. Total dissolved N concentration in streams in sewered suburban and urban watersheds were somewhat lower and less variable than in streams draining the agricultural watershed. Streams in urban and suburban watersheds may also experience high episodic N loading caused by combined sewer overflows (Driscoll et al., 2003c).

C.6.3. Timber Harvest and Fire

Timber harvest contributes to nutrient removal from the ecosystem via biomass export and acceleration of leaching losses (Bormann et al., 1968; Mann et al., 1988). In particular, logging contributes to loss of N and Ca^{2+} from the soil (Tritton et al., 1987; Latty, 2004). The extent of nutrient loss is determined, at least in part, by the intensity of the logging and whether or not it is accompanied by fire (Latty, 2004). The species composition of the regrowth vegetation also has important effects on nutrient cycling. Fire is sometimes followed by establishment of N-fixing vegetation that provides substantial sources of N_r (Johnson, 1995; Johnson et al., 2004). Tree species also vary dramatically in their N cycling properties, especially in their influence on litter mass and quality (Finzi et al., 1998; Ferrari, 1999; Ollinger, 2002). Thus, over time, the extent of effect of logging and fire on nutrient cycling can increase, depending largely on shifts in tree species composition and the degree to which C and N pools are altered in the mineral soil and the forest floor.

Dissolved N exports have been clearly shown to increase substantially after major watershed disturbance, often reaching peak concentrations in streamwater within 1 to 3 years of disturbance, and then returning to background concentrations after about 5 to 10 years (Likens et al., 1978; Bormann and Likens, 1979; Eshleman et al., 2000). Such transient NO_3^- leakage has been shown to occur subsequent to both logging (Dahlgren and Driscoll, 1994; Martin et al., 1984; Yeakley et al., 2003) and insect infestation (Eshleman et al., 1998, 2004).

The extent to which timber harvesting influences leaching of NO_3^- and base cations from soils to drainage waters depends on changes in primary productivity, nutrient uptake by plants and microorganisms within the terrestrial ecosystem, and hydrological pathways for transferring nutrients to drainage water (Hazlett et al., 2007). Because of the variety of responses and interactions of environmental and forest litter and soil conditions, it is difficult to generalize about the influence of harvesting on N cycling (Grenon et al., 2004; Hazlett et al., 2007).

It is known, however, that land use history constitutes a major influence on N leaching from forested watersheds that receive moderate to high levels of atmospheric N deposition (Pardo et al., 1995; Aber and Driscoll, 1997; Goodale et al., 2000; Lovett et al., 2000a). The severity of effect and length of the recovery period probably vary according to the nature of the past disturbance. Extensive past logging appears to have considerable and long-lasting effects on nutrient cycling (Goodale and Aber, 2001; Fisk et al., 2002). Latty et al. (2004) compared soil nutrient pools and N cycling among three forest stands in the Adirondack Mountains: old growth, selectively logged, and selectively logged and then burned. The logging and fire had occurred about 100 years previously. Results suggested that even relatively light logging, plus burning, may influence the extent of subsequent N limitation over time scales of decades to centuries (Latty, 2004). Models of forest ecosystem response to disturbance incorporate such long-lasting effects of land use on C and N storage, cycling, and release (Aber et al., 1997).

Chen and Driscoll (2004) simulated the response of five forested watersheds in the Adirondack and Catskill regions of New York to changes in atmospheric deposition and land disturbance. Simulation results suggested that forest harvesting caused increased leaching of base cations and NO_3^- from the watersheds. These changes also affected model projections of future pH and acid neutralizing capacity (ANC) of lake water. Model results suggested that lakewater pH and ANC were lower in response to forest cutting as compared with undisturbed conditions.

Nitrification rates at old growth sites in the White Mountains of New Hampshire (63 ± 4.3 kg N/ha/yr) were approximately double those at previously burned (34 ± 4.4 kg N/ha/yr) and previously logged (29 ± 4.7 kg N/ha/yr) sites (Goodale, 2001). Fire and logging disturbances had occurred about 100 years previously on these study sites. Nitrification increased as forest floor C:N ratio decreased, resulting in higher NO_3^- concentrations in streamwater. These results suggest that forest disturbance can have long-lasting effects on N cycling and the potential for N saturation.

Thus, disturbance can affect N cycling and the response of forest ecosystems to N deposition. In addition, it also appears that vegetative changes stimulated by N deposition may affect the frequency and

severity of disturbance. Excess N_r deposition is thought to be impacting essential ecological attributes associated with terrestrial ecosystems and how they respond to disturbance. Effects of N_r deposition influence habitat suitability, genetic diversity, community dynamics and composition, nutrient status, energy and nutrient cycling, and frequency and intensity of natural fire disturbance regimes. For example, several lines of evidence suggest that N_r deposition may be contributing to greater fuel loads and thus altering the fire cycle in a variety of ecosystem types (Fenn et al., 2003c). Invasive grasses, which can be favored by high N deposition, promote a rapid fire cycle in many locations (D'Antonio and Vitousek, 1992). The increased productivity of flammable understory grasses increases the spread of fire and has been hypothesized as one mechanism for the recent conversion of coastal sage shrub (CSS) to grassland in California (Minnich and Dezzani, 1998).

High grass biomass has also been associated with increased fire frequency in the Mojave Desert (Brooks, 1999; Brooks and Esque, 2002; Brooks et al., 2004). This effect is most pronounced at higher elevation, probably because the increased precipitation at higher elevation contributes to greater grass productivity. Increased N supply at lower elevation in arid lands can only increase productivity to the point at which moisture limitation prevents additional growth. Fire was relatively rare in the Mojave Desert until the past two decades, but now fire occurs frequently in areas that have experienced invasion of exotic grasses (Brooks, 1999).

C.6.4. Insect Infestation and Disease

Insect infestation and plant disease, via atmospheric N deposition, can alter the effects of nutrient enrichment on forest ecosystems. Such disturbances alter the pool of N_r in the forest floor with short-term impacts on NO_3^- and base cation leaching. Positive influences of N deposition on root and seed biomass of an annual plant, common ragweed, were suppressed by herbivory, which increased with higher available plant shoot N (Throop, 2005).

Eshleman et al. (2004) applied a regional lithology-based unit N export response function model to simulate NO_3^- export to streams in the Chesapeake Bay watershed. The model considered the geographic distribution of bedrock classes and the timing and extent of defoliation by gypsy moth (*Lymantria dispar*) larvae. Modeling results suggested that the regional annual NO_3^--N export increased during the year following peak insect defoliation by about 1500%, from an initial rate of 0.1 kg N/ha/yr to nearly 1.5 kg N/ha/yr.

Between the mid-1980s and the early 1990s, the southward expanding range of the gypsy moth traversed Shenandoah National Park, VA (Webb, 1999). Some areas of the park were heavily defoliated 2 to 3 years in a row. The White Oak Run watershed, for example, was more than 90% defoliated in both 1991 and 1992. The gypsy moth population in White Oak Run then collapsed due to pathogen outbreak. This insect infestation of the forest ecosystem resulted in substantial effects on streamwater chemistry. The most notable effects of the defoliation on park streams were dramatic increases in the concentration and export of N and base cations in streamwater. Figure C-6 shows the increase in NO_3^- export that occurred in White Oak Run. Following defoliation, NO_3^- export increased to previously unobserved levels and remained high for over 6 years before returning to predefoliation levels. The very low baseline levels of NO_3^- export in park streams were consistent with expectations for N-limited, regenerating forests (e.g., Aber et al., 1989; Stoddard, 1994). Release of NO_3^- to surface waters following defoliation was likewise consistent with previous observations of increased N export due to forest disturbance (e.g., Likens et al., 1970; Swank, 1988). The exact mechanisms have not been determined, but it is evident that the repeated consumption and processing of foliage by the gypsy moth larva disrupted the ordinarily tight cycling of N in the forests within this park.

Change in Annual Streamwater Nitrate Flux
Following Watershed Defoliation
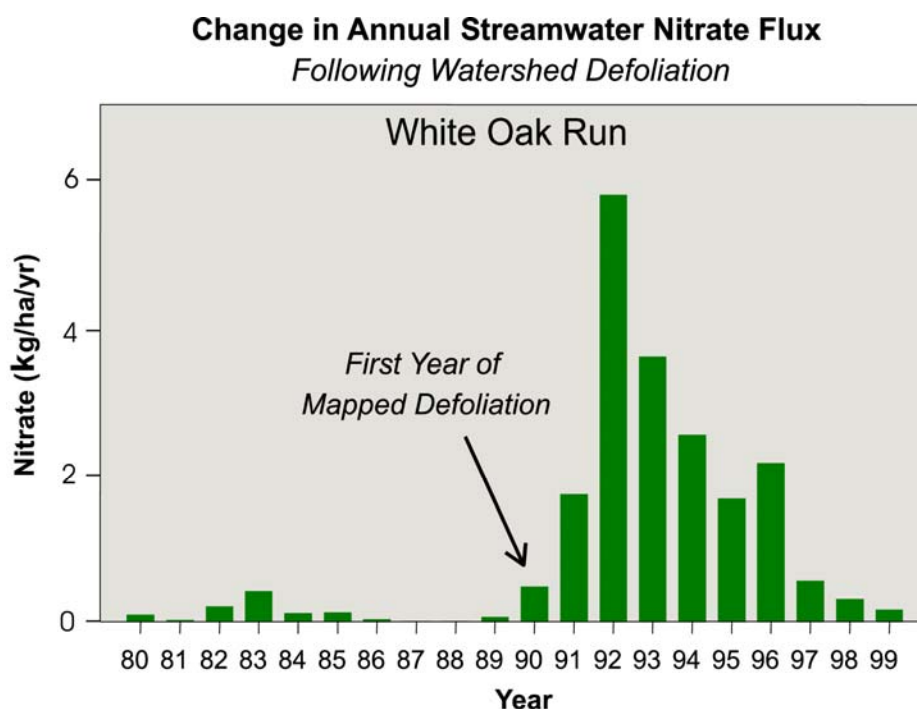
Source: Sullivan et al. (2003).

Figure C-6. Effect of watershed defoliation by the gypsy moth caterpillar on NO_3^- flux in streamwater. White Oak Run was heavily defoliated for three consecutive years. The watershed area defoliated was 46.5% in 1990, 92.9% in 1991, and 90.4% in 1992. In 1993, the gypsy moth population collapsed and there was no further defoliation.

The elevated concentrations of NO_3^- following defoliation did not appear to contribute to baseflow acidification in White Oak Run. This was due to a concurrent increase in concentrations of base cations in streamwater (Webb et al., 1995). Both NO_3^- and base cation concentrations also increased during high-runoff conditions, although the increase in base cations did not fully compensate for the episodic increase in NO_3^-. As a consequence, episodic acidification became more frequent and more extreme (Webb et al., 1995).

Large trees in old growth forests may resorb less N from foliage than do younger trees on previously logged or burned sites (Killingbeck, 1996). This process would be expected to contribute to an alleviation of N limitation on plant processes in old-growth forests (Latty et al., 2004). This effect might also extend to herbivores, which are often N-limited (Mattson, 1980). Latty et al. (2004) attributed the high severity of beech bark disease in old growth forests to such a mechanism. Beech bark disease is caused by an introduced scale insect (*Crytococcus fagisuga*), which has high N requirements (Wargo, 1988; Houston, 1994). The N-rich foliage in the old growth forest may improve insect fitness, contributing to a higher rate of infestation in the old growth stands (Latty et al., 2004).

C.6.5. Urbanization

Perhaps the most noteworthy impact of urban land use on processes of nutrient enrichment from N deposition concerns the transport of Nr to N-limited estuarine and near-coastal waters. In agricultural, and especially in forested areas, it is generally expected that most atmospherically deposited N is taken up by terrestrial vegetation. Relatively little of the deposited N is available for transport to downstream

receiving waters. This is not the case for urban land use. Urbanization often involves substantial clearing of vegetation and compaction of soil (Poff et al., 1997; Burges et al., 1998; Jones et al., 2000; Trombulak and Frissell, 2000; Alberti et al., 2007). Due to the relatively large impervious surface area in the urban landscape (buildings, roads, parking lots, etc.), a higher percentage of precipitation is routed directly to surface waters, with less opportunity for vegetative uptake of deposited N (Arnold and Gibbons, 1996; Montgomery and Buffington, 1998). Therefore, atmospheric N deposition contributes proportionately more NO_3^- to surface waters in urban settings than it does with other land uses. The reduction in riparian and wetland coverage and functionality also diminishes the ability of the urban watershed to filter contaminants from runoff, including atmospherically deposited N (Peterjohn and Correll, 1984). Because many large urban areas are both located close to the coastline and expected to receive relatively high NO_X deposition, they can constitute sizeable sources of body contribution to estuarine and marine waters.

C.6.6. Agriculture

Agricultural ecosystems are not sensitive to levels of N deposition typically found in the U.S. Rather, such ecosystems often act as net sources of NH_3 emissions rather than as sinks (Grünhage et al., 1992; Krupa, 2003). Atmospheric N deposition can contribute a quantitatively important component of the Nr requirements of pastures and croplands. In such settings, atmospheric N deposition provides an additional chronic source of N fertilizer. This may be viewed as a beneficial outcome. Nevertheless, some of the N that is atmospherically deposited on agricultural land may eventually leach to drainage waters and contribute to eutrophication, especially in estuarine and near-coastal marine environments. Industrial livestock operations also contribute substantial amounts of NH_Y to the atmosphere, some of which is deposited on coastal waters.

Agriculture also experiences indirect effects of NO_X emissions through the formation of ground-level O_3. Such effects are not considered in this review.

C.6.7. Other Disturbances

In some ecosystems, chronic additions of atmospherically derived N may have had irreversible consequences that involve interactions with invasive, non-native plants. For example, California has many plant species that occur in shrub, forb, and grasslands that receive high N deposition. There are up to 200 sensitive plant species in southern California coastal sage scrub (CSS) communities alone (Skinner and Pavlik, 1994). About 25 plant species are thought to be extinct in California, most of them forbs that occurred in sites that have experienced conversion to annual grassland (U.S. EPA, 2005a). As CSS vegetation continues to convert to grassland dominated by invasive species, loss of additional rare plant species may occur. Invasive plant species are often identified as a major threat to rare native plant species. However, the occurrence of invasive species may combine with other stress factors, including N deposition, to promote increased productivity of invasive species at the expense of native species.

As sensitive vegetation is lost, wildlife species that depend on these plants can also be adversely affected. There are several threatened or endangered wildlife species listed by the U.S. Fish and Wildlife Service, including the desert tortoise (*Gopherus agassizii*) and checkerspot butterfly that are native to plant communities in California thought to be sensitive to atmospheric N input. A native to the San Francisco Bay area, the bay checkerspot butterfly has declined in association with invasion of exotic grasses that replaced the native forbs on which the butterfly depends. In particular, the larval stage of the butterfly is dependent on *Plantago erecta*, which is increasingly being outcompeted by exotic grasses (U.S. EPA, 2005a).

Decline in the population of the desert tortoise may be due to a number of co-occurring stresses, including grazing, habitat destruction, drought, disease, and a declining food base. In the desert shrub

inter-spaces, sites where native forbs once flourished, invasive grasses now dominate, reducing the nutritional quality of foods available to the tortoise (Fenn et al., 2003a; Nagy et al., 1998). N deposition contributes to the productivity and density of grasses at the expense of native forbs (Brooks, 2003).

C.6.8. Multiple Stress Response

Ecosystems are often subjected to multiple stressors, of which nutrient enrichment from atmospheric deposition of N is only one. Additional stressors are also important, including O_3 exposure, climatic variation, natural and human disturbance, the occurrence of invasive non-native plants, native and non-native insect pests, and disease. Atmospheric N deposition interacts with these other stressors to affect ecosystem patterns and processes in ways that are only beginning to beunderstood.

For example, terrestrial ecosystems at many locations are subjected to high N deposition and high exposure to O_3. This is especially true in portions of southern California and the Appalachian Mountains. Mixed conifer forests in the San Bernardino and San Gabriel mountains in southern California are exposed to high levels of atmospheric O_3 and receive atmospheric N deposition in the range of about 5 to over 30 kg N/ha/yr (Takemoto et al., 2001). Spatial variability in N deposition is high due to the patchy characteristics of these forests and associated canopy effects on dry deposition processes. The forest ecosystems have reached N-saturation, as evidenced by high NO_3^- concentrations in stream water. However, evaluation of N effects on vegetation is complicated by the concurrent effects of O_3, which has damaged sensitive plant species, especially Ponderosa and Jeffrey pine. Bytnerowicz (Bytnerowicz, 2002) summarized N/O_3 interactions and consequent effects.

Peak diurnal concentrations of atmospheric O_3 and NO_2 co-occur at Tanbork Flat in the San Bernardino Mountains (Bytnerowicz et al., 1987). They can have counteracting effects, with O_3 reducing growth and N deposition enhancing growth of pine trees (Grulke and Balduman, 1999).

Jeffrey and Ponderosa pine are the most sensitive western coniferous tree species to injury from O_3 pollution (Miller et al., 1983; Duriscoe and Stolte, 1989). In some areas of the western Sierra Nevada Mountains, O_3 concentrations have been high enough to cause visible foliar injury to these species and reduced needle retention (Bytnerowicz, 2002). Reduced radial growth has also been observed (Peterson et al., 1987, 1991). In the San Bernardino Mountains, trees of these species that exhibit severe foliar injury from O_3 do not show growth reductions (Arbaugh et al., 1999), and this has been attributed to the fertilizing effects of high N deposition (Bytnerowicz, 2002; Takemoto et al., 2001). This may be an example of counteracting effects from O_3 and N air pollution. It is also possible that N deposition in the western Sierra Nevada Mountains may increase growth of pines, especially on nutritionally poor granitic soils (Takemoto et al., 2001).

Table C-9. Ecological effects of N deposition described for study sites in the Western U.S.

Ecological or Environmental Impact	Location	Level of Uncertainty	Possibility of Broader Occurrence (at other sites)	Reference
EFFECTS IN AQUATIC SYSTEMS				
Elevated NO_3^- in runoff; most severe in southern California and in chaparral catchments in the southwestern Sierra Nevada	Transverse ranges of southern California; low-elevation catchments in the Sierra Nevada; high-elevation catchments in the Colorado Front Range	Well-documented response	It is unclear how widespread this phenomenon is outside the ecosystems listed, because there is littler information from low-elevation systems in the Sierra Nevada and elsewhere.	Fenn and Poth (1999) Fenn et al. (2003a) Williams et al. (1996a)
N enrichment and shifts in diatom communities in alpine lakes	Colorado Front Range; Lake Tahoe (California/Nevada border)	Documented for two lakes east of the Continental Divide and Lake Tahoe	These effects seem likely in other N-enriched lakes but have not been investigated.	Baron et al. (2000) Goldman (1988) Wolfe et al. (2001)
Reduced lake water clarity and increased algal growth	Lake Tahoe (California/Nevada border); high-elevation lakes throughout central and southern Sierra Nevada	Well-documented response; N and P deposition believed to be important factors	Lake Tahoe is an unusual case because of its renowned lake clarity; extent of occurrence elsewhere in northern Sierra Nevada is unknown.	Jassby et al. (1994) Sickman et al. (2003a)
Increased NO_3^- concentrations in high-elevation lakes	Several regions, mainly downwind of urban centers	Fairly well established from lake surveys, but more data needed for improved definition of frequency and severity	Evidence suggests that urban plumes and agricultural emissions affect lake NO_3^- levels. There is also evidence of impacts on low-elevation lakes.	Sickman et al. (2002)
EFFECTS IN TERRESTRIAL SYSTEMS				
Enhanced growth of invasive species	Costal sage scrub, southern California; San Francisco Bay area	N deposition, fertilization studies, and plant community data supportive, but moderate uncertainty remains	It is not known if this effect occurs elsewhere, but it is expected that nitrophilous species will be selected for if N accumulates in soil.	Allen et al. (2008) Weiss (1999)
Lichen community changes	Parts of the Pacific Northwest; many areas in California; north and central Colorado	Well-established response; a highly sensitive air pollution indicator	Because of the sensitivity of many lichen species, it is likely that this effect occurs elsewhere.	Nash and Sigal (1999)

Deleterious effects on threatened and endangered species	San Francisco Bay area; southern California	Supportive evidence, but high degree of uncertainty about the precise role of N deposition	There is a high likelihood of effects in some habitats where N accumulates in soils	Weiss (1999), Brooks (2003)
Altered fire cycle	Coastal sage scrub in southern California	Hypothesis based on observations, fertilization studies, and N deposition and N cycling data; high level of uncertainty	Because it has not been studied elsewhere, it is uncertain whether this effect occurs in other areas.	Allen et al. (2008)
Altered forest C cycling and fuel accumulation	San Bernardino Mountains	Documented response	It is uncertain whether this effect occurs in other areas.	Grulke and Balduman (1999)
Physiological perturbation of overstory species	San Bernardino Mountains	Documented response	This effect has not been widely studied but is expected for sensitive plant species exposed to O_3 and adapted to N limitation but growing in N-enriched soils.	Grulke et al. (1998) Grulke and Balduman (1999) Takemoto et al. (2001)
Forest expansion into grasslands	Great Plains of western Canada	Supportive evidence found, but high degree of uncertainty as to the role of N deposition	It is not known whether this effect occurs in other areas.	Köchy and Wilson (2001)
N emissions as a major contributor to regional haze problem	National forests and parks throughout California, the Pacific Northwest, and some sites in the Interior West	Well-established effect; contribution from Nous pollutants has been quantified	This is known to occur in areas far removed from emissions sources because of long-range transport.	Fenn et al., (2003a) IMPROVE data (4 March 2003; http://vista.circa.colostate.edu/improve)
NO_X emissions as precursors for phytotoxic levels of O_3, leading to O_3 injury to sensitive plant species	Southern California; Sierra Nevada	Well-established effect	Significant O_3 injury to vegetation has not been reported from other sites downwind of urban centers but cannot be ruled out as urban regions expand.	Miller and McBride (1999) Carroll et al. (2003)

Note: Summary includes the degree of uncertainty regarding the role of N deposition in each effect and the likelihood that these effects may occur elsewhere in the West.

Annex D. Critical Loads

D.1. Background

Critical loads and critical levels are used to express how much deposition of an atmospheric pollutant (a "load") or how large a concentration of an airborne pollutant (a "level") can be tolerated by natural or artificial systems without significant harm or change occurring in those systems (see Section D.2.1). The critical load and critical level approaches to quantifying the effects of pollutants attempt to estimate the atmospheric deposition load or concentration that would be likely to cause environmental harm. The expectation is that environmental harm can be avoided by keeping pollution levels or loads below these critical values. This approach is commonly used to estimate loads or levels of pollution required to protect lakes, streams, or forest soils from environmental harm. The basic principles are, however, transferable to any sensitive receptor. Since the present evaluation deals primarily with the effects of atmospheric deposition of S and N compounds, this chapter focuses on critical loads more than critical levels.

Most critical load studies in North America have been undertaken in Canada. The critical load approach has been used in Canada to design emission reduction programs (Jeffries and Lam, 1993; RMCC, 1990). Modeling of critical loads for the 1997 Canadian Acid Rain Assessment (Jeffries, 1997) was conducted for six regional clusters of lakes, four in eastern Canada, one in Alberta, but also the Adirondack Mountains in New York. More recently, critical loads have been determined and mapped for waters (Aherne et al., 2004; Dupont et al., 2005; Henriksen et al., 2002; Hindar et al., 2001; Watmough et al., 2005) and forest soils (Arp et al., 1996; Moayeri et al., 2001; Ouimet et al., 2006; Watmough and Dillon, 2003), for a number of regions in eastern Canada. There have also been a number of regional critical loads studies (cf. Henriksen and Dillion, 2001; Ouimet et al., 2006) focused on acid-sensitive lakes on the Canadian pre-Cambrian shield. Much of this work is summarized and presented, along with steady state critical load maps for eastern Canada, in the 2004 Canadian Acid Deposition Science Assessment (Jeffries et al., 2005).

At the regional, cross-border level, critical loads in northeastern North America have been developed by a joint U.S.-Canadian cooperative. The Conference of New England Governors and Eastern Canadian Premiers (NEG/ECP) has undertaken a program with the objective to "estimate sustainable acidic deposition rates and exceedances for upland forests representative of the New England States and the Eastern Canadian Provinces…" (NEG/ECP Forest Mapping Group, 2001). The Forest Mapping Working Group within the NEG/ECP conducts regional assessments of the sensitivity of northeastern North American forests to current and projected S and N emissions levels. The group is charged with identifying specific forested areas most sensitive to continued S and N deposition and estimating deposition rates required to maintain forest health and productivity at large spatial scales (Miller and McDonald, 2006). The NEG/ECP has also provided estimates of critical loads for surface waters in northeastern North America (Dupont et al., 2005).

Aside from the NEG/ECP studies, the use of critical loads to assess S and N deposition effects in the U.S. has not been as geographically extensive as elsewhere in North America or Europe. Most critical loads studies in the U.S. have focused on smaller sub-regional areas or individual sites. Critical loads studies for forests in the U.S. have been centered in the northeast and have usually used a catchment-based approach (Aber et al., 2003; Driscoll et al., 2003d; Pardo and Driscoll, 1993, 1996). Critical load studies for surface waters have been more extensive along the eastern seaboard. Critical loads have been estimated for lakes in the Northeast (Driscoll et al., 2001b; Pembrook, 2004) and for streams in the Mid-Atlantic States and central Appalachians (Sverdrup et al., 1992; Sullivan et al., 2004). In the western U.S. there have been a few studies of critical loads for acidification of surface waters (Sullivan et al., 2004).

The primary concern in the West, however, has been the critical load of N deposition affecting both terrestrial and aquatic resources through eutrophication and/or through N enrichment and its impact on community structure (Baron et al., 1994, 2000; Baron, 2006; Bowman et al., 2006; Burns, 2004; Fenn, 2003a; Nydick et al., 2003, 2004b; Stevens et al., 2004; Williams and Tonnessen, 2000; Wolfe et al., 2003).

The critical load approach has been used extensively in Europe for organizing information about effects, and for specifying emissions reductions that would be required to protect ecosystems and other sensitive receptors from the harmful effects of atmospheric S and N) deposition. During the 1970s, it was recognized that transboundary air pollution in Europe had adverse ecological and economic consequences. In response, the countries of the UN Economic Commission for Europe (UNECE) developed the Convention on Long-range Transboundary Air Pollution (LRTAP), the first international legally binding instrument to deal with problems of air pollution on a broad regional basis (see http://www.unece.org/env/lrtap). Signed in 1979, it entered into force in 1983. The LRTAP Convention requires that its Parties cooperate in research into the effects of S compounds and other major air pollutants on the environment, including agriculture, forestry, natural vegetation, aquatic ecosystems, and materials. To this end, the Executive Body for the Convention established a Working Group on Effects (WGE) that is supported by a number of International Cooperative Programmes (ICPs). The ICP for Mapping and Modeling generated maps of critical loads for all of Europe in 1995 (Posch et al., 1995). Those maps are modified on a continuing basis (e.g., Posch et al., 2001). By comparing current or expected future deposition to the critical loads maps, mapped estimates of exceedances have been generated. An exceedance is the amount of S and N deposition that occurs at some specific time (past, current, or future), above the critical load of deposition that would be required to protect against adverse effects on the environment. The maps of estimated exceedances are used in negotiations to regulate pollutant emissions in Europe (for example, the 1999 Gothenberg Protocol via the UNECE Convention on LRTAP).

Outside of North America and Europe, there is an increasing use of critical loads for assessment purposes, and to inform policy development. Examples include studies in Siberia (Bashkin et al., 1995), Thailand (Milindalekha et al., 2001), and South Africa (Van Tienhoven et al., 1995). In China, several studies have been carried out to study the sensitivity of surface waters to acidification and the critical loads of acid deposition (Duan et al., 2000; Li et al., 2000; Ye et al., 2002; Hao et al., 2001), and to calculate the critical loads of S and N acidity for soils at both the local and regional scales (Xie et al., 1995; Zhao and Seip, 1991; Duan et al., 2000b, 2001).

D.1.1. The Critical Load Process

The process of estimating critical loads is not a purely scientific enterprise. Management or policy input to the process is needed to insure that the appropriate science is included and the appropriate questions are addressed. The critical load process integrates knowledge of a multitude of physical, chemical and biological mechanisms affected by ambient air quality, and presents the current scientific understanding in a format that is most useful for assessing current or future management practices and policy decisions regarding air quality, or the resources affected. The critical loads process provides decision-making insight based on both scientific evidence and policy priorities.

Science and policy are closely coupled in the critical loads process. In the development of critical load estimates, it is important to identify those elements that are essentially scientific in nature as opposed to those elements that are driven by management or policy priorities. The scientific elements include tasks such as: relating ambient air quality to pollutant deposition, quantifying the relationships between pollutant deposition and resource responses, identifying the resources at risk to adverse effects, understanding the temporal and spatial responses of resources to pollutant deposition, and more. The policy-dependent elements include tasks such as: identifying the environmental resources to be protected,

establishing appropriate criteria for different land use areas (e.g., Class I areas, national parks, wildlife refuges), defining significant harm to protected resources, and more. When all elements are integrated, it is apparent that the critical load process provides a framework for alternate ways of examining and understanding the cascade of effects from ambient air quality to resource effects, described in the preceding four annexes. Changing scientific assumptions or understanding may result in different critical load estimates for the same resources. Changing policy or management assumptions or priorities may also result in different critical load estimates.

There is, therefore, no single "definitive" critical load for a natural resource. Critical load estimates are explicitly linked to policy, but their reliability is conditioned on the soundness of the underlying science. As elements of the critical load process change, the critical load estimates will change to reflect both the current state-of-knowledge and policy priorities. Changes in scientific understanding may include: new dose-response relationships, better resource maps and inventories, larger survey datasets, continuing time series monitoring, improved numerical models, etc. Changes in the policy elements may include: new definitions of harm, new mandates for resource protection, focus on new pollutants, or inclusion of perceived new threats that may exacerbate the pollutant effects (e.g., climate change).

The critical load process is thus an iterative process — as science changes, the content is updated; as policy needs change, the content is re-directed. Being iterative, the process allows incremental improvement in understanding resource responses to ambient air quality. Individual elements of the process can be replaced as needed to reflect new science or policy. Continuing to update the process may reduce uncertainty and risk, as new data or techniques allow refinement of existing pieces. The piecewise nature of the process provides adaptability as new policy concerns arise, such as new pollutants or mandates. As the critical load process advances, a "library" of critical load estimates will result. Examining and comparing these accumulated results, and their underlying scientific and policy bases, may produce a "weight of evidence" consensus, even if any single estimate entails substantial uncertainty.

D.1.2. Organization of this Annex

This Annex is intended as a review of the current state of critical loads science. It is not the intention to address questions of management or policy other than to point out where these activities influence the critical loads process. The material in Section D.2 presents necessary definitions and describes the conceptual framework for a critical load analysis. This framework identifies those elements that are primarily scientific in nature and those elements that require policy input. The framework also describes the steps that are taken in deriving a critical load estimate for a given resource. It is not an objective of this Annex to provide details of all critical loads studies that have been implemented in the U.S. or elsewhere. The conceptual framework, however, provides a generalized summary of the steps most critical loads studies have followed. Section D.3 discusses the time frame of responses for implementation of a critical load. Time frames of resource response are often ignored, or assumed implicitly, in defining a critical load analysis. The time required to implement the policy and technology to achieve a critical load can also affect the responses of the resources at risk. The time frames of response are important for selecting the data and models used to estimate critical loads. Section D-4 summarizes the tools (models and modeling approaches) commonly used in calculating critical loads. The Annex concludes in Section 5 with a summary of the current agreement on critical loads uses in the U.S. that was a product of the Multi-Agency Workshop on Critical Loads held in 2006. The workshop produced a series of recommendations for current and future activities related to critical loads analyses in the U.S.

D.2. Definitions and Conceptual Approach

D.2.1. Critical Load Definitions

Critical loads and critical levels are used to express how much deposition of an atmospheric pollutant (a "load") or how large a concentration of an airborne pollutant (a "level") can be tolerated by natural or artificial systems without significant harm or change occurring in those systems. The generally accepted definition of a critical load or a critical level of atmospheric pollutants emerged from a pair of international workshops held in the late 1980s. The workshop participants defined a critical load or a critical level as "a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge."

This evaluation deals primarily with the effects of atmospheric deposition of S and N compounds. This Annex, therefore, will deal exclusively with the concept of critical loads of S and N compounds from atmospheric deposition. Critical levels of pollutant concentration will not be addressed. As discussed in previous annexes, the deposition of both S and N has acidifying effects on receptors (Annex B), and the deposition of oxidized and/or reduced N compounds can produce eutrophication or nutrient-enrichment effects in receptors (Annex C). The following material, therefore, will focus on critical loads of S and N for acidification effects, and on critical loads of N for nutrient effects.

In addition to the generic definition of a critical load/level presented above, the participants in the second international workshop (the Skokloster Workshop) developed a number of specific definitions related to known atmospheric pollutants. Two of those definitions are relevant to this Annex.

Recognizing that both S and N compounds contribute to the acidity of deposition, the workshop participants developed a definition for critical loads of S and N for acidification of an ecosystem: "the highest deposition of acidifying compounds that will not cause chemical changes leading to long-term harmful effects on ecosystem structure and function according to present knowledge." Recognizing that N in both oxidized ($NO_Y = NO +$, $NO_2 + NO_2 +$, NO_3^-) and reduced ($NH_X = NH_3 + NH_4^+$) forms in deposition may influence the eutrophication and nutrient balances of ecosystems, the workshop participants defined the critical load of N for nutrient effects in an ecosystem as "the highest deposition of N as NH_X and/or NO_Y below which harmful effects in ecosystem structure and function do not occur according to present knowledge."

All three definitions can be applied to different receptors in a number of different environments (e.g., terrestrial ecosystems, transitional ecosystems, aquatic ecosystems, groundwater, agricultural crops, etc.). A sensitive element can constitute a part of, or the whole of, an ecosystem. Harmful effects can occur to individual organisms, to populations, or to entire communities within an ecosystem. Harmful effects can also be defined at the level of the ecosystem itself as changes in ecosystem processes, structure, and/or function.

While the concepts expressed in these definitions of critical loads and levels are easily understood and intuitively satisfying, the application of the critical load concept requires careful consideration and definition of a number of terms and procedures. It is apparent that there can be many different critical load values for a given atmospheric pollutant depending on the receptor or sensitive element(s) being considered. There can also be multiple different atmospheric pollutants that can produce the same harmful effects in a given receptor. Therefore, the critical load of a given pollutant can potentially be dependent on the deposition and/or atmospheric concentration of other pollutant species. Finally, the same atmospheric pollutant can produce a variety of different disturbances in a sensitive ecosystem that might occur at different pollutant loads. For example, N deposition produces both nutrient and acidification effects and the critical load of N for each type of disturbance may be different.

Therefore, to derive a quantitative estimate of the critical load of an atmospheric pollutant, a number of factors must be identified and defined Figure D-1. These include disturbance type, receptor, sensitive elements, and definition of what constitutes significant harm. In addition, a numerical relationship between pollutant deposition and the identified receptor response must be formulated, generally based on either an empirical dose-response relationship or a steady state or dynamic numerical model simulation. The next section outlines the steps (decisions) that must be taken to implement this process.

D.2.2. Critical Load Analysis Procedures

The development of a quantitative critical load estimate requires a number of steps. In this discussion, Figure D-1 is used to illustrate the procedure. The figure is simplified to facilitate general discussion and does not represent the full complexity of the choices that must be made, or the scientific understanding underlying those choices.

Table D-1 An example of the matrix of information that must be considered in the definition and calculation of critical loads. Note that multiple alternative biological indicators, critical biological responses, chemical indicators, and critical chemical limits

1) Disturbance	Acidification				Eutrophication	
2) Receptor	Forest		Lake		Grassland	Lake
3) Biological indicator	Sugar Maple	Norway Spruce	Brook trout	Fish species richness	Species diversity	Primary productivity
4) Critical biological response	Failure to reproduce	Seedling death	Presence absence	Species loss	Species loss	Excess productivity
5) Chemical indicator	Soil % Base Saturation	Soil Ca/Al ratio	Lakewater ANC	Lakewater ANC	Soil C/N ratio	Lakewater NO_3
6) Critical chemical limit	10%	1.0	0 µeq/L	50 µeq/L	20	10 µeq/L
7) Atmospheric pollutant	SO_4, NO_3, NH_4	SO_4, NO_3, NH_4	SO_4, NO_3, NH_4	SO_4, NO_3, NH_4	NO_3, NH_4	NO_3, NH_4
8) Critical pollutant load	???	???	???	???	???	???

There are eight general steps that must be taken to define the basic critical load question in any analysis.

1. Identify the ecosystem disturbance of concern (acidification, eutrophication, etc.). Not all disturbances will occur in all regions or at all sites, and the degree of disturbance may vary across landscape areas within a given region or site.

2. Identify the landscape receptors subjected to the disturbance (forests, surface waters, crops, etc.) Receptor sensitivity may vary locally and/or regionally, and the hierarchy of receptors most sensitive to a particular type of disturbance may vary as well.

3. Identify the biological indicators within each receptor that are affected by atmospheric deposition (individual organism, species, population, or community characteristics). Indicators will vary geographically and perhaps locally within a given receptor type

4. Establish the critical biological responses that define "significant harm" to the biological indicators (presence/absence, loss of condition, reduced productivity, species shifts, etc.). Significant harm may be defined differently for biological indicators that are already at risk from other stressors, or for indicators that are perceived as "more valued."

5. Identify the chemical indicators or variables that produce or are otherwise associated with the harmful responses of the biological indicators (stream water pH, Al concentration, soil base saturation, etc.). In some cases, the use of relatively easily measured chemical indicators (e.g., surface water pH or ANC) may be used as a surrogate for chemical indicators that are more difficult to measure (e.g., Al concentration).

6. Determine the critical chemical limits for the chemical indicators at which the harmful responses to the biological indicators occur (e.g., pH <5, base saturation <5%, Al concentrations >100 µg/L, etc.). Critical limits may be thresholds for indicator responses such as presence/absence, or may take on a continuous range of values for continuous indicator responses such as productivity or species richness. Critical limits may vary regionally or locally depending on factors such as temperature, existence of refugia, or compensatory factors (e.g., high calcium concentration mitigates the toxicity of Al to fish and plant roots).

7. Identify the atmospheric pollutants that control (affect) the pertinent chemical indicators (deposition of SO_4^{2-}, NO_3, NH_4, HNO_3, etc.). Multiple pollutants can affect the same chemical variable. The relative importance of each pollutant in producing a given chemical response can vary spatially and temporally.

8. Determine the critical pollutant loads (often in units of kg/ha/yr deposition of S or NO_3^-N, etc.) at which the chemical indicators reach their critical limits. Critical pollutant loads usually include both wet and dry forms of pollutant deposition. The critical pollutant load may vary regionally within a receptor or locally within a site (as factors such as elevation or soil depth vary) and may vary temporally at the same location (as accumulated deposition alters chemical responses).

The definition of the critical load problem for a region or individual site generally requires working down the table from top to bottom (Table D-1) What is the disturbance? What receptors are affected? What indicator organisms are, or were previously present and observable? What chemical indicators are changing and can be measured? What atmospheric pollutant is driving the changes in the chemical indicators?

The derivation of a quantitative estimate of a critical load generally requires working from the bottom of the table back towards the top, as indicated by the arrows in Table D-1. What is the maximum load of a pollutant that will cause a shift in the chemical indicator to its critical limit such that a critical indicator response occurs, or does not occur? From this point of view, it can be seen that steps 8 and 6 require the development of dose-response functions for the components of the ecosystem being considered (arrows in Table D-1). Step 8 describes the response of the chemical indicator as a function of the pollutant load, and Step 6 describes the responses of the biological indicator as a function of the chemical variable. As discussed in later sections, these response functions can be derived using empirical (e.g., statistical) or process-based (e.g., mechanistic) models that are either time-invariant (static or steady state) or time-variable (dynamic).

Each step in the development of the critical load, as summarized in Table D-1 can be classified as either a predominantly scientific task or as a task benefiting from, or perhaps requiring, collaboration and input from scientists, decision-makers, and other interested parties. For instance, tasks 1, 2, and 3 can be viewed as predominantly scientific tasks that can be completed by asking questions of fact. At task 4, however, questions of what defines "significant harm" entail subjective elements that cannot be determined by scientific techniques alone. In anticipation of the ultimate use of the critical load definition to set policy or establish management strategies, it is appropriate that political, socioeconomic, or perhaps ethical considerations be brought to bear in defining "significant harm." To define "harm" is to imply a corrective action, the cost of which will have to be borne by someone. Having reached agreement on task 4, however, tasks 5, 6, 7, and 8 are again predominantly scientific in nature, requiring determination of the causal links, represented as response functions or models, leading from the loading of the pollutant to the defined "significant harm."

This procedure will almost certainly result in calculation of multiple critical load values for a given pollutant and analysis location. The multiple solutions derive from the nested sequence of disturbances, receptors, and biological indicators that must be considered for a given pollutant. Multiple critical load values may also arise from an inability to agree on a single definition of "significant harm" at step 4. Finally, there is the inescapable heterogeneity of all natural environments. Consider soils for instance. The high spatial variability of soils almost guarantees that for any reasonably sized soil-based "receptor" that might be defined in a critical load analysis, there will be a continuum of critical load values for any indicator chosen. The range of this continuum of values may be narrow enough to be ignored, but in any critical load analysis there is nevertheless an a priori expectation of multiple values, or of a range of values.

The existence of multiple estimates of critical loads for a given pollutant and receptor should present no real problem. Examination of the range of critical loads derived may be deemed useful in subsequent discussions of the analysis, and in the decision-making steps that may follow critical load calculation. For instance, the lowest critical load of all those derived may be adopted as "the" critical load, as is often done in Europe. This however, is a policy choice. The scientific task is the derivation of the multiple values using best available information.

D.2.3. Target Load Definition

As seen in the previous section, it is expected that a potentially large number of critical load values may be objectively determined for a given atmospheric pollutant and a given receptor. Like the definition of "significant harm," the choice of which critical load value to use for management or decision-making is subjective, and should be driven by socioeconomic, political, and ethical considerations. The target load concept was developed to address these issues. Target loads are deposition loads of a given pollutant, based on critical load estimates for the pollutant, which incorporate policy and/or management decisions about the amount of pollutant deposition, and therefore the amount of resource damage that is deemed acceptable. Target loads can be set at, above, or below the various critical loads. If the target load is set above some of the estimated critical loads, one accepts the inevitability that some of the ecosystem components, generally the most sensitive, will be adversely affected. If the target load is set below all of the estimated critical loads, a safety margin has been established to account for uncertainty inherent in the process.

Given the spatial heterogeneity of natural systems, target loads might also be used to provide some measure of "cumulative resource protection." As discussed above, there typically exists a range of critical loads for a particular "significant harm" in a particular receptor. Selecting a target load within the range will provide protection for the fraction of the receptor with critical loads above the chosen target load, whereas that fraction with critical loads below the chosen target load will be expected to suffer some harm at that deposition level. In this way, it is possible to use the target load to define protection for some

cumulative proportion of the receptor (i.e., a target load for protection of 95% of the resource from "significant harm").

While most of the steps involved in estimating critical loads depend on sound, objective scientific analysis, the selection of target loads is almost entirely a subjective judgment. The selection of target loads must begin with reliable estimates of critical loads to set the constraints, and define the expected consequences of the target load choices. Nevertheless, the final decisions of which indicators are the key indicators, how much cumulative resource should be protected, how much sooner or later resource protection will be implemented, cannot be answered scientifically. Political, socioeconomic, and ethical considerations will form the basis of the final target load selections. Frequently, the legal mandates for various public lands would have a determinant influence on the selection of target loads. For instance, Federal Class I areas may be held to one standard of harm because of mandates to protect "natural condition," whereas Federal mixed-use lands may be held to a different standard of harm, and cropland to yet another standard of harm.

It is also important to note that scientific understanding, modeling approaches, and the data used to estimate critical loads are continually improving. Furthermore, the political, economic, and social environments surrounding selection of target loads are also constantly shifting. Therefore, the analysis and estimation of critical and target loads must be an iterative process.

D.3. Time Frame of Response

The critical load definitions and procedures discussed in the previous section do not explicitly consider the time frame of ecosystem response. When is "significant harm" expected? How long will it be before existing harm is reversed? When should critical loads be implemented? How long should a critical load be maintained? The use of critical and target loads in resource management always has some time frame of expected response, and some context of management priorities. For instance, it may be that a target load well below the critical load would hasten the recovery of a receptor with existing harm. Or, it may be that a receptor that has not yet been damaged can sustain a target load above the critical load for some finite period before incurring "significant harm." Such time frames can be very long (many decades or centuries).

The time frame of response between implementation of a critical load and the corresponding changes in biological or chemical indicators is a potentially important factor in establishing critical load analysis procedures and in selecting the final target load. Analyses can be designed to provide estimates of either "steady state critical loads" or "dynamic critical loads" depending on the perceived, or mandated, importance of the time frame of response and the types of models (transfer functions) used.

Steady state critical loads analyses provide estimates of the long-term sustainable deposition of a pollutant that will not cause "significant harm" to a receptor. This is the relevant information needed for any receptor to provide protection from damage by the pollutant in perpetuity as the receptor comes into equilibrium with the pollutant critical load (the implicit purpose of steady state analyses). However, no information is given concerning the time to achieve the equilibrium or what may happen to the receptor along the path to equilibrium. Estimated steady state critical loads for receptors that are currently damaged provide no information concerning when the desired long-term sustainable protection will occur and the existing "significant harm" will be mitigated. There exists the possibility that receptors with no current damage could suffer "significant harm" while waiting for implementation of the critical load. The possible occurrence, timing, and duration of such "interim periods of harm" are not the subject of steady state analyses.

Dynamic critical loads analyses provide estimates of a specifically scheduled deposition load of a pollutant that will not result in "significant harm" to a receptor at a specified time. This is the relevant information needed for any receptor to provide protection from damage by the pollutant within a specified time frame (the explicit purpose of dynamic analyses). However, care should be taken in interpreting the

results of dynamic analyses to ensure that "significant harm" to the receptor does not occur after the specific timetable has been completed. Many receptors can tolerate higher loads of a pollutant for a few decades (a common length of specified schedules for dynamic analyses) than can be sustained over longer periods. The use of dynamic critical load estimates in such cases may provide protection from harm during a time frame of immediate interest, but ultimately fail to provide long-term protection, unless these issues are considered.

D.3.1. Steady State Critical Loads

If the time frame of response is not important, for instance, if the target load is to provide long-term sustainable protection and the immediacy of the responses is not relevant, the use of static or steady state models (response functions) is justified in the critical load analysis procedure. Using steady state models to estimate critical loads and compare the estimated critical load to current or future deposition, only two cases can be distinguished: current or future deposition is below the critical load; or current or future deposition exceeds the critical load. In the first case, no problem is apparent, and no target load is deemed necessary, unless increases in deposition are anticipated. In the second case, there is by definition an increased risk of "significant harm" to the receptor and selection of a target load for resource protection is indicated.

The lack of explicit consideration of time in a steady state critical load analysis can lead to assumptions that are frequently not warranted. The critical load derived in a steady state analysis is an estimate of the long-term, constant deposition that a receptor can tolerate with no significant harm after it has equilibrated with the critical load deposition. However, biological and geochemical processes that affect a receptor may delay the attainment of equilibrium (steady state condition) for years, decades, or even centuries. By definition, steady state critical loads do not provide any information on these time scales. As a result, it is often assumed that reducing deposition to, or below the steady state critical load value will immediately eliminate or mitigate "significant harm." That is, it is assumed that the chemical indicator affected by the atmospheric pollutant immediately attains a non-critical value upon implementation of the critical load, and that there is immediate biological recovery as well. As discussed in the next section, these assumptions may not be valid.

D.3.2. Dynamic Critical Loads

The time frame of receptor response is important if the establishment of target loads is tied to defined schedules of deposition change or receptor responses. The use of time-dependent or dynamic model response functions will be necessary if the critical load analysis considers the response time frame. In the cascade of events that occur from changed deposition of an atmospheric pollutant to development of responses of key biological indicators, there are many processes in natural systems that are time and/or resource dependent and therefore can introduce delays in the response pattern. In the decision-making process leading to the adoption of target loads, there are likewise considerations of when deposition changes can be initiated and completed and when biological indicator responses are desired. With dynamic models, either empirical or process-based, a wide range of estimated critical loads can be derived for comparison with current or future deposition depending on the temporal constraints imposed on the critical load analysis. Temporal constraints that can be imposed on a given critical load analysis are determined by: the receptor responses—the characteristic time scales and inherent lags of the receptor being analyzed (a function of hydrobiogeochemical processes in the receptor); and the deposition schedules—the years designated for beginning and completing the changes in deposition and for evaluating the indicator responses (a function of political, socioeconomic, and management constraints).

D.3.3. Receptor Responses

The general conceptual model of the linkages among pollutant deposition and the responses of chemical and biological indicators can be characterized as a series of delays. In the causal chain from deposition of pollutant to damage to key biological indicators there are two major links that can give rise to delays. First, hydrological and biogeochemical processes in catchments can delay the responses of chemical indicators. Second, biological processes and population dynamics can further delay the response of biological indicators. The pattern of chemical and biological indicator responses can be represented conceptually (Figure D-1) (adapted from Jenkins et al., 2003; Posch et al., 2003). Five stages in the conceptual pattern can be distinguished (Figure D-1):

- Stage 1: Pollutant deposition is below the critical load for either the critical chemical limit or the critical biological response, and there is no "significant harm" to the receptor. As long as deposition stays below the critical load, this is the 'ideal' situation.

- Stage 2: Pollutant deposition rises above the critical load, but chemical and biological indicators still do not violate their respective criteria because there is a delay. No damage is likely to occur at this stage, despite the exceedance of the critical load. The time between the first exceedance of the CL and first violation of the biological criterion (first occurrence of "significant harm") is called the Damage Delay Time (DDT = t3–t1).

- Stage 3: Pollutant deposition is above the critical load and both the chemical and biological criteria are violated. Measures to reduce emissions are taken to avoid further harm to the receptor and pollutant deposition begins to decrease.

- Stage 4: Pollutant deposition has been reduced to a level below the critical load, but the chemical and biological criteria are still violated, and thus "recovery" has not yet occurred. The time between the first non-exceedance of the critical load and the subsequent non-violation of both criteria can be called the Recovery Delay Time (RDT = t6–t4).

- Stage 5: This stage is similar to Stage 1. Pollutant deposition has been reduced to a level below the critical load and neither the chemical nor biological criteria are violated. Only at this stage can the receptor be considered to have recovered to an undamaged level.

Stages 2 and 4 can be further subdivided into two sub-stages each: chemical damage and recovery delay times (DDTc = t2–t1 and RDTc = t5–t4; dark grey in Figure D-1 and (additional) biological damage and recovery delay times (DDTb = t3–t2 and RDTb = t6–t5; light grey). Given opportunities for "confounding effects" (i.e., mechanisms not related to acidic deposition but affecting biological indicators, such as forest pest infestation or climate change) occurring during the "delay periods," it is clear that unambiguous short-term patterns of recovery of biological indicators are unlikely to be observed, even in the presence of rather large declines in pollutant deposition. This has important implications for recovery expectations.

D.3.4. Deposition Schedules

Dynamic critical loads, by definition, must explicitly account for the receptor time scales and lags described above. Therefore, the process of estimating dynamic critical load values for a given pollutant must be based on a planned or assumed deposition schedule for changing the pollutant deposition and for assessing the receptor responses. Three different time periods are specified, as illustrated in Figure D-2. [The nomenclature used here for the three years specified in the deposition schedule conforms to that used in European "dynamic target loads analyses" (Posch et al., 2003)].
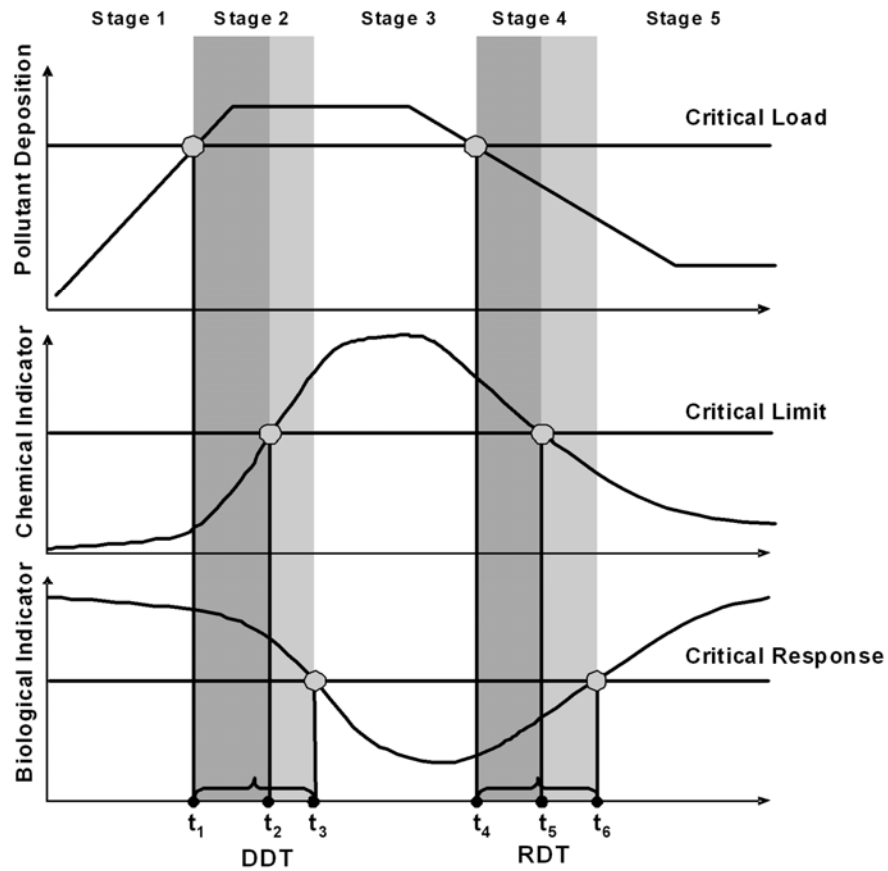
Figure D-1.   Conceptual patterns of pollutant deposition effects on a chemical indicator and a corresponding biological indicator during increasing and decreasing deposition. Critical limits and responses for the chemical and biological indicators are indicated as horizontal lines, along with the critical load of deposition that produces these levels. The delays between the exceedance of the critical load (t1), the violation of the critical chemical limit (t2), and the crossing of the critical biological response (t3) are indicated in grey shades, highlighting the DDT. Similar delays in chemical and biological recovery during deposition reductions (t4, t5, and t6) define the RDT of the system.
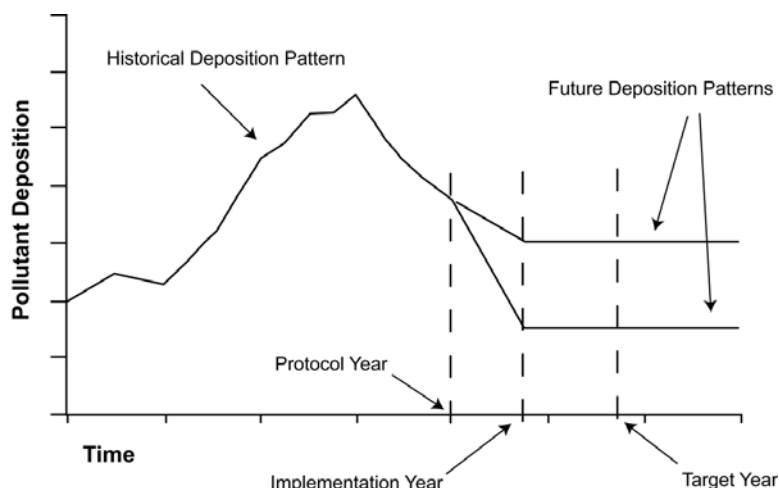
Figure D-2. Pollutant deposition patterns for defining the temporal parameters of dynamic critical loads analyses. The deposition schedule requires that three years be specified: (1) the year in which changes in pollutant deposition are begun, called the protocol year; (2) the year in which changes in pollutant deposition are completed, called the implementation year; and (3) the year in which the chemical or biological response indicator is evaluated, called the target year.

The first time period is the protocol year when deposition changes moving toward the critical load are begun. It will be the case that voluntary or mandated changes in deposition will require a number of years to get underway once a critical load has been calculated or target load has been selected. These delays in moving toward the critical load will affect the dynamic responses of the chemical and biological indicators and, therefore, must be included in the dynamic modeling of receptor response. Before the protocol year, it must be assumed that pollutant deposition will be continuing along the pattern of recent or historical deposition change or along the pattern dictated by future deposition scenarios already planned and assumed to take effect.

The second time period is the implementation year when deposition changes are complete and pollutant deposition has reached the desired critical or target load. It is likely that a number of years will elapse between the time changes in deposition toward the critical load are initiated, and the time when they are completed. During this transition period, pollutant deposition continues at a rate higher, or lower, than the critical load. The effects of these years of deposition inputs above or below the critical load value will affect the dynamic responses of the chemical and biological indicators, and must also be included in the dynamic modeling of receptor response. It is assumed in dynamic critical loads analyses that the pollutant deposition to the receptor remains constant at the critical load for all years after the implementation year.

The final time period is the target year when the biological indicators are evaluated. Recognizing that there are inherent lags in receptor responses following changes in pollutant deposition, it a number of years will frequently be allowed to elapse after the implementation year before the receptor responses are assessed. It must also be recognized that receptor responses will continue to change over time. Thus, selection of the target year will affect attainment of the critical limit.

The deposition schedule for a dynamic critical load analysis can be driven by a number of considerations, and can be organized from protocol year to target year or vice versa. The selection of the protocol and implementation years is often a matter of political will and economic possibility. Large-scale pollution abatement programs take time to negotiate. Costs or engineering difficulties may delay the start of the abatement program and affect the length of time it takes to complete the program once it is begun. Once these constraints have been established, it is then possible to select a reasonable target year for

evaluation of the receptor responses. Alternately, resource management mandates might require that "significant harm" to receptor indicators be mitigated or eliminated by a certain time. This establishes the target year for the dynamic analysis and the protocol and implementation years must be selected to allow time for any lags in the receptor responses to occur.

Clearly, there is tension between the two approaches when developing a deposition schedule. It is possible, for instance, to defer the protocol and implementation years so far into the future that extensive "significant harm" occurs to the receptor indicators in the intervening years. If that damage is especially severe, the critical load, when the target year is finally reached, may not be achievable. Similarly, if a receptor is currently suffering harm, it is possible to choose a target year for receptor response too close to the present day to allow time for the receptor to recover, even if the pollutant deposition was reduced to zero immediately.

Both of these hypothetical scenarios raise important points about dynamic critical load estimates. Because time is explicitly incorporated, there are certain dynamic critical loads questions that have no answer. Commonly called "you can't get there from here" problems, these deposition schedules choose protocol, implementation, or target years that are inconsistent with the time scales of receptor response. For example, setting a target year 5 years in the future for achievement of no "significant harm" in a receptor that is currently badly damaged, and has a history of high pollutant loading, may be asking the impossible. Critical load estimates derived in this case would require having set the pollutant deposition to zero some years in the past. In other words, the state of no significant harm cannot be reached within the specified five years regardless of how deposition is changed within that 5 year period ("you can't get there from here"). This problem is moot for steady state critical loads. Steady state critical loads analyses will always provide some sensible estimate (zero or finite) of long-term sustainable pollutant deposition for every receptor because time is not a factor. Dynamic critical loads analyses, on the other hand, may frequently provide non-quantitative results, but these results nonetheless convey useful information concerning the current status of the receptor and point out the necessity to continue the analysis with modified assumptions or expectations to develop realistic and achievable target load values.

D.3.5. Long-Term Implications

The explicit inclusion of time in critical loads estimation provides useful information for managers or policymakers when deciding when and how much to alter pollutant emissions and deposition, but the dynamic approach leads to implicit assumptions that must be recognized. Focus on the near-term aspects of receptor responses (the years included in the deposition schedule) can be misleading. The implicit assumption is that having attained the desired biological or chemical response in the target year, nothing more will happen, or at least that further changes in the receptor, if they do occur, will not produce "significant harm." Available dynamic model critical load estimates suggest that this is not always true, and the long-term implications of dynamic critical load estimates should be examined carefully.

The dynamic critical loads procedure assumes that pollutant deposition remains constant at the critical load from the implementation year until the target year, and the assessment of receptor response. Model simulations can be continued, assuming deposition at the constant critical load value, for a number of years after the specified target year to ensure that lags in the receptor response will not result in "significant harm" appearing at some later date, even though it was not present in the target year. Some receptors have chemical or biological lags that are many decades long, or longer. Critical loads analyses based on deposition schedules that cover only 20 to 30 years can produce the unwanted result of estimating a dynamic critical load that avoids "significant harm" to the receptor in the target year, only to have the receptor suffer damage some years later.

It is important to determine which receptor responses and which deposition schedules might lead to such an unwanted result. There are some general guidelines concerning this potential problem. For any receptor for which there is currently no "significant harm," the estimated critical load provided by the

dynamic approach will be one that brings the biological or chemical indicators to the threshold of harm without crossing it (the definition of the critical load). However, this dynamic critical load has then put the biological or chemical indicator on a trajectory away from its currently good status and toward the threshold of harm. In most cases, the trajectory toward harm will continue past the target year and "significant harm" will occur in these receptors some time after the target year.

On the other hand, in any receptor for which there currently is "significant harm," the estimated critical load provided by the dynamic approach will be one that brings the biological and chemical indicators to the threshold of harm and crosses it, just to return to a state of no harm. This dynamic critical load puts the biological or chemical indicator on a trajectory away from harm and towards good status. In most cases, it is likely that the upward trajectory will continue past the target year and significant further recovery will occur in these receptors after the target year.

These are, however, merely generalizations. Depending on the geochemical and biological process affecting a receptor, there exist possibilities that upward trajectories could become downward trajectories sometime after the target year and vice versa. The most straightforward procedure is to run the model(s) used in the dynamic critical loads analyses for a sufficiently long time after the target year so that any reasonable chance of delayed damage to the receptor or delayed recovery is either discovered or discounted.

D.3.6. Steady State and Dynamic Critical Loads: Complementary Information

There is no "correct" choice to be made between steady state and dynamic critical loads analyses. Both provide estimates of pollutant loads that are intended to avoid "significant harm" to a receptor. Both are valid scientific expressions of the receptor's sensitivity to the pollutant. They differ primarily in the time scales implicit in their use. Steady state analyses provide critical load estimates for long-term sustainable protection, but ignore questions of near-term recovery and avoidance of interim harm. Dynamic analyses provide critical load estimates that can be used to examine short-term or long-term options for recovery of damaged systems and avoidance of interim harm, but may ignore the ultimate long-term sustainability of the estimated deposition, which may evolve over centuries. Clearly, the two approaches provide complementary information.

The complementary nature of the two critical loads approaches can be exploited in the selection of a target load estimate for a receptor. Selecting the lower of the two critical load estimates for the receptor (steady state or dynamic) should result in facilitation of recovery, or avoidance of harm, in the short-term, as well as long-term sustainability once the receptor has reached equilibrium with the selected target load. Multiple lines of evidence reflecting multiple critical load values can provide important information that collectively provides the foundation for management decision-making.

The procedures, data requirements, and computational resources needed for each of the two critical loads approaches may differ significantly depending on the models (response functions) adopted for the analyses. Differences in the approaches may also depend on the disturbance, receptor, or indicator being evaluated. The next two sections discuss the disturbances, receptors, and indicators relevant to deposition of S and N, and the models used for calculation of critical load estimates by each approach.

D.4. Calculation of Critical Loads

The derivation of quantitative estimates of critical loads requires the development of dose-response functions (models) for the components of the ecosystem being considered. Models are needed to describe two different classes of dose-response function. Geochemical models describe the changes in the

chemical indicators that occur as functions of changes in the pollutant loads. Biological response models describe the changes in the biological indicators as functions of changes in the chemical variables.

Models for either class of dose-response function can be developed using two general approaches. Empirical models are based on direct observations of indicator response to pollutant deposition. They are usually developed using statistical techniques and generally do not contain a mechanistic pathway linking pollutant deposition to indicator response. Process-based models are based on conceptual representations of chemical and biological mechanisms, and use mathematical equations to express the inter-relationships among system components. Whereas process-based models frequently also use observations of receptor responses to pollutant deposition for calibration and validation, they are fundamentally different from empirical models in that mechanistic pathways from pollutant deposition to indicator response are explicitly included in the model structures. In general, the geochemical models used to link S and N deposition to chemical indicator response are mostly process-based, whereas biological responses to acidification by S and N are mostly modeled using empirical approaches. Finally, both geochemical models and biological response models, whether developed using either empirical or process-based approaches, can be further classified as static or dynamic depending on whether or not time is included among variables.

D.4.1. Empirical Models

Empirical models can be constructed relating either chemical or biological indicators to pollutant deposition. The empirical models currently in use for calculating critical loads employ steady state approaches. This is not a necessary constraint, however, because even with no knowledge of the underlying mechanisms, there exist many statistical techniques for relating the time-series of outputs and inputs of ecosystems. The reason empirical critical loads models are usually based on a steady state approach is primarily because time-series data of long enough duration to parameterize dynamic empirical models are not generally available. In general, empirical models require less complex datasets, are more straightforward to implement, and are easier to understand than process-based models. For some receptors, the lack of conceptual understanding of the mechanisms of indicator response to pollutant deposition renders the use of process-based models problematic, and the use of empirical models is then the only viable critical load analysis approach.

D.4.2. Acidification Effects of Sulfur and Nitrogen

Empirical models of critical loads for acidity assign critical loads to soils on the basis of soil mineralogy and chemistry (UNECE, 2004). For example, at the Critical Loads Workshop at Skokloster soil forming materials were divided into five classes on the basis of the dominant weatherable minerals. A critical load range, rather than a single value, was assigned to each of these classes according to the amount of acidity that could be neutralized by the base cations produced by mineral weathering. The classification of soil materials developed at Skokloster used a relatively small range of primary silicate minerals and carbonates. A larger range of minerals was classified by Sverdrup and Warfvinge (1988) and Sverdrup et al. (1990) for use in the PROFILE model (Warfvinge and Sverdrup, 1992).

D.4.3. Nutrient Effects of Nitrogen

Empirical models of critical loads for nutrient N have been developed in Europe within LRTAP to set critical loads for atmospheric N deposition (e.g., UNECE, 2004). Empirical critical loads of N for natural and semi-natural terrestrial ecosystems and wetland ecosystems were first presented in a

background document for the 1992 workshop on critical loads held under the UNECE LRTAP Convention at Lökeberg, Sweden (Bobbink et al., 1992b). A number of European expert workshops have taken place to reach agreement among specialists regarding the impacts of N for various ecosystems and related critical loads (Achermann and Bobbink, 2003; Bobbink et al., 1992b, 1996.; Hornung et al., 1995; Nilsson and Grennfelt, 1988). Empirical relationships have also recently been developed in the U.S., particularly for western ecosystems (e.g., Baron et al., 1994, 2000; Burns, 2004; Fenn et al., 2003; Nydick et al., 2004a; Williams and Tonnessen, 2000).

D.4.4. Process-Based Models

A number of process-based models are currently in use for calculating critical loads using both steady state and dynamic approaches. Developing a process-based modeling approach that includes all appropriate chemical and biological indicators is a complex task. Some process models incorporate both geochemical and biological response mechanisms in one program. An alternate approach is to chain individual process-based models, for example taking the output of a geochemical model and passing it as input to a biological-response model. In either approach, the level of process complexity varies a great deal among the various available models. The choice of a particular process-based modeling approach to be used in a critical load analysis (dynamic or steady state, all-in-one or chained, etc.) will depend on the scope of the analysis, the quality and quantity of available data, and the availability of resources (time and money) for the analysis. The following is a brief overview of some of the process-based biogeochemical models that are commonly used to calculate critical loads.

D.4.5. Steady State Models

The Simple Mass Balance (SMB) model is the standard model for calculating critical loads for terrestrial ecosystems under the LRTAP Convention (Sverdrup et al., 1990; Sverdrup and De Vries, 1994). The SMB model is a single-layer model. There also exist multi-layer steady state models for calculating critical loads in terrestrial ecosystems. Examples are the MACAL model (De Vries, 1988) and the widely used PROFILE model (Warfvinge and Sverdrup, 1992), which has at its core a model for calculating weathering rates from total mineral analyses.

The Steady State Water Chemistry (SSWC) model (Henriksen et al., 1992; Henriksen and Posch, 2001; Sverdrup et al., 1990) calculates critical loads of acidity for surface waters, based on the principle that acid loads should not exceed the balance of non-marine, non-anthropogenic base cation sources and sinks in a catchment, minus a buffer to protect selected biota from being damaged.

The First-order Acidity Balance (FAB) model for calculating critical loads for surface waters takes into account sources and sinks within the lake and its terrestrial catchment. The original version of the FAB model was developed and applied to Finland, Norway, and Sweden by Henriksen et al. (1992) and Posch et al. (1997). A modified version was first reported in Hindar et al. (2000, 2001) and is described in more detail by Henriksen and Posch (2001).

D.4.6. Dynamic Models

MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on surface water chemistry (Cosby et al., 1985a, 1985b, 2001). The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in these waters. MAGIC consists of: a sub-model in which the

concentrations of major ions are assumed to be governed by simultaneous reactions involving $SO_4{2-}$ adsorption, cation exchange, dissolution-precipitation-speciation of Al, and dissolution-speciation of inorganic carbon (C); and a mass balance sub-model in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering, net uptake and loss in biomass, and losses to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change of surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils. MAGIC is described in more detail in Annex C.

PnET-BGC is an integrated dynamic biogeochemical model that simulates chemical transformations of vegetation, soil, and drainage water. It was formulated by adding the sub-model BGC (biogeochemistry) to PnET-CN, a model of C, water, and N balances (Aber and Federer, 1992; Aber and Driscoll, 1997; Aber et al., 1997), to expand the model to include vegetation and organic matter interactions of major elements (i.e., Ca_2^+, $Mg2^+$, K^+, Na^+, Si, S, P, Al_3^+, Cl^-, F^-), abiotic soil processes, solution speciation, and surface water processes (Gbondo-Tugbawa et al., 2001). The model was initially developed for, and applied to, the northern hardwood forest ecosystem. It was tested extensively at the Hubbard Brook Experimental Forest, New Hampshire, including a detailed sensitivity analysis of parameter values. The model has subsequently been applied to intensively-studied watersheds in the Adirondack and Catskill regions of New York and applied regionally to the Adirondacks (Chen and Driscoll, 2005b) and northern New England (Chen and Driscoll, 2005a, 2005b). See additional description in Annex C.

Simulation Model for Acidification's Regional Trends (SMART2) is a soil acidification and nutrient cycling model and is an extension of the dynamic soil acidification model SMART (Kros et al., 1995). The original model was a relatively simple simulation of the response of soil and soil water quality to atmospheric inputs. Improvements in SMART2 include processes of canopy interactions, litter fall, root decay, mineralization, and root uptake of nutrients. SMART2 has been used primarily in European critical loads studies.

The Soil Acidification in Forest Ecosystems model (SAFE) was developed at the University of Lund in Sweden (Alveteg and Sverdrup, 2002; Warfvinge et al., 1993). The main differences between the SAFE and MAGIC models are: (a) weathering of base cations is not calibrated for SAFE, but it is modeled with the PROFILE sub-model, using soil mineralogy as input (Warfvinge and Sverdrup, 1992); (b) SAFE is oriented to soil profiles in which water is assumed to move vertically through several soil layers, (c) cation exchange between Al, H, and (divalent) base cations is modeled in SAFE with Gapon exchange reactions rather than Gaines-Thomas reactions, and the exchange between the soil matrix and soil solution is diffusion-limited. The standard version of SAFE does not include S adsorption although a version, in which S adsorption is dependent on SO_4^{2-} concentration and pH of soil solution, has recently been developed (Martinson et al., 2003).

ForSAFE is a mechanistic model that simulates N and C cycling and soil chemistry. Climatic drivers within the model include temperature, precipitation, radiation, and deposition. ForSAFE combines three established models (SAFE, PnET-CN, and DECOMP). SAFE simulates soil chemistry (e.g., chemical weathering, cation exchange, leaching, and solution equilibrium reactions). PnET-CN (Aber et al., 1997) is used to predict forest growth within ForSAFE, through the simulation of C fixation, litterfall, and C and nutrient allocation. DECOMP (Walse et al., 1998) is a dynamic, multi-layered process-oriented decomposition model that incorporates the influences of temperature, moisture, pH, and Al. Very Simple Dynamic soil acidification model (VSD) only includes a few key processes, such as cation exchange and N immobilization, and a mass balance for cations and N (Posch et al., 2003). VSD does not consider seasonal variations, as the time step in the model is one year. The VSD model is based on mass balance equations that describe soil input-output fluxes and equations describing the rate-limited (e.g., uptake and silicate weathering) and equilibrium (e.g., cation exchange) soil processes. Soil solution chemistry is based solely on the net element input from the atmosphere (i.e., deposition minus net uptake minus net

immobilization) and geochemical interactions in the soil (i.e., CO_2 equilibria, weathering of carbonates and silicates, and cation exchange). VSD simulates a single soil layer with a constant density and a fixed depth. The concentration of the soil water leaving the compartment is assumed to be equal to the annual precipitation excess.

D.5. Use of Critical Loads in the U.S. – Current Status

At the Multi-Agency Critical Loads Workshop for Sulfur and Nitrogen Deposition Effects on Freshwater and Terrestrial Ecosystems, convened by the U.S. EPA, the U.S. Forest Service (USFS), the National Park Service (NPS), and the USGS in May 2006, approximately 75 scientists, conservation representatives, and state and federal agency officials gathered to share information, discuss scientific advances, and develop a broad federal strategy for advancing critical loads in the U.S. (U.S. EPA, 2006c). The conclusions and recommendations of that workshop are presented below. These conclusions and recommendations represent the current understanding of critical loads as scientific tool and policy instrument in the U.S.

The conclusions and recommendations below were reached by the Federal Agencies sponsoring the workshop. It is worth noting that some state agencies have pursued the use of critical loads independently to link science and policy in addressing the management of natural resources. For instance, in the State of Colorado, critical loads for N deposition that were developed for Rocky Mountain National Park (Baron, 2006) are being used to develop goals for N emissions reductions by the State of Colorado, U.S. EPA, and NPS. (See "Nitrogen Deposition Reduction Plan" at http://www.cdphe.state.co.us/ap/rmnp.html)

D.5.1. Current Recommendations on Critical Loads Uses in the U.S.

The participants in the Multi-Agency Critical Loads Workshop developed a set of findings and recommendations to help advance critical loads usage in the U.S. The "areas of agreement" published in the workshop report (U.S. EPA, 2006c) included the following:

- A critical load is defined as: a quantitative estimate of the exposure to one or more pollutants below which significant harmful effects on specific sensitive elements of the environment do not occur according to present knowledge (Nilsson and Grennfelt, 1988).

- Despite reductions in S and N emissions in the U.S., deposition rates still exceed preindustrial levels and acidification and eutrophication effects remain widespread.

- Critical loads can be used to better understand impacts of atmospheric deposition, assess the effectiveness of emissions programs, and guide natural resource management.

- The development of critical loads is a process that is subject to continued development and improvement as knowledge advances.

- Adequate information exists to move forward with the development and limited application of critical loads in some regions and ecosystems in the U.S.

- An intensive research and monitoring agenda should be pursued to support the development and refinement of critical loads in the U.S.

- Critical loads should be based on a matrix of biological and chemical indicators for aquatic and terrestrial ecosystems that account for acidification, N saturation, and eutrophication effects and are relevant to the geographic area or ecosystem of concern.

- Adequate information exists to establish harmful effect thresholds for some indicators based on specific protection and recovery objectives defined by policymakers and managers.

- Dynamic models provide the most accurate site-specific information and account for time-dependent processes, but are generally too data intensive to be applied across large geographic areas at present. Simple mass balance models can be applied to current conditions in large geographic areas, but in some instances do not adequately highlight some sensitive areas because they tend to average conditions across the landscape. Hybrid approaches that link observational datasets with dynamic and steady state models represent a useful approach for regionalizing site-specific information.

D.5.2. Questions and Limitations Regarding Critical Loads Uses in the U.S.

The participants in the Multi-Agency Critical Loads Workshop also developed a set of "Questions Needing Further Discussion" (U.S. EPA, 2006c):

- What are the appropriate applications of critical load estimates to policy and management issues given current knowledge? For applications where buy-in to an incremental process does not exist, greater investment in critical loads methods may be needed before this application can be pursued.

- How strong is the relationship between specific indicators, thresholds, and biological responses?

- What are the suitable interpretations and uses of existing databases for the development of national simple mass balance critical load models?

D.5.3. Critical Loads Research and Monitoring Needs

Finally, the participants in the Multi-Agency Critical Loads Workshop presented a list of "Critical Loads Research and Monitoring Needs" (U.S. EPA, 2006c), which are summarized below.

D.5.3.1. Emissions and Deposition

- Update N and S emissions inventories on a state-by-state basis back to the 1900s to correspond with methods used in current emissions inventories.

- Develop NH_3 emissions inventory.

- Improve dry deposition estimates for S and N.

- Improve total S and N deposition estimates.

- Measure gaseous NH_3 concentrations.

- Add NH_3 deposition measurements to current networks.

- Improve estimates of total deposition in complex terrain.

- Develop N and S deposition maps for North America.

D.5.3.2. Soils

- Improve spatial coverage and representativeness of soil chemistry databases, particularly in sensitive terrain.

- Increase soil monitoring.

- Improve estimates of mineral weathering rates.

- Develop soil archiving and well characterized reference samples to promote cross-laboratory comparisons.

- Expand research on the nature and size of soil nutrient pools.

- Conduct research on threshold values of soil quality for biologic responses.

- Determine N supply rates in different soil types.

- Investigate N soil accumulation rates in arid lands and implications for critical loads.

D.5.3.3. Surface Waters

- Incorporate TIME and LTM surface water monitoring programs into a larger network with better geographic coverage (e.g., the West and Southeast).

- Improve spatial coverage and representativeness of surface water chemistry databases, particularly in sensitive and complex terrain.

- Integrate fixed-site monitoring with regional probability monitoring design.

- Continue to monitor major drivers of acidity.

- Build critical loads considerations (e.g., validation, improvement, regionalization) into monitoring from the start by combining chemistry, hydrology, deposition and biology, and integrating site-specific models and measurements into regional contexts.

- Expand research to understand what is driving dissolved organic carbon (DOC) changes in the East.

- Analyze the impact of groundwater transport on recovery times.

D.5.3.4. Biological Effects

- Develop better understanding of the link between chemical indicators and biological response (e.g., quantify the minimum N level at which plankton communities shift).

- Conduct additional research on the sequential impacts of N and relationship between N deposition and ecosystem impacts.

- Integrate critical load estimates with biodiversity and climate change interactions.

- Undertake more research on biological change and "harmful effects" to help establish appropriate critical loads thresholds (e.g., in arid lands, what level of productivity of exotic invasive species will cause the reduction versus the extinction of native species?).

- Collect sediment cores from lakes that vary in rates of N deposition to track changes in diatom assemblages.

D.5.3.5. Critical Loads Models

- Improve representation of N dynamics in models.

- Expand models to include NH_3.

- Improve explicit consideration of changing base cations and DOC.

- Conduct ground-truthing of forest sensitivity and other models.

- Integrate water flowpaths into nutrient cycling models since lateral and vertically upward flowpaths are common.

- Understand and quantify uncertainties in models.

- Conduct site level model comparisons of dynamic and simple mass balance models.

- Integrate observational databases with steady state and dynamic models.

- Incorporate capacity to understand and evaluate climate change interactions.

Table D-2. **Biological indicators for the effects of elevated N deposition and related empirical critical loads for major ecosystem types (according to the Eunis classification) occurring in Europe.**

Ecosystem Type	Biological Effect Indicators	Empirical Critical Load (kg N/ha/yr)
GRASSLANDS AND TALL FORB HABITATS (E)		
Sub-Atlantic semi-dry calcareous grassland	Increased mineralization, nitrification and N leaching; increased tall grasses; decreased diversity	15–25
Non-Mediterranean dry acid and neutral closed grassland	Increase in nitrophilous graminoids, decline of typical species	10–20
Inland dune grasslands	Decrease in lichens, increase in biomass, accelerated succession	10–20
Low and medium elevation hay meadows	Increased tall grasses, decreased diversity	20–30
Mountain hay meadows	Increase in nitrophilous graminoids, changes in diversity	10–20
Moist and wet oligotrophic grasslands	Increase in tall graminoids, decreased diversity, decrease in bryophytes	10–25
Alpine and subalpine meadows	Increase in nitrophilous graminoids, changes in diversity	10–15
Moss and lichen dominated mountain summits	Effects on bryophytes and lichens	5–10
HEATHLAND HABITATS (F)		
Northern wet heaths	Decreased heather dominance, transition heather to grass, decline in lichens and mosses	10–20
Dry heaths	Transition heather to grass, decline in lichens	10–20
Arctic, alpine, and subalpine scrub habitats	Decline in lichens, mosses, and evergreen shrubs	5–15

COASTAL HABITAT (B)		
Shifting coastal dunes	Increased biomass, increased N leaching	10–20
Coastal stable dune grasslands	Increase in tall grasses, decreased prostrate plants, increased N leaching	10–20
Coastal dune heaths	Increase in plant production, increased N leaching, accelerated succession	10–20
Moist to wet dune slacks	Increase in biomasss and tall graminoids	10–25
MIRE, BOG, AND FEN HABITATS (D)		
Raised and blanket bogs	Changed species composition, N saturation of Spagnum	5–10
Poor fens	Increased sedges and vascular plant, negative effects on mosses	10–20
Rich fens	Increase in tall graminoids, decreased diversity, decrease of characteristic mosses	15–35
Mountain rich fens	Increase in vascular plants, decrease in bryophytes	15–25
FOREST HABITATS (G)		
Mycorrhizae	Reduced sporocarp production, reduced below ground species composition	10–20
Ground vegetation	Changed species composition, increased nitrophilous species; increased susceptibility to parasites (insects, fungi, virus)	10–15
Lichens and algae	Increase in algae; decrease in lichens	10–15

Source: Achermann and Bobbink (2003). Reprinted with permission.

Annex E. Effects of NO_Y, NH_X, and SO_X on Structures and Materials

E.1. Introduction

The purpose of this chapter is to summarize the research published since the most recent AQCDs on materials and structures damage caused by: (1) NO, NO_2, and their combination (NO + NO_2 = NO_X); the organic and inorganic reaction products of NO_X (denoted as NO_Z); and the combination of NO_X and NO_Z (NO_X + NO_Z = NO_Y), (2) the effects of NH_3 and NH_X, and of (3) SO_X. Materials and structures exposed to the environment are subject to damage from exposure to sunlight, moisture, salt, windblown dust, and cycles of temperature and humidity, whether or not air pollutants are present. However, NO_Y, NH_X, and SO_X air pollutants may cause such damage to be greater or occur more rapidly than with natural environmental factors alone. Damage to materials and structures may be physical, potentially affecting the durability or maintenance needs of a material or structure, or may be purely aesthetic, affecting only the outward appearance of the material or structure. In the case of historical buildings, monuments, or artifacts, aesthetic damage may be a relevant concern.

Note that very extensive work related to materials damage from acidic deposition related to S and N was conducted in the 1980s as part of the National Acid Precipitation Assessment Program (NAPAP) (NAPAP, 1991). The results of that work are well known to the U.S. EPA (1991) and so are not discussed here. In compiling information for this chapter on NO_Y/NH_X/SO_X effects, the information presented in the 1993 NO_X AQCD (U.S. EPA, 1993a) and the 2004 PM AQCD (U.S. EPA, 2004) was updated by literature searches reaching back to approximately 1992. This update was based on peer-reviewed literature, with a focus on studies that were conducted in the U.S., that evaluated effects at realistic ambient air pollutant levels, and that treated NO_Y/NH_X/SO_X as components of a complex mixture of air pollutants. These latter two factors result in an emphasis on studies done with exposures to ambient atmospheric pollution, rather than exposures at high levels, e.g., in test chambers. The studies cited in this chapter were selected from those found in a broad literature search based on criteria that they address damage caused by exposure to atmospheric contaminants; focus on S and N containing species; provide a clear link between pollutant concentrations and damage; and give complete information on methods and data analysis used.

Broadly speaking, the pace of research on NO_Y, NH_X, and SO_X materials effects has slowed considerably since the publication of the previous AQCDs. In particular, although the literature searches conducted for this update emphasized studies conducted in the U.S., the great majority of the relevant publications found originated in Europe or Asia. The relative scarcity of recent U.S. studies on structural and materials damage from NO_Y/NH_X/SO_X may be a natural fall-off in research in this area, following the extensive efforts that were summarized in the previous AQCDs and in the NAPAP report. Certainly the greater number and age of aesthetically valuable buildings and archeological sites in Europe and Asia, relative to the U.S., may be a driving force for current research in those geographic areas. In this chapter, each discussion of the effects of NO_Y/NH_X/SO_X on a material type begins with a brief summary of the state of knowledge as represented in the previous AQCDs, and then continues with a description of recent research on that type of material.

E.2. Environmental Exposures of Materials

E.2.1. Mechanisms of Materials Damage

As noted in the introduction to this chapter, materials damage may occur by natural physical processes without the involvement of $NO_Y/NH_X/SO_X$ air pollutants. When those pollutants are involved, the destructive processes may be chemical, physical, or even biological. Chemical processes include direct reactions with gaseous pollutants such as NO_2, SO_2, or nitric acid (HNO_3), reaction with electrolytes (proton (H^+), ammonium (NH_4^+), nitrate (NO_3^-), SO_4^{2-}, etc.) in water on material surfaces, and reactions with chemicals in deposited particulate matter. An example of a physical process is the deterioration of stone that occurs when gypsum ($CaSO_4 \cdot 2H_2O$) forms from reaction of SO_2 with the calcium carbonate ($CaCO_3$) in the stone. The gypsum thus formed occupies a larger volume than the original stone, causing the surface to deteriorate. Biological degradation can occur when deposited pollutants are oxidized to acids by fungi or bacteria.

A key factor affecting damage to certain materials, primarily metals and stone, is the frequency and duration of wetting of the surface. Liquid water on materials surfaces can dissolve deposited pollutants, producing reactive electrolyte solutions, and can serve as a reaction medium in which S and N oxides are converted to more damaging acids. Pollutants deposited on surfaces may contain or form hygroscopic salts, which enhance the formation of liquid water and thereby increase materials damage. As Dubowski et al. (2004) have shown, the deposition of HNO_3 onto surfaces can increase the extent of wetting of surfaces, and promote the damaging effects of both HNO_3 and other pollutants.

E.2.2. Deposition Processes

Air pollutants come into contact with surfaces through both dry and wet depositional processes. Dry deposition occurs in the absence of precipitation and is governed by factors such as atmospheric turbulence, the chemical and physical properties of the pollutant (e.g., water solubility and reactivity for gases; size, density, and shape for particles), and surface properties (e.g., reactivity, roughness, moisture level, and pH). The deposition rate of a pollutant is proportional to the atmospheric concentration of that pollutant. Dry deposition of gases depends primarily on the water solubility of the gas, the moisture level on the surface, and the pH of the electrolyte formed on the surface of a material. Nitric acid and NH_3 are deposited very efficiently to most surfaces regardless of the surface properties of the material. Particle size plays an important role in determining the rate of deposition of particles to a surface. For very small particles, Brownian diffusion is the dominant deposition mechanism. For larger particles, inertial impaction and gravitational settling are important deposition processes. Particles between 0.05 and 2 μm, which include most atmospheric particles containing NO_3^-, SO_4^{2-}, and NH_4^+, may have long atmospheric lifetimes in the absence of moisture.

Wet deposition occurs when gas or particle species come into contact with moisture (as rain, fog, snow, or ice). Atmospheric species can be dissolved into moisture and then deposited as the moisture falls to the ground. Solubility and the chemical reactions of the dissolved species determine the degree of wet deposition. For acid gases, high dissolution is observed due to the dissociation of the dissolved species in water. Wet deposition of pollutants occurs at a faster rate than dry deposition, but is only an important mechanism when moisture is present.

E.2.3. Chemical Interactions of Nitrogen and Sulfur Oxide Species

N and S oxide species are subject to many atmospheric reactions in both the gaseous and particulate phase. Emissions of S and N oxides are primarily in the form of gas phase SO_2 and NO_X. In the atmosphere, these species can be oxidized by reaction with other atmospheric species to gas and particle phase product species. On the surface of materials, the oxides are generally oxidized to their acid forms (nitrous acid (HNO_2), HNO_3, sulfurous acid (H_2SO_3), and sulfuric acid (H_2SO_4)), which then dissociate to form nitrite, nitrate, sulfite, and sulfate ions. These acids are the primary species responsible for damage to materials by S and N pollutants. NH_3, the primary gaseous basic compound in the atmosphere, can partly or completely neutralize these acids in particulate matter or in the aqueous phase, forming NH_4^+ ions.

On the surfaces of materials, N and S species can react to form a variety of degradation products. On metals and stone, the possible degradation products include nitrite, nitrate, sulfite, and sulfate species as well as minerals that incorporate nitrate or sulfate into a more complex composition. These degradation products may be more or less reactive to further degradation than the original material. Degradation products that are more reactive, or those that are soluble in water, do not have long lifetimes on a material surface. They undergo further chemical reactions and are transformed to other species, or they are washed off the surface by precipitation. Products which are less reactive and less soluble in water than the original material may form a protective layer on the surface of the material which inhibits or prevents further damage from atmospheric pollutants. Products that are more reactive or water-soluble than the original material are readily removed, exposing the surface to more damage. The protectiveness of the products formed depends on the complex mixture of species present and the physical/chemical properties of the material.

Synergistic effects, which influence the rate of degradation of materials, are possible in atmospheres containing a complex mixture of pollutants. NO_X may enhance the oxidation of sulfite to sulfate and lead to faster rates of corrosion. The deposition velocity of SO_2 and NO_X may be influenced by the presence of HNO_3 deposited to the surface due to the increased degree of surface wetting.

E.2.4. Materials Damage Experimental Techniques

The $NO_Y/NH_X/SO_X$ air pollutants are comprised of numerous distinct chemical species, which may exist in the gaseous and/or particulate phases in the atmosphere, as well as in dissolved form in atmospheric precipitation and in condensed water on surfaces. To test the damaging effects of $NO_Y/NH_X/SO_X$ species on man-made materials, it is often necessary to simplify the system by testing under controlled laboratory conditions, typically with a very limited set of pollutants in a test chamber. Such tests generally use pollutant concentrations that are greatly elevated relative to ambient atmospheric levels, and may also use exaggerated temperature, humidity, or wetting, to accelerate the development of materials damage so that it can be detected. Chamber tests may not accurately mimic the mass transfer of pollutants in the atmosphere, and efforts in such tests to isolate the effects of one pollutant from the complex mixture present in the atmosphere are unrealistic. As a result, chamber tests may provide valuable information on potential effects and mechanisms involving ambient air pollutants, but cannot accurately predict the corrosion rates or effects of such pollutants in real situations.

Exposing materials of interest to the ambient atmosphere for extended time periods can provide a realistic look at the effects of air pollutants on materials. However, such ambient exposure tests are limited by the occurrence of natural (i.e., non-air pollutant) materials damage, and by the complexity of the $NO_Y/NH_X/SO_X$ system. While it is relatively easy to determine which materials suffer more or less damage during equivalent exposures to ambient air pollution, it is extremely difficult to determine which air pollutants are responsible for the observed damage. This is due to the co-occurrence of all air

pollutants simultaneously, complexities in accurately measuring the suite of $NO_Y/NH_X/SO_X$ species, and interconversions among species (e.g., SO) and SO_4^{2-}, NO_X and HNO_3) related to contact with materials or with moisture. The amount of time that surfaces are wet is a key factor in the extent of materials damage, and this factor may be difficult to determine in ambient exposures, because the presence of air pollutants themselves may enhance surface wetness on the microscale beyond that expected based on meteorological conditions (Dubowski et al., 2004). Ambient exposure tests lead to retrospective analyses, in which meteorological and air pollutant data, surface analyses, and measurements of chemical and physical properties are evaluated statistically to estimate the impacts of air pollutants on the exposed materials.

E.3. Effects on Dyes and Textiles

E.3.1. Fading of Dyes

The fading of dyes by N oxides has long been recognized, and dye manufacturers have worked to produce products less susceptible to this effect, through both improved dye chemicals and the use of inhibitors in dye formulations to minimize fading. Fading has been observed with both red and blue dyes, both on natural fibers (e.g., cotton, silk, wool) and on synthetics (e.g., nylon, rayon, polyester). The fading effect of NO_2 is generally reported to be greater than that of NO on various dyes with various fabrics. In exposures of dyed fabrics to ambient air, test samples must be shielded from sunlight, to avoid the substantial fading of dyes that results from sunlight exposure. Under such conditions, NO_2 and ozone (O_3) are often found to be about equally important in the fading of dyed fabrics.

E.3.2. Degradation of Textile Fibers

N oxides can degrade a variety of synthetic fibers, with the greatest effects seen with nylon. With NO_2, the damage to nylon occurs due to breaking of the polymer chain (i.e., chain-scissioning). Similar weakening of nylon has been observed in tests with elevated concentrations of HNO_3. A synergistic effect was observed between mechanical stress and NO_X in the degradation of oriented nylon-6 fibers (Smith and DeVries, 1993).

E.4. Effects on Plastics and Elastomers

The group of materials called plastics includes a wide variety of polymeric materials such as polyethylene, polypropylene, polystyrene, polyurethanes, acrylic polymers, phenolics, and fluorocarbon polymers, among others. Plastic materials may include other components such as hardeners or plasticizers, and fillers that may impart properties such as physical strength. Elastomers are polymers that can stretch to at least their twice their normal dimensions and then return to their original dimensions when the stress is removed. Examples of elastomers include various rubber formulations and neoprene. Plastics and elastomers can be damaged by NO_2, SO_2, and O_3, as well as by UV radiation in sunlight, and some studies have been designed to separate the effects of these factors.

Chamber studies at relatively high pollutant concentrations with sunlight or UV light have generally shown greater damage than from the pollutants alone. NO_2 is damaging to a variety of polymers

and elastomers, causing either chain-scissioning or cross-linking (formation of additional bonds between polymer chains) depending on the polymer. Polypropylene is reported to be damaged more severely by SO_2 than by NO_2. Elastomers are damaged more severely than plastics. In tests where light and NO_2 have been present simultaneously, much of the damage observed in chamber tests has been attributed to O_3, produced by the interactions of the pollutants and UV light, rather than to NO_2 alone. In studies in which the same pollutant concentrations are present both with and without light, the greater damage observed in samples exposed to the light is often attributed to the light itself, when in fact chemical processes initiated by light (such as the formation of O_3) undoubtedly also play a part.

Cellulose nitrate can break down through hydrolytic, thermal, and photochemical reactions. Addition of plasticizer to cellulose nitrate slows the degradation substantially. NO_2 is of particular interest with regard to cellulose nitrate because it is not only capable of causing damage, but is also produced as a result of damage to the material (Shashoua, 2006). NO_2 is formed when N-O bonds connecting cellulose rings are broken. The NO_2 formed will then further degrade cellulose nitrate, thus the degradation is an autocatalytic process.

E.5. Effects on Metals

Metals are considered to be the materials most subject to damage from the $NO_Y/NH_X/SO_X$ air pollutants, and have been the subject of a great deal of research. The nature and concentration of the pollutant, its rate of deposition, and especially the duration of wetting of the surface are key factors in the corrosion of metals. Numerous studies have indicated corrosion rates of metal surfaces on the order of 1 to several micrometers per year (µm/yr) under real or simulated atmospheric conditions.

Table E-1 summarizes the materials tested, exposure conditions, and findings of recent studies related to the effects of $NO_Y/NH_X/SO_X$ air pollutants on metals. The studies listed in Table E-1 are discussed where applicable in the following sections.

Table E-1.   Studies on corrosive effects of $NO_Y/NH_3/SO_X$ effects on metals.

Materials	Exposure Conditions	Findings	Reference
Zinc Mild Steel	Samples were exposed to fly-ash in clean air and in air with SO_2 and/or HCl (presentation rates of 27×10^{-6} and 4.7×10^{-6} mg/cm²s, respectively). A synthetic acid rain solution was used to model wet deposition.	Corrosion was found to depend on the surface electrolyte irrespective of the presence of particles. Inert particles were found to increase corrosion rates in relatively unpolluted atmospheres. With higher pollution levels, species leached from particulate matter contribute to the conductance of the surface electrolyte and thus increase the corrosion rate.	Askey et al. (1993)
Copper	Copper samples were exposed to 264 ppb NO_2 in a laboratory setting. Exposures were limited to 72 h to study the initial corrosion behavior.	The corrosion rate of copper in the presence of NO_2 was much greater than in clean air. The surface electrolyte was found to contain predominantly nitrate with only trace levels of nitrite. After 24 h, the electrolyte had become sufficiently acidic to dissolve the copper oxide layer. Once the copper oxide was dissolved, corrosion proceeded at a significantly faster rate.	Dante and Kelly (1993)
Zinc	Zinc samples were exposed to SO_2 (0.78 ppm) and/or NO_2 (1.06 ppm) for 420 h. Some samples were treated with NaCl before exposure.	SO_2 slowed the corrosion of zinc with moderate to high surface concentrations of NaCl due to the formation of sodium zinc hydroxychloride sulfate. NO_2 (which, alone, is unreactive toward zinc) accelerated the corrosion of zinc in the presence of small amounts of NaCl.	Svensson and Johansson (1993b)
Galvanized Iron Zinc	Samples were exposed to SO_2 or NH_3 in the laboratory. Air was supplied at 5 cm/s and the pollutant gases at 3 cm/s. The concentrations of the gases were very high to accelerate the tests.	Corrosion rates in SO_2 were found to be largely dependent on relative humidity. No such humidity dependence was observed for corrosion induced by NH_3. Corrosion rates in both gases decreased sharply with time (approaching steady state values after 30 h).	Dehri et al. (1994)
Aluminum Zinc	Samples were exposed to ambient air for 4 years at 6 sites. SO_2 deposition rates ranged from 10 mg/m²day to non-detectablelevels across the sites. Time of wetness was also measured at each site.	Corrosion products that developed in rural environments were found to be easily removed from the surface and thus result in poor protectiveness. Corrosion products formed in more aggressive environments were found to be more protective against continuing corrosion.	Vilche et al. (1995)
Zinc	Samples were exposed at temperatures of 4, 14, 22, and 30 C with 95% relative humidity. SO_2 was supplied at 500 ($\pm$ 5) ppb and 107 ($\pm$ 2) ppb.	SO_2 induced corrosion was found to be inversely dependent on temperature. The maximum corrosion rate (at 107 ppb SO_2) of 11 mg/cm2d was observed at 4 C. The corrosion rate at 30 C was 6.8 mg/cm2d.	Svensson and Johansson (1996)

Materials	Exposure Conditions	Findings	Reference
Copper Zinc Aluminum	Samples were exposed in the laboratory to SO_2 (1.5 ppb, 0.5 ppm, 10 ppm), NO_2 (10 ppm), NO (10 ppm), or O_3 (10 ppm).	NO was found to have no effect on the corrosion of copper, zinc, or aluminum. Copper in the presence of SO_2 (10 ppm) and NO_2 led to significant material loss initially with a slowing of the rate with increasing time. O_3 was found to have the strongest influence on the corrosion of copper. Only very slight mass gains were observed for copper exposed to 0.5 ppm SO_2. A small effect on zinc was observed for NO_2 with SO_2 (10 ppm) resulting in the largest weight gain. SO_2 at 0.5 ppm had a much larger effect on zinc than on copper. For aluminum, O_3 had the largest effect followed by SO_2 and NO_2.	Oesch and Faller (1997)
Copper	Powdered samples of copper patina compounds (tenorite, cuprite, brochantite, antlerite, and atacamite) were exposed to SO_2 (476 ppb) alone or in combination with NO_2 (450 ppb) or O_3 (500 ppb). Some samples were pretreated with carbon.	Tenorite reacted rapidly with SO_2 to form brochantite and other sulfate containing products. Cuprite reacted slowly with SO_2 alone but addition of O_3 formed antlerite and brochantite. NO_2 did not produce the same effect. For samples with carbon on the surface, the oxidation reaction was greatly enhanced. Brochantite and antlerite were found to be stable in atmospheres with SO_2 in combination with O_3 or NO_2.	Strandberg (1998)
Copper	Samples were exposed to atmospheres containing approximately 200 ppb of SO_2, SO_2 and O_3, or SO_2 and NO_2. O_3 and NO_2 were introduced at different times in the exposure scenarios.	Copper sulfite and cuprous oxide formed on copper surfaces exposed to SO_2. With O_3 present, an increased rate of mass gain was measured, and copper sulfite was converted to copper sulfate. NO_2 increased the mass gain to a lesser extent than O_3 and resulted in the formation of copper nitrate in addition to copper sulfate.	Aastrup et al. (2000)
Mild Steel	Steel samples were exposed to the atmosphere in 47 marine atmospheres with varying levels of chloride and SO_2. Atmospheres were separated for data analysis based on chloride and SO_2 deposition rates.	Samples exposed at sites with moderate SO_2 and chloride deposition rates formed compact, rounded corrosion structures. Samples at sites with high SO_2 and moderate chloride exhibited cracking in the corrosion products. Samples at sites with high chloride and moderate SO_2 exhibited the highest corrosion rates of the mixed atmospheres. The 1 site with high chloride and high SO_2 exhibited a lower corrosion rate than expected.	Almeida et al. (2000)

Materials	Exposure Conditions	Findings	Reference
Steel	Two types of steel were exposed to urban-industrial and rural atmospheres for 20 years. Avg SO_2 concentrations were 90 and <10 μg/m^3 (34 and <4 ppb) for urban and rural environments, respectively.	The corrosion rates of the two grades of steel were similar with values of 0.1 and 0.08 mm/yr for the urban and rural environments, respectively. The initial rate of corrosion was significantly faster and steady state values were approached after 4000 days exposure. The similar corrosion rates measured for the samples were thought to be due to similar time of wetness at both sites.	Damian and Fako (2000)
Copper Zinc	Samples were exposed in the field at 8 sites. SO_2, NO_2, and O_3 concentrations were monitored over a 4–yr exposure duration at each of the sites.	The highest corrosion losses for copper were observed at the site with the highest combination of SO_2 and O_3. For zinc, the highest corrosion losses were observed at the site with the highest SO_2 concentration. Both metals showed a decrease in corrosion rate with time. Runoff rates from copper were much smaller than from zinc. 90% of the corrosion products remained on the copper surface after 4 years; only 40% of the zinc corrosion products remained after 4 years.	Leuenberger-Minger et al. (2002)
Nickel	Nickel samples were exposed in the field at 3 sites (urban, industrial, and rural) for 1 year. Concentrations of NO (41.1, 9.7, and 2.9 μg/m^3) (33, 8, and 2 ppb), NO_2 (50.1, 24.2, and 8.7 μg/m^3) (26, 13, and 5 ppb), SO_2 (22.3, 29.0, and 12.2 μg/m^3) (8, 11, and 5 ppb), and O_3 (25.8, 47.1, and 60.1 μg/m^3) (13, 24, and 30 ppb) were measured at the urban, industrial, and rural sites, respectively.	Mass loss rates of 320, 570, and 200 μg/cm2y were determined for urban, industrial, and rural environments, respectively. Mass loss was found to increase with increasing SO_2 concentration. Soluble corrosion products were formed on the surface and then removed by rainfall events. Hydrated nickel sulfates were the main corrosion products formed on the nickel surface.	Jouen et al. (2004)
Iron	Samples were exposed to humidified air in the laboratory. Samples were exposed to clean air, SO_2 (200 ppb), SO_2 and NO_2 (each 200 ppb), or SO_2 and O_3 (each 200 ppb). The same exposure conditions were used for iron samples with NaCl deposited on the surface.	No corrosion products were detected on samples exposed to humidified air alone. The addition of SO_2 alone was not enough to initiate a change in corrosion behavior of the samples. When an oxidant (NO_2 or O_3) was added to the humidified air/SO_2 system, a significant increase in corrosion rate was observed. SO_2 was found to inhibit the NaCl induced corrosion of iron, but the combination of SO_2 and NO_2 was found to accelerate NaCl induced corrosion.	Weissenrieder et al. (2004)

Materials	Exposure Conditions	Findings	Reference
Aluminum	Aluminum samples were exposed to SO_2 (96 ppb) either alone or in the presence of other pollutants (NaCl, NO_2, or O_3).	SO_2 alone resulted in the loss of metallic luster. 50% of the surface had developed corrosion products after 672 h. Samples exposed to NaCl alone showed significantly larger mass gain than samples exposed to only SO_2. The combination of SO_2 and NaCl resulted in the largest mass gain (fastest corrosion rate). While the rate of mass gain was highest with a combination of SO_2 and NaCl, the pitting observed in the presence of NaCl alone was significantly reduced. O_3 was found to slightly increase the deposition rate of SO_2, no effect on SO_2 deposition rate was observed for NO_2.	Blucher et al. (2005)
Copper Zinc Steel	Samples were exposed to HNO_3 (50–180 ppb) in a laboratory exposure chamber. Tests were conducted at 65% and 85% relative humidity.	The corrosion effects of HNO_3 on carbon steel were larger than on zinc or copper. The corrosion effect of HNO_3 was found to be larger than corrosion from SO_2 alone or a mixture of SO_2 with O_3 or NO_2. No increase in corrosion was observed at 85% relative humidity compared to 65% relative humidity.	Samie et al. (2007)

E.5.1. Role of NO_Y, NH_X, and SO_X in the Corrosion Process

In the atmosphere the $NO_Y/NH_X/SO_X$ pollutants occur together, along with other pollutants such as O_3 or chloride salts. While wetting of metals surfaces is the single greatest factor promoting corrosion, an important observation is the enhanced damage that occurs due to interactions among this mixture of pollutants. It must be noted that in many studies the various $NO_Y/NH_X/SO_X$ species have not been adequately separated or quantified, and this may be the cause of conflicting observations from some studies. However, some generalizations can be made. Sulfur and chloride pollutants are generally more important at causing metals corrosion than N pollutants, however NO_X (or NO_Y) and SO_2 together have been shown to be more damaging than SO_2 alone. The combination of NO_2 and SO_2 has been shown to result in a synergistic effect where the total damage from the mixture is greater than the additive damage from the two pollutants separately (Svensson and Johansson, 1993a). This effect may be due to enhanced wetting of the surfaces caused by NO_Y pollutants, resulting in corrosion at lower relative humidities than would otherwise be the case. This enhancement has been attributed to the formation of hygroscopic nitrate salts, but may also be caused directly by the deposition of gaseous HNO_3 onto the surface (Dubowski et al., 2004). The corrosion effect of HNO_3 on zinc, copper, and steel is larger than that of SO_2 alone or a mixture of SO_2 and NO_2 (Samie et al., 2007).

Although deposition of $NO_Y/NH_X/SO_X$ species in particulate matter can soil metal surfaces, such deposition does not directly result in substantial metals damage. However, under wet conditions these soluble species form an electrolytic solution that can cause corrosion. Corrosion of steel and zinc has been found to depend on the surface electrolyte irrespective of the presence of particles (Askey et al., 1993).

Temperature has been found to have a complex effect on metals corrosion. Lower temperatures tend to increase surface wetness, but decrease the diffusivity of gaseous pollutants, and may reduce the

rates of some reactions that convert SO_2 and NO_X to sulfuric and nitric acids. Thus, the effect of temperature changes on long-term corrosion rates can be hard to predict.

E.5.2. Effect on Economically Important Metals

Steel is the most common and economically important structural metal, and is often used in galvanized form (i.e., with a protective coating of zinc). SO_2 is generally reported to be more corrosive than NO_X, however for well-protected steel the effects of ambient air pollutants are usually a small increment on top of the natural weathering process. The N pollutants can have an enhancing effect on the corrosion caused by the S pollutants. This is attributed to the increased wetting that can result from the presence of hygroscopic NO_3 salts. Relative humidity has been shown to be very important in the corrosion of steels by SO_2 with much slower corrosion rates observed when the relative humidity is below 70% (Dehri et al., 1994). The presence of SO_2 has been shown to reduce the corrosion pitting of iron induced by sodium chloride (NaCl) but there may be an overall synergistic effect among SO_2, NO_2, and NaCl (Weissenrieder et al., 2004). Steel corrosion rates have been shown to decrease over time (Almeida et al., 2000; Damian and Fako, 2000) approaching steady state rates after approximately 4000 days (Damian and Fako, 2000).

Zinc corrosion has been shown to be inversely dependent on temperature (Svensson and Johansson, 1996). Corrosion products formed on zinc in polluted environments are less water soluble, and therefore more protective against further corrosion, than corrosion products formed in clean environments (Vilche et al., 1995). The combination of SO_2 and NO_2 showed synergistic (i.e., greater than simply additive) corrosive effects on zinc (Svensson and Johansson, 1993a). SO_2 slowed the $NaCl^-$induced corrosion of zinc while NO_2 accelerated that corrosion (Svensson and Johansson, 1993b).

Aluminum is naturally protected from corrosion by a formation of a durable surface film, but some effects of the $NO_Y/NH_X/SO_X$ pollutants have been observed. Minimal damage is caused to Al by NO_X. The mixture of SO_2 and NO_X is variously said to be either more or less corrosive to Al than SO_2 alone. The deposition rate of SO_2 to Al was shown to increase in the presence of O_3, but no effect on SO_2 deposition rate was found for NO_2 (Blucher et al., 2005). Interaction between SO_2 and NaCl results in an increased corrosion rate but decreased pitting of Al compared to NaCl alone (Blucher et al., 2005). Oesch and Faller (1997) found that SO_2 is more corrosive to Al than NO_2 and that there is no difference in Al corrosion rate when exposed to NO or clean air.

Mixtures of NO_X and SO_2 are more corrosive to copper than either pollutant alone. When hydrogen sulfide (H_2S) and O_3 were also evaluated for damage to copper, they also were found to be more damaging to copper than NO_X. The corrosion rate of copper exposed to SO_2 or NO_2 has been shown to slow over time (Leuenberger-Minger et al., 2002; Oesch and Faller, 1997). The corrosion rate of copper in the presence of NO_2 is greater than in clean air. In the first 24 h of exposure to NO_2, an acidic electrolyte is formed on the surface that dissolves copper oxides and results in an increased corrosion rate (Dante and Kelly, 1993). Synergistic effects have been seen between SO_2 and O_3 (strong) and NO_2 (weak) (Aastrup et al., 2000). High corrosion rates were observed for field exposures of copper at sites with a combination of SO_2 and O_3. After four years of exposure, 90% of the corrosion products formed on copper remained on the surface (Leuenberger-Minger et al., 2002). The copper hydroxy sulfates brochantite and antlerite are stable copper corrosion products formed in the presence of SO_2, O_3, and NO_2 (Strandberg, 1998).

Nickel is also damaged more severely by SO_2 or chloride salts than by NO_X. Nickel samples deployed at urban, industrial, and rural sites showed that corrosion rates increase with SO_2 concentrations. Soluble hydrated nickel sulfates were the main corrosion products and are easily removed from the surface by rainfall events, thereby exposing the underlying surface (Jouen et al., 2004).

Kim et al. (2004) conducted a study of the effects of ambient SO_2 and NO_2 on steel, bronze, copper, and marble at sites in China, Korea, and Japan. Both sheltered and unsheltered samples were exposed with the corrosion rates of the unsheltered samples higher in all cases. The corrosion rate of steel was the highest, followed by marble, bronze, and copper. Higher corrosion rates (especially for unsheltered samples) were found to be correlated with high SO_2 concentrations.

E.5.3. Effects on Electronics

The increasingly wide penetration of electronic devices into daily life offers greater opportunities for environmental damage to sensitive components. The hardware of communication systems may be exposed to pollutants in outdoor air, and the ubiquitous cell phones may be exposed in both indoor and outdoor environments. Sulfur and N oxides have been shown to corrode the metallic contacts in electronic equipment, which are often made of copper or brass coated with a precious metal such as gold, palladium, or nickel. Such materials are corroded more by NO_2 than by SO_2, but a mixture of these two pollutants is more corrosive than either alone. The combination of SO_2 and H_2S is also less damaging than either NO_2 alone or a combination of NO_2 and these pollutants. NO_2 is also moderately corrosive to solder in electronic components.

E.6. Effects on Paints

Painted surfaces are extremely common as a means of preventing damage to other materials, and may be categorized as architectural coatings (e.g., house paint), product coatings (e.g., automobile finishes), and special-purpose coatings (e.g., bridge paint). Environmental damage to painted surfaces is expected, and periodic repainting is normal, but any factor that causes more rapid degradation or discoloration of paints will require more frequent repainting and thus result in higher costs. Paint formulations may differ widely for different applications, so the extent of air pollution damage in a given application cannot necessarily be predicted from published information. Previous work at elevated pollutant concentrations has shown that oil-based house paint is readily damaged by SO_2 and moisture, and is more subject to damage by SO_2 than by NO_2. Sample weights increased with increasing NO_2, but it is not clear if this indicates direct reaction of NO_2 or an enhancement of the effects of SO_2 and moisture by NO_2. The effect of SO_2 may be due to reaction with $CaCO_3$ and zinc oxide (ZnO) present in the paint. Tests with various paints showed that NO_X becomes incorporated into the paint surface upon long exposure, apparently by reaction with polymers that make up the cured paint. In other tests HNO_3 was found to produce substantially more damage to paints containing both low and high levels of carbonate (CO_3^-) than did an equal mixing ratio of NO_2.

Grosjean et al. (1994) studied the fading of colorants on cellulose paper. Twelve colorants were exposed to various atmospheres including purified air, NO_2, SO_2, and a mixture of oxidants (O_3, NO_2, and peroxyacetyl nitrate [PAN]). Not all colorants were tested in each atmosphere. The mixture of oxidants resulted in the largest color change for each tested colorant. Only one colorant was exposed to SO_2, NO_2, and the mixture. For that colorant, the color change induced by the mixture of oxidants was approximately three times the color change with NO_2 alone; the color change with SO_2 was approximately 70% of the color change with NO_2. An increase in relative humidity results in increased fading of colorants (Grosjean et al., 1993, 1994). Of 35 colorants exposed to a mixture of O_3, NO_2, and PAN, nine exhibited substantial color changes and three exhibited moderate color changes (Grosjean et al., 1993).

Paint samples were exposed to UV light, NO_X, SO_2, and a combination of the treatments by Colombini et al. (2002). The exposure conditions were chosen to produce accelerated aging of paint samples. Non-pigmented paints were chosen to isolate degradation of the paint binder from synergistic effects with pigments. Exposure to the combination of treatments resulted in increased cross-linking in the paint binder as well as formation of organic acids. An examination of paint samples taken from naturally aged paintings confirmed the presence of organic acids as degradation products.

E.7. Effects on Stone and Concrete

The effects of NO_Y/NH_X/SO_X air pollutants on stone and concrete are undoubtedly the most widely studied because of their impact on historic buildings, monuments, and archeological treasures. Table E-2 summarizes studies of the effects of NO_Y/NH_X/SO_X on stone, concrete, and mortars. Calcareous stone (i.e., that consisting of $CaCO_3$, such as marble, limestone, and cement) is most susceptible to damage. Mortar used in stone construction is often more porous than calcareous stone, and therefore more subject to damage. The damage to such materials is attributed primarily to the effect of SO_2 in forming gypsum ($CaSO_4 \cong 2H_2O$):

$$CaCO_3 + SO_2 + 2H_2O \longrightarrow CaSO_4 \cdot 2H_2O + CO_2$$
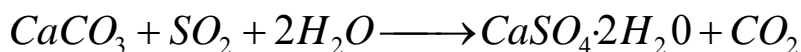
The gypsum thus formed occupies a larger volume than the original carbonate, so the stone surface becomes pitted and damaged. Gypsum is also more soluble than the carbonate, so it can be removed by precipitation, exposing the surface to further reaction and damage. As a result, dry deposition of SO_2 to the stone surface between rain events is important, as it causes continued damage. The reaction of SO_2 with calcareous stone is more energetically favorable than the reaction of N oxides, and thus SO_2 is the primary cause of damage to stone, however the combination of SO_2 and NO_X is more damaging than SO_2 alone. This effect may be due to enhanced wetting of the stone, to oxidation of SO_2 by the N oxides, or to formation of calcium nitrate ($Ca(NO_3)_2$), which is much more soluble than $CaCO_3$ and is easily washed off the stone surface by precipitation. Removal of the nitrate salts in this way may result in underestimation of the role of N oxides in stone damage when surface layers are analyzed for chemical composition.

Table E-2. Studies on corrosive effects of $NO_Y/NH_3/SO_X$ on stone.

Materials	Exposure Conditions	Comments	Reference
Marble	Laboratory exposure to HNO_3 ranging from 54 to 4174 $\mu g/m^3$ (21 to 1603 ppb). Field exposures were conducted in several stages in Greece. Avg concentrations for field exposures were 1.41 $\mu g/m^3$ (0.5 ppb) HNO_3, 2.39 $\mu g/m^3$ (3 ppb) NH_3, 4.84 $\mu g/m^3$ NO_3^-, 14.61 $\mu g/m^3$ SO_4^{2-}, and 5.01 $\mu g/m^3$ NH_4+.	Marble was found to be a very good sink for HNO_3. The extent of corrosion by sulfates and nitrates were found to be of the same order of magnitude. Corrosion was found to be caused by acid and salt species (HNO_3, H_2SO_4, etc.) on the surface rather than the oxides (SO_2, NO_X).	Sikiotis and Kirkitsos (1995)
Limestone	Samples of differing thickness were exposed in the field and runoff water collected for 5 mos. The avg SO_2 concentration was 60 $\mu g/m^3$ (23 ppb).	Damage functions were developed to try to determine the ionic sulfate content in runoff water from the ambient SO_2 concentration. It was determined that the ambient SO_2 concentration alone does not determine the sulfate concentration in runoff water.	Torfs and van Grieken (1996)
Marble	Laboratory exposure to 10 ppm of SO_2 and NO_2. Field exposure to either dry deposition or dry and wet deposition in Louisville, Kentucky. Avg concentrations of 10 ppb SO_2 and 25 ppb NO_2 for field exposures.	Gypsum crust thickness of 1.9 μm for rain sheltered samples after 1 year of exposure. SO_2 was found to be the dominant factor in crust formation. Surface recession due to rain washing was 14.5 $\mu m/yr$ and due to dissolution of the gypsum crust as well as dissolution of the original marble.	Yerrapragada et al. (1996)
Marble Brick	Samples exposed in the field for 8 days with multiple fog episodes. Over 3 measurement campaigns, the mean pollutant concentrations were 17.2 $\mu g/m^3$ (7 ppb) SO_2, 265 $\mu g/m^3$ (139 ppb as NO_2) NO_X, and 131 $\mu g/m^3$ suspended particles.	For all samples, gypsum was the only stable mineral formed following exposure to fog water in a polluted environment. Exposure to fog water may be a significant cause of corrosion for materials sheltered from rainwater, but is of lesser importance if a material is exposed to rain.	Del Monte and Rossi (1997)
Marble Limestone Mortars	Samples were exposed to urban environments in both sheltered and unsheltered configurations. Pollutant concentrations were not reported.	Sulfation was the primary damage mechanism and was more intense on mortars than on stones due to higher porosity. Higher concentrations of degradation products were found on samples sheltered from rain than on samples exposed to rain.	Zappia et al. (1998)
Jaumont limestone	Samples were exposed to 340 $\mu g/m^3$ (125 ppb) SO_2 and 98 $\mu g/m^3$ (50 ppb) NO_2 in the laboratory. Samples were either exposed naked or sprinkled with fly-ash particles. Field exposure was conducted for 1 year with samples sheltered from rainwater. Avg SO_2 concentration during the field exposure was 107 $\mu g/m^3$ (40 ppb).	Sulfation (gypsum formation) was found to proceed with greater intensity for samples sprinkled with fly-ash than for naked samples. The growth of gypsum crystals fixed the fly-ash to the surface of the limestone. Fly-ash was found to be an important factor in crust formation by facilitating gypsum crystal formation. Fly-ash particles also darken gypsum crusts from gray to black.	Ausset et al. (1999)
Calcium carbonate	Powdered calcium carbonate was exposed to 10 ppm SO_2 and 90% relative humidity for 124 days.	Reaction between calcium carbonate and SO_2 was found to take place in a liquid film on the calcium carbonate surface. The presence of several different types of airborne particles was found to increase the extent of sulfation by 20%. The SO_2 concentration used is unrealistic for ambient conditions.	Boke et al. (1999)
Mortars	A wide range of mortar and plaster samples were collected from sites throughout Europe. Pollutant concentrations over the life of the buildings were not reported.	Sulfation was the primary damage mechanism observed. Sulfite was found as an intermediate damage product in the sulfation process. Ettringite was also found as a secondary damage product due to a reaction between gypsum and calcium aluminum hydrates.	Sabbioni et al. (2001)

Materials	Exposure Conditions	Comments	Reference
Mortars	Plaster and mortar samples were collected from buildings in the Old Venice Arsenal. Pollutant concentrations over the life of the building were not reported.	Gypsum was found to be the primary damage product on all of the mortars sampled. A secondary damage mechanism was found where gypsum reacts with calcium aluminum hydrates to form ettringite, an insoluble sulfate. The presence of sulfur in the damage products indicates SO_2 as the most aggressive atmospheric pollutant toward mortars.	Sabbioni et al. (2002)
Concrete	Samples were collected from the interior of a tunnel in Italy. The tunnel formerly held a railway and currently houses a road with heavy automobile traffic. SO_2 levels have declined from 350 µg/m^3 (132 ppb) in 1970 to ~10 µg/m^3 (4 ppb) in 2002. NO_X concentrations have remained relatively constant around 100 µg/m^3 (52 ppb as NO_2) over the same time period.	The urban mixture of pollutants (SO_2, NO_X, CO_2, and particles) results in formation of dendritic crusts on concrete. Nitrates were found to be present in the largely gypsum crusts. Soot particles were found embedded in the crusts as well. Low quality starting materials provide a more porous media that is more susceptible to degradation by atmospheric pollutants. The degradation of concrete is more similar to that of sandstone than of limestone.	Marinoni et al. (2003)
Marble	Samples exposed to atmosphere and sheltered from rain at 4 sites. SO_2 concentrations ranged from ~2 to 20 ppb across the sites.	Sulfation was the primary damage mechanism observed. Marble containing dolomite was less sensitive to SO_2 than calcite marble. For relative humidity greater than 72%, humidity was an important factor in determining the sulfation rate.	Lan et al. (2005)
Limestone Sandstone	Samples were collected from 3 facades of a historical building in Spain. Samples were collected from the surface as well as 5 mm below the surface to determine degradation and original compositions, respectively. Pollutant concentrations over the life of the building were not reported.	The main decay products on the surface were found to be nitrate compounds. Samples with black crusts on the surface were found to have predominantly gypsum and soot, but nitrate compounds were identified in the crusts as well. Sandstone samples were much more damaged than limestone samples due to their higher porosity.	Martinez-Arkarazo et al. (2007)

Concrete is more susceptible to damage from N oxides than are the calcareous stones, because concrete contains calcium hydroxide ($Ca(OH)_2$), which can react to form calcium nitrate ($Ca(NO_3)_2$). This product is soluble and can be washed out of the concrete, weakening the material.

Deposition of particulate matter onto stone primarily results in soiling of the stone, due to the elemental carbon and organic compound content of the deposited particles. The orientation of the surfaces and size of the particles affect deposition: vertical surfaces are more affected by deposition of fine particles, whereas horizontal surfaces are more affected by large particles. The fine particles carry the bulk of the carbon and organic material. Metal oxides present in deposited particles may enhance the reaction of SO_2 to form gypsum.

Gypsum crusts form more readily in rain-sheltered environments than on rain-washed stone surfaces (Zappia et al., 1998). The presence of fog water has been shown to increase the rate of gypsum formation on surfaces sheltered from rain washing (del Monte and Rossi, 1997). Gypsum crust formation has been shown to proceed at a faster rate when the stone surface is sprinkled with fly-ash particles. In addition, fly-ash (or other carbonaceous particles) can become entrained in the gypsum matrix and affixed to the stone surface. Normally, gypsum crusts are gray in color, but when carbon containing particles are entrained, they become black (Ausset et al., 1999). While gypsum crusts are composed primarily of sulfates, they have been found to contain nitrate compounds as well (Marinoni et al., 2003; Martinez-Arkarazo et al., 1999). The inclusion of nitrates in gypsum crusts suggests that N oxides, as well as SO_2, play a role in the degradation of stone exposed to the atmosphere. The presence of particulate matter, in addition to SO_2, has been shown to increase gypsum formation by 20% (Böke et al., 1999). Ambient SO_2 concentrations alone are not adequate to predict the degree of damage to stone samples (Torfs and Van Grieken, 1996).

Dolomite has been shown to be less sensitive to sulfation than calcite (Lan et al., 2005). Corrosion of marble due to S species has been found to be of the same order of magnitude as that caused by N species. Damage is caused not by the gas phase oxides (SO_2, NO_2, NO) but by acid (H_2SO_4, HNO_3) and salt (SO_4^{2-}, NO_3^-) species present in the electrolyte which forms on the marble surface (Sikiotis and Kirkitsos, 1995). The rate of marble surface recession by rain washing is faster than the rate of gypsum crust formation due to dry deposition of S and N containing pollutants. Marble is damaged by rain washing through two mechanisms, dissolution of the gypsum crust and dissolution of the underlying marble. The gypsum crust is more soluble in water than marble and is rapidly dissolved in rain. The naturally occurring acidity in rainwater from the dissolution of carbon dioxide (CO_2) is an important mechanism by which stone samples are degraded, but additional acidity from the dissolution of SO_2 and NO_2 in rainwater does not greatly increase the solubility of marble in rainwater (Yerrapragada et al., 1996).

While gypsum is the primary degradation product found on stone, mortar, and concrete samples, other damage products do occur. Sulfite species have been found on mortars as intermediate damage products. On mortars, a secondary damage mechanism exists in which gypsum reacts with calcium Al hydrates present in the mortar to produce ettringite ($3CaO \cong Al_2O_3 \cong 3CaSO_4 \cong 32H_2O$). Ettringite is an insoluble sulfate that may cause damage by expansion and lead to cracking of mortars (Sabbioni et al., 2001, 2002).

E.8. Effects of NO_X on Paper and Archival Materials

The cellulose fibers that make up paper are reactive with NO_2 and other NO_Y species, and storage condition standards have been set regarding accepTable levels of NO_X for archives, libraries, and museums. Exposure of archival materials to NO_Y species in such facilities can arise from normal outdoor or indoor sources, but also from generation of such NO_Y species from the materials themselves. Specifically, stored materials that include cellulose nitrate, e.g., in the form of photographic film, adhesives, or recording media, can slowly decompose to release NO_X and product species such as HNO_3. These emissions can degrade archival materials, and even be a safety hazard if allowed to accumulate. In terms of outdoor air pollutants, it is likely that HNO_3 is a key reactant in the degradation of paper archives. The rapid deposition velocity of HNO_3 and the numerous surfaces in archival facilities provide opportunity for attack by HNO_3, and probably result in the effects of HNO_3 being underestimated, relative to those of NO_X, based on indoor air measurements. Artists' pigments can also be damaged by extended exposure to ambient atmospheric NO_2.

The effects of SO_2 and O_3 on paper were studied by Johansson and Lennholm (2000). The deposition rate of SO_2 to fresh paper was found to decrease rapidly with time and approached steady state after ten hours. The deposition rate of SO_2 to fresh paper in the presence of O_3 was found to be elevated compared to SO_2 alone. The deposition rates to aged paper were much lower and there was no effect on the SO_2 deposition rate observed in the presence of O_3. The decrease in deposition rate with time is thought to be due to protonation of all available carboxylate ions to carboxylic acid.

Pigments in works of art can be degraded or discolored by atmospheric pollutants. H_2S has been shown to react with both copper and lead pigments, but only lead white has been seen to darken over time (Smith and Clark, 2002). A synergistic effect has been detected between NO_2 and both benzene and toluene resulting in an increased rate of attack on pigment oxides (Agelakopoulou et al., 2007). Deposition of S to the surface of paintings, either as SO_2 or ammonium sulfate ((NH_4)$_2SO_4$) particles, can damage, varnish, or cause discoloring of paint (Gysels et al., 2004). Paint models subjected to accelerated aging in SO_2 (10 ppm) and NO_X (10 ppm) as well as UV radiation for 15 days exhibited a variety of

damage markers. Both nitrate and sulfate damage mechanisms were observed with sulfation sometimes masking other processes (Arbizzani et al., 2004).

E.9. Costs of Materials Damage from NO_Y, NH_X, and SO_X

Materials exposed to the ambient atmosphere are degraded and damaged through a number of mechanisms. Damage associated with air pollutants result in effects such as decreased usable lifetime, increased maintenance frequency, and loss of aesthetic appeal. It is difficult to separate the costs associated with air pollutants from costs associated with other damage mechanisms. Some estimates of cost have been based on empirically derived dose-response functions for specific materials. Other estimates have been developed using inspection of actual materials damage and maintenance guidelines for the materials (Cowell and Apsimon, 1996). Estimation of costs over large geographic areas is subject to considerable uncertainty due to unknown distribution of materials at risk and spatial variations in pollutant concentrations. A cost estimate for material cost savings from SO_2 emission reductions in Europe was performed by Cowell and Apsimon (1996). In this study, the cost savings of theoretical future emission reductions across Europe was modeled using cost data extrapolated from a study conducted in three Norwegian cities. Total theoretical SO_2 reductions of 15,904 kilotons per year resulted in modeled annual cost savings of $9,504 million total for Europe (Apsimon and Cowell, 1996).

E.10. Summary

Many types of materials, including metals, electronics, plastics, paints, stone, and paper may be damaged by atmospheric NO_Y/NH_X/SO_X species. Damage occurs due to dry and/or wet deposition of the pollutants onto the surface of a material and subsequent formation of an electrolytic solution in water present on the surface. At low relative humidity, when little water is present on surfaces, damage rates have been observed to be much lower, and in some cases, no damage has been observed. Both SO_2 and NO_2 have been implicated in damage processes for different materials. In general, damage to materials by SO_2 is greater than by NO_2. Little work has been conducted to investigate the effects of NO on material damage. What work has been conducted shows no damage, or very minor damage for NO containing environments compared to clean air. Synergistic effects between SO_2 and NO_2 lead to increased damage rates for the gases in combination. Other species such as O_3, NaCl, organics, or particulate matter have also been shown to have synergistic effects with SO_2 and NO_2. The corrosive effects of nitric acid have been found to be stronger than effects of other NO_Y/NH_X/SO_X species. Costs associated with damage to materials by atmospheric pollutants are difficult to estimate because of the many sources of uncertainty in the estimation process. For heavily polluted environments, the cost savings due to decreased rates of material degradation could offset a significant portion of the costs to reduce emissions. In general, for polluted environments, reductions in SO_2 or HNO_3 concentrations will reduce damage rates more than reductions in NO_2, NO, or NH_3. In areas with low SO_2 concentrations, reductions in NO_2, O_3, or particulate matter concentrations may reduce damage rates.

Annex F. Valuation of the Environmental Effects of N and S (non-materials)

F.1. Introduction

The monetary valuation of ecological effects associated with NO_X and SO_X emissions starts with natural science endpoints. These may be things that people value directly, such as loss of a particular species, or some remote effect on a resource that is not clearly understood by the general public or not valued by the public for itself, such as forest soils. Of course, damage to forest soils will affect the terrestrial ecosystem in ways that may be valuable to humans, such as tree growth, habitat, and even the aesthetics of the forest. This Annex is a review of the literature that estimates such values for various ecosystem endpoints or that provide values for effects that can be reasonably inferred from what is provided.

The purpose of this Annex is to provide an assessment of the economics literature on the effects of NO_X and SO_X emissions on terrestrial, transitional, and aquatic ecosystems.

F.1.1. Valuation in the Context of NO_X and SO_X

Figure F-1 provides a schematic representation of how economic valuation is derived from changes to NO_X and SO_X secondary standards. Starting at the upper left-hand side, the NO_X and SO_X standards are set and emissions reductions occur to change the ambient concentrations of NO_X and SO_X. Reading down from "Change in Ambient Concentrations," these reductions will lead to changes in a variety of ecological endpoints (as identified in the ISA) in terrestrial, transitional, and aquatic ecosystems. The box below, "Change in Economic Endpoints," refers to physical endpoints that people care about, in which changes can be valued (at least in principle) in monetary terms. Many times, these are referred to as ecosystem services. In a few cases, such as agricultural crop growth and yield, ecological and economic endpoints are nearly the same. Finally, at the bottom of this diagram is a box labeled "Valuation Methods," which notes alternative approaches for placing monetary values on these economic endpoints. As endpoints are discussed in detail in the ISA, this Annex focuses solely on valuation.

F.1.1.1. Ecosystem Services

Broadly defined, ecosystem services are the benefits that people obtain from ecosystems (Millennium Ecosystem Assessment, 2003). In the Millennium Ecosystem Assessment (MA), ecosystem services are classified into provisioning, regulating, supporting, and cultural services. Provisioning services denote the products people obtain from ecosystems; regulating services are associated with the ecosystem functions that regulate climate, nutrient cycle, water filtration, and so forth; supporting services are ecosystem functions, such as primary productivity and production of O_2, that support the provision of ecosystem services; and cultural services are the non-material benefits ecosystems provide to people through spiritual enrichment, cognitive development, reflection, recreation, and aesthetic experiences.

Ecosystems are productive systems in which various biological and physical factors, as well as their interactions, serve various functions in the production of ecosystem services. However, economic valuation of the environment has focused mostly on the contributions of individual goods and services to

human well-being. Alternately, ecosystem services valuation is based on the various benefits generated by the ecosystem (Polasky et al., 2005). In this case, benefits include both marketed and non-marketed services, and their valuation considers the environment as a natural capital asset that generates returns on investment in ecosystem protection and management.
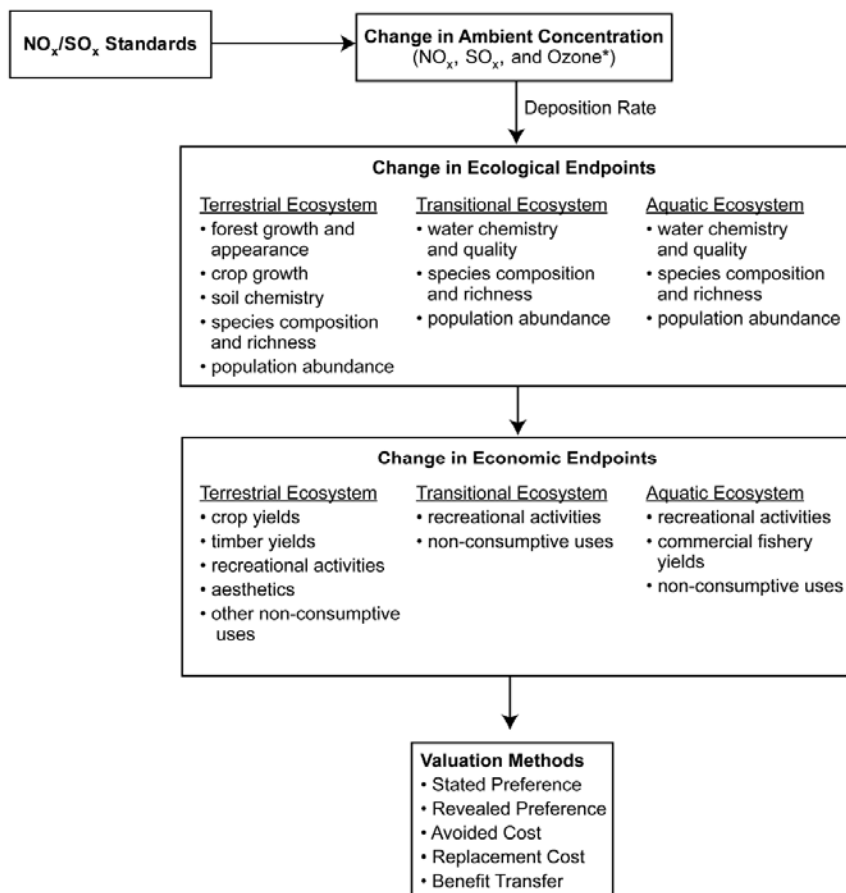
Figure F-1.   Illustration chart of the assessment.

For example, wetlands constitute a form of natural capital. They serve as flood barriers, soaking up excess water and slowing and preventing floodwaters from spreading uncontrollably. Wetlands help replenish groundwater and improve both ground and surface water quality by slowing down the flow of water, and absorbing and filtering out sediments and contaminants. They also provide spawning habitat for fish, supporting the regeneration of fisheries. In addition, wetlands provide habitat for many wildlife species and support commercial and sport fishing, as well as hunting and other forms of recreation.

Though different functions and processes of ecosystems, such as water filtration, may be economically important, they need to be viewed as inputs of or mechanisms for the production of economically valuable services, such as drinking water, timber, or recreational benefits. The end products, not the elements of the production process, ultimately generate economic well-being. Along these lines, Boyd and Banzhaf (2007) advocate defining ecosystem services as "components of nature, directly enjoyed, consumed, or used to yield human well-being." In other words, ecosystem services are the end products of nature to which ecosystems contribute as intermediate inputs or production technologies. Though this distinction may at first seem unimportant, it is crucial for the accurate valuation of ecosystem

services. Regarding the incorporation of ecosystem services into the measurements of national income and the value of goods and services produced in an economy, such as gross domestic product (GDP) accounts, Boyd and Banzhaf (2007) note that if intermediate and final goods are not distinguished, the value of intermediate goods is double-counted because the value of intermediate goods is embodied in the value of final goods. For example, clean drinking water, which is consumed directly by a household, is dependent on a range of intermediate ecological goods, but these intermediate goods should not be counted in an ecosystem service welfare account. Also important is that ecosystem services are attributed only the incremental value they contribute to the production of valuable end products. Using the above example, the value of ecosystem services associated with drinking water denotes the marginal contribution of ecosystems in the production of drinking water, not the full value of the final product.

If intermediate and final goods are not distinguished, the value of intermediate goods is double-counted because the value of intermediate goods is embodied in the value of final goods. For example, clean drinking water, which is consumed directly by a household, is dependent on a range of intermediate ecological goods, but these intermediate goods should not be counted in an ecosystem service welfare account. Also important is that ecosystem services are attributed only the incremental value they contribute to the production of valuable end products. Using the above example, the value of ecosystem services associated with drinking water denotes the marginal contribution of ecosystems in the production of drinking water, not the full value of the final product.

Given the complexity and variety of ecosystems and their services, their valuation poses several challenges. According to the National Academy of Sciences' Committee on the Valuation of Ecosystem Services, the importance of ecosystem functions and services is often taken for granted and overlooked in environmental decision making. Moreover, the key challenge in the valuation of ecosystem services lies in the difficult integration of economic valuation and ecological production theory. This is no straightforward task, because many ecosystem goods and services are not quantifiable using available methods, and the application of economic valuation methods may be subject to judgment, uncertainty, and bias (Heal et al., 2005).

A study by Costanza et al. (1997), seeking to determine the value of global ecosystem services, exemplifies the problems and pitfalls in the valuation of ecosystem services. Deriving and summing value estimates from the existing literature for a wide range of ecosystem attributes and services, this study suggested that the total value of global ecosystem services likely ranges from $16 to $54 trillion annually, or roughly one to three times global GDP. The study has been influential and widely quoted and used, especially among scientists and environmentalists. Economists consider it fundamentally problematic both conceptually and methodologically, preferring to focus on the value of changes to ecosystem services, which is relevant for policy, or what is termed the marginal value of ecosystem services. The estimate of the value of global ecosystem services by Costanza et al. (1997) has therefore been characterized as a "serious underestimate of infinity" (cf. Smith, 2007; Toman, 1998).

F.1.1.2. Use of the Valuation Literature to Define Adversity

A secondary standard, as defined in Section 109(b)(2) of the CAA, must "specify a level of air quality the attainment and maintenance of which, in the judgment of the Administrator, based on such criteria, is required to protect the public welfare from any known or anticipated adverse effects associated with the presence of [the] pollutant in the ambient air." One way to quantify adverse effects is through monetary valuation.

Adversity is difficult to quantify and measure, and there are several challenges to using a monetary valuation approach. A major effect that is geographically extensive might be considered to be more adverse than a more severe effect limited to one geographic location. Another problem is aggregation. Any change in pollution may have multiple effects (i.e. effects on many types of ecosystem services) leading to difficulty in aggregating in a consistent way.

Monetary values on any service or resource degradation reflect human preferences about what is a severe effect. Larger unit values correlate with more severe effects, other things equal. Also, more extensive effects, will contribute to larger welfare loss (or gain). In addition, since monetary units can be added, the aggregation issue can be addressed by "simply" summing the welfare losses (or gains). Although this is not strictly true (e.g., values for improvements in water quality and fish populations may not be additive), in principle the differences in how people conceptualize ecosystem improvements can be captured in the way resource improvements are valued in monetary terms.

Clearly, there are many practical problems associated with using monetary value as a way of defining adversity. First, many resources and services have not been valued and efforts to credibly transfer the results of valuation studies to other areas and resources have been minimal. Second, studies addressing multiple effects are particularly difficult to transfer and few in number. Finally, even with the first two problems addressed, a judgment would still need to be made on whether the air quality standard was the contributing factor for eliminating adverse (highly monetarily valued) effects.

F.1.1.3. Methods for Selecting Literature for this Assessment

Assessing the economics literature on the effects of NO_X and SO_X emissions on terrestrial, transitional, and aquatic ecosystems requires identifying and reviewing relevant studies addressing these effects. Multiple methods were used for this Annex: searching existing databases of this valuation literature; conducting systematic searches of the economics literature; reviewing a large number of key articles, reports, authors, and journals; and identifying studies based on the expertise and familiarity with the relevant literature of lead researchers.

Two existing databases on environmental valuation studies – the Environmental Valuation Reference Inventory (EVRI) and the Beneficial Use Values Database (BUVD) – were particularly useful for this assessment. The EVRI database, which includes nearly 1,900 valuation articles/studies on environmental and human health effects, was screened according to criteria regarding the potential relevancy of geographical location (U.S.), types of environmental goods and services valued (ecological functions, extractive uses, non-extractive uses, passive uses); and environmental stressor. This resulted in over 200 articles/studies of interest. BUVD is a relatively small database (131 articles/studies), so it was imported into the literature review database in its entirety, with unrelated articles/studies later excluded on an individual basis.

A large number of additional journals and literature databases were identified that publish and cover research potentially relevant to this assessment. The selected peer-reviewed journals[1] and library databases[2] were then reviewed using search engines and a range of key words developed to find studies addressing relevant ecological endpoints (aquatic, transitional, terrestrial) and their economic values. The tables of contents of those journals that could not be searched electronically were reviewed in hard copy and relevant articles were added to the literature review database. These searches were augmented by reviews of the bibliographies of the following EPA reports: *EPA Report to Congress: The Benefits and Costs of the CAA 1990–2010* (U.S. EPA 1999b); *Air Quality Criteria for Ozone and Related Photochemical Oxidants* (U.S. EPA 2006b); *Air Quality Criteria for Particulate Matter* (U.S. EPA 2004).

---

[1] American Economic Review, American Journal of Agricultural Economics, Canadian Journal of Economics, Canadian Journal of Forestry, Contemporary Economic Policy, Ecological Economics, Environment and Development Economics, Environmental and Resource Economics, Environmental Science and Technology, Forest Science, Forestry Chronicle, Journal of Agricultural and Applied Economics, Journal of Applied Econometrics, Journal of Agricultural and Resource Economics, Journal of Agricultural Economics, Journal of Environmental Economics and Management, Journal of Forest Economics, Journal of Forestry, Journal of Political Economy, Journal of Risk and Uncertainty, Land Economics, Marine Resource Economics, Resource and Energy Economics, Review of Agricultural Economics, Review of Economics and Statistics, Water Resources Research.

[2] AgEcon Search, Agricola, BioOne, CSA Illumina, EconLit, GeoRef, Google Scholar, SciSearch/Science Citation Index (Web of Science), SCOPUS, Sportfishing Values Database, SSRN.

The results from these searches were checked for duplicates and clearly irrelevant studies, after which over 500 potentially relevant articles/studies were identified for initial assessment. Relevancy of each study for this assessment was determined according to the following key criteria.

- Does the study address an ecological endpoint sensitive to reductions in NO_X and SO_X emissions?

- Does the study value quality changes in the ecological endpoint, which is actually or potentially attributed to reductions in NO_X and SO_X emissions?

- Is the study peer-reviewed and preferably, published in an academic journal?

- Very few, if any studies fully satisfy all above criteria. For this reason, studies that at least partially satisfy these criteria were deemed potentially relevant for this project. Finally, reviews and meta-analyses were included in the assessment whenever they were available and dealt with potentially relevant ecological endpoints.

In the initial assessment, each record's potential relevancy to the assessment was rated on a scale of 1 to 4, with 1 indicating that the record appears directly relevant to this assessment (the study addresses quality change of an ecological endpoint, which is actually or potentially attributable to NO_X/SO_X). Records rated 2 only partially satisfied the "relevancy criteria," but were considered important to be referenced in this report. Records rated 3 were to be reviewed more closely to determine their usefulness, and those rated 4 were found not relevant for the purposes of this assessment. Because the goal in the initial assessment was to avoid missing potentially relevant studies, borderline cases have been classified to the lower number category.
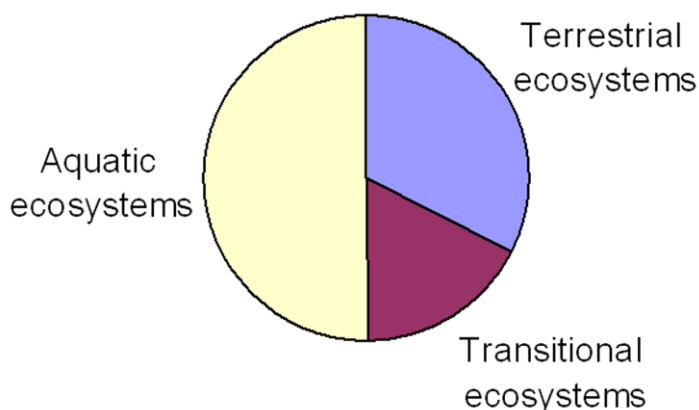
Figure F-2.   Reviewed studies by ecosystem addressed.

All studies rated 1 through 3 were next reviewed using several attributes, including ecological endpoints, valuation techniques, geographical area, use vs. non-use value category, and other details of interest. Of those studies, about half addressed aquatic ecosystems (Figure F-2). The reviewed studies addressed many different ecological endpoints, such as sport fishing, commercial fisheries, aquatic recreation (e.g., swimming and boating), general water quality, ecosystems services provided by aquatic ecosystems, and coral reefs (Figure F-3). Nearly one third of the studies addressed terrestrial ecosystems (e.g., forestry/commercial timber, outdoor recreation, and agriculture); the rest dealt with transitional ecosystems (e.g., ecosystems services provided by wetlands and wetlands recreation).

F.2. Conceptual Framework

F.2.1. Taxonomy of Values for Environmental Goods and Services

The economic value derived by society from these ecological goods and services can be categorized as either "use" or "non-use" values. Use values comprise values for those goods and services that can be used either directly or indirectly. Non-use values denote the characteristics of the ecological goods and services that are not used at all but still hold economic value. The schematic in Figure F-4 illustrates these divisions of values for environmental goods and services.

Direct use values are held for those goods and services which can be directly consumed or utilized by individuals or society. Some direct use goods, such as fish caught or timber cut are sold in markets and thus valued using market data. Other direct uses, such as recreational use of ecosystems for fishing, hunting, and sightseeing, are usually not bought or sold through a market and are therefore more difficult to value. Similarly, changes in their value are more difficult to quantify. Thus, direct use can be subdivided into directly used market and non-market goods or services.
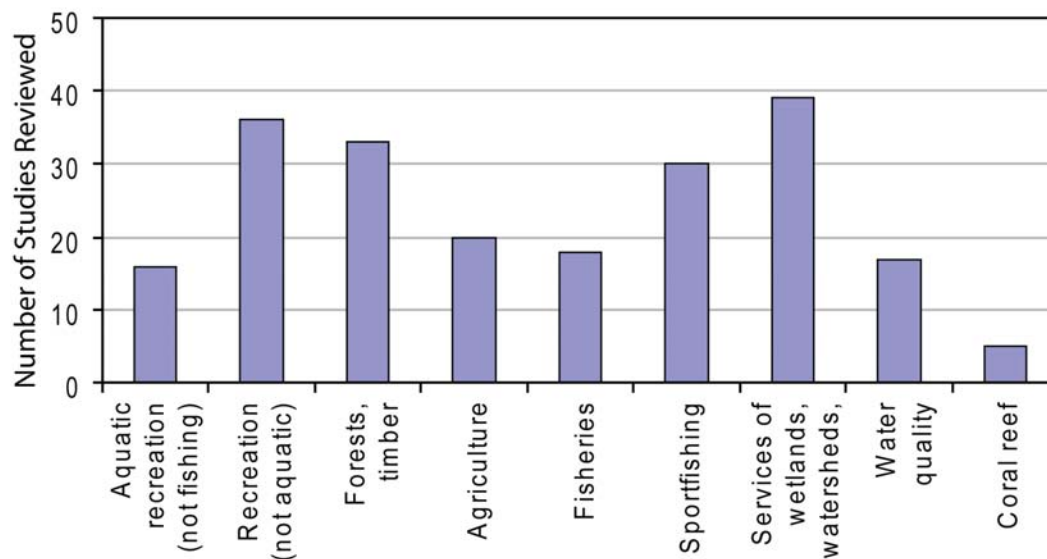
Figure F-3.   Reviewed studies by ecological endpoint.
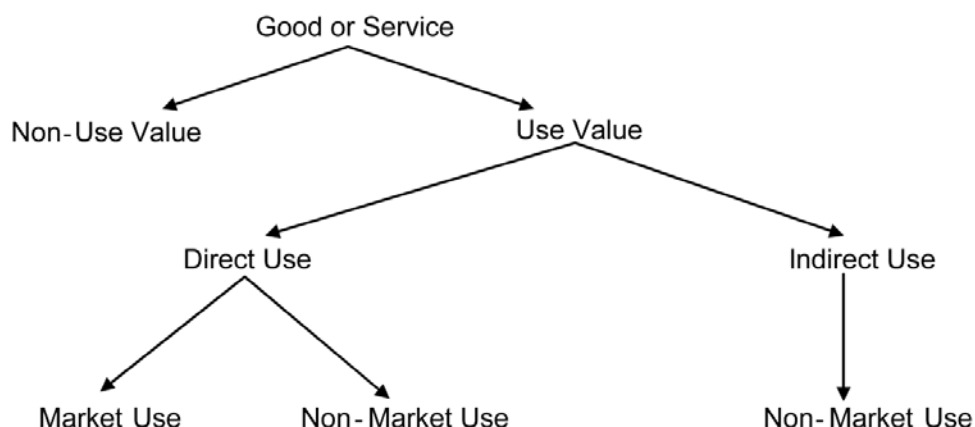
Source: U.S. EPA (2002a).

Figure F-4.   Taxonomy of values for environmental goods and services.

Examples of direct, market uses of ecological goods and services include commercially sold food sources (fish, crops, other animals); building materials (wood, stone); fuel sources (wood, coal, oil); drinking water (groundwater, surface water); chemicals; and minerals (U.S. EPA, 2002a). Examples of direct, non-market uses of ecological goods and services include recreational fishing and hunting; beach use (sunbathing, swimming, and walking); boating; hiking; camping; wildlife watching; and sightseeing (U.S. EPA, 2002a).

Indirect use values capture those ecological services that are not used directly but still provide benefits of economic value to society. These services include flood control, storm water treatment, ground water recharge, climate control, pollution mitigation, wave buffering, soil generation, nutrient cycling, habitat value, and biodiversity (U.S. EPA, 2002a).

Non-use values denote the characteristics of the ecological goods and services that are not used at all but still hold economic value. These non-use values include what are known as existence and bequest values–the value of simply knowing that certain ecosystems exist and of ensuring that they continue to exist for future generations, respectively. These services are also not traded in a market and quantifying their value is a challenge.

Importantly, empirical methods for addressing non-use value generally estimate the total value of a resource. Distinguishing between the use and non-use values often is not possible, and the valuation results including non-use values should therefore generally be considered total valuation rather than non-use valuation studies. Examples of non-use values of ecological goods and services include existence value, cultural/historical value, intrinsic value, bequest value, and altruistic value (U.S. EPA, 2002a).

In this Annex, the focus is on the potential incremental benefit that might be realized from reducing levels of SO_X or NO_X by a relatively small amount, rather than the total value of the affected ecosystems. Therefore, the term "total value" in this Annex generally denotes total marginal benefits that contain both use and non-use values, not the total value of the entire resource. This notation is consistent with the principles of economic valuation of the environment, which generally focus on predicting damages or benefits from marginal changes in environmental conditions.

F.2.2. Welfare Economics

Any environmental goods or services that somehow contribute to human well-being are economically valuable. Their economic value reflects the capacity of the environment to satisfy different human needs, which is related to the direct consumption of different goods and services derived from the

environment. It also includes different indirect, passive, and non-use values for environmental goods and services, such as recreational benefits, enjoyment of natural landscape, purity of air and water, and provision of habitat for species other than humans.

Economic valuation is rooted in the basic principle of consumer sovereignty. Rather than judging whether an individual's choices are right or wrong, each person is considered able to make rational choices that advance his or her well-being, given the possibilities available. The principle of consumer sovereignty extends also to the valuation of environmental goods and services. Even in the absence of markets for environmental benefits, each individual is considered able to assess the importance of changes in environmental quality on personal well-being or, as economists commonly refer to it, utility.

Consumer (CS) and producer surpluses (PS) are the basic monetary measures of well-being (or welfare) in economics. They denote the "excess utility" consumers and producers enjoy when consuming or producing specific goods or services after paying for them. Producer surplus is measured by profit, the value of production after accounting for all costs. Consumer surplus, which is a more subtle concept, can be thought of as the difference between the price and the maximum value that an individual holds for a good or service. However, it generally is not an exact measure of changes in welfare because CS does not fix the baseline level of utility, thereby ignoring the income effects of a changing baseline

CS has two exact (Hicksian) measures: willingness-to-pay (WTP) and willingness-to-accept (WTA). In the context of environmental valuation, WTP denotes an individual's maximum willingness to pay for an environmental good or service. WTA, on the other hand, stands for the minimum compensation an individual is willing to accept to forgo an environmental good or service. Though WTP and WTA both are exact measures of CS, they generally are not equal, meaning that the CS in general does not have a unique measure. WTP and WTA for usual marketed goods and services are similar and within narrow bounds of income effects (Willig, 1976). Similar findings can be expected with environmental goods and services only when they have close substitutes (Hanemann, 1991; Shogren et al., 1994).

Since many environmental goods and services cannot be easily substituted, WTP and WTA are expected to differ, sometimes substantially. In fact, the WTP-WTA divergence can range from zero to infinity, depending on the substitutability of an environmental good and other market or non-market goods (Hanley et al., 1997). Using WTA to measure welfare changes might often be justified on the grounds of economic theory and property rights, but many studies choose to estimate WTP for its practicality. In addition, WTP generally is lower than WTA and therefore is conservative, providing another justification for using WTP for valuing the environment. Finally, both WTP and WTA can be difficult to measure, and valuation studies therefore sometimes estimate the ordinary CS. It approximates WTP and WTA and is between these two exact measures of welfare. In the special case of no income effects, all different measures of consumer welfare coincide.

Various methods have been developed to determine the value of different ecological goods and services by estimating the change in social welfare or WTP for changes in the quantity or quality of a given environmental resource (see Table F-1). Some valuation techniques obtain WTP from observing people's actions (revealed preferences or RP) while others rely on people's responses to hypothetical situations (stated preferences or SP). Yet another set of valuation methods relies on other studies, either by transferring their estimates into another context (benefits transfers) or by conducting statistical meta-analyses of earlier studies to examine their systematic findings. See Section F.2.3 for details about these approaches.

As noted by Kramer et al. (2003), several forest protection valuation studies also considered the sensitivity of contingent valuation estimates to various preference elicitation methods, including dichotomous choice, payment card, and open-ended techniques. Haefele et al. (1992) used payment card and dichotomous choice techniques in a contingent valuation survey measuring the WTP of Southern Appalachian residents for protecting high-elevation spruce-fir trees from exotic insects and air pollution. Estimates for mean WTP were $20.86 per year using a payment card method, and $99.57 per year using a discrete choice method. Sample sizes for each method were relatively small (232 and 236 respondents, respectively). Another limitation concerns the wide span between the two valuation statistics, which

despite a large difference in the mean estimates showed no overlap of the 95% confidence intervals. Similar studies have been performed by Loomis et al. (1996) and Kramer and Mercer (1997).

F.2.3. Benefit Estimation Approaches

Table F-1 introduces different valuation techniques and indicated which type of value (direct use, indirect use, total value) each can be used to estimate. Studies addressing non-use values are referred to in this Annex as total valuation studies. This is because non-use valuation methods in fact generally estimate the total value of a resource, including both its use and non-use components.

Travel cost (including site choice models) and hedonic pricing methods are perhaps the most regularly applied revealed preference (RP) methods for valuing the environment, whereas contingent valuation and choice experiments are the most popular stated preference (SP) methods. One of the key differences between the RP and SP methods is that RP methods can only fully address direct and indirect use values, whereas SP methods are required for the estimation of total values of environmental resources, including their non-use value component.

Travel cost studies predict use values for ecological resources, such as natural parks, by examining individuals' travel expenditures to utilize that resource (most often at a park or some other recreational site), including the opportunity cost of work time missed while traveling to and utilizing the resource. Travel cost studies commonly use a random utility framework, which infers individuals' WTP for an ecological resource (again usually a recreational site) by observing their choice from among one or more alternatives. While the travel cost method uses changes in the quality of one resource to ascertain its value, the random utility model uses individuals' choices among various options of various qualities at various prices to do the same.

Hedonic price studies predict the value of ecological resources by examining their effect on property values. Assuming that all the benefits from living in a specific location and house are capitalized into the market value of the property, hedonic models estimate the independent effects of different housing characteristics on housing prices. Controlling for all observable housing and location characteristics, hedonic pricing models examine environmental values for, for example, proximity to forests or particular watersheds by estimating the implicit incremental price people are willing to pay for that proximity. Hedonic pricing relies on assumptions such as efficiently functioning housing market and perfect information and mobility by individuals. However, because WTP is not necessarily tied to ecosystem changes, this Annex does not consider property values as a method of valuation.

Other market or RP-based approaches to valuing changes in ecological goods and services include the alternative/replacement cost method; avoidance expenditures/averting behavior method; referendum method; user fee method; market price and market simulation method; and a host of different variations of these and other valuation approaches. See, for example, Freeman (2003) for the theory and applications of different methods for valuing environmental quality.

The RP methods have the advantage of gleaning their value estimates from individuals' real world actions. However, because they do not include the non-use value of ecological resources, none of them capture total value. This problem has given rise to the development of a variety of non-market valuation methods that use surveys to elicit preferences for public goods. Because these methods are generally based on eliciting "stated" rather than "revealed" preferences, they are broadly categorized as SP methods.

The contingent valuation method is the most common SP method. It involves developing and administering surveys, in which respondents are presented with a scenario or a program with specified environmental outcomes and costs. Each respondent is asked to indicate approval or disapproval of the proposed environmental scenario and its monetary cost. Researchers vary the proposed costs across different survey respondents and use their choices to estimate how much people on average are willing to pay for different scenarios to improve the environment. Because some of the respondents may use a

public good also for direct enjoyment, say viewing an endangered bird, the surveys actually capture total value for the improvements, rather than just their non-use value.

Choice experiment methods (including contingent ranking, contingent choice, and conjoint analysis) separate an environmental good into its constituent attributes, recombine those attributes into different bundles, and elicit respondents' preferences for those bundles. Often a monetary value can be assigned to those attributes and thus the process allows researchers to determine WTP for the bundle and each attribute. Conjoint analysis usually is performed by choosing the most preferred attribute bundle from a group (choice experiment, contingent choice) or via ranking a series of attribute bundles (contingent ranking). Using conjoint analysis, researchers may be able to simultaneously value various relevant goods or services that an environmental resource provides. For example, improving a public body of water provides improved recreational opportunities, drinking water, and support of aquatic ecosystems.

Valuing the environment as a factor of production monetizes the incremental benefits from using the environment as an input to production. In other words, this method treats the environment as a production input comparable to other raw materials and infrastructure, such as land, capital, labor, and so forth. This method is appropriate for valuing environmental effects that have direct value as a factor of production. Examples of such cases include the effects of water quality on the productivity of commercial fisheries, or the impact of soil characteristics on agricultural productivity. However, this method is limited to market goods and services and can only address their role as part of the production process. This method does not address non-market environmental goods and services or non-use values.

Benefits transfer approaches translate the entire estimated demand function from one application to another. Sometimes the function is adjusted to meet the specific criteria of the target site, and then new WTP value estimates are generated for the environmental good/service at the new site using the demand function. Using the transferred demand function, both changes in the level of use and the unit value benefits for the new site can be estimated (U.S. EPA, 2002a). There are four general types of benefits transfer technique: mean unit value transfer/ adjusted unit value transfer, benefit/demand function or model transfer, meta-function transfer, and structural benefits transfer. The first three methods dominate the literature (Smith et al., 2006b).

Mean unit value transfer/adjusted unit value transfer entails taking the value of a specific environmental good or service (such as recreational hunting), sometimes from a single study of the same good and sometimes estimated by averaging a range of value estimates from various primary studies, and transferring that value to the same good or service at a new site.

Benefit/demand function or model transfer is the translation of the entire estimated demand function from one site to another. Sometimes the function is adjusted to meet the specific criteria of the target site, and then new WTP value estimates are generated for the environmental good/service at the new site using the demand function. Using the transferred demand function, both changes in the level of use and the unit value benefits for the new site can be estimated (U.S. EPA, 2002a). *Meta-function transfer* involves the use of meta-regressions to combine the results of numerous valuation studies and allows researchers to account for influencing factors, thus enabling them to create value estimates for new policy sites. *Structural benefits transfer*, also known as preference calibration, requires selection of a preference model which can describe individual choices over a set of market and associated non-market goods to maximize utility when faced with budget constraints (Rosenberger and Loomis, 2001; Smith et al., 2006b).

Meta-study review provides a useful way of summarizing the literature on the valuation of ecological endpoints from reductions in NO_X and SO_X, though there are few studies exactly on this topic. But there are studies summarizing monetary valuation efforts for particular sets of endpoints, such as the economic valuation of fresh water ecosystem services. Where such studies are available, they are summarized in the appropriate section of this annex.

Even more valuable are **meta-analyses**, which perform statistical analyses of the results of original studies. Such studies explain variation in monetary value estimated for various endpoints using features of the original studies' methodologies as well as the characteristics of the site being studied and other factors.

Smith and Pattanayak (2002) defined meta-analysis as the practice of using a collection of formal and informal statistical methods to synthesize the results found in a well-defined class of empirical studies.

In general, the three uses of meta-analysis are: synthesize or "take stock" of the literature on a particular valuation topic; test hypotheses with respect to the effects of explanatory variables on the value construct of interest; and use the estimated meta-analysis model to predict estimates of the value construct across time and space (Bergstrom and Taylor, 2006). Bergstrom and Taylor (2006) provided a review of the techniques and theory behind the use of meta-analysis for benefits transfer. They noted that to conduct a successful meta-analysis for benefits transfer, it is important to be as comprehensive as possible in terms of the studies to be included. Excluding a study would be equivalent to applying a zero weight to the information in that study. The authors list some additional criteria to be considered when identifying studies for inclusion in a meta-analysis, including controlling for the valuation method and estimated welfare measure, as well as addressing the temporal and spatial scales of the valued commodity.

Extensive evaluation of the relative merits of, and issues with, different environmental valuation methods is not within the scope of this Annex. Vast amounts of research have been conducted to develop and evaluate alternative environmental valuation methods. For example, the Handbook of Environmental Economics recently dedicated an entire 1,100–page volume to addressing methods for valuing environmental changes (Mäler and Vincent, 2005).

The validity of environmental valuation methods is sometimes questioned, in particular that of SP methods. Because survey-based valuation methods are based on what people say rather than what they do, there is a tendency to question the credibility of the results. For this reason, nonmarket valuation researchers, following the lead of the National Oceanic and Atmospheric Administration (NOAA) Expert Panel that reviewed the highly publicized studies valuing damages from the Exxon Valdez oil spill, often build into their surveys a series of validity tests, such as testing for the sensitivity of WTP to the scope of resource being valued (Federal Register, 1993). Additionally, SP surveys are vulnerable to a variety of issues dealing with the design and administration of surveys, as well as analyzing their data (e.g., Carson and Hanemann, 2005).

Though examining actual choices lends credence to RP methods, they are not free of problems. For example, hedonic pricing studies of housing markets rest on the assumptions that the housing market is at equilibrium and that housing choices accurately reflect the attributes of interest, such as air pollution or environmental amenities associated with the residential location. Hedonic studies and other RP studies, such as recreation trip demand analysis, are also susceptible to potential biases. These include the omission of important variables, which may thwart the efforts to accurately value environmental quality.

A number of studies have compared SP analyses with RP analyses, such as hedonic property value studies. Generally, these comparisons have suggested that when similar environmental values are examined, RP methods generally yield somewhat higher value estimates than SP methods. For example, Carson et al. (1996) reviewed over 80 studies which included comparisons of SP and RP methods, and concluded that SP methods are on average about 75% to 90% of corresponding RP values.

F.3. Valuation of Forests and Terrestrial Ecosystems

F.3.1. Use Values

The impacts of NO_X and SO_X can occur over many different terrestrial ecosystems and use-value efforts must look at each of these ecosystems individually. One serious threat to agriculture from NO_X emissions comes from ambient ozone (O_3), which is a byproduct of atmospheric reactions between Volatile Organic Compounds (VOCs) and NO_X. In commercial forests, air pollution effects have not been addressed in economics beyond evaluating the potential effects of O_3. Unlike in agriculture, the scientific

understanding of O_3 effects on trees is more limited and related mostly to visual injury to leaves in young saplings, an indicator that is difficult to link to tree growth in mature forests. However, the valuation of O_3 has already been evaluated in detail in the 2006 O_3 AQCD (U.S. EPA, 2006b), and will not be covered in this Annex or the ISA (see also Tables F-2 and F-3).

Some studies have attempted to specifically measure use values associated with forest quality, without regard to the factor that is altering forest quality. For example, an early study by Leuschner and Young (1978) considered the effects of crown density changes due to insect infestation around 19 lakeside campgrounds in east Texas. A travel-cost model estimated the CS losses from a 10% reduction in crown density to fall between 0.69% and 6.5%, depending on the number of substitute recreation sites available. More studies that look at how forest quality affects various uses are listed in Table F-4. Also, Table F-5 lists value estimates from a meta-analysis but does not reflect the considerable variation of value estimates across underlying studies.

Figure F-5 depicts the linkages between aesthetic welfare benefits and air pollution. One such linkage that is shown is the visual quality of forests. Changes in woodland appearances are monitored using scientific indicators of ecosystem change, such as crown condition, mortality, foliar damage, vegetation structure, and plant diversity (McLaughlin and Percy, 1999). However, in comparison to valuation of changes in commercial timber, measuring the economic value of aesthetic changes in forests and natural ecosystems can be more directly based on scientific information regarding the effects of pollution on forest health. Although the scientific linkages between air pollution and visual forest quality include large degrees of uncertainty, historic examples of air pollutant effects on forest aesthetics facilitate their empirical valuation. Figure F-6 shows the regions and species that have been identified as historically affected by air pollutants.
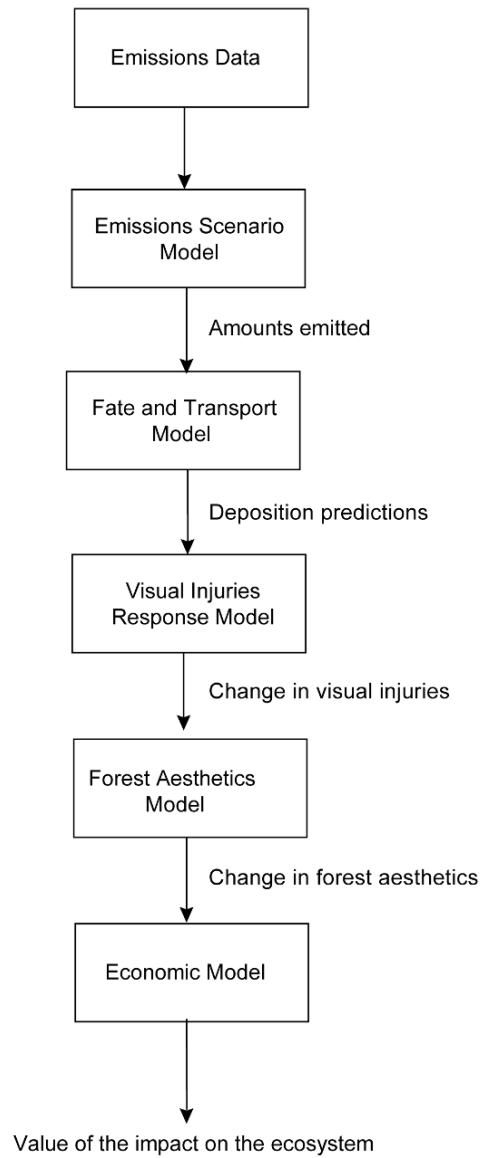
Figure F-5.   Linkages from emissions to forest aesthetics.

U.S. Major Forest Types Affected by Air Pollution-Induced Visual Injuries

Note: Only areas affected by non-point source pollution are shown. Scientific certainty varies with location. Direct ozone-induced injuries also occur in several other locations not indicated. (e. g., Southern Forests, Berraug et al., 1995.)
Sources: NAPAP (1991); White and Cogbill (1992).
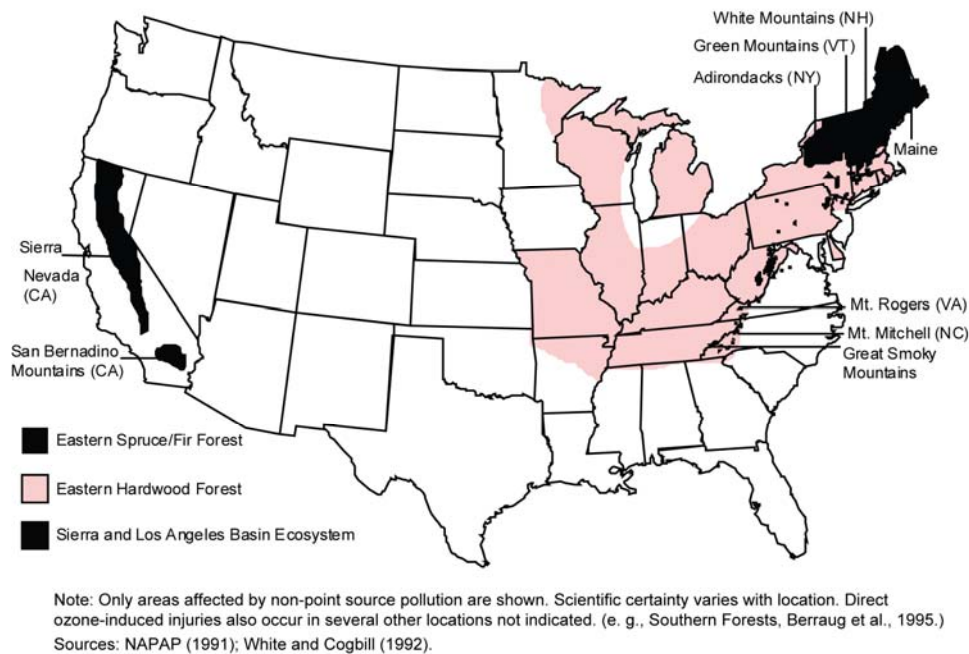
Source: Figure 2 in IEc (1999a).

Figure F-6.   Geographic distribution of forested areas historically affected by air pollution.

When the aesthetic quality of forests is important to people, visible injuries to trees can affect consumer welfare. Loss of or damage to foliage, changes in tree density, changes in species composition, and changes in vegetation structure can all affect the enjoyment that people derive from forests, and are therefore appropriate for economic assessment. Estimation of the aesthetic value of forest condition uses RP or SP methods and often focuses on long-term outcome stressors, rather than current intermediate situations. Nevertheless, there are few scientific studies that relate changes in pollution concentrations to these endpoints, and that make a direct linkage between science and economics. A memorandum by Industrial Economics, Inc. (IEc) (1999c) produced for *Benefit-Cost Analysis of the CAA 1999*, provided a comprehensive review of early forest aesthetics valuation literature. A recent literature review by Kramer et al. (2003) also summarized several key studies described in this report. Table F-5 lists and describes studies which have estimated monetary value for the types of non-consumptive use and non-use values for forests and natural ecosystems which may be affected by N and sulfur emissions.

F.3.2. Total Values

Several studies were reviewed by Kramer et al. (2003), and measured the total WTP of the general public for forest aesthetics and attempted to separate contributions of use values and non-use values. Most of these studies indicated that in the aggregate, non-use values (including option, bequest, and existence value) were significantly greater than use values (recreation).

Walsh et al. (1990) employed a contingent valuation study using an iterative bidding technique to estimate WTP of Colorado residents for protecting Ponderosa pine (*Pinus ponderosa*) forests from the mountain pine beetle (*Dendroctonus ponderosae*). Presented with pictures of mid-level forest quality representing current conditions (100 to 125 live trees measuring more than 6–inches in diameter per acre), respondents were asked their WTP to prevent the lowest forest quality (0 to 50 trees per acre) and to attain

the highest forest quality (125 to 175 trees per acre). Overall mean WTP for changes in forest quality was estimated at $47 per household. In addition, respondents decomposed total value into four categories of value (recreational use, option, existence, and bequest). Results showed that use values accounted for 27.4% of total value, and non-use values accounted for 72.6% of total value. The study was limited by small sample size (200 respondents) and possible bias from framing the scenario as "one of the most important issues facing Colorado residents."

A study by Haefele et al. (1992) that measured WTP to protect Southern Appalachian spruce-fir forests, used a decomposition approach to determine dominate influences on total values. The authors found that non-use values (bequest and existence values) overshadowed use values as reasons to protect forests. Holmes and Kramer (1996) relied on results from Haefele et al. (1992) to compare WTP between recreational forest users and members of the general public. Mean household estimates for forest-users ($36.22) were substantially larger than estimates for nonusers ($10.37).

Kramer et al. (2003) used a dichotomous-choice, contingent-valuation format to determine WTP of Southern Appalachian residents for protecting spruce-fir forests from insects and air pollution. The study measured incremental levels of forest protection using two scenarios: the first increment occurred along road and trail corridors, a scenario that would appeal to people valuing the ecosystem primarily for recreational use; the second level was for the entire ecosystem, a scenario that would appeal to people valuing the continued existence of the entire threatened ecosystem. Using randomly assigned values between $2 and $500 dollars, respondents were asked if they would pay a certain tax amount for each scenario. Results suggested that preferences for forest ecosystem protection created a well-behaved demand curve, with incremental WTP increasing at a decreasing rate.

F.3.3. National-Scale Valuation

An EPA-contracted valuation study by IEc (1999b) developed a benefits-transfer model using results from Holmes and Kramer (1996), Peterson et al. (1987), and Walsh et al. (1990) to estimate national benefits from the 1990 CAAA. Calculations applied WTP values from these previous studies across all households in the affected states. (See Table F-6 for more information on the underlying original studies, and Table F-7 for benefits transfer results.) Estimates for the total value of avoiding air pollution-induced damage to forest aesthetics in the U.S. during the period 1990–2010 were found to range from $3 to $17 billion. Due to limitations in the original studies and the simplicity of the benefits-transfer model, the authors warned that the estimates should only be used to consider the general magnitude of benefits to forest aesthetics (in the range of billions of dollars) rather than as precise values.

F.3.4. Valuation of Degrees of Injury

A few studies—Hollenhorst et al. (1993); Ruddell et al. (1989); Hammitt et al. (1994); Buhyoff et al. (1982)—measured general preferences for forest aesthetics without estimating changes in welfare. Hollenhorst et al. (1993) considered the effect of tree mortality on perceived forest aesthetics. On a 1 to 10 scale for visual and recreational appeal, 400 respondents ranked pictures of 25 sites with tree mortality ranging from 6% to 98% from gypsy moth (*Lymantria dispar*) damage. The results produced a hill-shaped function, whereby site appeal increased with mortality at levels as high as 40% but then declined. The authors speculated that respondents had a general distaste for tree mortality but valued light penetration to the forest understory, which allows for the growth of wild flowers and lower-level vegetation.

Other studies confirmed this visual preference for light penetration, including Ruddell et al. (1989) and Hammitt et al. (1994), who observed positive responses to forest edges and open middle grounds without light-obstructing tree canopies. Buhyoff et al. (1982) tested how awareness of environmental

damages affects perception of aesthetic losses. The study compared aesthetic rankings of photographs between a control group and a group that is informed about the cause of forest damage before the ranking session. Results show a heightened level of sensitivity to forest damage by the "informed" group of subjects.

Several other studies investigated the notion of aesthetic thresholds, or discontinuous jumps in aesthetic preferences across small changes in visual injuries. Of particular interest to early studies were thresholds at the lower limit of visual perceptibility.

Contingent valuation studies by Vaux et al. (1984) and Flowers et al. (1985) assessed aesthetic preferences at recreational areas with fire damage and found that small differences in site appearance can produce large changes in recreation preferences. This finding is generally consistent with the results from two early studies by Buhyoff et al. (1979) and Buhyoff and Wellman (1980), which asked respondents to rate various levels of insect damage. The authors found that preferences seemed to be most affected by the presence or absence of insect damage, as opposed to the degree of damage.

Crocker (1985) surveyed 100 recreationists for their WTP for recreational experiences at forested sites with slight injury, moderate injury, or severe injury. Mean WTP estimates for the environment with slight injury were three times higher than WTP for environments with moderate and severe injury, suggesting that people are willing to pay a premium for recreational access below the lower limit of perceptibility. As a group, respondents did not indicate a clear preference ordering between the moderate and severe injury environments.

Holmes et al. (2006) use a hedonic method to predict the impact of forest damage due to the hemlock woolly adelgid (*Adelges tsugae*), an invasive insect, on the value of residential properties. Examining 3,379 residential property sales in New Jersey between 1992 and 2002, the study analyzed how the appearance/health of the forest on the home's parcel and within 0.1, 0.5, and 1 km buffers around it affects the housing market. Controlling for other relevant variables, the study estimated that hemlock health status had a statistically significant effect on property values. The estimation results suggest, for example, that a 1-point increase (e.g., from 10% to 11%) in the percentage of healthy hemlocks (less than 25% foliar damage) of all forests on the home's parcel was associated with a 0.66% sales price increase. Similar changes in the hemlock forests and their health status in the home's near proximity are predicted to be associated with yet larger increments in the sales price.

At least one study seems to provide evidence against the concept of thresholds at the lower limit of perceptibility. A referendum-type contingent valuation survey by Jenkins et al. (2002) used two sample populations to value a forest protection program. The initial forest condition was described as "pristine" for one group and already "somewhat damaged" for another group. The degree of forest damage incurred in the absence of a forest protection program was the same for both sample groups. Regressions for the entire sample population showed no statistically (Jenkins et al., 2002) significant difference in WTP for forest protection between the two groups.

Further analysis of Jenkins et al. (2002) suggested that aesthetic preferences and thresholds differ between recreational groups. Comparisons among recreational groups revealed that consumptive forest users (hunters and anglers) held values that were sensitive to change in forest condition, while non-consumptive forest users (hikers and campers) held values that were insensitive to the same amount of change. Overall, however, non-consumptive forest users expressed higher values than consumptive forest users. Aesthetic thresholds also seem apparent for recovering forests. Paquet and Belanger (1997) found that the aesthetic effects of clear cutting were largely removed once re-growth reached a height of 4 m.

Finally, there is substantial literature related to the amenity value of urban/suburban forests and open space. McConnell and Walls (2005) recently reviewed this literature, evaluating more than 60 published articles that have attempted to estimate the value of different types of open space. Two lines of research emerge in this literature: studies that estimate the hedonic value of open space proximity to residential properties, and studies that use SP methods to value preservation of open space. Unfortunately, neither line of research generally comprises studies that provide information on the WTP for quality changes to open space that might be caused by changes in NO_X and SO_X emissions. In most cases, the proximity or preservation of open space or urban/suburban forest is valued without reference to the

quality or even the type of open space or forest. Although this literature demonstrates the value of the availability and preservation of open space, its relevancy for the purposes of this assessment is at best limited.

F.3.5. Limitations and Uncertainties

Shortcomings in the air pollution terrestrial valuation literature have been well documented in recent reviews (Adams et al., 2003; U.S. EPA, 2006b). In existing economics literature, the effects of O_3 on terrestrial endpoints overshadow assessments of other effects of NO_X and SO_X pollution, such as acid deposition and N fertilization. The latter effects have been well documented in the scientific literature, but the lack of valuation studies related to them limits full assessments of terrestrial damages from NO_X and SO_X pollution. Incomplete scientific understanding of the effects of air pollutants on ecosystems and economic endpoints extends to many valuation studies. Even in the valuation of O_3 effects, which have been relatively thoroughly studied, improvements in noneconomic input data could play an important role in evaluating the magnitude of vegetation damages from O_3.

Economic models should incorporate more specific temporal (dynamic) and spatial data regarding terrestrial effects of air pollution to reflect more realistic situations. For example, the O_3 effects valuation literature analyzes air pollution effects across a period of time using only two or three scenarios that represent large, static changes. In the real world, however, these changes would occur gradually and incrementally. Future studies should try to consider more dynamic models that can describe effects of marginal air quality changes. From a spatial perspective, previous studies often assumed that producer responses are similar across large geographic areas. However, regional factors may be important, suggesting a possible need for finer-scale agricultural and forestry data that would allow models to consider micro-level physical and economic factors (Adams et al., 2003).

With regards to the effects of air pollution on agricultural crops, most economics studies date from the 1980s and many focus on O_3. Therefore, there is a general need for updated valuation studies that consider agricultural damages from air pollution, especially with regards to the roles played by NO_X and SO_X. Specific issues include the need to develop new exposure-response functions for sensitive crops and the effects of air pollution on crop yields under actual farm conditions.

Assessments of welfare losses in commercial forestry from air pollution are mainly limited by scientific uncertainty regarding the extent of ecological damage. Restrained by the large size and slow growth of trees, scientific research has primarily considered O_3 effects on seedlings and has little transferability to mature trees.

Existing literature on valuation of changes in forest aesthetics has focused primarily on historical cases of acute air pollution or insect infestation and may be overly simplistic. Although these valuations are useful, no existing assessments have examined the effects of reduced air pollution on forest aesthetics. Understanding the effects of marginal changes in air pollution would require the collection of long-term high-quality data about forest health, as well as improved casual linkages between air pollutants and visible injuries to trees. Scientific advancements at this scale would require a sophisticated monitoring network operating over several decades. Until the impacts of pollution on the foundational services of terrestrial ecosystems are better understood, valuation assessments may be premature. Additionally, most studies also fail to distinguish between marginal values of forest health and average values of forest health, an oversight that may create bias in final estimates.

A major limitation of both non-economic and economic forest health assessments concerns the limited extent of documented ecosystem-level changes. Most forest health surveys focus on average forest conditions that allow for modeling of near-term trends in economic value, but fail to detect fundamental changes in ecosystem processes that sustain natural capital in the long run (McLaughlin and Percy, 1999). Quantifications of impacts on species effectively conform to existing valuation methods; however, these effects may be overshadowed by long-term or irreversible reductions in ecosystem structure and function

(U.S. EPA, 1999b). Assessing ecosystem-level changes presents new challenges to both science and economics as they include a large degree of uncertainty in the scale and nature of effects. In particular, economic assessments of ecosystem impacts may require regional- to national-scale modeling of numerous ecosystem functions rather than analyses of specific service flows that directly contribute to human welfare (U.S. EPA, 1999b). In spite of these challenges, the relationship between air pollution and forest health has enormous implications for policy development and should be addressed in future research.

More advanced methods to address uncertainty and irreversibility are essential to future modeling of complex ecosystem-level impacts. Several alternative methods to address ecological uncertainties are currently being developed and should play a central role in future models (U.S. EPA, 1999b).

F.4. Valuation of Transitional Ecosystems

The economic analysis of the benefits on wetlands (transitional ecosystems) from reduced emissions are limited in this Annex to three recent and comprehensive meta-analyses. Brander et al. (2006) provided a comprehensive review and meta-analysis of the wetland valuation literature. This study improved upon previous similar studies (Brouwer et al., 1999; Woodward and Wui, 2001) by including tropical wetlands estimates from other valuation methodologies, other wetland services, and estimates from more countries.

It is well known that wetlands serve a variety of potentially valuable ecological functions, including flood and flow control, storm buffering, sediment retention, groundwater discharge, and habitat for plant and animal species. Wetlands also contribute to climate stabilization, carbon sequestration, and the overall quality of the natural environment. Brander et al. (2006) (Table F-8) described these functions and their associated goods and services, as well as their values as determined by common valuation methods.

F.4.1. Use and Non-Use Values

The Brander et al. (2006) meta-analysis included 191 different wetland valuation studies from 25 different countries. Eighty of those studies, half of which were from North America, provided useful empirical data for the meta-analysis. A total of 215 individual observations were gleaned from those studies for use in meta-regressions. The study reviewed the literature, discussed valuation techniques, calculated average wetland values using the results from the combined data set, and then performed a meta-regression of the data to determine which explanatory variables had the greatest effect on wetland value. Non-market use values of wetlands, as well as non-use/existence values, were also included in the analysis. Because not all of the studies generated WTP value estimates, wetland size and population statistics were used to convert estimates from the diverse valuation methodologies to 1995 dollar values per hectare per year, following the example of Woodward and Wui (2001), which is described below.

The results of the Brander et al. (2006) meta-analysis showed an average value for wetlands of $2800/ha/yr (1995 dollars), and median value of $150/ha/yr. Individual values were calculated by wetland type, the wetland service provided, contingent, and valuation method used. The meta-regression also revealed that studies using the contingent valuation method consistently returned the highest wetland values. It is noted that this may have been due to the type of wetland values that this method was applied to, rather than something intrinsic to the methodology.

To look at the value differences from a reduction specifically in N emissions, there is a focus on Brander et al.'s (2006) analysis of wetland value changes that resulted from a small change in water quality or some other ecosystem service. These results are valuable because they may be related to

changes in acid deposition as a result of changes in the concentrations of NO_X or SO_X. In the meta-regression results of Brander et al. (2006), the only such ecosystem service which was shown to have a statistically significant effect on wetland value was hunting. Hunting had an unexpected negative influence on wetland value. Although not statistically significant, water quality, habitat and nursery service (specifically support for commercial fisheries and hunting), fishing, and biodiversity all had positive effects on wetland value. The accuracy of the value transfer exercise in Brander et al. (2006) seems to be in line with other similar efforts, with an average transfer error of 74%. Overall, the value transfer function from Brander et al. (2006) produced higher-value transfer error for less valuable wetlands (and systematically over-predicted their value) and lower value transfer error for more valuable wetlands (and slightly under-predicted their value).

Woodward and Wui (2001) found 39 studies that contained sufficient data for inter-study comparison, including peer-reviewed and gray literature. Similar to the approach of Brander et al. (2006), Woodward and Wui (2001) assumed that a wetland's value is a function of its ecological characteristics and socio-economic environment, and that there exists a true public WTP at a given moment for a particular wetland. With these assumptions, they attributed variability in wetland value to two principal sources: differing characteristics of the wetland and error in the estimation of the true value (Woodward and Wui, 2001).

Brouwer et al. (1999) analyzed the WTP of 30 CV studies addressing ecosystem functions of wetlands, providing a total of 103 estimates. The studies were mostly conducted in the U.S., but were not in any way comprehensive spatially. They ranged from 1981 to 1997 and covered a wide range of commodity definitions, including preserving wetlands threatened by flooding, maintaining or improving current catch levels and fish populations, saving the bald eagle (*Haliaeetus leucocephalus*), improving/maintaining habitat, water quality ladder changes, preventing shellfish bed closures, increasing the number of protected rivers, and explicitly preserving a measure of water quality. No attempt was made to standardize the degree of change being valued. Instead, the authors attempted to address differences in the studies through the use of dummy variables and some degree of sub-setting.

Based on all of the included studies, Brouwer et al. (1999) estimated that the average WTP for the addressed ecosystem functions was about $90 per household per year. These studies covered types of wetlands (primarily fresh water systems), ecosystem functions (water quality and biodiversity, and to a lesser extent water quantity and flood control), and wetlands size. Cutting across types of systems, location, and function enhanced, the WTP for salt and fresh water improvements was about the same. Within fresh water wetland systems, riverine wetland improvements appeared to be more highly valued than palustrine wetland improvements. Across ecosystem function, flood control was more highly valued than biodiversity, water quality and water generation, in that order. Improvements to larger wetlands appeared to be somewhat more highly valued than to improvements to smaller wetlands. Improvements in use values averaged slightly more than $100 per household per year, whereas improvements in non-use values only showed values about half this size. Spatially, values were higher in California, followed by Georgia and Louisiana.

The review of outdoor recreation valuation studies by Rosenberger and Loomis (2001) included 13 studies and 59 value estimates associated with waterfowl hunting, a popular activity in transitional ecosystems. On average, these studies estimated that the value of waterfowl hunting is about $32 per person per day (1996 dollars). However, different value estimates ranged from about $2 to over $160 per person per day. In their meta-analysis, Rosenberger and Loomis (2001) predicted a $40 value per person for a day for waterfowl hunting (Table F-4). These results demonstrate potential benefits from waterfowl hunting, but do not address changes in the quality of transitional ecosystems that may possibly be associated with reduced NO_X/SO_X emissions.

F.4.2. Limitations and Uncertainties

Meta-analyses of wetland value (and the underlying original studies) are not directly useful because they do not measure changes in ecosystem services that would follow from some tightening or loosening of the standard for NO_X or SO_X. Nevertheless, they have indirect use by pointing out the importance of various methodologies, the overall values commonly assigned to wetland improvement, and types of ecosystem services that might be affected by air pollutants. For example, both Brander et al. (2006) and Woodward and Wui (2001) found that CV studies generally yielded greater value per acre than travel cost studies. This is not surprising, as the former would generally include non-use values. Furthermore, Woodward and Wui's (2001) meta-analysis showed that the availability of bird hunting, bird watching, and amenity services affect wetland value. For example, bird watching (which could be affected by bird populations which, in turn, could be affected by nutrient enrichment) contributes more value to an ecosystem than any of the other ecosystem services. This is mainly due to the popularity of bird watching and the large numbers of people who engage in this recreational activity.

F.5. Valuation of Aquatic Ecosystems

As discussed in the ISA and the preceding annexes, acidification and eutrophication are the two main effects of NO_X and SO_X on aquatic ecosystems. In economic valuation of the effects of NO_X and SO_X deposition on aquatic ecosystems, these effects are reflected partly in the WTP for recreational fishing (with effects on the catch rate and fishing quality in a particular aquatic ecosystem) and partly on aesthetic and non-use (and total) values. Valuation methods used to assess the value of aquatic ecosystems include contingent valuation (CV) (open-ended, discrete choice, etc.), choice experiments, hedonic-pricing valuation, travel cost (TC) (hedonic travel cost and traditional travel cost), cost-effectiveness analysis, avoided-damage cost, replacement cost, market analysis, and so forth. The CV method has gained popularity for total (use plus non-use) value estimation, whereas the travel cost method plays an important role in deriving use values. Currently, there is also a tendency to use stated and RP techniques together for the valuation of recreational activities. Supplemental to the below discussions about valuation of acidification and eutrophication on aquatic ecosystems, Table F-9 describes different aquatic valuation studies according to the ecological effect examined (acidification, eutrophication) and lists their relevant details.

An extensive literature review by Wilson and Carpenter (1999) provides an excellent starting point to the valuation literature on aquatic ecosystems. This paper examined 30 studies published between 1971 and 1997 that estimated the value of nonmarket ecosystem services provided by fresh water bodies in the U.S. Sixteen were SP studies, with the rest split between travel cost and hedonic pricing approaches. The travel cost studies covered very specific water bodies and stressors, such as a boaTable to swimmable change in water quality for 13 recreation sites along the Monongahela River in Pennsylvania (Smith and Desvousges, 1986), and a change in water quality measured by the Uttormark's Lake Condition Index for recreational use of Pike Lake in Wisconsin (Bouwes and Schneider, 1979). Beyond spatial and stressor differences, the studies differ in their units for expressing value. The Monongahela River study used benefits per household, with the largest value expressed for a change from boatable to swimmable ($51). The Bouwes and Schneider (1979) study concluded that the total (aggregate) annual mean CS was almost $86,000.

There are several additional meta-analyses that describe methods of valuation for aquatic ecosystems, but not specifically relating to effects caused by NO_X or SO_X. Van Houtven et al. (2007) analyzed WTP for fresh water quality improvements, covering 131 valuation estimates from 18 SP studies that used or could be transformed to use the water quality ladder (boatable, fishable, swimmable) modified into a 10–point scale. The analysis started with 90 studies but found that most were not

sufficiently comparable for statistical analyses. The studies ranged from 1977 to 2003 and covered rivers, lakes and estuaries.

A meta-analysis by Johnston et al. (2005) examined the value of fish catch based on a total of 48 studies published in the U.S. and Canada between 1977 and 2001. The study statistically examined WTP for fish relative to variations in resource, context, angler, and policy attributes, as well as methodological attributes of the studies themselves. The attributes examined included species targeted, geographic region, water body type, catch rate, angler demographics, and fishing method. Among 391 WTP observations, 122 were estimated using CV methods, 59 using TC methods and the remaining from discrete choice models.

Johnston et al. (2005) found that SP studies have generally resulted in lower WTP estimates than RP studies, which is consistent with earlier multiple study reviews and meta-analyses. Dichotomous choice CV also has produced lower WTP estimates than choice experiment or conjoint surveys, compared to the default of open-ended surveys (including payment cards and iterative bidding). However, these findings were not robust across all regression model specifications. The study supported previous findings (Poe et al., 2000) that WTP is systematically associated with variations in resource, context, and angler attributes. The study also concluded that WTP per fish varies systematically across study methods, but the variation due to methodology accounted for a relatively small proportion of total WTP variation. Again, these results demonstrate the value of recreational fishing, but do not address changes in water quality that may be associated with reduced NO_X/SO_X emissions.

F.5.1. Acidification

The Adirondack Park in New York is the best documented of all areas affected by acidic deposition in the U.S. Due to air pollution that largely originated from power plants and other sources to the west and southwest of the park, many watersheds in the park have experienced slow acidification of water and soil since the late 18th century. This park has been the subject of numerous valuation studies in recent decades.

Morey and Shaw (1990) applied the travel cost model and estimated recreational fishing values associated with water quality change resulting from acidic deposition in the Adirondack Park area. The results showed that the aggregate expected conditional compensating variation for a 50% increase in catch rate of two trout species at four sites was $3,863 (1977 dollars; $13,175 in 2007 dollars), based on 607 survey respondents with an estimated standard deviation of $89 ($304 in 2007 dollars).

A travel cost model was also applied by Mullen and Menz (1985) to link acidic deposition and recreational fishing in the Adirondack Park. A net average economic value per angler day was calculated to be $20 (1976 dollars; $73 in 2007 dollars) for lakes, ponds, and streams in the Adirondacks, with an estimated total loss in net economic value of $1.07 million (1976 dollars; $3.89 million in 2007 dollars) per year for a 5% reduction in fishable area. These estimates excluded streams because limited knowledge existed to assess the effect of pH fluctuations on aquatic life in streams. Shaw (1989) questioned the reliability of these results, arguing that the demand equation was not compatible with economic theory and that aggregating separate CS measures from different equations was inappropriate.

Englin et al. (1991) assessed the economic impact on recreational fishing in four upper northeastern states resulting from acidic deposition control. Biological effects of acidification were linked with hedonic travel cost and random utility models through the acid stress index (ASI) and fish catch per unit effort (CPUE). The analysis was based on multiple data sources and yielded positive social welfare for 2030 under a scenario of reducing by 50% the ambient deposition in 1989. This level of decline in acidic deposition was expected to occur on the basis of analyses conducted by the National Acid Precipitation Assessment Program (NAPAP).

Cameron and Englin (1997) measured welfare under an assumption that people are not certain about participation in fishing. Based on WTP results from a survey and a random utility model, surpluses

were estimated for preventing a 20% loss in the availability of high-elevation lakes for fishing in northeastern states.

Randall and Kriesel (1990) employed a SP method to value a National Pollution Control Program, which led to improved air and water quality by 25% within 5 years. A nationwide survey conducted in multiple modes found an estimated annual willingness to pay of $694 ($1,098 in 2007 dollars) per household. The researchers concluded that the estimated value was lower than their multimarket hedonic estimates.

Banzhaf et al. (2006) conducted a CV survey, which was designed to estimate the total value (use plus non-use values) of reducing acidification by liming the lakes and forests in the Adirondack Park to a degree matching recent SO_X and NO_X reductions under emissions trading programs. The mean WTP for improving 600 lakes "of concern," and small increases in populations of two bird species and one tree species was $48 (2003 dollars; $54 in 2007 dollars) per year per New York household. The mean WTP for improving 900 lakes "of concern," four bird species and three tree species was $54 (2003 dollars; $61 in 2007 dollars) per year per New York household.

Sequential implementation of several regulations, including in particular the CAA, has substantially reduced acidic deposition, especially in the eastern part of the U.S. Burtraw et al. (1997) conducted a benefit-cost analysis for the NAPAP program. Besides improving public health and visibility, emissions controls contributed to decreased lake acidification which was projected to have economic benefit associated with improved recreational fishing in the Adirondack Park. The ASI and CPUE approaches were used in the Tracking and Analysis Framework (TAF) model to capture the response of three recreationally fished species to water quality improvement in 33 statistically selected Adirondack lakes. The per capita recreational fishing benefits in 2010 were estimated to be $0.62 (1990 dollars; $0.98 in 2007 dollars) annually per angler fishing in the Adirondack area.

F.5.2. Eutrophication

As is the case for acidification, the endpoints most studied in the valuation literature for nutrient enrichment concern fishing and non-use (or total) values. Change in aquatic recreational behavior is another endpoint for looking at valuation of such ecosystems, although it is difficult to link those changes due to ambient NO_X or SO_X concentrations.

F.5.2.1. Recreation

Bockstael et al. (1989b) measured the benefits of improvements in water quality of the Chesapeake Bay using travel cost and SP methods. A telephone survey with 959 respondents revealed an aggregate WTP for water quality improvement from current level to a level acceptable for swimming and/or other water activity of about $91 million (1987 dollars; $166 million in 2007 dollars) for households in Maryland. Based on three other surveys, a travel cost model yielded aggregate use values of about $34.7, $4.7, and $1.4 million ($63.1, $8.6, and $2.6 million in 2007 dollars) for a 20% water quality improvement for beach use, boating, and sport fishing, respectively.

Morgan and Owens (2001) simulated water quality change under a baseline (without additional pollution control) and a scenario with pollution control in the Chesapeake Bay watershed and then calculated aggregate benefits for beach use, boating, and striped bass sport fishing by transferring the benefits from Bockstael et al. (1989b). Lower bound aggregate benefits for beach use, boating, and sport fishing were $288.8, $6.7, and $288.8 million (1996 dollars; $380.4, $8.8, and $380.4 million in 2007 dollars), respectively for a 60% improvement in Chesapeake Bay water quality.

Lipton (2003) mailed out an open-ended contingent valuation survey to 2,510 randomly selected Maryland boaters regarding willingness to pay for one unit improvement in the water quality of the Chesapeake Bay. The boaters ranked their perception of water quality on a scale of one to five. The

median WTP for a one step improvement in water quality was $17.50 ($19.66 in 2007 dollars) per year and the mean was $63 ($71 in 2007 dollars), with 38% of respondents expressing a zero WTP. It was found that the boaters who keep their boats in the water would pay more than those who keep them on trailers. Individuals who ranked ambient water quality lower and had more concern for the health effects from water quality degradation would likely pay more for water quality improvement. The aggregated WTP for the Chesapeake Bay boaters in Maryland was approximately $7.3 million ($8.2 million in 2007 dollars) per year with a $146 million ($164 million in 2007 dollars) present value (a 5% discount rate).

Smith et al. (1991) estimated the recreational fishing value of Albemarle-Pamlico Estuary in North Carolina using a hedonic travel cost model. The analysis was based on an intercept survey with 1,012 interviews at 35 boat sites and 44 bank sites in 1981 and 1982. The estimated benefit derived from the application of a conventional demand model to the boat site sample ranged from $1.49 to $2.58 (1982 dollars; $3.19 to $5.53 in 2007 dollar), and for the bank site sample ranged from $0.65 to $1.11 ($1.39 to $2.38 in 2007 dollars) for an increase in catch rate of one fish per hour per person.

Four years later, Kaoru (1995) and Kaoru et al. (1995) used the information collected from the same survey to estimate the recreation value from improvements in Albemarle and Pamlico Sounds using a household production model and a random utility model. They linked the effluent loading and quality of sport fishing with the fisherman's decision on site selection. Instead of fish availability being estimated as the average number of fish caught per person per hour for each entry point, Kaoru et al. (1995) used total catch per trip per person as their key measure of fishing success. They included not only the estimated N loadings but also the effect on biochemical O_2 demand as an influence on fishing quality. The results suggested that depending on aggregation methods, CS ranged between $7.05 and $36.19 ($9.56 and $49.08 in 2007 dollars) for a 5% increase in total catch. The CS was $1.27 to $6.52 ($1.72 to $8.84 in 2007 dollars) for a 36% decrease in N loadings at all sites.

Whitehead et al. (2000) used a joint stated and RP model to estimate recreation value of improvements to Albemarle and Pamlico Sounds in terms of CS per trip and per season. A telephone survey was conducted in 1995 to learn how North Carolina residents would value improvements of water quality resulting in a 60% increase in fish catch and a 25% increase in open shellfish beds. The analysis was based on 765 completed responses. The CS per trip was estimated at $64 (1995 dollars; $87 in 2007 dollars) for current quality and $85 ($115 in 2007 dollars) for improved quality and the CS per season was $121 ($164 in 2007 dollars) for current and $155 ($210 in 2007 dollars) for improved quality.

The Catawba River in North and South Carolina is used for electric power generation, recreation, drinking water, and wastewater assimilation. With population growth and land use change, the health and vitality of the river system are declining as the river flows downstream. Through a mail-phone survey of 1,085 residents randomly selected from 16 counties of Catawba River Basin, Kramer and Eisen-Hecht (2002) presented a management plan designed to maintain the water quality at the current level over time. The water quality in the entire watershed was classified as good, fair or poor on maps to illustrate the distribution of the tributaries with different water quality. The mean WTP was estimated to be $139 ($160 in 2007 dollars) for protecting current water quality from deterioration.

A site choice model applied jointly with a trip frequency model was used by Needelman and Kealy (1995) to assess the relative benefits of eliminating eutrophication, fecal bacteria, and oil and grease in New Hampshire lakes. The site choices analysis was based on 53 individuals and 1,021 trips, while the trip frequency model was based on a total of 519 individuals including the responses for the site choices model. The mean seasonal benefits were valued at $1.40 ($1.90 in 2007 dollars) for eliminating eutrophication from all sources ($1.33; $1.80 in 2007 dollars) for eliminating nonpoint source pollution alone and $0.09 ($0.12 in 2007 dollars) for eliminating point source pollution alone) with an aggregate seasonal benefit of $1.16 million ($1.57 million in 2007 dollars), with $1.11 million for nonpoint source and $0.08 million for point source pollution. However, the economic benefit estimates were exclusively for swimming and day trips. The measures of water quality were not from the year of the survey (1989) but from a range of years from 1976 to 1991.

The Tar-Pamlico River has experienced declining fish catches, disease in fish and shellfish beds, algae blooms, and aquatic grass losses. More than half of the pollution impairing one third of the river

was estimated to come from agricultural nonpoint sources. Whitehead and Groothuis (1992) proposed a management program in which farmers used best management practices (BMPs) to significantly improve the water quality of the Tar-Pamlico River such that recreational anglers would be able to catch twice as many fish per trip. A mail survey was sent to 179 households in four counties in Tar-Pamlico River basin (with a 61% response rate). The mean WTP for doubling fish catch was estimated at $25 ($38 in 2007 dollars), which was bounded from above by a $35 use value ($53 in 2007 dollars) and from below by a $21 ($32 in 2007 dollars) non-use value. The benefits of water quality improvement in the study area were aggregated at $1.62 million (1991 dollars; $2.46 million in 2007 dollars) each year. The researchers believed that non-use value could account for as high as 84% of the estimate. However, the study suffered from small sample size and relatively high non-response rate (11%) to the WTP questionnaire.

Some portions of the coastal coral reefs in the Florida Keys are projected to disappear within 10 to 25 years. In 2000, the U.S. government announced a long-term plan to save coral reefs proposing that 20% of all coral reefs in American-controlled waters would become ecological preserves by 2010. Park et al. (2002) investigated the WTP to preserve current water quality and health of the coral reefs in the Florida Keys. Based on 460 responses to a CV survey and 4,035 respondents to a travel cost survey (460 responses used in the analysis), the annual use value was estimated at $481 per person per snorkeling trip ($553 in 2007 dollars). The mean predicted WTP per trip from a Tobit model was $735 ($844 in 2007 dollars). Over 85% of the predicted WTP value was within plus or minus $50 ($57 in 2007 dollars) of the total trip expenses from the contingent valuation scenario.

F.5.2.2. Commercial Fisheries

As one of six background studies for the National Science and Technology Council (NSTC), Diaz and Solow (1992) used a time series estimation approach to examine the effects from hypoxia[1] in the Gulf of Mexico. The study failed to confirm the relationship between the annual occurrence of hypoxia and commercial fishery health, based on catch rate per unit effort of three major species from the 1960s to 1990s. Although the benefit assessment did not detect effects attributable to hypoxia, this does not necessarily mean that the economic effects would not occur. NSTC (2000) identified alternatives for reducing the adverse effects of hypoxia and examined the costs associated with reduction of N and P inputs. A net cost estimated by the U.S. Mathematical Programming Model for Agriculture was about $0.8 per kilogram ($0.36 per pound; $0.96 per kilogram/$0.36 per pound in 2007 dollars) for a 20% edge-of-field N loss reduction on agricultural lands, whereas restoring 5 million acres of wetland would have a net cost of $1.00 per kilogram ($0.45 per pound) ($1.2 per kilogram/$0.54 per pound in 2007 dollars) of N removal.

The Neuse River in North Carolina is important to the commercial blue crab (*Callinectes sapidus*) fishery in the eastern U.S. It accounted for about a quarter of the blue crab harvest from 1994 to 2002. Smith and Crowder (2005) simulated the progress of eutrophication in the Neuse River using a series of ordinary differential equations, which linked changes in the quantity of nutrients, algal growth, spatial population distribution of blue crab and its prey species with fishing efforts. Results suggested that a 30% reduction in N loading in the Neuse River watershed over a 50–yr period would result in about a $2.56 million ($2.71 million in 2007 dollars) discounted present value generated in fishery rent (the difference between fishing revenues and costs including fixed and opportunity cost).

---

[1] Hypoxia (DO depletion) is a phenomenon resulting from the overloading of nutrients (usually N or P) in water. Most fresh waters are P-limited, and therefore added N from atmospheric deposition does not have a substantial effect on productivity. In contrast, marine and estuarine waters tend to be N-limited, and are therefore expected to respond to additional N inputs by increasing algal productivity. Excessive production of algae can deplete the water of oxygen when those algae die and are decomposed by oxygen-consuming microorganisms. If the concentration of DO decreases to very low levels, fish, and other life forms can die.

F.5.2.3. Water Clarity

In addition to effects on fish populations, eutrophication reduces water clarity due to excessive growth of algae. Boyle et al. (1999) studied the social welfare related to water clarity of four lakes in Maine employing a two-stage hedonic demand model. Based on data from 1990 to 1995 on property sales for 25 lakes, tax records, mail survey, and water clarity data from the Maine Department of Environmental Protection (DEP), the CS for water clarity improvement from the average ambient level (3.78 m) to 5.15 m was estimated to be $3,677, $3,765, and $12,870 ($4,562, $4,671, and $15,967 in 2007 dollars) for differently specified demand systems (Cobb-Douglas, semilog, and linear demand models, respectively). Social welfare loss for visibility deterioration from an average level to 2.41 m ranged from $25,388 to $46,750 ($31,497 to $57,989 in 2007 dollars). One of the interesting findings in the study was that the slope of the Cobb-Douglas demand model increased to 3.0 m, a threshold used by the Maine Department of Environmental Protection to indicate improved water quality and public preferences for it.

Poor et al. (2006) evaluated water quality in a small watershed of Maryland using a hedonic property valuation model. The watershed is located in a peninsula surrounded by the Potomac and Patuxent Rivers and the Chesapeake Bay. Due to nonpoint source pollution runoff, water quality has deteriorated, which might have negative impacts on residential housing prices, especially for those close to the river. To estimate the possible extent of the impact, total suspended solids (TSS) and dissolved inorganic nitrogen (DIN) were averaged by year and included in the model as indicators of ambient water quality. The estimates showed that a marginal increase in TSS reduced average housing prices by $1,086 ($1,113 in 2007 dollars), and a marginal increase in DIN decreased housing prices by $17,642 ($18,087 in 2007 dollars).

F.5.3. Avoided Costs

Based on a model projection, IEc (1999c) estimated the benefits of decreased N deposition to the estuaries in the eastern U.S. using the avoided cost method. According to their results, the annual avoided cost in 2010 would range from $26 to $102 million if 12.8 million pounds of N loading was reduced annually in Long Island Sound. An annual reduction of 58 million pounds of N loading into Chesapeake Bay would avoid an annual cost of $349 to $1,278 million. Uncertainty associated with model assumptions and the inappropriate use of avoided cost estimates to value benefits or damages are two major sources of potential error in generating such estimates. In addition, the avoided costs method generally does not measure values conceptually accurately, and these values also are not linked to benefits from reduced pollution.

F.5.4. Limitations and Uncertainties

Several general limitations apply to the valuation of water quality changes. First, the definition of water quality is too ambiguous to quantify comparisons across studies. Second, the degree of water quality improvement is not often clear. A common obstacle in any environmental economic valuation is the availability of data. Problems stemming from lack of data extend from biological data on the populations of target species to limitations of the available economic data on the value of commercial and recreational fisheries to small samples of survey respondents (Smith and Crowder, 2005).

The geographical focus of valuation studies is another limitation. The studies reviewed here largely focused on the eastern part of the U.S., represented by the Adirondacks, Chesapeake Bay, and Albemarle and Pamlico Sounds. Several studies investigated the total value of aquatic ecosystems and most the studies calculated recreational values of water quality improvement. Only a few studies addressed the

economic value of commercial fisheries. There is considerable uncertainty in the estimates of benefits as they vary significantly even for studies in the same area, with similar changes in the commodity, and use of the same valuation methodology.

Almost every study reviewed here mentioned the problem of uncertainties about the natural science (Diaz and Solow, 1992; National Science and Technology Council, 2000). For example, the processes involved in the development of hypoxia are not fully known. There is also no clear connection between a decrease in pollution level and an increase in catch rate (Bockstael et al., 1989b). Additionally, uncertainty arises from the selection of parameter values (Smith and Crowder, 2005) and models (Burtraw et al., 1997). Due to the uncertainty about water quality improvement in tributaries of the Chesapeake Bay, the estimates provided by Morgan and Owens (2001) excluded benefits from water recovery in the tributaries.

Study coverage also affects benefit estimates. For example, Morey and Shaw (1990) only included those fishermen who could make day trips to one or more of the study sites, fishermen with complete records, and fishermen whose distance to the farthest site was less than 200 miles. Morey and Shaw (1990) evaluated four sites and two kinds of trout in the Adirondacks while Englin et al. (1991) valued only one trout species and lakes in four states.

Many studies relied on information from surveys, which may suffer from various biases. For example, several studies reviewed here used intercept surveys, which are not necessarily representative of the target population (Bockstael et al., 1989b; Smith et al., 1991). Double counting of values may also introduce errors into value estimation. For example, people who are boating may also go fishing (Bockstael et al., 1989b).

F.6. Summary

Previous ecosystem valuations presented in AQCDs were very limited because they considered only studies that could directly attribute monetary values to changes in emissions. The assessment of the literature in this Annex has a different approach: the voluminous literature that values various ecosystem services affected by emissions is included, whether or not the actual linkages all the way from emissions to those effects have been quantified. This approach nevertheless necessitates that the natural science underpinnings be examined in the context of preferences, that is, descriptions of damages (or benefits) from NO_X and SO_X emissions (or reductions in those emissions) from the natural sciences that translate into things that the public cares about. These include, for example, whether the water is boatable or swimmable, the marketable yield associated with changes in a forest or a crop, and effects on aesthetics of wetlands.

The physical endpoints and their corresponding valuation studies are divided into different ecological and value endpoints applicable to terrestrial, transitional, and aquatic ecosystems. There is significant valuation literature on the effects of O_3 on crops (and to a far lesser degree on forest yield), but this topic is beyond of the scope of this assessment. Beyond the O_3 effects, there is little quantification of the science describing the effects of pollution related to NO_X and SO_X on ecosystems. Valuation studies are themselves classified into meta-analyses and original studies, the latter into market studies (e.g., commercial fishing), RP studies (e.g., those related to recreation behavior, property values, etc.), and SP studies (those that ask people survey questions about their WTP for hypothetical ecosystem improvements).

For valuation of terrestrial effects, survey methods are most common. Supplemented by travel cost approaches, this literature leads to a variety of estimates of WTP for improved forest quality that could prove useful for estimating benefits of N and S reductions (provided a number of linkages can be made), even though some of the endpoints valued are related to insect damage. One meta-analysis is available that summarizes this valuation literature.

For wetland valuation, three meta-analyses are available that summarized the valuation literature. This literature is problematic because it focuses on values per wetland acre rather than WTP for changes in services provided by a wetland affected by deposition of N and S pollutants. However, some of the available studies provide WTP for discreet ecosystem services, which is helpful in matching these values to services affected by reductions in N and S deposition. Nevertheless, because there is a very poor understanding of the scientific basis for linking NO_X and SO_X emissions to ecosystem health endpoints, the ability to make the necessary linkages to estimate benefits of pollution reductions is very limited.

The aquatic service valuation literature is the most voluminous of the three categories reviewed. It contains many recreation value studies, a number of property value studies, some total (use plus non-use) value studies, some studies on commercial fishery damages and several good meta-analyses of primary valuation studies, which provide estimates of the WTP of households for improvements in the aquatic ecosystem related to N and S changes. Again, however, there is little focus on NO_X or SO_X as the cause of alterations to the aquatic ecosystem.

Overall, there is a robust literature valuing a variety of ecosystem services that could be related to reductions in N and S emissions. Therein addition, issues affecting the credibility of any individual study and even the studies grouped by technique, such studies can only be used for general valuation purposes. The most important limitation is establishment of the linkages between the physical, chemical, and biological effects of air pollutants on natural ecosystems and changes in exposure to NO_X and SO_X.

Table F-1.   Commonly adopted environmental valuation methods based on revealed or state preferences.

Methods	Description	Direct Use	Indirect Use	Total Value
Revealed Preference Methods	Observing individual choices and behavior to predict their preferences for environmental goods and services.			
Avoided expenditure method	Predicting the cost of mitigating the effects of reduced environmental quality.	X	X	
Derived demand functions	Estimate the value of environmental goods and services by deriving the demand functions of households or firms for them (e.g., water use)	X	X	
Hedonic valuation method	Estimating an implicit price for the environmental quality attributes of marketable goods, such as housing.	X	X	
Market analysis	Used for valuing market goods using data on prices and quantities of outputs and inputs. May use prices of close substitutes, methods of deriving shadow prices, or simulation of changes in market conditions.	X	X	
Referenda	Examining voting results related to environmental resources to predict values for them.	X	X	
Replacement cost	Measures expenditures incurred in replacing or restoring environmental good or service lost (e.g., water filtration). Provides accurate valuation only under strict assumptions usually not met.	X	X	
Travel cost method	Values the environmental attributes of recreational sites by examining visitation frequency and cost differential incurred in reaching site with different attributes.	X	X	
User fee	Examine user fees paid to gain access to an ecological resource such as a park to estimate the lower bound of society's value for that resource.	X	X	
Stated Preferences Approach	Directly surveying individuals to predict their preferences for environmental goods and services.			

Methods	Description	Direct Use	Indirect Use	Total Value
Choice experiments, conjoint analysis	Elicits individuals' choices from several alternatives associated with different environmental and cost outcomes. Elicits data on WTP indirectly (by eliciting cost-environmental outcome tradeoffs, similar to contingent ranking).	X	X	X
Contingent valuation	Elicits data on individuals' willingness to pay for environmental goods and services (hypothetical setting, limited by potential biases). Often implemented using a hypothetical referenda.	X	X	X
Contingent ranking	Elicits data on the ranking of several alternatives associated with different environmental and cost outcomes. Elicits data on WTP indirectly (by eliciting cost-environmental outcome tradeoffs, similar to choice experiments, conjoint analysis).	X	X	X

Table F-2.   Economic effects of ozone and other pollutants on agriculture, as reported in the 1996 ozone criteria document.

Study	Region	Pollutant and Concentration	Model Features				Results (Annual 1980 U.S. Dollar)			
			Price Changes	Output Sub-stitu-tions	Input Substi-tutions	Quality Changes	Crops	Consumer Benefits	Producer Benefits	Total Benefits (Costs)
Adams et al. (1986a, 1986b)	U.S.	Ozone, 25% reduc-tion from 1980 level for each statec	Yes	Yes	Yes	No	Corn, soy-beans, cot-ton, wheat, sorghum, barley	1160×106	550×106	1700×106
Kopp et al. (1985)b	U.S.	Ozone, universal reduction from 53 ppb to 40 ppba	Yes	Yes	Yes	No	Corn, soy-beans, wheat, cot-ton	Not reported	Not re-ported	Not re-ported
Adams et al. (1986b)	U.S.	Acid deposition, 50% reduction in wet acidic deposition	Yes	Yes	Yes	No	Soybeans	172×106	–30×106	142×106
Adams and Crocker (1989)	U.S.	Ozone, seasonal standard of 50 ppb with 95% compli-anced; Includes adjustments for 1985 Farm Bill	Yes	Yes	Yes	No	Corn, soy-beans, cot-ton, wheat, sorghum, rice, hay, barley	905×106	769×106	1674×106

[a] Seven hour growing season geometric mean. Given a long-normal distribution of air pollution events, a 7-h seasonal ozone level of 40 ppb is approximately equal to an hourly standard of 80 ppb, not to be exceeded more than once a year (Heck et al., 1983). [b] Reported in 1986 criteria document. [c] Reported All studies except Garcia et al. use NCLAN data to generate yield changes due to ozone. [d] Seven- and twelve-h growing season geometric mean. Analysis includes both fixed rollbacks (e.g., 25% and seasonal standards (with variable compliance rates). Source: Adams and Horst (2003).

Table F-3.   Economic effects of ozone on marketable benefits from forests.

Reference	Pollutant/Coverage	Response and Air Quality Data	Economic Model	Annual Damages or Benefits of Control
Callaway et al. (1986a)	All pollutants. Forest products (hardwood and softwood) in the eastern U.S.	Assumes three arbitrary growth reductions (10%, 15%, and 20%) for hardwood and softwood tree species.	Spatial equilibrium models of softwood and hardwood stumpage and forest products industries in the U.S.	$340 to $510 million; damage in 1984 dollars for assumed reductions in growth levels.
Crocker (1985)	Acid deposition. Forest products and forest ecosystem service flows for eastern U.S.	Assumes a 5% reduction in products due to acid deposition: assumes a pristine background pH of approximately 5.2.	Naive; assumed changes in output multiplied by avg value of those goods or services.	$1.75 billion damage in 1978 dollars from current levels of acid deposition.
Crocker and Forster (1986)	Acid deposition. Forest products and forest ecosystem services for eastern Canada.	Assumes 5% reduction in forest productivity for all eastern Canadian forests receiving $10 kg/ha/yr sulphate deposition.	Naive; assumed changes in output multiplied by avg value of goods or services.	$1.5 billion damage in 1981 Canadian dollars from current levels of acid deposition.
Haynes and Adams (1992)	Air pollutants, including acid precipitation. Losses estimated for eastern U.S. softwoods.	None; paper demonstrates a methodology for assessing economic effects of yield (growth and inventory) reductions due to any course. Assumes losses from 6% to 21% for softwoods.	Econometric model of U.S. timber sector (TAMM).	Damages of $1.5 to $9.0 billion in 1988 dollars.b
Bentley and Horst (1998)	Ozone. All hardwoods and softwoods except western hardwoods.	Dose-response based on survey of experts scaled to partial attainment of secondary standard relative to the current primary standard. SUM06 exposure metric is based on a cumulative daytime exposure during the growing season.	Econometric model of U.S. timber sector (TAMM).	Benefits of $14 million in 2010 (1990 dollars) for partial attainment of 0.08 ppb 3rd max secondary standard. This standard was considered during the standard development process.

aWe used the updated version of Crocker (1986), while Adams and Horst (2003) cited a prior version, from Crocker (1985).
bWe drew different numbers from the Crocker and Forster (1986) study than those reported by Adams and Horst (2003).
Source: Adams and Horst (2003), exceptions: Table 2 in Bentley and Horst (1998).

Table F-4.   Forecasted average values for select activities, per day per person in 1996.

Activity	Northeast	Southeast	Intermountain	Pacific Coast	Alaska	USA
Swimming	14	9	19	9	14	14
General recreation*	30	25	34	25	30	30
Fishing	37	32	41	32	37	37
Waterfowl hunting	40	35	44	34	40	39
Big game hunting	45	40	50	40	45	45

*The activity category includes camping, picnicking, sightseeing, hiking, small game hunting, wildlife viewing, and other general recreation. In the meta-analysis, values for these activity categories do not differ statistically significantly. Source: from the meta-analysis benefit function by Rosenberger and Loomis (2001), Table 6.

Table F-5.   Typical impacts of specific pollutants on the visual quality of forests.

Pollutant	Geographic Extent	Injury Type	Major Types of Visual Injuries	Notes
Ozone	Area or regional effects	Direct injuries	Foliar injuries (e.g., pigmented stipple), increased needle/leaf abscission, premature senescence of leaves. Pattern, size, location, and shape of foliar injuries to indicator species can be specific for ozone.	
		Indirect Injuries	Increased susceptibility to visual injuries may result from other adverse environmental factors, such as insect attacks. For example, increased needle/leaf abscission, elevated mortality rates, and/or changes in species composition.	
Acidic Deposition	Area or regional effects	Indirect Injuries	Increased susceptibility to visual injuries may result from other adverse environmental factors, such as climatic factors. For example, increased needle/leaf abscission, elevated mortality rates, and/or changes in species composition.	Acidic deposition can also cause direct foliar injuries. Acids are, however, more likely to indirectly affect the visual appearance of forest trees, unless exposure levels are very high.
Sulfur Dioxide	Point source pollution	Direct Injuries	Foliar injuries including leaf/needle discoloration and necrosis. Pattern, size, location, and shape of foliar injuries to indicator species can be specific for sulfur dioxide. At high concentrations, elevated mortality rates of sensitive species and changes in species composition may occur.	Sulfur dioxide may also cause indirect injuries. Indirect injuries, however, are not well documented.
Hydrogen Fluoride	Point source pollution	Direct Injuries	Foliar injuries including leaf/needle discoloration and necrosis. Pattern, size, location, and shape of foliar injuries to indicator species can be specific for sulfur dioxide. At high concentrations, elevated mortality rates of sensitive species and changes in species composition may occur.	Hydrogen fluoride may also cause indirect injuries. Indirect injuries, however, are not well documented.

Source: Exhibit 2 Industrial Economics (IEc) (1999a)

Table F-6.   Economic valuation studies related to forest aesthetics.

Study	Method	Study Area	Description	Economic Endpoint	Economic Value
Crocker (1985)	CV (open ended)	Southern California	Evaluating visits to recreational sites with slight, moderate, and severe O_3 induced damages to Ponderosa and Jeffery pine stands.	Household WTP (per trip)	Slight damage: $2.09 Moderate damage: $0.66 Severe damage: $0.74
Haefele et al. (1992)	CV (payment card, dichotomous choice)	Southern Appalachian Mountains	Protect high-elevation spruce firs from insect and air pollution	Household WTP (per year)	PC: $21 DC: $100
Holmes and Kramer (1996)	CV (payment card, dichotomous choice)	Southern Appalachian Mountains	Protect high-elevation spruce firs from insect and air pollution. Analysis compared forest users and non-users.	Household WTP (per year)	Forest users: $36 Non-users: $10
Holmes et al. (1996)	Hedonic pricing	New Jersey	Evaluate the effects of hemlock forest health status on housing prices. Hemlock health status is potentially deprived by hemlock woolly adelgid; an exotic forest insect.	Housing price	Hemlock forest health status is positively associated with housing prices. For example, a 1–point increment in (e.g., from 10% to 11%) in the % of healthy hemlocks of all forests on the home parcel was associated with a 0.66% sales price increase. Similar changes in home's near proximity are associated with yet larger price increments.
IEc (1999b)[b]	Benefits transfer	National	Protect trees from various different types of damage (see description of source studies)	Welfare Loss (1990–2010)	$3 to $17 billion
Jakus and Smith (1991)	CV (dichotomous choice)	Maryland and Pennsylvania	Protect private homeowner property and surrounding public lands from gypsy moth damages (reduce tree defoliation by 25%)	Household WTP (for entire program)	Private Property Prgm (only): $254 to $420 Private and Public Prgm: $314 to $527
Jenkins (2002)	CV (open ended)	Southern Appalachian Mountains	Protect high-elevation spruce firs from insects and air pollution along roads and throughout ecosystem	Household WTP (per year)	$153
Kramer et al. (2003)	CV (dichotomous choice)	Southern Appalachian Mountains	Protect high-elevation spruce firs from insects and air pollution along roads and throughout the entire ecosystem	Household WTP (per year)	Road side only: $18 Entire ecosystem: $28 Non-use: 87% of total value Use: 13% of total value
Kramer and Mercer (1997)	CV (payment card and dichotomous choice)	National (USA)	Protect 10% of tropical rainforests as national parks or forest reserves.	Household WTP (per year)	PC: $31 DC: $21

Study	Method	Study Area	Description	Economic Endpoint	Economic Value
Loomis et al. (1996)	CV (dichotomous choice, open ended)	Oregon	Protect old growth forests of Pacific Northwest from fires.	Household WTP (per year)	DC: $98 OE: $33
Leuschner and Young (1978)	TCM	Texas	Reduce crown density in recreational areas.	Consumer Surplus (losses)	–0.69 to –6.5% (depending on level of substitute sites)
Miller and Lindsey (1993)	CV (dichotomous choice)	New Hampshire	Protect private homeowner property from gypsy moth damages (reduce tree defoliation by various amounts)	Household WTP (per year)	$55 to $86 (depending on level of reduction in tree defoliation)
Peterson et al. (1987)	CV, hedonic property	Los Angeles area	Avoid O_3 induced damages to trees in local national forests for recreationists (in greater LA area) and homeowners (with property bordering forest).	Household WTP (per year) Consumer Welfare	Recreationist: $43 Homeowner: $131 $31 to $161 million
Treiman (2006)	CV (dichotomous choice)	Missouri	Improve residential tree care and maintenance in different sized cities.	Household WTP (per year)	Urban areas: $14 to $16
Walsh et al. (1989)	TCM	Colorado Rockies	Reduce tree density in recreational areas.	Consumer Surplus (losses)	–8.5 to –23.2% (for reductions in tree density ranging between 10 to 30%)
Walsh et al. (1990)	CV (iterative bidding)	Colorado	Protect Ponderosa pine forests from damages caused by the mountain pine beetle.	Household WTP (per year)	$47 Non-use: 73% of total value Use: 27% of total value

[a]Holmes and Kramer study applies same results found in Haefele et al. (1991). [b]Benefits transfer was based on results from Holmes and Kramer (1996), Peterson et al. (1987), Walsh et al. (1990).

Table F-7.   Summary of the monetized estimates of the annual value of forest quality changes

Reference	Aesthetic Change Valued	Value of Change per Household (Current Dollars)	Value of Change per Household (1990 Dollars)i	Total Value of Change for Region (Current Dollars)	Total Value of Change for Region (1990 Dollars)i
Peterson et al. (1987a)	Ozone damage to San Bernardino and Angeles National Forests	$6.31 - $32.70ii	$7.26 - $37.62	$27 - $140 million	$31 - $161million
Walsh et al. (1990)	Visual damage to Colorado's Front Range	$47	$61.68	$55.7 million	$73.09 million
Holmes and Kramer (1996)	Visual damage to spruce-fir forests in southern Appalachia	$10.81 nonusers $36.22 users	$10.37 nonusers $34.76 users	NA	NA

Source: Exhibit 4 Industrial Economics (IEc) (1999c).

Table F-8.   Estimated value of avoiding forest damage in the U.S.

Affected System	States Included	Value per Household	Householdsi	Total Annual Value	Cumulative Value (1990–2010)ii
Sierra Nevada and Los Angeles Basin	CA	$7.26 - $37.62	10.4 million	$75.5 million - $391.2 million	$1.02 billion - $5.27 billion
Eastern Spruce Fir and Selected Eastern Hardwood	ME, VT, NH, MA, NY, PA, WV, TN, KY, NC, VA	$7.26 - $37.62	23.2 million	$168 million - $872.8 million	$2.27 billion - $11.75 billion

Source: Exhibit 5 Industrial Economics (IEc) (1999c)

Table F-9. Ecological wetland functions, economic goods and services, types of value, and applicable valuation methods.

Ecological Function	Economic Goods and Services	Value Type	Commonly Used Valuation Method(s)[a]
Flood and flow control	Flood protection	Indirect use	Replacement cost Market prices Opportunity cost
Storm buffering	Storm protection	Indirect use	Replacement cost Production function
Sediment retention	Storm protection	Indirect use	Replacement cost Production function
Groundwater recharge/discharge	Water supply	Indirect use	Production function NFI Replacement cost
Maintenance/Nutrient retention	Improved water quality	Indirect use	CVM
	Waste disposal	Direct use	Replacement cost
Habitat and nursery for plant and animal species	Commercial fishing and hunting	Direct use	Market prices, NFI
	Recreational fishing and hunting	Direct use	TCM, CVM
	Harvesting of natural materials	Direct use	Market prices
	Energy resources	Direct use	Market prices
Biological diversity	Appreciation of species existence	Non-use	CVM
Micro-climate stabilization	Climate stabilization	Indirect use	Production function
Carbon sequestration	Reduced global warming	Indirect use	Replacement cost
Ecological Function	Economic Goods and Services	Value Type	Commonly Used Valuation Method(s)[a]
Natural environment	Amenity	Direct use	HP, CVM
	Recreational activities	Direct use	CVM, TCM
	Appreciation of uniqueness to culture/ heritage	Non-use	CVM

[a] Acronyms refer to the contingent valuation method (CVM), hedonic pricing (HP), net factor income (NFI), and the travel cost method (TCM).

Source: Table 1, Brander et al. (2006). Modifications adapted from Barbier (1991); Barbier et al. (1997); Brouwer et al. (1999); and Woodward and Wui (2001).

Table F-10.   Economic valuation studies related to acidification and eutrophication in aquatic ecosystems.

Reference	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
ACIDIFICATION						
Banzhaf et al. (2006)	Injured lakes in Adirondacks, NY	CV	Fish, bird species, and tree species	WTP (total value)	1. The mean WTP for base version was $48 per year per household in New York State while the mean WTP for scope version was $54 per year per household in New York State (discounting rate =3%)	1. Base version: improvement in fish population of 600 lakes, small improvements in the populations of two bird and one tree species. 2. Scope version: improvement in fish population of 900 lakes, improvement in the population of four bird and three tree species.
Bockstael et al. (1989b)	Chesapeake Bay, MA and DC	CV and TC	Fish	Aggregate benefit/ consumer surplus (recreational value)	1. 20%water quality improvement resulting in aggregate benefits for beach use, boating, and sportfishing were about $34.7, 4.7, and 1.4 millions. 2. aggregate WTP for water quality improvement from current to a level acceptable for water activity was about $91 million (1987 dollars)	1. TNP, product of N and P, was included in the model. 2. WTP was aggregated for households in Maryland.
Cameron and Englin (1997)	Northeast U.S.	CV and RUM	Trout fishing (uncertain about use)	Consumer surplus (recreational value, existence value)	1. For passive user, surplus for preventing a 20% loss in currently fishable high altitude lakes in the Northeast was $218 for S model and $215 for OP model. 2. For active user, surplus for preventing a 20% loss in currently fishable high altitude lakes in the Northeast was $283 for S model and $439 for OP-I model and $436 for OP-D.	1. S model: Surplus interpretation of the WTP responses 2. OP model: Option price interpretation of the WTP responses. 3. I: complete independence between year-to-year decisions 4. D: complete dependence on previous decisions

Reference	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Englin et al. (1991)	ME, NH, NY (excluding New York City) and VT	HTC and RUM	Catch per unit effort (number of fish caught in an h)	Consumer surplus (recreational value)	1. Under baseline scenario (1989), welfare loss was estimated at $0.27 m (HTC) and $1.75 (RUM) 2. Under NAPAP scenario 1, welfare loss was occurred in 2010 at $13.7 m (HTC) and $1.2 m (RUM) but social welfare would gain in 2030 at $3.5 m (HTC) and $5.5 m (TCM) 3. Under NAPAP scenario 4, welfare would gain in 2010 at $3 m (HTC) and $7.4 m (TCM) and also gain in 2030 at $4.4 m (HTC) and $9.7 m (TCM)	1. Acidic stress index (ASI) measuring fish biological tolerance to acidity was included in the model. 2. The benefits were valued in 1989 dollars 3. Multiple datasets were used in the analysis. 4. Only trout species fishing was included. 5. The benefit estimates were aggregated for four states by accounting income increase and population change resulting from baby boom.
Kaoru et al. (1995)	Albemarle and Pamlico Sounds, NC	CV and RUM	Fish	Consumer surplus (recreational value)	1. 35–site model: $36.19 for 5% increase of total catch at all sites (full-wage) 2. 35–site model: $6.52 for 36% decrease in N loadings at all sites (full-wage)	1. Estimated N loadings and biochemical O_2 demand, were used in household production models to measure fishing quality. 2. The paper also estimated benefit based on opportunity cost at 1/3 wage for 23−site and 11–site models.
Morey and Shaw (1990)	Four fishing sites in Adirondacks, NY	CV and TC	Brook and Lake Trout	Consumer surplus (conditional compensating variations) (recreational value)	1. $475.87 for 5% increase in catch rates for trout (1977 dollars) 2. $2162.04 for 25% increase in catch rates for trout (1977 dollars) 3. $3862.94 for 50% increase in catch rates for trout (1977 dollars)	1. Economic values were aggregate CCV for 607 survey respondents. 2. Catch rate, as an indicator of acid deposition, was included as a variable in the model.

Reference	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Morgan and Owens (Morgan and Owens)	Chesapeake Bay	Water quality model and Benefit transfer	Water quality	Aggregate benefit (recreational value)	1. Lower bound total benefit for beach use was $288.8m from a 60% improvement in Chesapeake Bay water quality. 2. Lower bound total benefit for trailered boating was $6.7m from a 60% improvement in Chesapeake Bay water quality. 3. Lower bound total benefit for striped bass sport fishing was $288.8m from a 60% improvement in Chesapeake Bay water quality.	1. The study also provided aggregate benefits at avg and high level for three recreational uses. 2. Benefit transfer was based on the results in Bockstael et al. (1988).
Mullen and Menz (1985)	Adirondack, NY	TC	Fish	Net economic value per angler day/ Consumer surplus (recreational value)	1. Net economic value per angler day was avgd at $19.90 for entire waterbody including lakes, ponds, and streams. 2. Total angler value was estimated $31.3 million for entire water body. 3. The loss in net economic value was estimated at $1.07 million for lakes and ponds due to reduction in angler visitation.	1. The values were in 1976 dollars. 2. Total value was aggregated by number of trips.
Randall and Kriesel (1990)	Nationwide, U.S.	CV	Water/air quality	WTP (total value)	1. The estimated annual willingness to pay was $694.42 per household.	1. The study valued a National Pollution Control Program, which improved air and water quality by 25 percent in 5 years.

Reference	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Smith et al. (1991)	Albemarle and Pamlico Sounds, NC	HTC and demand function	Fish	Benefit/ consumer surplus (recreational value)	1. Conventional demand model: $2.58 for boat, $1.11 for bank fishing 2. Simple inverse demand model: $0.79 for boat, $0.62 for bank fishing 3. Detailed inverse demand model: $0.88 for boat, $0.79 for bank fishing	1. Benefit was calculated for an one-fish increase in catch rate per hour per person 2. Catch rate was included in the model. 3. The paper also estimated benefit based on opportunity cost at 1/3 wage.
Whitehead et al. (2000)	Albemarle and Pamlico Sounds, NC	CV and TCM	Fish catches and shellfish beds	Consumer surplus per season/ per trip (recreational value)	1. The consumer surplus per trip is $64 for current quality and $85 for 60% increase in fish catch and 25% more open shellfish beds. 2. The consumer surplus per season is $121 for current quality and $155 for 60% increase in fish catch and 25% more open shellfish beds.	1. The consumer surplus per trip difference between two baseline and scenario was not significant at the 0.10 level while the consumer surplus per season difference between two situations was. 2. The studies also estimated annual aggregate consumer surplus per season for 41 counties within the watershed.

EUTROPHICATION

Reference	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Boyle, et al. (1999)	Four lakes, ME	HTC (two stages, hedonic demand model	Water clarity (visibility)	Consumer surplus (recreational value)	1. The consumer surplus (+) for an avg visibility improvement from 3.78m to 5.15m was $3,765 and $3,677 for semi-log and Cobb-Douglas model. 2. The welfare losses (–) for an avg visibility decrease from 3.78m to 2.41m was $25,388 and $46,750 for semi-log and Cobb-Douglas model.	1. The welfare was also measured in linear demand model. However, the own price of water clarity is not significant.
Diaz and Solow (1992)	Gulf of Mexico	Time series	Brown shrimp, white shrimp, and Menhaden	Mean catch rate per unit effort	1. The study failed to quantify economic effects of hypoxia based on past data.	1. Hypoxia was measured in terms of area (zone) and index in the model to calculate correlation.

Reference	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Kramer and Eisen-Hecht (2002)	Catawba River, NC and SC	CV	Water quality	WTP (total value)	1. A mean willingness to pay was revealed at $139 for maintaining current water quality over time.	1. Phone-mail-phone and mail-phone survey formats applied.
Lipton (2003)	Chesapeake Bay, MA	CV	Water quality	WTP (use value)	1. The median WTP for a one scale improvement in water quality was $17.50 per boater per year and the mean was $63, with 38% expressing a zero WTP.	1. The aggregate WTP for the Chesapeake Bay boaters in Maryland was about $7.3 million per year, total improvement gets a $146 million present value.
Needelman and Kealy (1995)	Lakes, NH	Site choice model and a trip frequency model	Water quality	Benefit (recreational value)	1. The mean seasonal benefits estimates were $1.4 for eliminating eutrophication from all sources ($1.33 for nonpoint source and $0.09 for point source) and the aggregate seasonal benefits were estimated at $1,163,000 for eliminating eutrophication from all sources ($1,105,000 for nonpoint source and $75,000 for point source).	1. The study also reported mean and aggregate seasonal benefits for eliminating bacteria, oil and grease, eutrophication problems, and all pollution from all sources. 2. The benefit estimates address exclusively swimming and day trips.
vNSTC (2000)	Gulf of Mexico, Mississippi-Atchafalay River Basin	Cost effective, simulation model (US Mathematic Programming Model in Agriculture)	Fish, shrimp, and marine ecosystem	Social cost for reduction/ restoration	1 For 20% edge-of-field N-loss reduction, the net cost was estimated at $0.8/kg ($0.36/pound), while restoring 5 million acres of wetland would have net cost of $1.00/kg ($0.45/pound).	1. The benefit to reduce N loadings to the Gulf was difficult to calculate because economic analysis failed to show direct effects on Gulf fisheries, which was a background study conducted by Diaz and Solow (1992).
Park et al. (2002)	Florida Keys, FL	CV	Water quality and health of coral reefs	WTP per trip expenses (recreational value)	1. The annual avg use value was $481.15 per person per snorkeling trip.	

Reference	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Poor et al. (2006)	St. Mary's River watershed, MA	HPVM	Ambient water quality	Avg housing price within the watershed (commercial value)	1. One unit (mg/L) increase in TSS resulted in a $1,086 loss on avg housing prices within the watershed. 2. One unit increase in the dissolved inorganic N resulted in a $17,642 loss on avg housing prices.	1. Total suspended solids and dissolved inorganic N included as indicators of ambient water quality.
Smith and Crowder (2005)	Neuse River, NC	Bio-economic model	Blue crab	Fish rent (commercial value)	1. A 30% reduction in N loadings over a 50–yr time period increases present value rents by 2.56 million, total catch by 12.4 million pounds, and total trips by 91,000.	1. Discounting rate was 2.5%.
Whitehead and Groothuis (1992)	Tar-Pamlico River, NC	CV	Catch rate	WTP (total value, use, and non-use value)	1. The mean WTP resulting from a 61% response rate was estimated at $25, which was bounded from above by a $35 use value, and from below a $21 nonuse value. 2. The aggregate benefits from water quality improvement estimated at $1.62 million each year.	1. The study proposed a program in which farmers are required to use BMPs to improve the water quality of the Tar-Pamlico River so that anglers would catch twice as many fish per trip. 2. A mail survey was sent to 179 households in four counties in Tar-Pamlico River basin.
VARIOUS EFFECTS						
Johnston et al. (2005)	U.S. and Canada	Meta-analysis	Catch rate	WTP (recreational use)	1. WTP per fish over the sample ranged from $.048 to $612.79, with a mean of $16.82	1. This study supports previous findings that WTP is systematically associated with resource, context, and angler attributes.

Glossary

Acid Neutralizing Capacity (ANC)
> A key indicator of the ability of water to neutralize acidifying inputs. This ability depends largely on associated biogeochemical characteristics.

Acidification
> The process of decreasing the pH of a system. Systems that can be acidified by atmospheric deposition of acidic or acidifying compounds include lakes, streams, and forest soils.

Algae
> Photosynthetic, often microscopic and planktonic, organisms occurring in aquatic ecosystems.

Algal bloom
> A rapid and extreme increase of an algae population in a lake, river, or ocean.

Alpine
> The biogeographic zone made up of slopes above the *tree line*, and characterized by the presence of rosette-forming herbaceous plants and low, shrubby, slow-growing woody plants.

Anthropogenic
> Resulting from human activity or produced by human beings.

Arid region
> An area receiving <250 mm precipitation per year.

Atmosphere
> The gaseous envelope surrounding the Earth. The dry atmosphere consists almost entirely of nitrogen and O_2, together with trace gases including carbon dioxide and ozone.

Base cation saturation
> The degree to which soil cation exchange sites are occupied with base cations (e.g., Ca^{2+}, Mg^{2+}, K^+) as opposed to Al_3^+ and H^+. Base cation saturation is a measure of soil acidification, with lower values being more acidic. A marked increase in the sensitivity of soils to changes in base saturation occurs at a threshold of approximately 20%.

Bioaccumulation
> The gradual increase in accumulation of some compounds in organisms with increasingly higher trophic levels.

Biodiversity
> The total diversity of all organisms and ecosystems at various spatial scales (from genes to biomes).

Buffering capacity
> The ability of a body of water and its watershed to resist changes in pH.

Carbon sequestration
> The process of increasing the carbon content of a reservoir other than the atmosphere.

Catchment

An area that collects and drains rainwater.

Climate

Climate in a narrow sense is usually defined as the 'average weather', or more rigorously, as the statistical description in terms of the mean and variability of relevant quantities over a period of time ranging from months to thousands or millions of years. These quantities are most often surface variables such as temperature, precipitation, and wind. Climate in a wider sense is the state, including a statistical description, of the *climate system*. The generally accepted period of time is 30 years, as defined by the World Meteorological Organization (WMO).

Critical load

A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge.

Denitrification

The anaerobic reduction of oxidized nitrogen (e.g., nitrate or nitrite) to gaseous nitrogen (e.g., N_2O or N_2), normally accomplished by denitrifying bacteria.

Dry deposition

The movement of gases and particles from the atmosphere to surfaces in the absence of precipitation (e.g., rain or snow) or occult deposition.

Ecological community

An assemblage of populations of different species, interacting with one another

Ecosystem services

Ecological processes or functions having monetary or non-monetary value to individuals or society at large. They may be classified as (i) supporting services such as productivity or biodiversity maintenance; ii) provisioning services such as food, fibre, or fish; iii) regulating services such as climate regulation or carbon sequestration; and (iv) cultural services such as tourism or spiritual and aesthetic appreciation.

Ecosystem

The interactive system formed from all living organisms and their abiotic (physical and chemical) environment within a given area. Ecosystems cover a hierarchy of spatial scales and can comprise the entire globe, *biomes* at the continental scale, or small, well-circumscribed systems such as a small pond.

Eutrophication

The enrichment of a waterbody with nutrients, resulting in increased productivity (of algae or aquatic plants), and sometimes also decreased dissolved O_2 levels.

Eutrophy

Eutrophy generally refers to a state of nutrient enrichment, but it is commonly used to refer to condition of increased algal biomass and productivity, presence of nuisance algal populations, and a decrease in dissolved O_2 concentrations.

Evapotranspiration

The combined process of water evaporation from the Earth's surface and transpiration from vegetation.

Fen

A phase in the development of the natural succession from open lake, through reedbed, fen and carr, to woodland as the peat develops and its surface rises.

Freshet

A great rise or overflowing of a stream caused by heavy rains or melted snow.

Greenhouse gas

Those atmospheric gasses that absorb and emit radiation emitted by the Earth's surface, the atmosphere, and clouds within the infrared portion of the spectrum. This property causes the greenhouse effect. Water vapour (H_2O), carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), and ozone (O_3) are the primary greenhouse gases in the Earth's atmosphere. Besides these, the *Kyoto Protocol* also deals with the greenhouse gases sulphur hexafluoride (SF_6), hydrofluorocarbons (HFCs), and perfluorocarbons (PFCs).

Gross primary production

The total carbon fixfixed by plant through photosynthesis.

Heathland

A wide-open landscape dominated by low-growing woody vegetations such as heathers and heathland grasses. Heathlands generally occur on acidic, nutrient-poor, and often sandy and well-draining soils.

Hypoxic

Events that lead to a deficiency of O_2.

Invasive species and invasive alien species

A species aggressively expanding its range and population density into a region in which it is not native, often through outcompeting or otherwise dominating native species.

Leaching

The removal of soil elements or chemicals by water movement through the soil.

Lowland

In physical geography, lowland is any relatively flat area in the lower levels of regional elevation. The term can be applied to the landward portion of the upward slope from oceanic depths to continental highlands, to a region of depression in the interior of a mountainous region, to a plain of denudation, or to any region in contrast to a highland.

Net ecosystem exchange (NEE)

The net flux of carbon between the land and the atmosphere, typically measured using eddy covariance techniques. Positive values of NEE usually refer to carbon released to the atmosphere (i.e., a source), and negative values refer to carbon uptake (i.e., a sink)

Net ecosystem production (NEP)

The difference between net primary production (NPP) and heterotrophic respiration (mostly decomposition of dead organic matter) of that ecosystem over the same area. NEP = -NEE, with positive values indicating a sequestration of atmospheric carbon in to biosphere.

Net primary production (NPP)

The *gross primary production* minus autotrophic *respiration*, i.e., the sum of metabolic processes for plant growth and maintenance, over the same area.

Nitrification

The biological oxidation of ammonia to nitrite and then to nitrate. This process is primarily accomplished by autotrophic nitrifying bacteria that obtain energy by reducing ammonium and/or nitrite to nitrate.

Nitrogen mineralization

The conversion of organic nitrogen into plant-available inorganic forms (e.g., NH_3 or NH_4^+) by microorganisms.

Nitrogen-retention capacity

The length of time that an ecosystem can retain nitrogen in plants, microbes and soil-organic matter. Nitrogen-retention capacity is highly affected by soil, vegetative, topographic, and land-use factors.

Nitrogen saturation

The condition in which nitrogen inputs from atmospheric deposition and other sources exceed the biological requirements of the ecosystem.

Occult deposition

The transmission of gases and particles from the atmosphere to surfaces by fog or mist.

Ombrotrophic bog

An acidic peat-accumulating wetland that is fed by rainwater (instead of groundwater) and, thus, especially poor in nutrients.

pH

A measure of the relative concentration of hydrogen ions in a solution. The formula for calculating pH is: $pH = -\log_{10}[H^+]$, where $[H^+]$ represents the hydrogen ion concentration in moles per liter. The pH scale ranges from 0 to 14. A pH of 7 is neutral. A pH less than 7 is acidic and a pH greater than 7 is basic.

Phytoplankton

The plant forms of *plankton*. Phytoplankton are the dominant plants in the sea and are the basis of the marine food web. These single-celled organisms are the principal agents of photosynthetic carbon fixfixation in the ocean.

Primary Production

All forms of production accomplished by plants, also called primary producers. See *GPP, NPP,* and *NEP*.

Semi-arid regions

Regions of moderately low rainfall (100– and 250–mm precipitation per year), which are not highly productive and are usually classified as *rangelands.*

Sensitivity

The degree to which a system responds to pollution (e.g., acidification, n-nutrient enrichment, etc.). The response may be direct (e.g., a change in growth following a change in the mean, range, or variability of N deposition) or indirect (e.g., changes in growth due to alterations in competitive dynamics between species or decreased biodiversity , themselves following N deposition).

Streamflow

Water flow within a river channel. A synonym for *river discharge*.

Surface runoff

The water that travels over the land surface to the nearest surface stream; *runoff* of a drainage *basin* that has not passed beneath the surface since precipitation.

Throughfall

The precipitation falling through the canopy of a forest and reaching the forest floor.

Trophic level

The position that an organism occupies in a food web.

Tundra

A treeless, level, or gently undulating plain characteristic of the Arctic, sub-Arctic regions and some alpine regions characterized by low temperatures and short growing seasons.

Upland terrestrial ecosystem

Generally considered to be the ecosystems located at higher elevations directly above riparian zones and wetlands. Vegetation in an upland ecosystem is not in contact with groundwater or other permanent water sources.

Valuation

The economic or non-economic process of determining either the value of maintaining a given ecosystem type, state, or condition or the value of a change in an ecosystem, its components, or the services it provides.

Vulnerability

Susceptibility to degradation or damage from adverse factors or influences. Vulnerability is a function the exposure and its sensitivity.

Welfare effects

Effects on soils, water, crops, vegetation, man-made materials, animals, wildlife, weather, visibility and climate, damage to and deterioration of property, and hazards to transportation, as well as effects on economic values and on personal comfort and well-being, whether caused by transformation, conversion, or combination with other air pollutants (CAA 302(h)).

Wet deposition

The transmission of gases and particles from the atmosphere to surfaces by rain or other precipitation.

Wetland

Those areas that are inundated or saturated by surface or ground water at a frequency and duration sufficient to support a prevalence of vegetation adapted to water-saturated soil conditions. Wetlands include swamps, marshes, bogs, and similar areas.

Zooplankton

The animal forms of plankton. They consume phytoplankton or other zooplankton.

References

Aastrup T; Wadsak M; Leygraf C; Schreiner M. (2000). In situ studies of the initial atmospheric corrosion of copper influence of humidity, sulfur dioxide, ozone, and nitrogen dioxide. J Electrochem Soc, 147, 2543-2551.

Abbot DS; Palmer PI; Martin RV; Chance KV; Jacob DJ; Guenther A. (2003). Seasonal and interannual variability of North American isoprene emissions as determined by formaldehyde column measurements from space. Geophys Res Lett, 30, 1886. doi:10.1029/2003GL017336.

Aber JD; Nadelhoffer KJ; Steudler P; Mellilo JM. (1989). Nitrogen saturation in northern forest ecosystems. Excess nitrogen from fossil fuel combustion may stress the biosphere. Bioscience, 39, 378-386.

Aber JD; Mellilo JM; Nadelhoffer KJ; Pastor J; Boone RD. (1991). Factors controlling nitrogen cycling and nitrogen saturation in northern temperate forest ecosystems. Ecol Appl, 1, 303-315.

Aber JD. (1992). Nitrogen cycling and nitrogen saturation in temperate forest ecosystems. Trends Ecol Evol, 7, 220-224.

Aber JD; Federer CA. (1992). A generalized, lumped-parameter model of photosynthesis, evapotranspiration and net primary production in temperate and boreal forest ecosystems. Oecologia, 92, 463-474.

Aber JD; Driscoll CT. (1997). Effects of land use, climate variation, and N deposition on N cycling and C storage in northern hardwood forests. Global Biogeochem Cycles, 11, 639-648.

Aber JD; Ollinger S; Driscoll C. (1997). Modeling nitrogen saturation in forest ecosystems in response to land use and atmospheric deposition. Ecol Modell, 101, 61-78.

Aber JD; McDowell W; Nadelhoffer K; Magill A; Berntson G; Kamakea M; McNulty S; Currie W; Rustad L; Frenandez I. (1998). Nitrogen saturation in temperate forest ecosystems: Hypotheses revisited. Bioscience, 48, 921-934.

Aber JD; Ollinger SV; Driscoll CT; Likens GE; Holmes RT; Freuder RJ; Goodale CL. (2002). Inorganic nitrogen losses from a forested ecosystem in response to physical, chemical, biotic, and climatic perturbations. Ecosystems, 5, 648-658.

Aber JD; Goodale CL; Ollinger SV; Smith ML; Magill AH; Martin ME; Hallett RA; Stoddard JL. (2003). Is nitrogen deposition altering the nitrogen status of northeastern forests? Bioscience, 53, 375-389.

Aber JD; Magill AH. (2004). Chronic nitrogen additions at the Harvard Forest (USA): The first 15 years of a nitrogen saturation experiment. For Ecol and Manage, 196, 1-5.

Achermann B; Bobbink R. (2003). Empirical critical loads for nitrogen. Proceedings of an expert workshop held under the UNECE Convention on Long-range Transboundary Air Pollution held in Berne, Switzerland; November, 2002. (Environmental Documentation no. 164). Berne, Switzerland; Swiss Agency for the Environment, Forests, and Landscape (SAEFL).

Adams AB; Harrison RB; Sletten RS; Strahm BD; Turnblom EC; Jensen CM. (2005). Nitrogen-fertilization impacts on carbon sequestration and flux in managed coastal Douglas-fir stands of the Pacific Northwest. For Ecol Manage, 220, 313-325.

Adams MA; Iser J; Keleher AD; Cheal DC. (1994). Nitrogen and phosphorus availability and the role of fire in heathlands at Wilsons Promontory. Aust J Bot, 42, 269-281.

Adams MB; Edwards PJ; Wood F; Kochenderfer JN. (1993). Artificial watershed acidification on the Fernow Experimental Forest, USA. J Hydro1, 150, 505-519.

Adams MB; Angradi TR; Kochenderfer JN. (1997). Stream water and soil solution responses to 5 years of nitrogen and sulfur additions at the Fernow Experimental Forest, West Virginia. For Ecol Manage, 95, 79-91.

Adams MB. (1999). Acidic deposition and sustainable forest management in the central Appalachians, USA. For Ecol Manage, 122, 17-28.

Adams MB; Burger JA; Jenkins AB; Zelazny L. (2000). Impact of harvesting and atmospheric pollution on nutrient depletion of eastern U.S. hardwood forests. For Ecol Manage, 138, 301-319.

Adams MB. (2003). Ecological issues related to N deposition to natural ecosystems: Research needs. Environ Int, 29, 189-199.

Adams RM; Hamilton SA; McCarl BA. (1986a). The benefits of pollution control: The case of ozone and U.S. agriculture. Am J Agric Econ, 68, 886-893.

Adams RM; Callaway JM; McCarl BA. (1986b). Pollution, agriculture and social welfare: The case of acid deposition. Can J Agric Econ, 34, 3-19.

Adams RM; Crocker TD. (1989). The agricultural economics of environmental change: Some lessons from air pollution. J Environ Manage, 28, 295-307.

Adams RM; Horst RL Jr. (2003). Future directions in air quality research: Economic issues. Environ Int, 29, 289-302.

Adams SM; Greeley MS; Law JM; Noga EJ; Zelikoff JT. (2003). Application of multiple sublethal stress indicators to assess the health of fish in Pamlico Sound following extensive flooding. Estuaries, 26, 1365-1382.

Adamsen APS; King GM. (1993) Methane consumption in temperate and sub-arctic forest soils: Rates, vertical zonation, and responses to water and nitrtogen. Appl Environ Microbiol, 59, 485-490.

Aeschlimann U; Nosberger J; Edwards PJ; Schneider MK; Richter M; Blum H. (2005). Responses of net ecosystem CO_2 exchange in managed grassland to long-term CO_2 enrichment, N fertilization and plant species. Plant Cell Environ, 28, 823-833.

Aerts R; Berendse F. (1988). The effect of increased nutrient availability on vegetation dynamics in wet heathlands. Plant Ecology, 76, 63-69.

Aerts R. (1990). Nutrient use efficiency in evergreen and deciduous species from heathland. Oecologia, 84, 391-397.

Aerts R; Berendse F; De Caluwe H; Schmits M. (1990). Competition in heathland along an experimental gradient of nutrient availability. Oikos, 57, 310-318.

Aerts R; Toet S. (1997). Nutritional controls on carbon dioxide and methane emission from Carex-dominated peat soils. Soil Biol Biochem, 29, 1683-1690.

Aerts R; de Caluwe H. (1999). Nitrogen deposition effects on carbon dioxide and methane emissions from temperate peatland soils. Oikos, 84, 44-54.

Aerts R; Verhoeven JTA; Whigham DF. (1999). Plant-mediated controls on nutrient cycling in temperate fens and bogs. Ecology, 80, 2170-2181.

Agelakopoulou T; Bassiotis I; Metaxa E; Roubani-Kalantzopoulou F. (2007). Benzene and toluene influence with or without nitrogen dioxide on inorganic pigments of works of art-Part II. Atmos Environ, 41, 2009-2018.

Aherne J; Larssen T; Dillon PJ; Cosby BJ. (2004). Effects of climate events on elemental fluxes from forested catchments in Ontario, Canada: Modelling drought-induced redox processes. Water Air Soil Pollut, 4, 37-48.

Aherne J; Larssen T; Cosby BJ; Dillon PJ. (2006). Climate variability and forecasting surface water recovery from acidification: Modelling drought-induced sulphate release from wetlands. Sci Total Environ, 365, 186-199.

Ainsworth EA; Long SP. (2005). What have we learned from 15 years of free-air CO_2 enrichment (FACE)? A meta-analytic review of the responses of photosynthesis, canopy properties and plant production to rising CO_2. New Phytol, 165, 351-371.

Ainsworth EA; Rogers A. (2007). The response of photosynthesis and stomatal conductance to rising $[CO_2]$: Mechanisms and environmental interactions. Plant Cell Environ, 30, 258-270.

Akiyama H; Yagi K; Yan XY. (2005). Direct N_2O emissions from rice paddy fields: Summary of available data. Glob Biogeochem Cycles, *19,* doi:10.1029/2004GB002378.

Alban DH. (1982). Effects of nutrient accumulation by aspen, spruce, and pine on soil properties. Soil Sci Soc Am J, 46, 853-861.

Alberti M; Booth D; Hill K; Coburn B; Avolio C; Coe S; Spirandelli D. (2007). The impact of urban patterns on aquatic ecosystems: an empirical analysis in Puget lowland sub-basins. Landsc Urban Plan, 80, 345-361.

Albinet A; Leoz-Garziandia E; Budzinski H; Viilenave E. (2006). Simultaneous analysis of oxygenated and nitrated polycyclic aromatic hydrocarbons on standard reference material 1649a (urban dust).and on natural ambient air samples by gas chromatography-mass spectrometry with negative ion chemical ionisation. J Chromatogr A, 1121, 106-113.

Alcamo J; Shaw R; Hordijk L. (1990). The RAINS model of acidification: Science and stratigies in Europe. Dordrecht, The Netherlands: Kluwer Academic Publishers.

Alcorn SH; Lurmann FW. (2004). Southern California children's health study exposure database (final report). Petaluma, CA: Sonoma Technology, Inc., (Report no. STI-95230-2453-FR3). Prepared for Division of Environmental Health; University of Southern California School of Medicine.

Aldous AR. (2002). Nitrogen retention by Sphagnum mosses: Responses to atmospheric nitrogen deposition and drought. Can J Bot, 80, 721-731.

Alewell C; Gehre M. (1999). Patterns of stable S isotopes in a forested catchment as indicators for biological S turnover. Biogeochemistry, 47, 317-331.

Alexander RB; Smith RA; Schwarz GE. (2000). Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. Nature, 403, 758-761.

Alexander RB; Smith RA; Schwarz GE; Preston SD; Brakebill JW; Srinivasan R; Pacheco PA. (2001). Atmospheric nitrogen flux from the watersheds of major estuaries of the United States: An application of the SPARROW watershed model. In: Valigura R;, Alexander R; Castro M; Meyers T; Paerl H; Stacey P; Turner RE (Eds.), Nitrogen loading in coastal water bodies: An atmospheric perspective. (Vol. monograph 57, pp. 119-170). Washington, DC: American Geophysical Union.

Alexander RB; Johnes RJ; Boyer EW; Smith RA. (2002). A comparison of models for estimating the riverine export of nitrogen from large watersheds. Biogeochemistry, 57/58, 295-339.

Alexander RB; Boyer EW; Smith RA; Schwarz GE; Moore RB. (2007). The role of headwater streams in downstream water quality. J Am Water Resources Assoc, 43, 41-59.

Alicke B; Hebestreit K; Stutz J; Platt U. (1999). Iodine oxide in the marine boundary layer. Nature, 397, 572-573.

Allan BJ; McFiggans G; Plane JMC; Coe H. (2000). Observations of iodine monoxide in the remote marine boundary layer. J Geophys Res, 105, 14363-14369.

Allegrini I; Febo A; Perrino C. (Eds.) (1992). Field intercomparison exercise on ammonium measurement. Proceedings from Rome, Italy April 29-May 4, 1990. Air Pollution Research Report #37. Brussels, Belgium: Commission of European Communities (CEC).

Allen DJ; Pickering KE; Molod A. (1997). An evaluation of deep convective mixing in the Goddard Chemical Transport Model using ISCCP cloud parameters. J Geophys Res, 102, 25467-25476.

Allen DJ; Pickering K; Stenchikov G; Thompson A; Kondo Y. (2000). A three-dimensional total odd nitrogen (NO_Y).simulation during SONEX using a stretched-grid chemical transport model. J Geophys Res, 105, 3851-3876

Allen EB; Padgett PE; Bytnerowicz A; Minich R. (1998). Nitrogen deposition effects on coastal sage vegetation of southern California (No. PSW-GTR-166; pp 131-139): U.S. Forest Service; U.S. Department of Agriculture (USDA).

Allen EB; Sirulnik AG; Egerton-Warburton L; Kee SN; Bytnerowicz A; Padgett PE; Temple PJ; Fenn ME; Poth MA; Meixner T. (2005). Air pollution and vegetation change in southern California coastal sage scrub: A comparison with chaparral and coniferous forest. In: Kus BE; Beyers JL (Eds.), Planning for biodiversity: Bringing research and management together. (general technical report PSW-GTR-195; pp. 79-95). Albany, CA; Pacific Southwest Research Station; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Allen EB; Bytnerowicz A; Fenn ME; Minnich RA; Allen MF. (2007). Impact of anthropogenic N deposition on weed invasion, biodiversity, and the fire cycle at Joshua Tree National Park (No. PMIS 72123). University of California, Riverside. Center for Conserv Biol (CCB); and Forest Fire Laboratory of the U.S. Forest Service; U.S. Department of Agriculture (USDA).

Allen EB; Rao LE; Steers RJ. (2008). Impacts of atmospheric nitrogen deposition on vegetation and soils at Joshua Tree National Park. In: Webb RH; Fenstermaker LF; Heaton JS; Hughson DL; McDonald EV; Miller DM (Eds.), The Mojave Desert: Ecosystem processes and sustainability. Reno, NV: University of Nevada Press.

Allen NS; Hershey AE. (1996). Seasonal changes in chlorophyll *a* response to nutrient amendments in a North Shore tributary of Lake Superior. J North Am Benthol Soc, 15, 170-178.

Alley RB; Clark PU; Huybrechts P; Joughin I. (2005). Ice-sheet and sea-level changes. Science, 310, 456-460.

Almeida E; Morcillo M; Rosales B. (2000a). Atmospheric corrosion of zinc; Part 2: Marine atmospheres. British Corrosion Journal, 35, 289-296.

Almeida E; Morcillo M; Rosales B. (2000b). Atmospheric corrosion of mild steel. Part II - Marine atmospheres. Mater Corros, 51, 865-874.

Almer B; Dickson W; Ekström C; Hörnström E; Miller U. (1974). Effects of acidification on Swedish lakes. Ambio, 3, 30-36.

Altshuller AP; Linthurst RA. (Eds.). (1984). The acidic deposition phenomenon and its effects: Critical assessment review papers. (Report no. EPA-600/8-83-016-BF.). Washington, DC: U.S. Environmental Protection Agency.

Alvarez R; Weilenmann M; Favez J-Y. (2008). Evidence of increased mass fraction of NO_2 within real-world NO_X emissions of modern light vehicles—derived from a reliable online measuring method. Atmos Environ, 42, 4699-4707.

Alveteg M; Sverdrup H. (2002). Manual for regional assessments using the SAFE model (draft version 8 April 2002). Lund, Sweden: Department of Chemical Engineering II, Lund University.

Alvo R; Hussell DJT; Berrill M. (1988). The breeding success of common loons (*Gavia immer*) in relation to alkalinity and other lake characteristics in Ontario. Can J Zool, 66, 746-752.

Ambrose RA Jr; Woll TA; Martin JL. (1995). The water quality analysis simulation program, WASP5, Part A: Model documentation. Athens, GA; Ecosystems Division; National Exposure Research Laboratory; Office of Research and Development; U.S. Environmental Protection Agency.

Ambus P; Robertson GP. (2006). The effect of increased N deposition on nitrous oxide, methane and carbon dioxide fluxes from unmanaged forest and grassland communities in Michigan. Biogeochemistry, 79, 315-337.

Ambus P; Zechmeister-Boltenstern S; Butterbach-Bahl K. (2006). Sources of nitrous oxide emitted from European forest soils. Biogeosciences, 3, 135-145.

Ammann M; von Ballmoos P; Stalder M; Suter M; Brunold C. (1995). Uptake and assimilation of atmospheric NO_2^--N by spruce needles (Picea abies): A field study. Water Air Soil Pollut, 85, 1497-1502.

Ammann M; Kalberer M; Jost DT; Tobler L; Rossler E; Piguet D; Gaggeler HW; Baltensperger U. (1998). Heterogeneous production of nitrous acid on soot in polluted air masses. Nature, 395, 157-160.

Ammann M; Siegwolf R; Pichlmayer F; Suter M; Saurer M; Brunold C. (1999). Estimating the uptake of traffic-derived NO_2 from N-15 abundance in Norway spruce needles. Oecologia, 118, 124-131.

Amundson RG; McLean DC. (1982). Influence of oxides of nitrogen on crop growth and yield: An overview. In Schneider T; Grant L (Eds.), Air pollution by nitrogen oxides. (Series: Studies in environmental science Volume 21; Proceedings of the U.S.-Dutch international symposium held in Maastricht, The Netherlands in May 1982; pp 501-510). Amsterdam, The Netherlands: Elsevier Scientific Publishing.

Anastasio C; Newberg JT; Williams DK; Chu GB; Matthew BM. (1999). Photoformation of hydroxyl radical in sea salt particles. Presented at 1999 Fall Meeting December 13-17, 1999; San Francisco, CA. Sponsored by American Geophysical Union; Trans American Geophys Union, 80, Abstract F147.

Anderson HR; Spix C; Medina S; Schouten JP; Castellsague J; Rossi G; Zmirou D; Touloumi G; Wojtyniak B; Ponka A; Bacharova L; Schwartz J; Katsouyanni K. (1997). Air pollution and daily admissions for chronic obstructive pulmonary disease in 6 European cities: Results from the APHEA project. Eur Respir J, 10, 1064-1071.

Anderson NJ; Renberg I; Segerstrom U. (1995). Diatom production responses to the development of early agriculture in a boreal forest lake-catchment (Kassjon, Northern Sweden). J Ecol, 83, 809-822.

Andreae MO. (1991). Biomass burning: Its history, use, and distribution and its impact on environmental quality and global climate. In: Levine, JS (Ed.), Global biomass burning: Atmospheric, climatic, and biospheric implications (pp. 1-21). Cambridge, MA: MIT Press.

Andreae MO; Crutzen PJ. (1997). Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry. Science, 276, 1052-1058.

Andrews JA; Schlesinger WH. (2001). Soil CO_2 dynamics, acidification, and chemical weathering in a temperate forest with experimental CO_2 enrichment. Glob Biogeochem Cycles, 15, 149-162.

Aneja VP; Chauhan JP; Walker JT. (2000). Characterization of atmospheric ammonia emissions from swine waste storage and treatment lagoons. J Geophys Res, 105, 11535-11546.

Aneja et al., 1998 ambient NH3 concentration

Ansari AS; Pandis SN. (2000). Water absorption by secondary organic aerosol and its effect on inorganic aerosol behavior. Environ Sci Technol, 34, 71-77.

Antoine ME. (2001). Ecophysiology of the cyanolichen, *Lobaria oregana*. M.S. Thesis, Corvallis, OR; Oregon State University.

Antoine ME. (2004). An Ecophysiological approach to quantifying nitrogen fixation by *Lobaria oregano*. Bryologist, 107, 82-87.

Appel BR; Tokiwa Y; Haik M. (1981). Sampling of nitrates in ambient air. Atmos Environ, 15, 283-289.

Appel BR; Tokiwa Y; Kothny EL; Wu R; Povard V. (1988). Evaluation of procedures for measuring atmospheric nitric acid and ammonia. Atmos Environ, 22, 1565-1573.

Appel KW; Gilliland A; Eder B. (2005). An operational evaluation of the 2005 release of models-3 CMAQ version 4.5. Washington, DC: Atmospheric Sciences Modeling Division, Air Resources Laboratory, National Oceanic and Atmospheric Administration (NOAA).

Appelo CAJ; Postma D. (1993). Geochemistry, groundwater, and pollution. Rotterdam, The Netherlands: AA Balkema Publishers.

Appel K; Bhave PV; Gilliland AB; Sarwar G; Roselle SJ. (2008). Evaluation of the community multiscale air quality (CMAQ) model version 4.5: Sensitivities impacting model performance; Part IIâ€"particulate matter. Atmospheric Environment 42: 6057-6066.ApSimon HM; Cowell D. (1996). The benefits of reduced damage to buildings from abatement of sulphur dioxide emissions. Energy Policy, 24, 651-654.

Arbaugh MJ; Miller PR; Carroll JJ; Takemoto BL; Proctor T. (1998). Relationships of ozone exposure to pine injury in the Sierra Nevada and San Bernardino Mountains of California, USA. Environ. Pollut, 101, 291-301.

Arbaugh MJ; Peterson DL; Miller PR. (1999). Air pollution effects on growth of ponderosa pine, Jeffrey pine, and bigcone Douglas fir. In: Miller PR; McBride JR (Eds.), Oxidant air pollution impacts in the montane forests of southern California: A case study of the San Bernardino Mountains. (pp. 179-207). New York, NY: Springer-Verlag.

Arbaugh M; Bytnerowicz A; Grulke N; Fenn M; Poth M; Temple T; Miller P. (2003). Photochemical smog effects in mixed conifer forests along a natural gradient of ozone and nitrogen deposition in the San Bernardino Mountains. Environ Int, 29, 401-406.

Arbizzani R; Casellato U; Fiorin E; Nodari L; Russo U; Vigato PA. (2004). Decay markers for the preventative conservation and maintenance of paintings. Journal of Cultural Heritage, 5, 167-182.

Arey J; Zielinska B; Atkinson R; Winer AM; Ramdahl T; Pitts JN Jr. (1986). The formation of nitro-PAH from the gas-phase reactions of fluoranthene and pyrene with the OH radical in the presence of NO_X. Atmos Environ, 20, 2339-2345.

Arey J; Atkinson R; Zielinska B; McElroy PA. (1989). Diurnal concentrations of volatile polycyclic aromatic hydrocarbons and nitroarenes during a photochemical air pollution episode in Glendora, California. Environ Sci Technol, 23, 321-327.

Arey J. (1998). Atmospheric reactions of PAHs including formation of nitroarenes. In: Neilson AH (Ed.), Anthropogenic compounds. Part I. PAHs and related compounds - chemistry (Volume 3, Series: Hutzinger O (Ed.): The handbook of environmental chemistry. pp. 347-385). New York, NY: Springer-Verlag.

Arheimer B; Wittgren HB. (1994). Modelling the effects of wetlands on regional nitrogen transport. Ambio, 23, 378-386.

Arndt U; Billen N; Seufert G; Ludwig W; Borkhart K; Ohnesorge B. (1990). Visible injury responses. Environ Pollut, 68, 355-62

Arnebrandt K; Baath E; Soderstrom B. (1990). Changes in microfungal community structure after fertilization of scots pine forest soils with ammonium nitrate or urea. Soil Biol Biochem, 22, 309-312.

Arnold CL; Gibbons CJ. (1996). Impervious surface coverage: Emergence of a key environmental indicator. J Am Planning Assoc, 62, 243-258.

Arnold JR; Dennis RL; Tonnesen GS. (1998). Advanced techniques for evaluating Eulerian air quality models: Background and methodology. Paper presented at the American Meteorological Society 10th Joint Conference on the Applications of Air Pollution Meteorology with the Air & Waste Management Association January 11-16, 1998, Phoenix, AZ. (pp 1-5). Boston, MA: American Meteorological Society.

Arnold JR; Dennis RL. (2001). First results from operational testing of the U.S. EPA models-3/community multiscale model for air quality (CMAQ). In :Gryning S-E; Schiermeier FA (Eds.), Air pollution modelling and its application XIV. Proceedings of the Millennium NATO/CCMS international technical meeting on air pollution modeling and its application; May 15-19, 2000 in Boulder, Colorado. (Part 6: pp 651-658). New York, NY: Kluwer Academic Publishing.

Arnold JR; Dennis RL; Tonnesen GS. (2003). Diagnostic evaluation of numerical air quality models with specialized ambient observations: Testing the community multiscale air quality modeling system (CMAQ) at selected SOS 95 ground sites. Atmos Environ, 37, 1185-1198.

Arnold JR; Dennis RL. (2006). Testing CMAQ chemistry sensitivities in base case and emissions control runs at SEARCH and SOS99 surface sites in the southeastern U.S. Atmos Environ, 40, 5027-5040.

Arnold JR; Hartsell BE; Luke WT; Ullah SMR; Dasgupta PK; Huey LG; Tate P. (2007). Field test of four methods for gas-phase ambient nitric acid. Atmos Environ, 41, 4210-4226.

Arnold JR; Luke WT. (2007). Nitric acid and the origin and size segregation of aerosol nitrate aloft during BRACE 2002. Atmos Environ, 41, 4227-4241.

Arp PA; Oja T; Marsh M. (1996). Calculating critical S and N loads and current exceedances for upland forests in southern Ontario, Canada. Can J For Res, 26, 696-709.

Arrigo KR. (2005). Marine microorganisms and global nutrient cycles. Nature, 437, 349-355.

Arrington DV; Lindquist RC. (1987). Thickly mantled Karst of the Interlachen, Florida area. In: Beck BF; Wilson WL (Eds.), Karst hydrology: Engineering and environmental applications. Proceedings of the 2nd multidisciplinary conference on sinkholes and the engineering and environmental impacts of Karst. February 9-11, 1987 - Orlando Florida. (pp. 31-39). Rotterdam, The Netherlands; AA Balkema Publishers.

Arrow K; Solow R; Portney P; Leamer E; Radner R; Schuman H. (1993). Report of the NOAA Panel on Contingent Valuation. Federal Register 58(10), 4601-4614.

Ashby JA; Bowden WB; Murdoch PS. (1998). Controls on denitrification in riparian soils in headwater catchments of a hardwood forest in the Catskill Mountains, USA. Soil Biol Biochem, 30, 853-864.

Ashenden T. (1979). The effects of long-term exposures to SO_2 and NO_2 pollution on the growth of *Dactylis glomerata* L. and *Poa pratensis* L. Environ Pollut, 18, 249-258.

Ashendorff A; Principe MA; Seeley A; LaDuca J; Beckhardt L; Faber WJ; Mantus J. (1997). Watershed protection for New York City's supply. Journal of the American Water Works Association, 89, 75-88.

Ashworth SH; Allan BJ; Plane JMC. (2002). High resolution spectroscopy of the OIO radical: Implications for the ozone-depleting potential of iodine. Geophys Res Lett, 29, 1456, doi: 10.1029/2001GL013851.

Askey A; Lyon SB; Thompson GE; Johnson JB; Wood GC; Sage PW; Cooke MJ. (1993). The effect of atmospheric fly-ash particulates on the atmospheric corrosion of zinc and mild steel. Corros Sci, 34, 1055-1081.

Asman WAH; Drukker B; Janssen AJ. (1988). Modeled historical concentrations and depositions of NH_3 and NH_4 in Europe. Atmos Environ, 22, 725-735.

Asman WAH; van Jaarsveld JA. (1992). A variable-resolution transport model applied for NH_X for Europe. Atmos Environ, 26, 445-464.

Asman WAH; Sutton MA; Schjorring J. (1998). Ammonia: Emission, atmospheric transport and deposition. New Phytol, 139, 27-48.

Asner GP; Townsend AR; Riley WJ; Matson PA; Neff JC; Cleveland CC. (2001). Physical and biogeochemical controls over terrestrial ecosystem responses to nitrogen deposition, Biogeochemistry, 54, 1–39

Asp H; Berggren D. (1990). Phosphate and calcium uptake in beech (*Fagus sylvatica*) in the presence of aluminium and natural fulvic acids. Physiol Plant, 80, 307-314.

Atkinson R; Winer AM; Pitts JN Jr. (1986). Estimation of night-time N_2O_5 concentrations from ambient NO_2 and NO_3 radical concentrations and the role of N_2O_5 in night-time chemistry. Atmos Environ, 20, 331-339.

Atkinson R; Arey J; Zielinska B; Aschmann SM. (1990). Kinetics and nitro-products of the gas-phase OH and NO_3 radical-initiated reactions of naphthalene-d_8, fluoranthene-d_{10}, and pyrene. Int J Chem Kinetics, 22, 999-1014.

Atkinson R; Baulch DL; Cox RA; Hampson RF Jr; Kerr JA; Troe J. (1992). Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement IV, IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry. J Phys Chem Ref Data, 21, 1125-1568.

Atkinson R; Arey J. (1994). Atmospheric chemistry of gas-phase polycyclic aromatic hydrocarbons: Formation of atmospheric mutagens. Environ Health Perspect, 4, 117-126.

Atkinson R. (2000). Atmospheric chemistry of VOCs and NO_X. Atmos Environ, 34, 2063-2101.

Audet C; Wood CM. (1988). Do rainbow trout (*Salmo gairdneri*) acclimate to low pH? Can J Fish Aquat Sci, 45, 1399-1405.

Ausset P; Del Monte M; Lefèvre RA. (1999). Embryonic sulphated black crusts on carbonate rocks in atmospheric simulation chamber and in the field: role of carbonaceous fly-ash. Atmos Environ, 33, 1525-1534.

Avis PG; McLaughlin DJ; Dentinger BC; Reich PB. (2003). Long-term increases in nitrogen supply alters above and belowground ectomycorrhizal communities and increases dominance of *Russula* species. New Phytol, 160, 239-253.

Axler RP; Reuter JE. (1996). Nitrate uptake by phytoplankton and periphyton: Whole-lake enrichments and mesocosm-^{15}N experiments in an oligotrophic lake. Limnol Oceanogr, 41, 659-671.

Ayensu E; Claasen DVR; Collins M; Dearing A; Fresco L; Gadgil M; Gitay H; Glaser G; Juma C; Krebs J; Lenton R; Lubchenco J; McNeely JA; Mooney HA; Pinstrup-Andersen P; Ramos M; Raven P; Reid WV; Samper C; Sarukhán J, Schei P; Tundisi JG; Watson RT; Guanhua X; Zakri AH. (1999). Ecology: International ecosystem assessment. Science, 286, 685-686.

Babich P; Davey M; Allen G; Koutrakis P. (2000). Method comparisons for particulate nitrate, elemental carbon, and $PM_{2.5}$ mass in seven U.S. cities. J Air Waste Manage Assoc, 50, 1095-1105.

Baddeley JA; Thompson DBA; Lee JA. (1994). Regional and historical variation in the nitrogen content of *Racomitrium lanuginosum* in Britain in relation to atmospheric nitrogen deposition. Environ Pollut, 84, 189-196.

Baez S; Fargione J; Moore DI; Collins SL; Gosz JR. (2007). Atmospheric nitrogen deposition in the northern Chihuahuan desert: Temporal trends and potential consequences. J Arid Environ, 68, 640-651.

Baggs EM; Richter M: Cadisch G; Hartwig UA. (2003). Denitrification in grass swards is increased under elevated atmospheric CO_2. Soil Biol Biochem, 35. 729-732.

Baggs EM; Blum H. (2004). CH_4 oxidation and emissions of CH_4 and N_2O from Lolium perenne swards under elevated atmospheric CO_2. Soil Biol Biochem, 36, 713-723.

Bailey SW; Hornbeck JW; Driscoll CT; Gaudette HE. (1996). Calcium inputs and transport in a base-poor forest ecosystem as interpreted by Sr isotopes. Water Resour Res, 32, 707-719.

Bailey SW; Horsley SB; Long RP; Hallet RA. (1999). Influence of geologic and pedologic factors on health of sugar maple on the Allegheny Plateau, U.S. In: Horsley SB; Long RP. (Eds.), Sugar maple ecology and health: Proceedings of an international symposium (General technical report NE-261; pp. 63-65): Radnor, PA: Northeastern Research Station; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Bailey SW; Buso DC; Likens GE. (2003). Implications of sodium mass balance for interpreting the calcium cycle of a forested ecosystem. Ecology, 84, 471-484.

Bailey SW; Horsley SB; Long RP; Hallett RA. (2004). Influence of edaphic factors on sugar maple nutrition and health on the Allegheny Plateau. Soil Sci Soc Am J, 68, 243-252.

Bailey SW; Horsley SB; Long RP. (2005). Thirty years of change in forest soils of the Allegheny Plateau, Pennsylvania. Soil Sci Soc Am J, 69, 681-690.

Baird M; Zabowski D; Everett RL. (1999). Wildfire effects on carbon and nitrogen in inland coniferous forests. Plant Soil, 209, 233-243.

Bajwa R; Read DJ. (1985).The biology of the mycorrhizae in the Ericaceae. IX. Peptides as nitrogen sources for the ericoid endophyte and for mycorrhizal and non-mycorrhizzal plants. New Phytol, 101, 459-467.

Baker JL; Laflen JM. (1983). Water quality consequences of conservation tilage. J Soil Water Conserv, 38, 186-193.

Baker JP; Schofield CL. (1980). Aluminum toxicity to fish as related to acid precipitation and Adirondack surface water quality. In: Drabløs, D; Tollan A (Eds.), Ecological impact of acid precipitation: Proceedings of an international conference; held in Sandefjord, Norway in March 11-14, 1980. (SNSF project; pp. 292-295). Oslo, Norway: Swiss National Science Foundation (SNSF).

Baker JP; Schofield CL. (1982). Aluminum toxicity to fish in acidic waters. Water Air Soil Pollut, 18, 289-309.

Baker JP; Schofield CL. (1985). Acidification impacts on fish populations: A review. In: Adams D; Page WP (Eds.), Acid deposition: environmental, economic, and policy issues (pp. 183-221). New York and London: Plenum Press.

Baker JP; Gherini SA; Christensen SW; Driscoll CT; Gallagher J; Munson RK; Newton RM; Reckhow KH; Schofield CL. (1990a). Adirondack lakes survey: An interpretive analysis of fish communities and water chemistry, 1984-1987. Ray Brook, NY: Adirondack Lakes Survey Corporation.

Baker JP; Bernard DP; Christensen SW; Sale MJ. (1990b). Biological effects of changes in surface water acid-base chemistry. (State of science / technology report #13).Washington DC: National Acid Precipitation Assessment Program (NAPAP).

Baker JP; Christensen SW. (1991). Effects of acidification on biological communities in aquatic ecosystems. In: Charles DF; Christie S (Eds.), Acidic deposition and aquatic ecosystems: Regional case studies (pp. 83-106). New York, NY: Springer-Verlag New York, Inc

Baker JP; Van Sickle J; Gagen CJ; DeWalle DR; Sharpe WE; Carline RF; Baldigo BP; Murdoch PS; Bath DW; Kretser WA; Simonin HA; Wigington PJ Jr. (1996a). Episodic acidification of small streams in the northeastern United States: Effects on fish populations. Ecol Appl, 6, 423-437.

Baker LA; Brezonik PL. (1988). Dynamic model of in-lake alkalinity generation. Water Resour Res, 24, 65-74.

Baker LA; Pollman CD; Eilers JM. (1988). Alkalinity regulation in softwater Florida lakes. Water Resour Res, 24, 1069-1082.

Baker LA; Kaufmann PR; Herlihy AT; Eilers JM. (1990c). Acidic deposition: State of science and technology. In Report 9 - Current status of surface-water acid-base chemistry. Final report (No. PB-92-100452/XAB). Washington, DC: Prepared in cooperation with Council on Environmental Quality, and Wisconsin Univ.-Eau Claire. Dept. of Biology. National Acid Precipitation Assessment Program (NAPAP)

Baker LA. (1991a). Regional estimates of atmospheric dry deposition. In: Charles DF; Christie S (Eds.). Acidic deposition and aquatic ecosystems: Regional case studies. (pp 645-652). New York, NY: Springer-Verlag.

Baker LA; Kaufmann PR; Herlihy AT; Eilers JM. (1991a). Current status of surface water acid-base chemistry. In: Irving PM (Ed.). Acidic deposition: State of science and technology; Volume II: Aquatic processes and effects. (State of Science/Technology report no 9; pp. 9-5-9-367; 9-A1; 9-B1; 9-C1; 9-D1; and 9-CP1). Washington, DC: National Acid Precipitation Assessment Program (NAPAP).

Baker LA. (1991b). Appendix A: Ion enrichment analysis for the regional case studies project. In: Charles DF, Christie S (Eds.). Acidic deposition and aquatic ecosystems: Regional case studies. (pp. 641-644). New York, NY: Springer-Verlag.

Baker LA; Christensen SW. (1991). Effects of acidification on biological communities. In: Charles DF (Ed.).Acidic deposition and aquatic ecosystems: Regional case studies. New York, NY: Springer-Verlag, pp. 83-106.

Baker LA; Herlihy AT; Kaufmann PR; Eilers JM. (1991b). Acidic lakes and streams in the United States: The role of acidic deposition. Science, 252, 1151-1154.

Baker TR; Allen HL; Schoeneberger MM; Kress LW. (1994). Nutritional response of loblolly pine exposed to ozone and simulated acid rain. Can J For Res, 24, 453-461.

Baldigo BP; Murdoch PS. (1997). Effect of stream acidification and inorganic aluminum on mortality of brook trout (*Salvelinus fontinalis*) in the Catskill Mountains, New York. Can J Fish Aquat Sci, 54, 603-615.

Baldigo BP; Murdoch PS; Burns DA. (2005). Stream acidification and mortality of brook trout (*Salvelinus fontinalis*) in response to timber harvest in Catskill Mountain watersheds, New York, USA. Can J Fish Aquat Sci, 62, 1168-1183.

Baldigo BP; Lawrence GB; Simonin HA. (2007). Persistent mortality of brook trout in episodically acidified streams of the southwestern Adirondack Mountains, New York. Trans Am Fish Soc, 136, 121-134.

Balkanski YJ; Jacob DJ; Gardener GM; Graustein WC; Turekian KK. (1993). Transport and residence times of tropospheric aerosols inferred from a global three-dimensional simulation of ^{210}Pb. J Geophys Res, 98, 20573-20586.

Bamford HA; Baker JE. (2003). Nitro-polycyclic aromatic hydrocarbon concentrations and sources in urban and suburban atmospheres of the Mid-Atlantic region. Atmos Environ, 37, 2077-2091.

Banzhaf S; Burtraw D; Evans D; Krupnick A. (2006). Valuation of natural resource improvements in the Adirondacks. Land Econ, 82, 445–464.

Barbier EB. (1991). An approach to economic valuation of tropical wetlands: With examples from Guatemala and Nicaragua. In: Girvan NP; Simons D (Eds.). Caribbean ecology and economics, (pp 207-231). St Michael, Barbados: Caribbean Conservation Association.

Barbier EB; Acreman M; Knowler D. (1997). Economic valuation of wetlands: A guide for policy makers and planners. Prepared in collaboration with the Department of Environmental Economics and Environ Manage of the University of York, UK, the Institute of Hydrology, and IUCN-The World Conservation Union. Published in Gland, Switzerland by the Ramsar Convention Bureau, with financial support from the U.K. Department of the Environment and the Swedish International Development Cooperation Agency .

Bardwell CA; Maben JR; Hurt JA; Keene WC; Galloway JN; Boatman JF; Wellman DL. (1990). A technique using high-flow, dichotomous filter packs for measuring major atmospheric chemical constituents. Glob Biogeochem Cycles, 4, 151-163.

Barinaga M. (1990). Where have all the froggies gone? Science, 247, 1033-1034.

Barker DH; Vanier C; Naumburg E; Charlet TN; Nielsen KM; Newingham BA; Smith SD. (2006). Enhanced monsoon precipitation and nitrogen deposition affect leaf traits and photosynthesis differently in spring and summer in the desert shrub *Larrea tridentata*. New Phytol, 169, 799-808.

Barmuta LA; Cooper SD; Hamilton SK; Kratz KW; Melack JM. (1990). Responses of zooplankton and zoobenthos to experimental acidification in a high-elevation lake (Sierra Nevada, California, USA). Freshwater Biol, 23, 571-586.

Barnard R; Leadley PW; Hungate BA. (2005). Global change, nitrification, and denitrification: A review. Glob Biogeochem Cycles, 19, doi:10.1029/2004GB002282.

Barnes I; Bastian V; Becker KH; Overath RD. (1991). Kinetic studies of the reactions of IO, BrO and ClO with dimethylsulfide. Int J Chem Kinetics, 23, 579-591.

Baron J; Norton SA; Beeson DR; Hermann R. (1986). Sediment diatom and metal stratigraphy from Rocky Mountain lakes with special reference to atmospheric deposition. Can J Fish Aquat Sci, 43, 1350-1362.

Baron J. (1992).Surface waters. In: Baron J (Ed.). Biogeochemistry of a subalpine ecosystem: Loch Vale watershed. (Ecological Studies, series Volume 90, pp 142-186). New York, NY: Springer-Verlag.

Baron JS; Ojima DS; Holland EA; Parton WJ. (1994). Analysis of nitrogen saturation potential in Rocky Mountain tundra and forest: Implications for aquatic systems. Biogeochemistry, 27, 61-82.

Baron JS; Allstott J; Newkirk BK. (1995). Analysis of long term sulfate and nitrate budgets in a Rocky Mountain basin. In: Tonnessen KA; Williams MW; Tranter M (Eds.). Biogeochemistry of seasonally snow-covered catchments. Proceedings from an international symposium held during the XXI Assembly of the International Union of Geodesy and Geophysics in Boulder, CO, in July 1-14, 1995. (IAHS publication no 228, pp 255-261). Wallingford, Oxfordshire, U.K. Centre for Ecology and Hydrology: International Union of Geodesy and Geophysics (IAHS) Press.

Baron JS; Rueth HM; Wolfe AM; Nydick KR; Allstott EJ; Minear JT; Moraska B. (2000). Ecosystem responses to nitrogen deposition in the Colorado Front Range. Ecosystems, 3, 352-368.

Baron JS. (2006). Hindcasting nitrogen deposition to determine ecological critical load. Ecol Appl, 16, 433-439.

Barrie LA; Bottenheim JW; Schnell RC; Crutzen PJ; Rasmussen RA. (1988). Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere. Nature, 334, 138-141.

Barton L; Kiese R; Gatter D; Butterbach-Bahl K; Buck R; Hinz C; Murphy DV. (2008). Nitrous oxide emissions from a cropped soil in a semi-arid climate. Glob Chang Biol, 14, 177-192.

Bashkin VN; Kozlov MY; Priputina IV; Avrumuchev AV; Dedkova IS. (1995). Calculation and mapping of critical loads of S, N, and acidity of ecosystems of northern Asia. Water Air Soil Pollut, 85, 2395-2400.

Basiliko N; Moore TR; Jeannotte R; Bubier JL. (2006). Nutrient input and carbon and microbial dynamics in an ombrotrophic bog. Geomicrobiol J, 23, 531-543.

Battoe LE; Lowe EF. (1992). Acidification of Lake Annie, Highlands Co., FL. Water Air Soil Pollut, 65, 69-80.

Bauer GA; Bazaaz FA; Minocha R; Long S; Magill AH; Aber JD; Berntson GM. (2004). Effects of chronic N additions on tissue chemistry, photosynthetic capacity, and carbon sequestration potential of a red pine (*Pinus resinosa* Ait. .stand in the NE United States. For Ecol Manage, 196, 173-186.

Bayley SE; Schindler DW; Parker BR; Stainton MP; Beaty KG. (1992). Effects of forest fire and drought on acidity of a base-poor boreal forest stream: Similarities between climatic warming and acidic precipitation. Biogeochem, 17, 191-204.

Beamish RJ; Harvey HH. (1972). Acidification of the La Cloche Mountain lakes, Ontario, and resulting fish mortalities. J Fish Res Bd Can, 29, 1131-1143.

Beamish RJ. (1976). Acidification of lakes in Canada by acid precipitation and the resulting effects on fishes. Water Air Soil Pollut, 6, 501-514.

Beck MB. (1987). Water quality modeling: A review of the analysis of uncertainty. Water Resour Res, 23, 1393-1442.

Beck MB; Ravetz JR; Mulkey LA; Barnwell TO. (1997). On the problem of model validation for predictive exposure assessments. Stochastic Hydrology and Hydraulis, 11, 229-254.

Beck MB; Chen J. (2000). Assuring the quality of models designed for predictive tasks. In: Saltelli A; Chan K; Scott EM (Eds.), Handbook on sensitivity analysis. (pp 401-420). Chichester, UK: Wiley.

Becker DS; Bigham GN. (1995). Distribution of mercury in the aquatic food web of Onondaga Lake, New York. Water Air Soil Pollut, 80, 563-571.

Bedford BL; Walbridge MR; Aldous A. (1999). Patterns in nutrient availability and plant diversity of temperate North American Wetlands : Within-stand nutrient cycling in Wetland Ecosystems. Ecology, 80, 2151-2169.

Bedford BL; Godwin KS. (2003). Fens of the United States: Distribution, characteristics, and scientific connection versus legal isolation. Wetlands, 23, 608-629.

Beedlow PA; Tingey DT; Phillips DL; Hogsett WE; Olszyk DM. (2004). Rising atmospheric CO_2 and carbon sequestration in forests. Front Ecol Environ, 2, 315-322.

Beggs GL; Gunn JM. (1986). Response of lake trout (*Salvelinus namaycush* and brook trout (*S. fontinalis*) to surface water acidification in Ontario. Water Air Soil Pollut, 30, 711-717.

Behnke W; George C; Sheer V; Zetzsch C. (1997). Production and decay of $ClNO_2$ from the reaction of gaseous N_2O_5 with NaCl solution: Bulk and aerosol experiments. J Geophys Res, 102, 3795-3804.

Beier C; Hultberg H; Moldan F; Wright RF. (1995). MAGIC applied to roof experiments (Risdalsheia, N; Gårdsjön, S; Klosterhede, DK) to evaluate the rate of reversibility of acidification following experimentally reduced acid deposition. Water Air Soil Pollut, 85, 1745-1751.

Bell JNB. (1985). SO_2 effects on the productivity of grass species. In: Winner WE; Mooney HA; Goldstein RA (Eds.). Sulfur dioxide and vegetation: Physiology, ecology, and policy issues. (pp. 250-263). Stanford, CA: Stanford University Press.

Belnap J; Sigal L; Moir W; Eversman S. (1993). Identification of sensitive species, in lichens as bioindicators of air quality. In: Huckaby LS (Ed.), Lichens as bioindicators of air quality (pp. 67-88). Fort Collins, Colorado: Rocky Mountain Forest and Range Experimental Station, U.S. Forest Service, U. S. Department of Agriculture.

Benner RL; Stedman DH. (1989). Universal sulfur detection by chemiluminescence. Anal. Chem, 61, 1268-1271.

Benner RL; Stedman DH. (1990). Field evaluation of the sulfur chemiluminescence detector. Environ. Sci. Technol, 24, 1592-1596.

Bennett D; Goble R; Linthurst R. (1985). The acidic deposition phenomenon and its effects: Critical assessment document (Report no. EPA/600/8-85/001). Washington, DC: Office of Acid Deposition, Environmental Monitoring, and Quality Assurance; National Exposure Research Laboratory; Office of Research and Development; U.S. Environmental Protection Agency.

Benoit JM; Fitzgerald WF; Damman AWH. (1998). The biogeochemistry of an ombrotrophic bog: Evaluation and use as an archive of atmospheric mercury deposition. Environ Res, 78, 118-133.

Benoit JM; Gilmour CC; Mason RP; Heyes A. (1999). Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. Environ Sci Technol, 33, 951-957.

Benoit JM; Mason RP; Gilmour CC; Aiken GR. (2001). Constants for mercury binding by dissolved organic matter isolates from the Florida Everglades. Geochim Cosmochim Acta, 65, 4445-4451.

Benoit JM; Gilmour C; Heyes A; Mason RP; Miller C. (2003). Geochemical and biological controls over methylmercury production and degradation in aquatic ecosystems. In: Chai Y, Braids OC (Eds.), Biogeochemistry of environmentally important trace elements, ACS Symposium Series no. 835 (pp. 262-297). Washington, D.C.: American Chemical Society.

Benstead JP; Deegan LA; Peterson BJ; Huryn AD; Bowden WB; Suberkropp K; Buzby KM; Green AC; Vacca JA. (2005). Responses of a beaded Arctic stream to short-term N and P fertilisation. Freshw Biol, 50, 277-290.

Bentley J; Horst R. (1998). Commercial forestry benefits of alternative emission controls for the NO_X SIP Call (Report prepared by Science Applications International Corporation (SAIC #68-D-98-113) for the Office of Air Quality Planning and Standards). Research Triangle Park, NC; Office of Air Quality Planning and Standards; U.S. Environmental Protection Agency.

Berendse F. (1994). Competition between plant populations at low and high nutrient supplies. Oikos, 71, 253-260.

Berendse F; Breemen NV; Rydin H; Buttler A; Heijmans M; Hoosbeek MR; Lee JA; Mitchell A; Saarinen T; Vassander H; Wallen B. (2001). Raised atmospheric CO_2 levels and increased N deposition cause shifts in plant species composition and production in Sphagnum bogs. Glob Chang Biol, 7, 591-598.

Berg B. (2000). Initial rates and limit values for decomposition of Scots pine and Norway spruce needle litter: A synthesis for N-fertilized forest stands. Can J For Res, 30, 122-135.

Bergametti G; Remoudaki E; Losno R; Steiner E; Chatenet B. (1992). Source, transport and deposition of atmospheric phosphorus over the northwestern Mediterranean. J Atmos Chem, 14, 501-513.

Bergeron C; Husak J; Jason Unrine J; Romanek C; Hopkins W. (2007). Influence of feeding ecology on blood mercury concentrations in four species of turtles. Environ Toxicol Chem, 26, 1733-1741.

Berggren D; Mulder J. (1995). The role of organic matter in controlling aluminum solubility in acidic mineral soil horizons. Geochim Cosmochim Acta, 59, 4167-4180.

Bergman HL; Mattice JS; Brown DJA. (1988). Lake acidification and fisheries project: adult brook trout (*Salvelinus fontinalis*). Can J Fish Aquat Sci, 45, 1561-1562.

Bergström A; Blomqvist P; Jansson M. (2005). Effects of atmospheric nitrogen deposition on nutrient limitation and phytoplankton biomass in unproductive Swedish lakes. Limnol Oceanogr, 50, 987-994.

Bergström A; Jansson M. (2006). Atmospheric nitrogen deposition has caused nitrogen enrichment and eutrophication of lakes in the northern hemisphere. Glob Chang Biol, 12, 635-643.

Bergstrom JC; Taylor LO. (2006). Using meta-analysis for benefits transfer: Theory and practice. Ecol Econ, 60, 351-360.

Bernhardt ES; Likens GE. (2002). Dissolved organic carbon enrichment alters nitrogen dynamics in a forest stream. Ecology, 83, 1689-1700.

Bernot MJ; Dodds WK; Gardner WS; McCarthy MJ; Sobolev D; Tank JL. (2003). Comparing denitrification estimates for a Texas estuary by using acetylene inhibition and membrane inlet mass spectrometry. Appl Environ Microbiol, 69, 5950-5956.

Berresheim H; Eisele FL; Tanner DJ; McInnes LM; Ramsey-Bell DC; Covert DS. (1993). Atmospheric sulfur chemistry and cloud condensation nuclei (CCN) concentrations over the northeastern Pacific coast. J Geophys Res, 98, 12701-12711

Berresheim H; Wine PH; Davis DD. (1995). Sulfur in the atmosphere. In: Singh HB (Ed.), Composition, chemistry, and climate of the atmosphere (pp. 251-307). New York, NY: Van Nostrand Reinhold.

Bert D; Leavitt SW; Duponey JL. (1997). Variations in wood $\delta^{13}C$ and water-use efficiency of *Abies alba* during the last century. Ecology, 78, 1588-1595.

Bertness MD; Crain C; Holdredge C; Sala N. (2008). Eutrophication and consumer control of New England salt marsh primary productivity. Conserv Biol, 22, 131-9.

Bertram TH; Heckel A; Richter A; Burrows JP; Cohen RC. (2005). Satellite measurements of daily variations in soil NO_X emissions. Geophys Res Lett, 32, doi:10.1029/2005GL024640

Bey I; Jacob DJ; Yantosca RM; Logan JA; Field B; Fiore AM; Li Q; Liu H; Mickley LJ; Schultz MG. (2001). Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation. J Geophys Res, 106, 23073-23095.

Bezabeh DZ; Bamford HA; Schantz MM; Wise SA. (2003). Determination of nitrated polycyclic aromatic hydrocarbons in diesel particulate-related standard reference materials by using gas chromatography/mass spectrometry with negative ion chemical ionization. Anal Bioanal Chem, 375, 381-388.

Bhattacharya A; Mudgal R; Taneja A. (2004). Acid deposition and critical load analysis in Agra, India. J Hazard Mater, 106, 157-160.

Billen N; Schatzle H; Seufert G; Arndt U. (1990). Performance of some growth variables. Environ Pollut, 68, 419-434.

Billett MF; Parker-Jervis F; Fitzpatrick EA; Cresser MS. (1990). Forest soil chemical changes between 1949/50 and 1987. European Journal of Soil Science, 41, 133-145.

Billings WD. (1978). Plants and the ecosystem. (3rd Edition, pp 1-62; 83-108). Belmont, CA: Wadsworth Publishing Co.

Binkley D; Richter D. (1987). Nutrient cycles and H^+ budgets of forest ecosystems. Adv Ecol Res, 16, 2-52

Binkley D. (1995). The influence of tree species on forest soils: Processes and patterns. In: Mead DJ; Cornforth IS (Eds.). Proceedings of the Trees and Soil Workshop. (pp 1–33). Canterbury, New Zealand; Lincoln University Press.

Binkowski FS; Arunachalam S; Adelman Z; Pinto JP. (2007). Examining photolysis rates with a prototype online photolysis module in CMAQ. Journal of Applied Metereology and Climatology, 46, 1252-1256.

Birks HJB; Berge F; Boyle JF; Cumming BF. (1990). A palaeoecological test of the land-use hypothesis for recent lake acidification in south-west Norway using hill-top lakes. J Paleolimnol, 4, 69-65.

Bishop GA; Stedman DH. (1996). Measuring the emissions of passing cars. Acc Chem Res, 29, 489-495.

Blair RB. (1990). Water quality and the summer distribution of common loons in Wisconsin. Passenger Pigeon, 52, 119-126.

Blake L; Goulding KWT; Mott CJB; Johnston AE. (1999). Changes in soil chemistry accompanying acidification over more than 100 years under woodland and grass at Rothamsted Experimental Station, UK. Eur J Soil Sci, 50, 401-412.

Blanchard CL; Roth PM; Tanenbaum SJ; Ziman SD; Seinfeld JH. (2000). The use of ambient measurements to identify which precursor species limit aerosol nitrate formation. J Air Waste Manage Assoc, 50, 2073-2084.

Blanchard CL; Hidy GM. (2003). Effects of changes in sulfate, ammonia, and nitric acid on particulate nitrate concentrations in the southeastern United States. J Air Waste Manage Assoc, 53, 283-290.

Blanchard P; Brook JR; Brazil P. (2002). Chemical characterization of the organic fraction of atmospheric aerosol at two sites in Ontario, Canada. J Geophys Res, 107, 8348, doi:10.1029/2001JD000627.

Blancher PJ; McNicol DK. (1988). Breeding biology of tree swallows in relation to wetland acidity. Can J Zool, 66, 842-849.

Blancher PJ; McNicol DK. (1991). Tree swallow diet in relation to wetland activity. Can J Zool, 69, 2629-2637.

Blaschke H. (1990). Mycorrhizal populations and fine root development on Norway spruce exposed to controlled doses of gaseous pollutants and simulated acidic rain treatments. Environ Pollut, 68, 409-418.

Blett T; Geiser L; Porter E. (2003). Air pollution-related lichen monitoring in national parks, forests, and refuges: Guidelines for studies intended for regulatory and management purposes. (Report #NPS-D2292). http://www2.nature.nps.gov/air/Pubs/pdf/Lichen_Studies.pdf. Corvallis, OR and Denver, CO; Air Resources Division; National Prk Service; U.S. Forest Service ; U.S. Department of the Interior, U.S. Department of Agriculture (USDA).

Bloom AJ; Chapin FSI; Mooney HA. (1985). Resource limitation in plants - an economic analogy. Annu Rev Ecol Syst, 16, 363-392.

Bloom NS. (1992). On the chemical form of mercury in edible fish and marine invertebrate tissue. Can J Fish Aquat Sci, 49, 1010-1017.

Bloom SC; Takacs LL; Da Silva AM; Ledvina D. (1996). Data assimilation using incremental analysis updates. Monthly Weather Rev, 124, 1256-1271.

Bloom SC; da Silva A; Dee D; Bosilovich M; Chern J-D; Pawson S; Schubert S; Sienkiewicz M; Stajner I; Tan W-W; Wu M-L. (2005). Documentation and validation of the Goddard Earth Observing System (GEOS) data assimilation system--version 4. (Technical report series on global modeling and data assimilation, 104606, v. 26). Greenbelt, MD: Goddard Space Flight Center; National Aeronautics and Space Administration (NASA)

Bloss WJ; Lee JD; Johnson GP; Sommariva R; Heard DE; Saiz-Lopez A; Plane JMC; McFiggans G; Coe H; Flynn M; Williams P; Rickard AR; Fleming ZL. (2005). Impact of halogen monoxide chemistry upon boundary layer OH and HO_2 concentrations at a coastal site. Geophys Res Lett, 32, doi:10.1029/2004GL022084

Blucher DB; Svensson JE; Johansson LG. (2005). Influence of ppb levels of SO_2 on the atmospheric corrosion of aluminum in the presence of NaCl. J Electrochem Soc, 152, B397-B404.

Blum JD; Klaue A; Nezat CA; Driscoll CT; Johnson CE; Siccama TG; Eagar C; Fahey TJ; Likens GE. (2002). Mycorrhizal weathering of apatite as an important calcium source in base-poor forest ecosystems. Nature, 417, 729-731.

Bobbink R; Heil GW; Raessen MBAG. (1992a). Atmospheric deposition and canopy exchange processes in heathland ecosystems. Environ Pollut, 75, 29-37.

Bobbink R; Boxman D; Fremstad E; Heil G; Houdijk A; Roelofs J. (1992b). Critical loads for nitrogen eutrophication of terrestrial and wetland ecosystems based upon changes in vegetation and fauna. In: Grennfelt P, Thörnelöf E (Eds.), Critical loads for nitrogen. Nord (Miljörapport Volume 41, pp 111-159). Copenhagen; Nordic Council of Ministers.

Bobbink R; Hornung M; Roelofs JGM. (1996). Empirical nitrogen critical loads for natural and semi-natural ecosystems. Annex III. In: Manual on methodologies and criteria for mapping critical levels/loads and geographical areas where they are exceeded. (Procedings from UNECE Convention on Long-Range Transboundary Air Pollution). Berlin, Germany; Umvelt Bundes Arnt.

Bobbink R. (1998). Impacts of tropospheric ozone and airborne nitrogenous pollutants on natural and semi-natural ecosystems: A commentary. New Phytol, 139, 161-168.

Bobbink R; Hornung M; Roelofs JGM. (1998). The effects of air-borne nitrogen pollutants on species diversity in natural and semi-natural European vegetation. J Ecol, 86, 717-738.

Bobbink R; Ashmore M; Braun S; Flückiger W; van den Wyngaert IJJ. (2003). Empirical nitrogen critical loads for natural and semi-natural ecosystems: 2002 update. In: Achermann B; Bobbink R (Eds.), Empirical critical loads for nitrogen (pp. 43-170). Berne, Switzerland: Swiss Agency for Environment, Forest and Landscape SAEFL.

Bobrowski, N; Hönninger, G; Galle, B; Platt, U. (2003). Detection of bromine monoxide in a volcanic plume. Nature (London, U.K.), 423: 273-276.

Bockstael, NE; McConnell, KE; Strand, IE. (1988). Benefits from improvements in Chesapeake Bay water quality. Volume III of Benefit analysis using indirect or imputed market methods. Washington, DC: U.S. Environmental Protection Agency.

Bockstael N; McConnell K; Strand I. (1989a). A random utility model for sportfishing: Some preliminary results for Florida. Mar Resource Econ, 6, 245-260.

Bockstael NE; McConnell KE; Strand IE. (1989b). Measuring the benefits of improvements in water quality: The Chesapeake Bay. Mar Resource Econ, 6, 1-18.

Bodelier PLE; Roslev P; Heckel T; Frenze, P. (2000). Stimulation by ammonium-based fertilizers of methane oxidation in soil around rice roots. Nature, 403, 421-424.

Bodelier PLE; Laanbroek HJ. (2004). Nitrogen as a regulatory factor of methane oxidation in soils and sediments. FEMS Microbiol Ecol, 47, 265-277.

Boening DW. (2000). Ecological effects, transport, and fate of mercury: A general review. Chemosphere 40, 1335-1351.

Boersma KF; Eskes HJ; Brinksma EJ. (2004). Error analysis for tropospheric NO_2 retrieval from space. J Geophys Res, 109, doi: 10.1029/2003JD003962.

Boesch DF; Brinsfield RB; Magnien RE. (2001). Chesapeake Bay eutrophication: Scientific understanding, ecosystem resoration, and challenges for agriculture. J Environ Qual, 30, 303-320.

Boggs JL; McNulty SG; Gavazzi MJ; Myers JM. (2005). Tree growth, foliar chemistry, and nitrogen cycling across a nitrogen deposition gradient in southern Appalachian deciduous forests. Can J For Res, 35, 1901-1913.

Bohlke JK; Denver JM. (1995). Combined use of ground-water dating, chemical and isotopic analyses to resolve the history and fate of nitrate contamincation in 2 agricultural watersheds, Atlantic coastal-plain, Maryland. Water Resour Res, 31, 2319-2339.

Böke H; Göktürk EH; Caner-Saltik EN; Demirci S. (1999). Effect of airborne particle on SO_2–calcite reaction. Appl Surf Sci, 140, 70-82.

Bondietti EA; McLaughlin SB. (1992). Evidence of historical influences of acidic deposition on wood and soil chemistry. In: Johnson DW; Lindberg SE, (Eds.).Atmospheric deposition and forest nutrient cycling: a synthesis of the integrated forest study. (Series: Billings WD; Golley F; Lange OL; Olson JS; Remmert H, [Eds.] Ecological studies analysis and synthesis: Vol.ume 91, pp 358-377). New York, NY: Springer-Verlag.

Boonpragob K; Nash TH, III; Fox CA. (1989). Seasonal deposition patterns of acidic ions and ammonium to the lichen *Ramalina menziesii* Tayl. in southern California. Environ Exp Bot, 29, 187-197.

Boonpragob K; Nash THI. (1991). Physiological responses of the lichen *Ramalina menziesii* Tayl. to the Los Angeles urban environment. Environ Exp Bot, 31, 229-238.

Booth CE; McDonald DG; Simons BP; Wood CM. (1988). Effects of aluminum and low pH on net ion fluxes and ion balance in the brook trout (*Salvelinus fontinalis*). Can J Fish Aquat Sci, 45, 1563-1574.

Boring CB; Al-Horr R; Genfa Z; Dasgupta PK; Martin M. W; Smith, W. F. (2002).Field measurement of acid gases and soluble anions in atmospheric particulate matter using parallel plate wet denuder and alternating filter-based automated analysis system. Anal. Chem. 74: 1256-1268.

Borken W; Beese F; Brumme R; Lamersdorf N. (2002). Long-term reduction in nitrogen and proton inputs did not affect atmospheric methane uptake and nitrous oxide emission from a German spruce forest soil. Soil Biol Biochem, 34, 1815-1819.

Bormann FH; Likens GE. (1967). Nutrient cycling. Science, 155, 424-429.

Bormann FH; Likens GE. (1979). Pattern and process in a forested ecosystem. New York, NY: Springer Verlag.

Bormann FH; Likens GE; Fisher DW; Pierce RS. (1968). Nutrient loss accelerated by clear-cutting of a forest ecosystem. Science, 159, 822-884.

Bormann FH; Likens GE; Melillo JM. (1977). Nitrogen budget for an aggrading northern hardwood forest ecosystem. Science, 196, 981-982.

Borum J. (1996). Shallow waters and land/sea boundaries. In: Jorgensen BB; Richardson K, (Eds.). Eutrophication in coastal marine ecosystems. (pp 179-203). Washington DC: American Geophysical Union.

Bouwes NW; Schneider R. (1979). Procedures in estimating benefits of water quality change. Am J Agric Econ, 61, 535-539.

Bouwman AF; Van Drecht G; Knoop JM; Beusen AHW; Meinardi CR. (2005). Exploring changes in river nitrogen export to the world's oceans. Glob Biogeochem Cycles, 19, doi: 10.1029/2004GB002314.

Bovensmann H; Burrows JP; Buchwitz M; Frerick J; Noel S; Rozanov VV; Chance KV; Goede APH. (1999). SCIAMACHY: Mission objectives and mesurement modes. J Atmos Sci, 56, 127-150.

Bowden, RD, Melillo JM; Steudler PA; Aber JD. 1991. Effects of nitrogen additions on annual nitrous–oxide fluxes from temperate forest soils in the northeastern Unitied States. J Geophys Res, 96, 9321-9328.

Bowden RD; Rullo G; Stevens GR; Steudler PA. (2000). Soil fluxes of carbon dioxide, nitrous oxide, and methane at a productive temperate deciduous forest. J Environ Qual, 29, 268-276.

Bowden RD; Davidson E; Savage K; Arabia C; Steudler P. (2004). Chronic nitrogen additions reduce total soil respiration and microbial respiration in temperate forest soils at Harvard Forest. For Ecol Manage, 196, 43-56.

Bowen JL;Valiela I. (2001). Historical changes in atmospheric nitrogen deposition to Cape Cod, Massachusetts, USA. Atmos Environ, 35, 1039-1051.

Bowman WD. (1992). Inputs and storage of nitrogen in winter snowpack in an alpine ecosystem. Arct Alp Res, 24, 211-215.

Bowman WD; Theodose TA; Schardt JC; Conant RT. (1993). Constraints of nutrient availability on primary production in two alpine tundra communities. Ecology, 74, 2085-2097.

Bowman WD. (1994). Accumulation and use of nitrogen and phosphorus following fertilization in two alpine tundra communities. Oikos, 70, 261-270.

Bowman WD; Theodose TA; Fisk MC. (1995). Physiological and production responses of plant growth forms to increases in limiting resources in alpine tundra: Implications for differential community response to environmental change. Oecologia, 101, 217-227.

Bowman WD; Steltzer H. (1998). Positive feedbacks to anthropogenic nitrogen deposition in Rocky Mountain alpine tundra. Ambio, 27, 514-517.

Bowman WD. (2000). Biotic controls over ecosystem response to environmental change in alpine tundra of the Rocky Mountains. Ambio, 29, 396-400.

Bowman WD; Bilbrough CJ. (2001). Influence of a pulsed nitrogen supply on growth and nitrogen uptake in alpine graminoids. Plant Soil, 233, 283-290.

Bowman WD; Fisk MC. (2001). Primary production. In: Bowman WD; Seastedt TR. (Eds.). Structure and function of an alpine ecosystem: Niwot Ridge, Colorado. (pp 177-197). Oxford, UK: Oxford University Press.

Bowman WD; Gartner JR; Holland K; Wiedermann M. (2006). Nitrogen critical loads for alpine vegetation and terrestrial ecosystem response: are we there yet? Ecol Appl, 16, 1183-1193.

Boxman AW; Blanck K; Brandrud T-E; Emmett BA; Gundersen P; Hogervorst RF; Kjonass OJ; Persson H; Timmermann V. (1998a). Vegetation and soil biota response to experimentally-changed nitrogen inputs in coniferous forest ecosystems of the NITREX project. For Ecol Manage, 101, 65-79.

Boxman AW; van der Ven PJM; Roelofs JGM. (1998b). Ecosystem recovery after a decrease in nitrogen input to a Scots pine stand at Ysselsteyn, The Netherlands. For Ecol Manage, 101, 155-163.

Boyd J; Banzhaf S. (2007). What Are Ecosystem Services? The need for standardized environmental accounting units. Ecol Econ, 63, 616-626.

Boyer EW; Howarth RW. (2002). The nitrogen cycle at regional to global scales: report of the International SCOPE Nitrogen Project. Dordrecht, The Netherlands: Kluwer Academic Publishers.

Boyer EW; Goodale CL; Jaworski NA; Howarth RW. (2002). Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern USA. Biogeochemistry, 57/58, 137-169.

Boyer EW; Alexander RB; Parton WJ; Li C; Butterbach-Bahl K; Donner SD; Skaggs RW. (2006a). Modeling denitrification in terrestrial and aquatic ecosystems at regional scales. Ecol Appl, 16, 2123-2142.

Boyer E; Howarth RW; Galloway JN; Dentener FJ; Green PA; Vörösmarty CJ. (2006b). Riverine nitrogen export from the continents to the coasts. Glob Biogeochem Cycles, 20.

Boyle KJ; Poor PJ; Taylor LO. (1999). Estimating the demand for protecting freshwater lakes from eutrophication. Am J Agric Econ, 81, 1118-1122.

Boynton WR; Garber JH; Summers R; Kemp WM. (1995). Inputs, transformations, and transport of nitrogen and phosphorus in Chesapeake Bay and selected tributaries. Estuaries, 18, 285-314.

Bradford DF; Swanson C; Gordon MS. (1992). Effects of low pH and aluminum on two declining species of amphibians in the Sierra Nevada, California. J Herpetol, 26: 369-377.

Bradford DF; Tabatabai F; Graber DM. (1993). Isolation of remaining populations of the native frog, *Rana muscosa*, by introduced fishes in Sequoia and Kings Canyon National Parks, California. Conserv Biol, 7, 882-888.

Bradford MA; Ineson P; Wookey PA; Lappin-Scott HM. (2001). The effects of acid nitrogen and acid sulphur deposition on CH_4 oxidation in a forest soil: A laboratory study. Soil BiolBiochem, 33, 1695-1702.

Bradley K; Drijber RA; Knops J. (2006). Increased N availability in grassland soils modifies their microbial communities and decreases the abundance of arbuscular mycorrhizal fungi. Soil Biol Biochem, 38, 1583-1595.

Bradshaw J; Davis D; Crawford J; Chen G; Shetter R; Muller M; Gregory G; Sachse G; Blake D; Heikes B; Singh H; Mastromarino J; Sandholm S. (1999). Photofragmentation two-photon laser-induced fluorescence detection of NO_2 and NO: Comparison of measurements with model results based on airborne observations during PEM-Tropics A. Geophys Res Lett, 26, 471-474.

Bragazza L; Freeman C; Jones T; Rydin H; Limpens J; Fenner N; Ellis T; Gerdol R; Hajek M; Hajek T. Lacumin P; Kutnar L; Tahvanainen T; Toberman H. (2006). Atmospheric nitrogen deposition promotes carbon loss from peat bogs. Proc Natl Acad Sci USA, 103, 19386-19389.

Bragazza L; Freeman C. (2007). High nitrogen availability reduces polyphenol content in Sphagnum peat. Sci Total Environ, 377, 439-443.

Brand GJ; Nelson MD; Wendt DG; Nimerfro KK. (2000.). The hexagon/panel system for selecting FIA plots under an annual inventory. In: McRoberts RE; Reams GA; Van Deusen PC (Eds.) Proceedings of the first annual forest inventory and analysis symposium. (General technical report NC-213; pp. 8-13). St. Paul, MN; North Central Research Station; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Brander LM; Florax RJGM; Vermaat JE. (2006). The empirics of wetland valuation: A comprehensive summary and a meta-analysis of the literature. Environmental and Resource Economics, 33, 223-250.

Branfireun BA; Heyes A; Roulet NT. (1996). The hydrology and methylmercury dynamics of a Precambrian Shield headwater peatland. Water Resour Res, 32, 1785-1794.

Branfireun BA; Roulet NT; Kelly CA; Rudd WM. (1999). In situ sulphate stimulation of mercury methylation in a boreal peatland: toward a link between acid rain and methylmercury contamination in remote environments. Glob Biogeochem Cycles, 13, 743-750.

Branfireun BA; Bishop K; Roulet, NT; Granberg, G; Nilsson, M. (2001). Mercury cycling in boreal ecosystems: The long-term effect of acid rain constituents on peatland pore water methylmercury concentrations. Geophys Res Lett, 28, 1227-1230.

Brauer M; Koutrakis P; Keeler GJ; Spengler JD. (1991). Indoor and outdoor concentrations of inorganic acidic aerosols and gases. J Air Waste Manage Assoc, 41, 171-181.

Braun S; Schindler C; Volz R; Flückiger W. (2003). Forest Damages by the Storm 'Lothar' in permanent observation plots in Switzerland: The significance of soil acidification and nitrogen deposition. Water Air Soil Pollut, 142, 327-340.

Bredemeier M; Blanck K; Xu YJ; Tietema A; Boxman AW; Emmett B; Moldan F; Gundersen P; Schleppi P; Wright RF. (1998). Input-output budgets at the NITREX sites. For Ecol Manage, 101, 57-64.

Breiner J; Gimeno BS; Fenn M. (2007). Calculation of theoretical and empirical nutrient N critical loads in the mixed conifer ecosystems of southern California. ScientificWorldJournal, 7, 198-205.

Brenner M; Binford MW. (1988). Relationships between concentrations of sedimentary variables and trophic state in Florida lakes. Can J Fish Aquat Sci, 45, 294-300.

Brezonik PL; Baker LA; Perry TE. (1987). Mechanisms of alkalinity generation in acid sensitive softwater lakes. In: Hites R; Eisenreich SJ, (Eds.). Sources and fates of aquatic pollutants. (Advances in Chemistry Series Volume 216. pp 229-262). Washington, DC: American Chemical Society.

Brezonik PL; Eaton JG; Frost TM; Garrison PJ; Kratz TK; Mach CE; McCormick JH; Perry JA; Rose WA; Sampson CJ; Shelly BCL; Swenson WA; Webster KE. (1993). Experimental acidification of Little Rock Lake, Wisconsin: Chemical and biological changes over the pH range 6.1 to 4.7. Can J Fish Aquat Sci, 50, 1101–1121.

Bricker OP; Rice KC. (1989). Acidic deposition to streams: a geology-based method predicts their sensitivity. Environ Sci Technol, 23, 379-385.

Bricker SB; Clement CG; Pirhalla DE; Orlando SP; Farrow DGG. (1999). National estuarine eutrophication assessment: Effects of nutrient enrichment in the nation's estuaries. Silver Spring, MD: Special Projects Office and the National Centers for Coastal Ocean Science, National Ocean Service, National Oceanic and Atmospheric Administration (NOAA).

Bricker S; Longstaff B; Dennison W; Jones A; Boicourt K; Wicks C; Woerner J. (2007). Effects of nutrient enrichment in the nation's estuaries: A decade of change. http://ccmaserver.nos.noaa.gov/publications/eutroupdate/. (NOAA Coastal Ocean Program Decision Analysis Series No. 26). Silver Spring, MD: National Centers for Coastal Ocean Science, National Oceanic and Atmospheric Administration (NOAA).

Bridgham SD; Pastor J; McClaugherty CA; Richardson CJ. (1995). Nutrient-use efficiency: A litterfall index, a model, and a test along a nutrient availability gradient in North Carolina peatlands. American Naturalist, 145, 1–21.

Bridgham SD; Pastor J; Janssens J; Chapin C; Malterer T. (1996). Multiple limiting gradients in peatlands: A call for a new paradigm. Wetlands, 16, 45–65.

Britton KO; Berrang P; Mavity E. (1996). Effects of pretreatment with simulated acid rain on the severity of dogwood anthracnose. Plant Dis, 80, 646-649.

Broderick SJ; Cullen P; Maher W. (1988). Denitrification in a natural wetland receiving secondary treated effluent. Water Res, 4, 431-439.

Brook JR; Sirois A; Clarke JF. (1996). Comparison of dry deposition velocities for SO_2, HNO_3, and SO_4^{2-} estimated with two inferential models. Water Air Soil Pollut, 87, 205-218.

Brook JR; Dann TF. (1999). Contribution of nitrate and carbonaceous species to $PM_{2.5}$ observed in Canadian cities. J Air Waste Manage Assoc, 49, 193-199.

Brooks ML. (1999). Alien annual grasses and fire in the Mojave Desert. Madroño, 46, 13-19.

Brooks ML; Esque TC. (2002). Alien annual plants and wildfire in desert tortoise habitat: Status, ecological effects, and management. Chelonian Conserv Biol, 4, 330-340.

Brooks ML. (2003). Effects of increased soil nitrogen on the dominance of alien annual plants in the Mojave Desert. J Appl Ecol, 40, 344-353.

Brooks ML; D'Antonio CM; Richardson DM; Grace JB; Keeley J; DiTomaso JM; Hobbs RJ; Pellant M; Pyke D. (2004). Effects of invasive alien plants on fire regimes. Bioscience, 54, 677-688.

Brooks PD; Williams MW; Schmidt SK. (1996). Microbial activity under alpine snowpacks, Niwot Ridge, Colorado. Biogeochemistry, 32, 93-113.

Bröske R; Kleffmann J; Wiesen P. (2003). Heterogeneous conversion of NO_2 on secondary organic aerosol surfaces: A possible source of nitrous acid (HONO).in the atmosphere? Atmos Chem Phys, 3, 469-474.

Brouwer R; Langford IH; Bateman I; Turner K. (1999). A meta-analysis of wetland contingent valuation studies. Regional Environ Change, 1, 47-57.

Brown DJA. (1982). The effect of pH and calcium on fish and fisheries. Water Air Soil Pollut, 18, 343-351.

Brown DJA. (1983). Effect of calcium and aluminum concentrations on the survival of brown trout (*Salmo trutta*).at low pH Bull Environ Contam Toxicol, 30, 582-587.

Brown SS; Neuman JA; Ryerson TB; Trainer M; Dube WP; Holloway JS; Warneke C; De Gouw JA; Donnelly SG; Atlas E; Matthew B; Middlebrook AM; Peltier R; Weber RJ; Stohl A; Meagher JF; Fehsenfeld FC; Ravishankara AR. (2006a). Nocturnal odd-oxygen budget and its implications for ozone loss in the lower troposphere. Geophys Res Lett, 33, doi:10.1029/2006GL025900

Brown SS; Ryerson TB; Wollny AG; Brock CA; Peltier R; Sullivan AP; Weber RJ; Dubé WP; Trainer M; Meagher JF; Fehsenfeld FC; Ravishankara AR. (2006b). Variability in nocturnal nitrogen oxide processing and its role in regional air quality. Science, 311, 67-70.

Brühl C; Poschl U; Crutzen PJ; Steil B. (2000). Acetone and PAN in the upper troposphere: Impact on ozone production from aircraft emissions. Atmos Environ, 34, 3931-3938.

Brumme R; Beese F. (1992). Effects of liming and nitrogen fertilization on emission of CO_2 and N_2O from a temporate forest. J Geophys Res, 97, 12851-12858.

Brunet J, Diekmann, M, Falkengren-Grerup, U. (1998). Effects of nitrogen deposition on field layer vegetation in south Swedish oak forests. Environ Pollut, 102, 35-40.

Brunner I; Godbold DL. (2007). Tree roots in a changing world. J For Res, 12, 78-82.

Bubier JL; Moore TR; Bledzki LA. (2007). Effects of nutrient addition on vegetation and carbon cycling in an ombrotrophic bog. Glob Change Biol, 13, 1168-1186.

Buck S; Dodds W; Fisher J; Hart D; Parker A; Stevenson J; Watson V; Welch E. (2000). Nutrient criteria technical guidance manual: Rivers and streams (Report no EPA-822-B-00-002). Washington, DC; Office of Water; Office of Science and Technology; U.S. Environmental Protection Agency.

Buckler DR; Mehrle PM; Cleveland L; Dwyer FJ. (1987). Influence of pH on the toxicity of aluminum and other inorganic contaminants to east coast striped bass. Water Air Soil Pollut, 35, 97-106.

Bugas PE Jr; Mohn LO; Kauffman JW. (1999). Impacts of acid deposition on fish populations in the St. Marys River, Augusta County, Virginia. Banisteria 13, 191-200.

Buhr MP; Trainer M; Parrish DD; Sievers RE; Fehsenfeld FC. (1992). Assessment of pollutant emission inventories by principal component analysis of ambient air measurements. Geophys Res Lett, 19, 1009-1012.

Buhyoff GJ; Leuschner WA; Wellman JD. (1979). Aesthetic impacts of southern pine beetle damage. J Environ Manage, 8, 261-267.

Buhyoff GJ; Wellman JD. (1980). The specification of a non-linear psychophysical function for visual landscape dimensions. Journal of Leisure Research, 12, 257-272.

Buhyoff GJ; Wellman JD; Daniel, TC. (1982). Predicting scenic quality for mountain pine beetle and western spruce budworm damaged forests. Forest Science, 28, 827-838.

Buijsman E; Aben JMM; Van Elzakker BG; Mennen MG. (1998). An automatic atmospheric ammonia network in the Netherlands set-up and results. Atmos Environ, 32, 317-324.

Bukaveckas P; Shaw W. (1998). Phytoplankton responses to nutrient and grazer manipulations among northeastern lakes of varying pH. Can J Fish Aquat Sci, 55, 958-966.

Bulger AJ. (1986). Coincident peaks in serum osmolality and heat-tolerance rhythms in seawater-acclimated killifish (*Fundulus heteroclitus*). Physiol Zool, 59, 169-174.

Bulger AJ; Lien L; Cosby BJ; Henriksen A. (1993). Trout status and chemistry from the Norwegian thousand lake survey: Statistical analysis. Can J Fish Aquat Sci, 50, 575-585.

Bulger AJ; Dolloff CA; Cosby BJ; Eshleman KN; Webb JR; Galloway JN. (1995). The "Shenandoah National Park: fish in sensitive habitats" (SNP: FISH) Project. An integrated assessment of fish community responses to stream acidification. Water Air Soil Pollut, 85, 309-314.

Bulger AJ; Cosby, BJ; Dolloff, CA; Eshleman, KN; Webb, JR; Galloway, JN. (1999). SNP:FISH, Shenandoah National Park: Fish in sensitive habitats. Project final report -Volume I: Project description and summary of results; Volume II: Stream water chemistry and discharge, and synoptic water quality surveys. Volume III: Basin-wide habitat and population inventories, and behavioral responses to acid in a laboratory stream. Volume IV: Stream bioassays, aluminum toxicity, species richness and stream chemistry, and models of susceptibility to acidification. (Project Completion Report to the National Park Service). Charlottesville, VA, Department of Environmental Sciences; University of Virginia.

Bulger AJ; Cosby BJ; Webb JR. (2000). Current, reconstructed past, and projected future status of brook trout (*Salvelinus fontinalis*) streams in Virginia. Can J Fish Aquat Sci, 57, 1515-1523.

Bull KR; Roberts RD; Inskip MJ; Goodman GT. (1977) Mercury concentrations in soil, grass, earthworms and small mammals near an industrial emission source. Environ Pollut, 12, 135-140.

Burges SJ; Wigmosta MS; Meena JM. (1998). Hydrological effects of landuse change in a zero-order catchment. J Hydro Engr, 3, 86-97.

Burkholder JM; Dickey DA; Kinder CA; Reed RE; Mallin MA; McIver MR; Cahoon LB; Melia G; Brownie C; Smith J; Deamer N; Springer J; Glasgow HB; Toms D. (2006). Comprehensive trend analysis of nutrients and related variables in a large eutrophic estuary: a decadal study of anthropogenic and climatic influences. Limnol Oceanogr, 51, 463-487.

Burns DA; Kendall C. (2002). Analysis of $\delta^{15}N$ and $\delta^{18}O$ to differentiate NO_3^- sources in runoff at two watersheds in the Catskill Mountains of New York. Water Resour Res, 38, 1051. doi: 10.1029/2001WR000292.

Burns DA. (2004). The effects of atmospheric nitrogen deposition in the Rocky Mountains of Colorado and southern Wyoming, USA—A critical review. Environ Pollut, 127, 257-269.

Burrows JP; Weber M; Buchwitz M; Rozanov V; Ladstätter-Weißenmayer A; Richter A; DeBeek R; Hoogen R; Bramstedt K; Eichmann K-U; Eisinger M. (1999).The global ozone monitoring experiment (GOME): Mission concept and first scientific results. J Atmos Sci, 56, 151-175.

Burton AJ; Pregitzer KS; Hendrick RL. (2000). Relationships between fine root dynamics and nitrogen availability in Michigan northern hardwood forests. Oecologia, 125, 389-399.

Burton TM; Stanford RM; Allan JW. (1985). Acidification effects on stream biota and organic matter processing. Can J Fish, Aquat Sci, 42, 669-675.

Burtraw D; Krupnick A; Austin D; Farrell D; Mansur, E. (1997). The costs and benefits of reducing acid rain. (Discussion Paper 97-31-REV). Washington, DC: Resources for the Future (RFF).

Bushong SJ; Bachmann RW. (1989). In situ nutrient enrichment experiments with periphyton in agricultural streams. Hydrobiologia, 178, 1-10.

Butnor JR; Johnsen KH; Oren R; Katul, GG. (2003). Reduction of forest floor respiration by fertilization on both carbon dioxide-enriched and reference 17 year-old loblolly pine stands. Glob Change Biol, 9, 849-861.

Butterbach-Bahl, K; Gasche, R; Huber, C. H; Kreutzer, K; Papen, H. (1998). Impact of N-input by wet deposition on N-trace gas fluxes and CH_4-oxidation in spruce forest ecosystems of the temperate zone in Europe. Atmos. Environ. 32, 559-564.

Butterbach-Bahl, K; Breuer, L; Gasche, R; Willibald, G; Papen, H. (2002a). Exchange of trace gases between soils and the atmosphere in Scots pine forest ecosystems of the northeastern German lowlands. 1. Fluxes of N_2O, NO/NO_2 and CH_4 at forest sites with different N-deposition. For. Ecol. Manage. 167: 123-134.

Butterbach-Bahl, K; Gasche, R; Willibald, G; Papen, H. (2002b).Exchange of N-gases at the Hoglwald forest: A summary. Plant Soil 240: 117-123.

Bytnerowicz A; Miller PR; Olszyk DM. (1987a). Dry deposition of nitrate, ammonium and sulfate to a *Ceanothus crassifolius* canopy and surrogate surfaces. Atmos Environ, 21, 1749-1757.

Bytnerowicz A; Miller PR; Olszyk DM; Dawson PJ; Fox CA. (1987b). Gaseous and particulate air pollution in the San Gabriel Mountains of southern California. Atmospheric Environment 21: 1805-1814.

Bytnerowicz A; Fenn ME. (1996). Nitrogen deposition in California forests: A review. Environ Pollut, 92, 127-146.

Bytnerowicz A; Percy K; Riechers G; Padgett P; Krywult M. (1998a). Nitric acid vapor effects on forest trees: Deposition and cuticular changes. Chemosphere, 36, 697-702.

Bytnerowicz A; Dueck T; Godzik S. (1998b). Nitrogen oxides, nitric acid vapor, and ammonia. In: Flagler RB (Ed.), Recognition of air pollution injury to vegetaion: A pictoral atlas (2nd Edition, pp. 5-1-5-6). Pittsburgh, PA: Air & Waste Managment Association.

Bytnerowicz, A; Arbaugh, M. J; Schilling, S. L. (1998c). Proceedings of the international symposium on air pollution and climate change: Effects on forest ecosystems. Held in Riverside, CA in February 1996. http://www.fs.fed.us/psw/publications/documents/gtr-166/ (General technical report PSW-GTR-166). Albany, CA: Pacific Southwest Research Station; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Bytnerowicz A; Padgett P; Percy K; Krywult M; Riechers G; Hom J. (1999). Direct effects of nitric acid on forest vegetation. In: Miller PR, McBride J (Eds.), Oxidant air pollution impacts in the Montane forests of Southern California: The San Bernardino Mountains case study, Ecological Series 134. (pp. 270-287). New York: Springer.

Bytnerowicz A. (2002). Physiological/ecological interactions between ozone and nitrogen deposition in forest ecosystems. Phyton, 42, 13-28.

Bytnerowicz A; Tausz M; Alonso R; Jones D; Johnson R; Grulke N. (2002). Summer-time distribution of air pollutants in Sequoia National Park, California. Environ Pollut, 118, 187-203.

Byun DW; Ching JKS (Eds.). (1999). Science algorithms of the EPA models-3 community multiscale air quality model (CMAQ) modeling system. (Report EPA/600/R-99/030). Research Triangle Park, NC; Atmospheric Modeling Division; National Exposure Research Laboratory; Office of Research and Development; U.S. Environmental Protection Agency.

Byun D; Schere KL. (2006). Review of the governing equations, computational algorithms, and other components of the models-3 community multiscale air quality (CMAQ) modeling system. Appl Mech Rev, 59, 51-77.

Caddy, JF. (1993). Toward a comparative evaluation of human impacts on fishery ecosystems of enclosed and semi-enclosed seas. Rev. Fish. Sci. 1: 57-95.

Caffrey JM; Murrell M; Wigand C; McKinney R. (2007). Effect of nutrient loading on biogeochemical and microbial processes in a New England salt marsh. Biogeochemistry, 82, 251-264.

Caine, N. (1989).Hydrograph separation in a small alpine basin based on inorganic solute concentrations. J. Hydrol, 1, 89-101.

Cairns J Jr; Pratt JR. (1993). A history of biological monitoring using benthic macroinvertebrates. In: Rosenberg DM; Resh VH (Eds.), Freshwater biomonitoring and benthic macroinvertebrates (pp. 10-28). New York: Chapman and Hall.

Calanni J; Berg E; Wood M; Mangis D; Boyce; Weathers W; Sievering H. (1999). Atmospheric nitrogen deposition at a conifer forest: Response of free amino acids in Engelmann spruce needles. Environ Pollut 105: 79-89.

Caldeira, K; Wickett, ME. (2003). Anthropogenic carbon and ocean pH. Nature, 425, 365.

Caldwell TG; Johnson DW; Miller WW; Qualls RG. (2002). Forest floor carbon and nitrogen losses due to prescription fire. Soil Sci Soc Am J, 66, 262-267.

Callaway JM; Darwin, RF; Nesse, RJ. (1986). Economic valuation of acidic deposition damages: preliminary results from the 1985 NAPAP assessment. Water Air Soil Pollut. 31: 1019-1034.

Calvert JG; Su F; Bottenheim JW; Strausz OP. (1978). Mechanism of the homogeneous oxidation of sulfur dioxide in the troposphere. Atmos Environ, 12, 197-226.

Calvert JG; Yarwood G; Dunker AM. (1994). An evaluation of the mechanism of nitrous acid formation in the urban atmosphere. Res Chem Intermed, 20, 463-502.

Camargo JA; Alonso, A; Salamanca, A. (2005). Nitrate toxicity to aquatic animals: A review with new data for freshwater invertebrates. Chemosphere 58: 1255-1267.

Camargo JA; Ward, JV. (1995). Nitrate (NO_3^-N).toxicity to aquatic life: A proposal of safe concentrations for two species of nearctic freshwater invertebrates. Chemosphere 31: 3211-3216.

Cameron TA; Englin J. (1997). Welfare effects of changes in environmental quality under individual uncertainty about use. Rand J Econ, 28, s45-s70.

Camp DC; Stevens RK; Cobourn WG; Husar RB; Collins JF; Huntzicker JJ; Husar JD; Jaklevic JM; McKenzie RL; Tanner RL; Tesch JW. (1982). Intercomparison of concentration results from fine particle sulfur monitors. Atmos Environ, 16, 911-916.

Campbell DH; Clow DW; Ingersoll GP; Mast MA; Spahr NE; Turk JT. (1995). Processes controlling the chemistry of two snowmelt-dominated streams in the Rocky Mountains. Water Resour Res, 31, 2811-2821.

Campbell DH; Baron JS; Tonnessen KA; Brooks PD; Schuster PF. (2000a). Controls on nitrogen flux in alpine/subalpine watersheds. Water Resour Res, 36, 37-48.

Campbell, JL; Hornbeck, JW; McDowell, WH; Buso, DC; Shanley, JB; Likens, GE. (2000b). Dissolved organic nitrogen budgets for upland, forested ecosystems in New England. Biogeochemistry 49: 123-142.

Campbell DH; Kendall C; Chang CCY; Silva SR; Tonnessen KA. (2002). Pathways for nitrate release from an alpine watershed: determination using δ^{15}N and δ^{18}O. Water Resour Res, 31, 2811-2821.

Campbell DH; Muths E; Turk JT; Corn PS. (2004). Sensitivity to acidification of subalpine ponds and lakes in north-western Colorado. Hydrological Processes, 18, 2817-2834.

Campbell JL; Mitchell MJ; Groffman PM; Christenson LM. (2005). Winter in northeastern North America: An often overlooked but critical period for ecological processes. Front Ecol Environ, 3, 314-322.

Canary JD; Harrison RB; Compton JE; Chappell HN. (2000). Additional carbon sequestration following repeated urea fertilization of second-growth Douglas-fir stands in western Washington. For EcolManage, 138, 225-232.

Cape JN; Leith ID; Fowler D; Murray MB; Sheppard LJ; Eamus D; Wilson RHF. (1991). Sulfate and ammonium in mist impair the frost hardening of red spruce seedlings. New Phytol, 118, 119-126.

Cape JN; Sheppard LJ; Fowler D; Harrison AF; Parkinson JA; Dao P; Paterson IS. (1992). Contribution of canopy leaching to sulphate deposition in a Scots pine forest. Environ Pollut, 75, 229-236.

Cape JN. (1993). Direct damage to vegetation caused by acid rain and polluted cloud: Definition of critical levels for forest trees. Environ Pollut, 82, 167-180.

Cape JN. (1997). Photochemical oxidants: What else is in the atmosphere besides ozone? Phyton-Annales Rei Botanicae, 37, 45-57.

Cape JN. (2003). Effects of airborne volatile organic compounds on plants. Environ Pollut, 122, 145-157.

Cappellato R; Peters NE; Meyers TP. (1998). Above-ground sulfur cycling in adjacent coniferous and deciduous forests and watershed sulfur retention in the Georgia piedmont, USA. Water Air Soil Pollut, 103, 151-171.

Caraco NF; Cole JJ; Likens GE. (1989). Evidence for sulphate-controlled phosphorus release from sediments of aquatic systems. Nature, 341, 316-318.

Cardelino CA; Chameides WL. (2000). The application of data from photochemical assessment monitoring stations to the observation-based model. Atmos Environ, 34, 2325-2332.

Carlson RW. (1983). Interaction between SO_2 and NO_2 and their effects on photosynthetic properties of soybean *Glycine max*. Environ Pollut, 32, 11-38.

Carpenter LJ; Sturges WT; Penkett SA; Liss PS; Alicke B; Hebestreit K; Platt U. (1999). Short-lived alkyl iodides and bromides at Mace Head, Ireland: Links to biogenic sources and halogen oxide production. J Geophys Res, 104, 1679-1689.

Carpenter LJ. (2003). Iodine in the marine boundary layer. Chem Rev, 103, 4953-4962.

Carpenter SR; Caraco NF; Correll DL; Howarth RW; Sharpley AN; Smith VH. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol Appl, 8, 559-568.

Carreiro MM; Sinsabaugh RL; Repert DA; Parkhurst DF. (2000). Microbial enzyme shifts explain litter decay responses to simulated nitrogen deposition. Ecology, 81, 2359-2365.

Carroll MA; Bertman, SB; Shepson, PB. (2001). Overview of the program for research on oxidants, photochemistry, emissions and transport (PROPHET) summer 1998 measurements intensive. J Geophys Res, 106, 24275-24288.

Carroll JJ; Miller, PR; Pronos, J. (2003). Historical perspectives on ambient ozone and its effects on the Sierra Nevada. In: Bytnerowicz, A; Arbaugh, MJ; Alonso, R (Eds.). Ozone air pollution in the Sierra Nevada: Distribution and effects on forests; (Series: Developments in Environmental Science: Volume 2; pp. 33-54). New York, NY: Elsevier.

Carslaw DC. (2005). Evidence of an increasing NO_2/NO_X emissions ratio from road traffic emissions. Atmos Environ, 39, 4793-4802.

Carslaw DC; Beevers SD. (2005). Estimations of road vehicle primary NO_2 exhaust emission fractions using monitoring data in London. Atmos Environ, 39, 167-177.

Carslaw DC; Carslaw N. (2007). Detecting and characterising small changes in urban nitrogen dioxide concentrations. Atmos Environ, 41, 4723-4733.

Carson RT; Mitchell, RC. (1993).The value of clean water: The public's willingness to pay for boaTable, fishable, and swimmable quality water. Water Resour. Res., 29, 2445-2454.

Carson R; Flores NE; Martin KM; Wright. JL. (1996). Contingent valuation and revealed preference methodologies: Comparing the estimates for quasi-public goods. Land Econ, 72, 80–99.

Carson RT; Hanemann MW. (2005). Contingent Valuation. In: Mäler K-G; Vincent JR (Eds.), Handbook of environmental economics. Volume 2. Valuation of environmental changes (pp. 821-936). Amsterdam, The Netherlands: Elsevier.

Carter WPL. (1990). A detailed mechanism for the gas-phase atmospheric reactions of organic compounds. Atmos Environ, 24, 481-518.

Carter WPL. (1995). Computer modeling of environmental chamber studies of maximum incremental reactivities of volatile organic compounds. Atmos Environ, 29, 2513-2527.

CASAC. (2005). Recommendations to the Clear Air Act Advisory Committee (CASAC), Air Quality Management Work Group, phase I and next steps, January 2005. Washington, DC: Clean Air Act Advisory Committee.

Caspersen JP; Pacala SW; Jenkins JC; Hurtt GC; Moorcroft PR; Birdsey RA. (2000). Contributions of land-use history to carbon accumulation in U.S. forests. Science, 290, 1148-1151.

Castaldi S; Smith KA. (1998). The effect of different N substrates on biological N_2O production from forest and agricultural light textured soils. Plant Soil, 199, 229-238.

Castro MS; Steudler PA; Melillo JM; Aber JD; Millham S. (1992). Exchange of N_2O and CH_4 between the atmosphere and soils in spruce fir forests in the northeastern Unitied States. Biogeochem, 18, 119-135.

Castro MS; Morgan IRP. (2000). Input-output budgets of major ions for a forested watershed in western Maryland. Water Air Soil Pollut, 119, 121-137.

Castro MS; Driscoll CT; Jordan TE; Reay WG; Boynton WR; Seitzinger SP; Styles RV; Cable JE. (2001). Contribution of atmospheric depostition to the total nitrogen loads to thirty-four estuaries on the Atlantic and Gulf Coasts of the United States. In: Valigura RA; Alexander RB; Castro MS; Meyers TP; Paerl HW; Stacey PE; Turner RE (Eds.), Nitrogen loading in coastal water bodies: An atmospheric perspective (Monograph Voume 57, pp. 77-106). Washington, DC: American Geophysical Union.

Castro MS; Driscoll CT. (2002). Atmospheric nitrogen deposition to estuaries in the Mid-Atlantic and Northeastern United States. Environ Sci Technol, 36, 3242-3249.

Castro MS; Driscoll CT; Jordan TE; Reay WG; Boynton WR. (2003). Sources of nitrogen to estuaries in the United States. Estuaries, 26, 803-814.

CDC (2004). The health consequences of smoking: A report of the Surgeon General. http://www.cdc.gov/tobacco/data_statistics/sgr/sgr_2004/. Atlanta, GA; Office on Smoking and Health; National Center for Chronic Disease Prevention and Health Promotion; Centers for Disease Control and Prevention (CDC); U.S. Department of Health and Human Services.

Ceccotti SP; Messick DL. (1997). A global review of crop requirements, supply, and environmental impact on nutrient sulphur balance. In: Cram WJ; De Kok LJ; Stulen I; Brunold C; Rennenberg H (Eds.), Sulphur metabolism in higher plants (pp. 155-163). Leiden, The Netherlands: Backhuys Publishers.

Committee on Environment and Natural Resources (CENR).of the National Science and Technology Council. (1997+)

Centre for Ecology and Hydrology. (2003).Status of UK critical loads: critical loads methods, data & maps. http://www.airquality.co.uk/archive/reports/cat11/maintext_7may.pdf. Monks Wood, UK; UK National Focal Centre.

Certini G. (2005). Effects of fire on properties of forest soils: A review. Oecologia, 143, 1-10.

CFR. (2006). Lower detectable limit--(1).technical definition. (CFR 40: Section 53.23c.). Washington DC: U.S. Code of Federal Regulations (CFR).

Chadwick MA; Huryn, AD. (2003). Effect of a whole-catchment N addition on stream detritus processing. J. North Am. Benthol. Soc. 22: 194-206.

Chadwick MA; Huryn, AD. (2005). Response of stream macroinvertebrate production to atmospheric N deposition and channel drying. Limnol Oceanogr, 50, 228-236.

Chameides WL. (1984). The photochemistry of a remote marine stratiform cloud. J Geophys Res, 89, 4739-4755.

Chameides WL; Stelson AW. (1992). Aqueous-phase chemical processes in deliquescent sea-salt aerosols: A mechanism that couples the atmospheric cycles of S and sea salt. J Geophys Res, 97, 20565-20580.

Chan ASK; Steudler PA; Bowden RD; Gulledge J; Cavanaugh CM. (2005). Consequences of nitrogen fertilization on soil methane consumption in a productive temperate deciduous forest. Biol Fertil Soils, 41, 182-189.

Chanasyk DS; Whitson IR; Mapfumo E; Burke JM; Prepas EE. (2003). The impacts of forest harvest and wildfire on soils and hydrology in temperate forests: A baseline to develop hypotheses for the Boreal Plain. J Environ Eng Sci, 2, S51-S62.

Chang JS; Brost RA; Isaksen ISA; Madronich S; Middleton P. (1987). A three-dimensional Eulerian acid deposition model - physical concepts and formulation. J Geophys Res, 92, 14681-14700.

Chang MC; Sioutas C; Kim S; Gong H Jr; Linn WS. (2000). Reduction of nitrate losses from filter and impactor samplers by means of concentration enrichment. Atmos Environ, 34, 85-98.

Chang ME; Hartley DE; Cardelino C; Chang W-L. (1996). Inverse modeling of biogenic emissions. Geophys Res Lett, 23, 3007-3010.

Chang ME; Hartley DE; Cardelino C; Hass-Laursen D; Chang WL. (1997). On using inverse methods for resolving emissions with large spatial inhomogeneities. J Geophys Res, 102, 16023-16036.

Chapin FS III. (1980). The mineral nutrition of wild plants. Annu Rev Ecol Syst, 11, 233-260.

Chapin FS III; Bloom, AJ; Field, CB; Waring, RH. (1987). Plant responses to multiple environmental factors. BioScience 37: 49-57.

Chapin FS III. (1991). Integrated responses of plants to stress: a centralized system of physiological responses. BioScience 41: 29-36.

Chapin FS III; Moilanen, L; Kielland, K. (1993). Preferential use of organic nitrogen for growth by a non-mycorrhizal arctic sedge. Nature 361: 150-153.

Chapin FS III; Sala OE; Burke IC; Grime JP; Hooper DU; Lauenroth WK; Lombard A; Mooney HA; Mosier AR; Naeem S; Pacala SW; Roy J; Steffen WL; Tilman D. (1998). Ecosystem consequences of changing biodiversity. Bioscience, 48, 45-52.

Chapin FS.III; Ruess, RW. (2001). The roots of the matter. Nature, 411, 749, 751-752.

Chappelka, AH; Samuelson, LJ. (1998). Ambient ozone effects on forest trees of the eastern United States: A review. New Phytol. 139: 91-108.

Chapuis-Lardy L; Wrage N; Metay A; Chotte JL; Bernoux M. (2007). Soils, a sink for N_2O? A review. Glob Chang Biol, 13, 1-17.

Charbonneau R; Kondolf GM. (1993). Land use change in California: nonpoint source water quality impacts. Environ Manage, 17, 453-460.

Charles, DF; Norton, SA. (1986). Paleolimnological evidence for trends in atmospheric deposition of acids and metals. In: NRC (Ed.),.Acid deposition: Long-term trends. (NRC Committee on monitoring and assessment of trends in acid deposition; pp 335-435). Washington, DC: National Academy Press.

Charles DF; Batarbee RW; Renberg I; van Dam H; Smol JP. (1990a). Paleoecological analysis of lake acidification trends in North America and Europe using diatoms and chrysophytes. In: Acidic Precipitation; Series Volume 4: Soils, aquatic processes, and lake acidification. Advances in environmental science (pp. 207-276). New York: Springer-Verlag.

Charles DF; Binford MW; Furlong ET; Hites RA; Mitchell MJ; Norton SA; Oldfield F; Paterson MJ; Smol JP; Uutala AJ. (1990b). Paleoecological investigation of recent lake acidification in the Adirondack Mountains, NY. J Paleolimnol, 3, 195-241.

Charles DF. (1991). Christie, S. (Ed.). Acidic deposition and aquatic ecosystems: Regional case studies . New York: Springer-Verlag.

Chatfield RB; Crutzen PJ. (1984). Sulfur dioxide in remote oceanic air: cloud transport of reactive precursors. J Geophys Res, 89, 7111-7132.

Chen CW; Gherini SA; Dean JD; Hudson RJM; Goldstein RA. (1984a). Development and calibration of the integrated lake-watershed acidification model. In: Schnoor JL (Ed.), Modeling of total acid precipitation impacts (pp. 175-203). Stoneham, MA: Butterworth Publishers.

Chen CW; Gherini, SA. Peters NE; Murdoch, PS; Newton, RM; Goldstein, RA. (1984b). Hydrologic analyses of acidic and alkaline lakes. Water Resour Res, 20, 1875-1882.

Chen CW; Gomez LE. (1989). Comment on surface water chemistry. Environ Sci Technol, 23, 752-754

Chen CY; Stemberger RS; Kamman NC; Mayes BM; Folt CL. (2005). Patterns of Hg bioaccumulation and transfer in aquatic food webs across multi-lake studies in the Northeast U.S. Ecotoxicology, 14, 135-147.

Chen L; Driscoll, CT. (2004a). Modeling the response of soil and surface waters in the Adirondack and Catskill regions of New York to changes in atmospheric deposition and historical land disturbance. Atmos Environ, 38, 4099-4109.

Chen, L; Driscoll, CT. (2004b). A regional assessment of the response of the acid-base status of lake-watersheds in the Adirondack region of New York to changes in atmospheric deposition using PnET-BGC. (pp. 1-27). Syracuse, NY: Department of Civil and Environmental Engineering.

Chen L; Driscoll, CT. (2004c). An evaluation of processes regulating spatial and temporal patterns in lake sulfate in the Adirondack region of New York. Glob Biogeochem Cycles, 18, 10.

Chen L; Driscoll CT. (2005a). Regional application of an integrated biogeochemical model to northern New England and Maine. Ecol Appl, 15, 1783-1797.

Chen L; Driscoll CT. (2005b). Regional assessment of the response of acid-base status of lake-watersheds in the Adirondack region of New York to changes in atmospheric deposition using PnET-BGC. Environ Sci Technol, 39, 787-794.

Chen, L; Driscoll, CT. (2005c). A two-layer model to simulate variations in surface water chemistry draining a northern forest watershed. Water Resour Res, 41, doi: 10.1029/2004WR003625.

Chock DP; Winkler SL. (1994). A comparison of advection algorithms coupled with chemistry. Atmos Environ, 28, 2659-2675.

Choi S-C; Chase T Jr; Bartha R. (1994). Metabolic pathways leading to mercury methylation in *Desulfovibrio desulfuricans* LS. Appl Environ Microbiol, 60, 4072-4077.

Choi W; Leu M-T. (1998). Nitric acid uptake and decomposition on black carbon (soot) surfaces: Its implications for the upper troposphere and lower stratosphere. J Phys Chem, 102, 7618-7630.

Chorover J; Visousek, PM; Everson, DA; Esperanza, AM; Turner, D. (1994). Solution chemistry profiles of mixed-conifer forests before and after fire. Biogeochem, 26, 115-144.

Chow JC; Zielinska B; Watson JG; Fujita EM; Richards HW; Neff WD; Dietrich D; Hering SV. (1998). Northern Front Range air quality study. Volume A: Ambient measurements, Final Report. A companion document to the Northern Front Range air quality study final report (Watson et al., 1998a). http://www.nfraqs.colostate.edu/dri.html Fort Collins, CO; Prepared for Cooperative Institute for Research in the Atmosphere; Colorado State University Foothills Campus.

Chow JC; Watson JG. (1999). Ion chromatography in elemental analysis of airborne particles. In: Landsberger S, Creatchman M. (Eds.). Elemental analysis of airborne particles, (Series: Vo-Dinh T (Ed.).Advances in environmental industrial and process control technologies, Volume 1, pp 97-137). Newark, NJ: Gordon and Breach Science Publishers.

Christensen SW; Beauchamp JJ; Shaakir-Ali JA; Coe J; Baker JP; Smith EP; Gallagher J. (1990). Patterns of fish distribution in relation to lake/watershed characteristics: Regression analyses and diagnostics. In: Interpretative analysis of the Adirondack Lakes Survey. Final report to the Adirondack Lakes Survey Corporation (pp. A-1-A-62).

Christensen TR; Michelsen A; Jonasson S; Schmidt IK. (1997). Carbon dioxide and methane exchange of a subarctic heath in response to climate change related environmental manipulations. Oikos, 79, 34-44.

Christie CE; Smol JP. (1993). Diatom assemblages as indicators of lake rophic status in southeastern Ontario lakes. J Phycol, 29, 575-586.

Church MR; Shaffer PW; Thornton KW; Cassell DL; Liff CI; Johnson MG; Lammers DA; Lee JJ; Holdren GR; Kern JS; Liegel LH; Pierson SM; Stevens DL; Rochelle BP; Turner RS. (1992). Direct/delayed response project: Future effects of long-term sulfur deposition on stream chemistry in the mid-Appalachian region of the eastern United States (No. EPA/600/R-92/186). Corvallis, OR: U.S. Environmental Protection Agency.

Cione NK; Padgett PE; Allen EB. (2002). Restoration of a native shrubland impacted by exotic grasses, frequent fire and nitrogen deposition in southern California. Restor Ecol, 10, 376-384.

Civerolo KL; Dickerson RR. (1998). Nitric oxide soil emissions from tilled and untilled cornfields. Ag For Meteor, 90, 307-311.

Clair TA; Dennis IF; Amiro PG; Cosby BJ. (2004). Past and future chemistry changes in acidified Nova Scotian Atlantic salmon (*Salmo salar*) rivers: A dynamic modeling approach. Can J Fish Aquat Sci, 61, 1965-1975.

Clark CM; Cleland EE; Collins SL; Fargione JE; Gough L; Gross KL; Pennings SC; Suding KN; Grace JB. (2007). Environmental and plant community determinants of species loss following nitrogen enrichment. Ecol Lett, 10, 596-607.

Clark CM; Tilman D. (2008). Loss of plant species after chronic low-level nitrogen deposition to prairie grasslands. Nature, 451, 712-715.

Clarke JF; Edgerton ES; Martin BE. (1997). Dry deposition calculations for the Clean Air Status and Trends Network. Atmospheric Environment 31: 3667-3678.

Cleary PA; Wooldridge PJ; Cohen RC. (2002). Laser-induced fluorescence detection of atmospheric NO_2 with a commercial diode laser and a supersonic expansion. Appl Optics, 41, 6950-6956.

Clegg NA; Toumi R. (1998). Non-sea-salt-sulphate formation in sea-salt aerosol. J Geophys Res, 103, 31095-31102.

Cleland EE; Chiariello NR; Loarie SR; Mooney HA; Field CB. (2006). Diverse responses of phenology to global changes in a grassland ecosystem. Proc Natl Acad Sci USA, 103, 13740-13744.

Clemitshaw K. (2004). A review of instrumentation and measurement techniques for ground-based and airborne field studies of gas-phase tropospheric chemistry. Crit Rev Environ Sci Technol, 34, 1-108.

Cloern, JE. (2001). Our evolving conceptual model of the coastal eutrophication problem. Mar Ecol Prog Ser, 210, 223-253.

Cloern JE; Jassby AD; Schraga TS; Dallas KL. (2006). What is causing the phytoplankton increase in San Francisco Bay? In: The pulse of the estuary: Monitoring and managing water quality in the San Francisco estuary. (pp 62-70). http://www.sfei.org/rmp/pulse/2006/ThePulse2006_LowRes-Screen.pdf Oakland, CA: San Francisco Estuary Institute (SFEI) and The Regional Monitoring Program for Water Quality in the San Francisco Estuary.

Clough WS. (1975). The deposition of particles on moss and grass surfaces. Atmospheric Environment 9: 1113-1119.

Clow DW; Mast MA. (1999). Long-term trends in stream water and precipitation chemistry at five headwater basins in the northeastern United States. Water Resour Res, 35, 541-554.

Clow DW; Sueker JK. (2000). Relations between basin characteristics and stream water chemistry in alpine/subalpine basins in Rocky Mountain National Park, Colorado. Water Resour Res, 36, 49-62.

Clow DW; Sickman JO; Striegl RG; Krabbenhoft DP; Elliot JG; Dornblaser M; Roth, DA; Campbell DH. (2003). Changes in the chemistry of lakes and precipitation in high-elevation national parks in the western United States, 1985-1999. Water Resour Res, 39, 1171, doi: 10.1029/2002WR001533.

Cobourn WG; Husar RB; Husar JD. (1978). Continuous in situ monitoring of ambient particulate sulfur using flame photometry and thermal analysis. (In: Husar RB; Lodge, JP, Jr; Moore, DJ., (Eds.), Sulfur in the atmosphere: Proceedings of the international symposium; held in Dubrovnik, Yugoslavia; September 1977). Atmos Environ, 12, 89-98.

Cobourn, WG; Husar, RB. (1982). Diurnal and seasonal patterns of particulate sulfur and sulfuric acid in St. Louis, July 1977-June 1978. Atmos Environ, 16, 1441-1450.

Code of Federal Regulations. (2006). Lower detectable limit—(1) technical definition. CFR 40:§53.23c.

Coffman DJ; Hegg DA. (1995). A preliminary study of the effect of ammonia on particle nucleation in the marine boundary layer. J Geophys Res, 100, 7147-7160.

Cohen RC. (1999). Laser-induced fluorescence detection of atmospheric NO_2 at parts per trillion mixing ratios: Implications for nitrogen oxide photochemistry in the stratosphere and troposphere. Abstr Pap Am Chem Soc, 218, 262.

Cohn RD; Dennis RL. (1994). The evaluation of acid deposition models using principal component spaces. Atmos Environ, 28, 2531-2543.

Cole D; Rapp M. (1981). Elemental cycling in forest ecosystems. In: Reichle D (Ed.), Dynamic properties of forest ecosystems (Volume 23 from Series: International biological programme pp 341-409). Cambridge, UK: Cambridge University Press.

Collier TK. (2003). Forensic ecotoxicology: Establishing causality between contaminants and biological effects in field studies. Human and Ecological Risk Assessment: An International Journal, 9, 259-266.

Colombini MP; Modugno F; Fuoco R; Tognazzi A. (2002). A GC-MS study on the deterioration of lipidic paint binders. Microchem J, 73, 175-185.

Compeau GC; Bartha R. (1985). Sulfate-reducing bacteria: Principal methylators of mercury in aNO$_X$ic estuarine sediment. Appl Environ Microbiol, 50, 498-502.

Compton JE; Watrud LS; Porteous A; DeGrood S. (2004). Response of soil microbial biomass and community composition to chronic nitrogen additions at Harvard forest. For Ecol Manage, 196, 143-158.

Confer JL; Kaaret T; Likens GE. (1983). Zooplankton diversity and biomass in recently acidified lakes. Can J Fish Aquat Sci, 40, 36-42.

Conley DJ; Schelske CL; Stoermer EF. (1993). Modification of the biogeochemical cycle of silica with eutrophication. Mar Ecol Prog Ser, 101, 179-192.

Conley DJ; Markager S; Andersen J; Ellermann T; Svendsen LM. (2002). Coastal eutrophication and the Danish National Aquatic Monitoring and Assessment Program. Estuaries, 25, 848-861.

Conrad R. (1996). Soil microorganisms as controllers of atmospheric trace gases (H$_2$, CO, CH$_4$, OCS, N$_2$O, and NO). Microbiol Rev, 60, 609-640.

Cook, ER, Zedaker, SM. (1992).The dendroecology of red spruce decline. In: Eagar C; Adams MB (Eds.). Ecology and decline of red spruce in the eastern United States. (pp 192-231). New York, NY: Springer-Verlag.

Cook E. R; D'Arrigo, R. D; Mann, M. E. (2002).A well-verified, multiproxy reconstruction of the winter North Atlantic Oscillation Index since A.D. 1400. J Clim, 15, 1754-1764.

Cook RB; Kreis, RG Jr; Kingston JC; Camburn KE; Norton SA; Mitchell, MJ; Fry B; Shane LCK (1990). An acidic lake in northern Michigan. J Paleolimnol, 3, 13-34.

Cook RB; Jager HI. (1991). Upper Midwest: The effects of acidic deposition on lakes. In: Charles DF, Christie S. (Eds.). Acidic deposition and aquatic ecosystems: regional case studies. (pp 421-466). New York: Springer-Verlag.

Cook RB; Elwood JW; Turner RR; Bogle MA; Mulholland PJ; Palumbo AV. (1994). Acid-base chemistry of high-elevation streams in the Great Smoky Mountains. Water Air Soil Pollut, 72, 331-356.

Cooper AB. (1990). Nitrate depletion in the riparian zone and stream channel of a small headwater catchment. Hydrobiologia, 202, 13-26.

Cooper OR; Stohl A; Trainer M; Thompson AM; Witte JC; Oltmans SJ; Morris G; Pickering KE; Crawford JH; Chen G; Cohen RC; Bertram TH; Wooldridge P; Perring A; Brune W; Merrill J; Moody JL; Tarasick D; Nedelec P; Forbes G; Newchurch M; Schmidlin F; Johnson BJ; Turquety S; Baughcum SL; Ren X; Fehsenfeld FC; Meagher JF; Spichtinger N; Brown CC; McKeen SA; McDermid, IS; Leblanc T. (2006a).Large upper tropospheric ozone enhancements above mid-latitude North America during summer: In situ evidence from the IONS and MOZAIC ozone measurement network. J Geophys Res, 111, doi:10.1029/2006JD007306.

Cooper OR; Stohl A; Trainer M; Thompson A; Witte J; Oltmans S; Morris G; Pickering K; Crawford J; Chen G; Cohen R; Bertram T; Wooldridge P; Perring A; Brune W; Merrill J; Moody J; Tarasisck D; Nedelec P. (2006b). Influence of lightning NO$_X$ on the summertime upper tropospheric ozone enhancement above eastern North America. EOS Transactions, American Geophysical Union, 87.

Cooper SR; Brush GS. (1991). Long-term history of Chesapeake Bay aNO$_X$ia. Science, 254, 992-996.

Corn PS; Stolzenburg W; Bury RB. (1989). Acid precipitation studies in Colorado and Wyoming: interim report of surveys of mountain amphibians and water chemistry. (Biological report 80 [40.26]). U.S. Fish and Wildlife Service.

Cosby BJ; Hornberger GM; Galloway JN. (1985a). Modeling the effects of acid deposition: Assessment of a lumped parameter model of soil water and streamwater chemistry. Water Resour Res, 21, 51-63.

Cosby BJ; Wright RF; Hornberger GM; Galloway JN. (1985b). Modelling the effects of acid deposition: Estimation of long-term water quality responses in a small forested catchment. Water Resour Res, 21, 1591-1601.

Cosby BJ; Hornberger GM; Galloway JN; Wright RF. (1985c). Time scales of catchment acidification: a quantitative model for estimating freshwater acidification. Environ Sci Technol, 19, 1144-1149.

Cosby BJ; Jenkins A; Ferrier RC; Miller JD; Walker TAB. (1990). Modelling stream acidification in afforested catchments: Longterm reconstructions at two sites in central Scotland. J Hydrol, 120, 143-162.

Cosby BJ; Ryan PF; Webb JR; Hornberger GM; Galloway JN; Charles DF. (1991). Mountains of western Virginia. In: Charles DF; Christie S (Ed.), Acidic deposition and aquatic ecosystems: Regional case studies (pp. 297-318). New York, NY: Springer-Verlag.

Cosby BJ; Wright RF; Gjessing E. (1995). An acidification model (MAGIC) with organic acids evaluated using whole-catchment manipulations in Norway. J Hydrol, 170, 101-122.

Cosby BJ; Norton SA; Kahl JS. (1996). Using a paired catchment manipulation experiment to evaluate a catchment-scale biogeochemical model. Sci Total Environ, 183, 49-66.

Cosby BJ; Ferrier RC; Jenkins A; Emmett BA; Wright RF; Tietema A. (1997). Modelling the ecosystem effects of nitrogen deposition: Model of ecosystem retention and loss of inorganic nitrogen (MERLIN). Hydrol Earth Sys Sci, 1, 137-158.

Cosby BJ; Ferrier RC; Jenkins A; Wright RF. (2001). Modeling the effects of acid deposition: Refinements, adjustments and inclusion of nitrogen dynamics in the MAGIC model. Hydrol Earth Sys Sci, 5, 499-517.

Cosby BJ; Webb JR; Galloway JN; Deviney FA. (2006). Acidic deposition impacts on natural resources in Shenandoah National Park. (Technical Report NPS/NER/NRTR—2006/066) Philadelphia, PA; Northeast Region of the National Park Service; U.S. Department of the Interior.

Costanza R; d'Arge R; de Groot R; Farber S; Grasso M; Hannon B; Limberg K; Naeem S; O'Neill RV; Paruelo J; Raskin RG; Sutton P; van den Belt M. (1997). The value of the world's ecosystem services and natural capital. Nature, 387, 253-259.

Courchesne F; Cote B; Fyles JW; Hendershot WH; Biron PM; Roy AG; Turmel MC. (2005). Recent changes in soil chemistry in a forested ecosystem of southern Quebec, Canada. Soil Sci Soc Am J, 69, 1298-1313.

Cowardin LM; Golet FC; LaRoe ET. (1979). Classification of wetland and deepwater habitats of the United States; (Report no. FWS/OBS-79/31). Fish and Wildlife Service, U.S. Department of the Interior.

Cowell D; Apsimon H. (1996). Estimating the cost of damage to buildings by acidifying atmospheric pollution in Europe. Atmos Environ, 30, 2959-2968.

Cowling EB, Dochinger LS (1980). Effects of acidic precipitation on health and the productivity of forests. In: Miller PR (tech coordinator). Proceedings of symposium on effects of air pollutants on mediterranean and temperate forest ecosystems, June 22- 27, 1980, Riverside, CA. (General technical report PSW-43, pp 165–173). Berkeley, CA; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Cowling, EB; Chameides WL; Kiang CS; Fehsenfeld FC; Meagher JF. (2000). Introduction to special Section: Southern Oxidant Study Nashville/Middle Tennessee Ozone Study, part 2. J Geophys Res, 105, 9075-9077.

Cowling EB; Furiness C. (Eds.) (2001). The state of the southern oxidants study (SOS): Policy-relevant findings in ozone and PM$_{2.5}$ pollution research 1994–2000. (Report SOS-2). Raleigh, NC; SOS-Office of the Director; North Carolina State University.

Craig BW; Friedland AJ. (1991). Spatial patterns in forest composition and standing dead red spruce in montane forests of the Adirondacks and northern Appalachians. Environ Monit Assess, 18, 129-140.

Crain CM. (2007). Shifting nutrient limitation and eutrophication effects in marsh vegetation across estuarine salinity gradients. Estuaries and Coasts, 30, 26-34.

Crawford J; Davis D; Olson J; Chen G; Liu S; Fuelberg H; Hannan J; Kondo Y; Anderson B; Gregory G. Sachse G; Talbot R; Viggiano A; Heikes B; Snow J; Singh H; Blake D. (2000). Evolution and chemical consequences of lightning-produced NO_X observed in the North Atlantic upper troposphere. J Geophys Res, 105, 19795-19809.

Crill PM; Martikainen PJ; Nykanen H; Silvola J. (1994). Temperature and N-fertilization effects on methane oxidation in a drained peatland soil. Soil Biol Biochem, 26, 1331-1339.

Cristol DA; Brasso RL; Condon AM; Fovargue RE; Friedman SL; Hallinger KK; Monroe AP; White AE. (2008). The movement of aquatic mercury through terrestrial food webs. Science, 320, 335-335.

Crocker TD. (1985). On the value of the condition of a forest stock. Land Econ, 61, 244-254.

Crocker TD; Forster BA. (1986). Atmospheric deposition and forest decline. Water Air Soil Pollut, 31, 1007-1017.

Cronan CS; Reiners WA; Reynolds RC Jr; Lang GE. (1978). Forest floor leaching: Contributions from mineral, organic, and carbonic acids in New Hampshire subalpine forests. Science, 200, 309-311

Cronan CS; Aiken GR. (1985). Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York. Geochim Cosmochim Acta, 49, 1697-1705.

Cronan CS; Schofield CL. (1979). Aluminum leaching response to acid precipitation: Effects on high elevation watersheds in the Northeast. Science, 204, 304-306.

Cronan CS; Walker W; Bloom P. (1986). Predicting aqueous aluminum concentrations in natural waters. Nature, 140-143.

Cronan CS; Goldstein RA. (1989a). ALBIOS: A Comparison of aluminum biogeochemistry in forested watersheds exposed to acidic deposition. In: Adriano DC; Havas M. (Eds.). Acidic precipitation: Case studies. Volume 1 of series: Advances in environmental science. (pp 113-135). New York, NY: Springer-Verlag.

Cronan CS; April R; Bartlett RJ; Bloom PR; Driscoll CT; Gherini SA; Henderson GS; Joslin JD; Kelly JM; Newton RM; Parnell RA; Patterson HH; Raynal DJ; Schaedle M; Schofield CL; Sucoff EI; Tepper HB; Thornton FC. (1989b). Aluminum toxicity in forests exposed to acidic deposition: The ALBIOS results. Water Air Soil Pollut, 48, 181-192.

Cronan CS; Schofield CL. (1990). Relationships between aqueous aluminum and acidic deposition in forested watersheds of North America and northern Europe. Environ Sci Technol, 24, 1100-1105.

Cronan CS; Perdue EM; Gjessing ET. (1990a). Patterns of organic acid transport from forested watersheds to aquatic ecosystems. In: Perdue M; Glaze W; Gjessing ET (Eds.). Organic acids in aquatic ecosystems, (Report of the Dahlem workshop on organic acids in aquatic ecosystems; Berlin, Germany May 7-12, 1989). (pp. 245-260). New York, NY: John Wiley and Sons, Ltd.

Cronan, CS; Driscoll, CT; Newton, RM; Kelly JM; Schofield CL; Bartlett RJ; April R. (1990b). A comparative analysis of aluminum biogeochemistry in a northeastern and a southeastern forested watershed. Water Resour Res, 26, 1413-1430.

Cronan CS; Grigal DF. (1995). Use of calcium/aluminum ratios as indicators of stress in forest ecosystems. J Environ Qual, 24, 209-226.

Crosley DR. (1996). NO_Y blue ribbon panel. J Geophys Res, 101, 2049-2052.

Crutzen PJ. (1976). Upper limits on atmospheric ozone reductions following increased application of fixed nitrogen to the soil. Geophys Res Lett, 3, 169-172.

Crutzen PJ; Gidel LT. (1983). A two-dimensional photochemical model of the atmosphere. 2. The tropospheric budgets of the anthropogenic chlorocarbons, CO, CH_4, CH_3Cl and the effect of various NO_X sources on tropospheric ozone. J Geophys Res, 88, 6641-6661.

Cumming BF; Smol JP; Kingston JC; Charles DF; Birks HJB; Camburn KE; Dixit SS; Uutala AJ; Selle AR. (1992). How much acidification has occurred in Adirondack region lakes (New York, USA) since preindustrial times? Can J Fish Aquat Sci, 49, 128-141.

Cumming BF; Davey KA; Smol JP; Birks HJB. (1994). When did acid-sensitive Adirondack lakes (New York, USA).begin to acidify and are they still acidifying? Can J Fish Aquat Sci, 51, 1550-1568.

Cumming JR; Weinstein LH. (1990). Aluminum-mycorrhizal interactions in the physiology of pitch pine seedlings. Plant Soil, 125, 7-18.

Curtis CJ; Emmett BA; Reynolds B; Shilland J. (2006). How important is N_2O production in removing atmospherically deposited nitrogen from UK moorland catchments? . Soil Biol Biochem, 38, 2081-2091.

Dagnall RM; Thompson KC; West TS. (1967).Molecular-emission in cool flames. Part I. The behaviour of sulphur species in a hydrogen-nitrogen diffusion flame and in a shielded air-hydrogen flame. Analyst, 92, 506-512.

Dahlgren RA; Walker WJ. (1993). Aluminum release rates from selected spodosol Bs horizons: Effect of pH and solid-phase aluminum pools. Geochim Cosmochim Acta, 57, 57-66.

Dahlgren RA. (1994). Soil acidification and nitrogen saturation from weathering of ammonium-bearing rock. Nature, 368, 838-841.

Dahlgren RA; Driscoll CT. (1994). The effects of whole-tree clear cutting on soil processes at Hubbard Brook Experimental Forest, New Hampshire, USA. Plant Soil, 58, 239-262.

Dahlman L; Näsholm T; Palmqvist K. (2002). Growth, nitrogen uptake, and resource allocation in the two tripartite lichens *Nephroma arcticum* and *Peltigera aphthosa* during nitrogen stress. New Phytol, 153, 307-315.

Dahlman L; Persson J; Nasholm T; Palmqvist K. (2003). Carbon and nitrogen distribution in the green algal lichens *Hypogymnia physodes* and *Platismatia glauca* in relation to nutriend supply. Planta, 217, 41-48.

Dahlman L; Persson J; Palmqvist K; Näsholm T. (2004). Organic and inorganic nitrogen uptake in lichens. Planta, 219, 459-467.

Dail DB; Davidson EA; Chorover J. (2001). Rapid abiotic transformation of nitrate in an acid forest soil. Biogeochemistry, 54, 131-146.

Daily GC. (1997). Introduction: What are ecosystem services. In: Daily GC (Ed.). Nature's services: Societal dependence on natural ecosystems (pp. 1-10). Washington, DC: Island Press.

Daily GC; Ehrlich PR. (1999). Managing earth's ecosystems: An interdisciplinary challenge. Ecosystems, 2, 277-280.

Dalal RC; Wang WJ; Robertson GP; Parton WJ. (2003). Nitrous oxide emission from Australian agricultural lands and mitigation options: A review. Australian J Soil Res, 41, 165-195.

Dalsgaard T; Tharndrup B; Canfield DE. (2005). Anaerobic ammonium oxidation (anammox) in the marine environment. Res Microbiol, 156, 457-464.

Damian L; Fako R. (2000). Weathering structural steels corrosion in atmospheres of various degrees of pollution in Romania. Materials and Corrosion, 51, 574-578.

Dangles O; Malmqvist B; Laudon H. (2004). Naturally acid freshwater ecosystems are diverse and functional: evidence from boreal streams. Oikos, 104, 149-155.

Dante JF; Kelly RG. (1993). The evolution of the adsorbed solution layer during atmospheric corrosion and its effects on the corrosion rate of copper. J Electrochem Soc, 140, 1890-1897.

D'Antonio CM; Vitousek PM. (1992). Biological invasions by exotic grasses, the grass/fire cycle, and global change. Ann Rev Ecol Syst, 23, 63-87.

Darby FA; Turner RE. (2008). Below-and aboveground *Spartina alterniflora* production in a Louisiana salt marsh. Estuaries and Coasts, 31, 223-231.

Das B; Vinebrooke RD; Sanchez-Azofeifa A; Rivard B; Wolfe AP. (2005). Inferring sedimentary chlorophyll concentrations with reflectance spectroscopy: A novel approach to reconstructing historical changes in the trophic status of mountain lakes. Can J Fish Aquat Sci, 62, 1067-1078.

Dasch JM. (1987). Measurement of dry deposition to surfaces in deciduous and pine canopies. Environmental Pollution 44: 261-277.

Daum PH; Kleinman LI; Hills AJ; Lazrus AL; Leslie ACD; Busness K; Boatman J. (1990). Measurement and interpretation of concentrations of H_2O_2 and related species in the upper midwest during summer. J Geophys Res, 95, 9857-9871.

Daum PH; Kleinman LI; Newman L; Luke WT; Weinstein-Lloyd J; Berkowitz CM; Busness KM. (1996). Chemical and physical properties of plumes of anthropogenic pollutants transported over the North Atlantic during the North Atlantic Regional Experiment. J Geophys Res, 101, 29029-29042.

David MB; Driscoll CT. (1984). Aluminium speciation and equilibria in soil solutions of a haplorthod in the Adirondack Mountains (New York, USA). Geoderma, 33, 297-318.

David MB; Mitchell MJ; Scott TJ. (1987). Importance of biological processes in the sulfur budget of a northern hardwood ecosystem. Biol Fertil Soils, 5, 258-264.

David MB; Lawrence GB. (1996). Soil and soil solution chemistry under red spruce stands across the northeastern United States. Soil Sci, 161(3), 314-328.

David M; Vance G; Kahl J. (1999). Chemistry of dissolved organic carbon at Bear Brook Watershed, Maine: Stream water response to $(NH_4)_2SO_4$ additions. Environ Monit Assess, 55, 149-163.

Davidson CI; Wu Y-L. (1990). Dry deposition of particles and vapors. In Lindberg SE, Page AL, Norton SA (Eds.), Acidic precipitation: vol. 3, sources, deposition, and canopy interactions (pp. 103-216). New York: Springer-Verlag, Inc.

Davidson EA; Schimel JP. (1995). Microbial processes of production and consumption of nitric oxide, nitrous oxide and methane. In: Matson PA, Harriss RC (Eds.), Biogenic trace gases: Measuring emissions from soil and water (pp. 327-357). New York, NY: Blackwell Science.

Davidson EA; Kingerlee W. (1997). A global inventory of nitric oxide emissions from soils. Nutr Cycling Agroecosyst, 48, 37-50.

Davidson EA; Keller M; Erickson HE; Verchot LV; Veldkamp E. (2000). Testing a conceptual model of soil emissions of nitrous and nitric oxides. Bioscience, 50, 667-680.

Davidson EA; Chorover J; Dail DB. (2003). A mechanism of abiotic immobilization of nitrate in forest ecosystems: the ferrous wheel hypothesis. Glob Chang Biol, 9, 228-236.

Davidson EA; Seitzinger S. (2006). The enigma of progress in denitrification research. Ecol Appl, 16, 2057-2063.

Davies L; Bates JW; Bell JNB; James PW; Purvis OW. (2007). Diversity and sensitivity of epiphytes to oxides of nitrogen in London. Environ Pollut, 146, 299-310.

Davis RB; Anderson DS; Berge F. (1985). Paleolimnological evidence that lake acidification is accompanied by loss of organic matter. Nature, 316, 436-438.

Davis RB; Anderson DS; Norton SA; Whiting MC. (1994). Acidity of twelve northern New England (USA) lakes in recent centuries. J Paleolimnol, 12, 103-154.

Day DA; Wooldridge PJ; Dillon MB; Thornton JA; Cohen RC. (2002). A thermal dissociation laser-induced fluorescence instrument for in situ detection of NO_2, peroxy nitrates, alkyl nitrates, and HNO_3. J Geophys Res, 107, doi: 10.1029/2001JD000779.

Day DA; Dillon MB; Woolridge PJ; Thornton JA; Rosen RS; Wood EC; Cohen RC. (2003). On alkyl nitrates, O_3, and the missing NO_Y. J Geophys Res, 108, doi 10.1029/2003JD003685.

De Bakker AJ. (1989). Effects of ammonia emission on epiphytic lichen vegetation. Acta Bot Neerl, 38, 337-342.

De Coninck F. (1980). Major mechanisms in formation of spodic horizons. Geoderma, 24, 101-128.

De Haan DO; Brauers T; Oum K; Stutz J; Nordmeyer T; Finlayson-Pitts BJ. (1999). Heterogeneous chemistry in the troposphere: Experimental approaches and applications to the chemistry of sea salt particles. Int Rev Phys Chem, 18, 343-385.

de Laat ATJ; Zachariasse M; Roelofs GJ; Van Velthoven P; Dickerson RR; Rhoads KP; Oltmans SJ; Lelieveld J. (1999). Tropospheric O_3 distribution over the Indian Ocean during spring 1995 evaluated with a chemistry-climate model. J Geophys Res, 104, 13881-13894.

De Schrijver A; Verheyen K; Mertens J; Staelens J; Wuyts K; Muys B. (2008). Nitrogen saturation and net ecosystem production. (Brief communicatin arising from: F. Magnani et al. (2007). *Nature,* 447, 849–850; Magnani et al. reply). Nature, 451, E1.

de Steiguer JE; Pye JM. (1988). Using scientific opinion to conduct forestry air pollution economic analyses. In: Jöbstl A (Ed.). Proceedings of symposium on the economic assessment of damage caused to forests by air pollutants; held in Gmunden, Austria September 13-17, 1988. IUFRO Working Party S4.04-02 (pp. 133-142).

de Steiguer JE; Pye JM; Love CS. (1990). Air pollution damage to U.S. forests: A survey of perceptions and estimates of scientists. J For, 88, 17-22.

de Vries W. (1988). Critical deposition levels for nitrogen and sulphur on Dutch forest ecosystems. Water Air Soil Pollut, 42, 221-239.

de Vries W; Posch M; Kämäri J. (1989). Simulation of the long-term soil response to acid deposition in various buffer ranges. Water Air Soil Pollut, 48, 349-390.

de Vries W; Reinds GJ; Posch M; Kämäri J. (1994). Simulation of soil response to acidic deposition scenarios in Europe. Water Air Soil Pollut, 78, 215-246.

de Vries W; Reinds GJ; Vel E. (2003). Intensive monitoring of forest ecosystems in Europe: 2. Atmospheric deposition and its impacts on soil solution chemistry. For Ecol Manage, 174, 97-115.

de Vries W; Reinds GJ; Gundersen P; Sterba H. (2006). The impact of nitrogen deposition on carbon sequestration in European forests and forest soils. Glob Chang Biol, 12, 1151-1173.

de Vries W; Kros H; Reinds GJ; Wamelink W; Mol J; van Dobben H; Bobbink R; Emmett B; Smart S; Evans C; Schlutow A; Kraft P; Belyazid S; Sverdrup H; van Hinsberg A; Posch M; Hettelingh J-P. (2007). Developments in deriving critical limits and modelling critical loads of nitrogen for terrestrial ecosystems in Europe. (Alterra report no 1382). Wageningen, The Netherlands: Wageningen University and Research Centre - Alterra.

de Vries W; Solberg S; Dobbertin M; Sterba H; Laubhahn D; Reinds GJ; Nabuurs GJ; Gundersen P; Sutton MA. (2008). Ecologically implausible carbon response? (Brief communicatin arising from: F. Magnani et al. (2007). Nature, 447, 849–850; Magnani et al. reply). Nature, 451, E1-E3.

De Witt HA; Mulder J; Nygaard PH; Aamlid D. (2001). Testing the aluminium toxicity hypothesis: A field manipulation experiment in mature spruce forest in Norway. Water Air Soil Pollut, 130, 995-1000.

DeBano LF; Conrad CE. (1978). The effect of fire on nutrients in a chaparral ecosystem. Ecology, 59, 489-497.

DeBell LJ. (2006). Spatial and seasonal patterns and temporal variability of haze and its constituents in the United States: (CIRA IMPROVE network report IV). Fort Collins, CO; Cooperative Institute for Research in the Atmosphere (CIRA); Colorado State University.

DeCaria AJ; Pickering KE; Stenchikov GL; Scala JR; Stith JL; Dye JE; Ridley BA; Laroche P. (2000). A cloud-scale model study of lightning-generated NO_X in an individual thunderstorm during STERAO-A. J Geophys Res, 105, 11601-11616.

DeCaria AJ; Pickering KE; Stenchikov GL; Ott LE. (2005). Lightning-generated NO_X and its impact on tropospheric ozone production: a three-dimensional modeling study of a stratosphere-troposphere experiment: Radiation, aerosols and ozone (STERAO-A).thunderstorm. J Geophys Res, 110, doi:10.1029/2004JD005556.

DeConinck F. (1980). Major mechanisms in formation of spodic horizons. Geoderma, 24, 101-128.

Deevey ES; Binford MW; Brenner M; Whitmore TJ. (1986). Sedimentary records of accelerated nutrient loading in Florida lakes. Hydrobiologia, 143, 49-53.

DeForest JL; Zak DR; Pregitzer KS; Burton AJ. (2005). Atmospheric nitrate deposition and enhanced dissolved organic carbon leaching: Test of a potential mechanism. Soil Sci Soc Am J, 69, 1233-1237.

DeHayes DH; Schaberg PG; Hawley GJ; Strimbeck GR. (1999). Acid rain impacts on calcium nutrition and forest health. Bioscience, 49, 789-800.

Dehri I; Yazici B; Erbil M; Galip H. (1994). The effects of SO_2 and NH_3 on the atmospheric corrosion of galvanized iron sheet. Corros Sci, 36, 2181-2191.

Del Giorgio PA; Cole JJ; Cimberlic A. (1997). Respiration rates in bacteria exceed phytoplankton production in unproductive aquatic system. Nature, 385, 148-151.

Del Grosso SJ; Parton WJ; Mosier AR; Hartman MD; Brenner J; Ojima DS; Schimel DS. (2001). Simulated interaction of carbon dynamics and nitrogen trace gas fluxes using the DAYCENT model. In: Schaffer M; Ma L; Hansen S (Eds.), Modeling carbon and nitrogen dynamics for soil management, (pp 303-332). Boca Raton, Florida: CRC Press.

del Monte M; Rossi P. (1997). Fog and gypsum crystals on building materials. Atmos Environ, 31, 1637-1646.

Delaune RD; Lindau CW; Sulaeman E; Jugsujinda A. (1998). Nitrification and denitrification estimates in a Louisiana swamp forest soil as assessed by N-15 isotope dilution and direct gaseous measurements. Water Air Soil Pollut, 106, 149-161.

Delgado JA; Mosier AR; Follett RH; Follett RF; Westfall DG; Klemedtsson LK; Vermeulen J. (1996). Effects of N management on N_2O and CH_4 fluxes and N-15: Recovery in an irrigated mountain meadow. Nutr Cycling Agroecosys, 46, 127-134.

D'Elia CJ; Sanders JG; Boynton WR. (1986). Nutrient enrichment studies in a coastal plain estuary: phytoplankton growth in large-scale, continuous cultures. Can J Fish Aquat Sci, 43, 397-406.

Delmas R. (1982). On the emission of carbon, nitrogen and sulfur in the atmosphere during bushfires in intertropical savannah zones. Geophys Res Lett, 9, 761-764.

DeLucia EH; Hamilton JG; Naidu SL; Thomas RB; Andrews JA; Finzi A; Lavine M; Matamala R; Mohan JE; Hendrey GR; Schlesinger WH. (1999). Net primary production of a forest ecosystem with experimental CO_2 enrichment. Science, 284, 1177-1179.

Denning AS; Baron J; Mast MA; Arthur M. (1991). Hydrologic pathways and chemical composition of runoff during snowmelt in Loch Vale Watershed, Rocky Mountain National Park, Colorado, USA. Water Air Soil Pollut, 59, 107-123.

Dennis A; Fraser M; Anderson S; Allen D. (2002). Air pollutant emissions associated with forest, grassland, and agricultural burning in Texas. Atmos Environ, 36, 3779-3792.

Dennis RL; Binkowski FS; Clark TL; McHenry JN; McHenry SJ; Raynolds SK. (1990). Selected applications of the regional acid deposition model and engineering model, appendix 5F (part 2).of NAPAP SOS/T report 5. In: Irving PM, ed. National Acid Precipitation Assessment Program: State of Science and Technology, Volume 1. Washington, DC: National Acid Precipitation Assessment Program.

Dennis, R. (1997). Using the regional acid deposition model to determine the nitrogen deposition airshed of the Chesapeake Bay watershed. In: Baker JE (Ed.), Atmospheric deposition of contaminants to the Great Lakes and coastal waters. (pp 393-413). Pensacola, FL: Society of Environmental Toxicology and Chemistry Press.

Dennis RL; Mathur R. (2001). Airshed domains for modeling atmospheric deposition of oxidized and reduced nitrogen to the Neuse/Pamlico system of North Carolina. Hydrol Sci Technol, 17, 107-118.

Dennis RL; Tonnesen GS; Mathur R. (2001). Nonlinearities in the sulfate secondary fine particulate response to NO_X emissions reductions as modeled by the regional acid deposition model. In: Gryning S-E;. Schiermeier FA (Eds.), Air pollution modeling and its application, XIV (Proceedings of the millennium NATO/CCMS international technical meeting on air pollution modeling and its application, held May 15-19, 2000 in Boulder, Colorado pp 193-202). New York, NY: Kluwer Academic/Plenum Publishers.

Dennis TD; MacAvoy SE; Steg MB; Bulger AJ. (1995). The association of water chemistry variables and fish condition in streams of Shenandoah National Park (USA). Water Air Soil Pollut, 85, 365-370.

Dennis TE; Bulger AJ. (1995). Condition factor and whole-body sodium concentrations in a freshwater fish: Evidence for acidification stress and possible ionoregulatory over-compensation. Water Air Soil Pollut, 85, 377-382.

Dennis TE; Bulger AJ. (1999). The susceptibility of blacknose dace (*Rhinichthys atratulus*).to acidification in Shenandoah National Park. In: Bulger AJ; Cosby BJ; Dolloff CA; Eshleman KN; Galloway JN; Webb. JR (Eds.), Shenandoah National Park: Fish in sensitive habitats. Project final report, Volume IV: Stream bioassays, aluminum toxicity, species richness and stream chemistry, and models of susceptibility to acidification. Chapter 6B. Project completion report to the National Park Service. Charlottesville, VA; Department of Environmental Sciences, University of Virginia.

Dentener FJ; Crutzen PJ. (1993). Reaction of N_2O_5 on tropospheric aerosols: impact on the global distributions of NO_X, O_3, and OH. J Geophys Res, 98, 7149-7163.

Dentener F; Stevenson D; Cofala J; Mechler R; Amann M; Bergamaschi P; Raes F; Derwent R. (2005). The impact of air pollutant and methane emission controls on tropospheric ozone and radiative forcing: CTM calculations for the period 1990-2030. Atmos Chem Phys, 5, 1731-1755.

Dentener F; Stevenson D; Ellingsen K; Van Noije T; Schultz M; Amann M; Atherton C; Bell N; Bergmann D; Bey I; Bouwman L; Butler T; Cofala J; Collins B; Drevet J; Doherty R; Eickhout B; Eskes H; Fiore A; Gauss M; Hauglustaine D; Horowitz L; Isaksen IS; Josse B; Lawrence M; Krol M; Lamarque JF; Montanaro V; Muller JF; Peuch VH; Pitari G; Pyle J; Rast S; Rodriguez I; Sanderson M; Savage NH; Shindell D; Strahan S; Szopa S; Sudo K; Van Dingenen R; Wild O; Zeng G. (2006a). The global atmospheric environment for the next generation. Environ Sci Technol, 40, 3586-3594.

Dentener F; Drevet J; Lamarque JF; Bey I; Eickhout B; Fiore AM; Hauglustaine D; Horowitz LW; Krol M; Kulshrestha UC; Lawrence M; Galy-Lacaux C; Rast S; Shindell D; Stevenson D; Van Noije T; Atherton C; Bell N; Bergman D; Butler T; Cofala J; Collins B; Doherty R; Ellingsen K; Galloway J; Gauss M; Montanaro V; Müller JF; Pitari G; Rodriguez J; Sanderson M; Solman F; Strahan S; Schultz M; Sudo K; Szopa S; Wild O. (2006b). Nitrogen and sulfur deposition on regional and global scales: a multi-model evaluation. Glob Biogeochem Cycle, 20, doi: 10.1029/2005GB002672.

Derwent RG; Collins WJ; Johnson CE; Stevenson DS. (2001). Transient behaviour of tropospheric ozone precursors in a global 3-D CTM and their indirect greenhouse effects. Climatic Change, 49, 463-487.

DesGranges J-L; Darveau M. (1985). Effect of lake acidity and morphometry on the distribution of aquatic birds in southern Quebec. Holarctic Ecology, 8, 181-190.

DesGranges J-L; Houde B. (1989). Effects of acidity and other environmental parameters on the distribution of lacustrine birds in Quebec. In: DeGranges, JL (Ed.). Studies on the effects of acidification on aquatic wildlife in Canada: Lacustrine birds and their habitats in Quebec. (Canadian Wildlife Service occasional paper No. 67 pp 7-41). Ottawa, Ontario, Canada; Canadian Wildlife Service; Environment Canada.

Deviney FA; Rice KC; Hornberger GM. (2006). Time series and recurrence interval models to predict the vulnerability of streams to episodic acidification in Shenandoah National Park, Virginia. Water Resour Res, 42, doi:10.1029/2005WR004740.

Devito KJ; Dillon PJ; LaZerte BD. (1989). Phosphorus and nitrogen retention in five Precambrian Shield wetlands. Biogeochemistry, 8, 185-204.

Devito KJ; Hill AR. (1997). Sulphate dynamics in relation to groundwater-surface water interactions in headwater wetlands of the southern Canadian Shield. Hydrol Process, 11, 485-500.

Devito KJ; Hill AR. (1999). Sulphate mobilization and pore water chemistry in relation to groundwater hydrology and summer drought in two conifer swamps on the Canadian Shield. Water Air Soil Pollut, 113, 97-114.

Devol A. (2003). Solution to a marine mystery. Nature, 422, 575-576.

DeWald LE; Sucoff EI; Ohno T; Buschena CA. (1990). Response of northern red oak (*Quercus rubra* L.) seedlings to soil solution aluminum. Can J For Res, 20, 331-336.

DeWalle DR; Dinicola RS; Sharpe WE. (1987). Predicting baseflow alkalinity as an index to episodic stream acidification and fish presence. Water Resour Bull, 23, 29-35.

DeWalle DR; Swistock BR. (1994a). Causes of episodic acidification in five Pennsylvania streams on the northern Appalachian Plateau. Water Resour Res, 30, 1955-1963.

DeWalle DR; Swistock BR. (1994b). Differences in oxygen-18 content of throughfall and rainfall in hardwood and coniferous forests. Hydrol Processes, 8, 75-82.

DeWalle DR; Kochenderfer JN; Adams MB; Miller GW; Gilliam FS; Wood F; Odenwald-Clemens SS; Sharpe WE. (2006). Vegetation and acidification. In: Adams MB; DeWalle DR; Hom JL (Eds.), The Fernow watershed acidification study. (Volume 11 of Environmental Pollution Series, pp 137-188). Dordrecht, The Netherlands: Springer.

Diaz RJ; Solow A. (1999). Ecological and economic consequences of hypoxia: Topic 2 Report for the integrated assessment on hypoxia in the Gulf of Mexico. (NOAA Coastal Ocean Program Decision Analysis Series No 16).http://www8.nos.noaa.gov/nccos/pubinfo.aspx?id=514 . Silver Spring, MD: National cean Service Coastal Ocean Program; National Oceanic and Atmospheric Administration (NOAA). U.S. Department of Commerce.

Dibb JE; Arsenault M; Peterson MC. (2002). Fast nitrogen oxide photochemistry in Summit, Greenland snow. Atmos Environ, 36, 2501-2511.

Dickerson RR; Huffman GJ; Luke WT; Nunneracker LJ; Pickering KE; Leslie ACD; Lindsey CG; Slinn WGN; Kelly TJ; Daum PH; Delany AC; Greenberg JP; Zimmerman PR; Boatman JF; Ray JD; Stedman DH. (1987). Thunderstorms: An important mechanism in the transport of air pollutants. Science, 235, 460-464.

Dickerson RR; Rhoads KP; Carsey TP; Oltmans SJ; Burrows JP; Crutzen PJ. (1999). Ozone in the remote marine boundary layer: a possible role for halogens. J Geophys Res, 104, 21385-21395.

Dickson W. (1978). Some effects of the acidification of Swedish lakes. (Proceedings from the 20th Congress, internationale vereinigung fur theoretische und angewandte limnologie; held in Copenhagen, Denmark; August 8, 1977). Verh Internat Verein Limnol, 20, 851-856.

Diemer M. (1997). Effects of elevated CO_2 on gas exchange characteristics of alpine grassland. Acta Oecologica, 18, 177-182.

Dierberg FE; Brezonik PL. (1983). Nitrogen and phosphorus mass balances in natural and sewage-enriched cypress domes. J Appl Ecol, 20, 323-337.

Dighton J; Tuininga AR; Gray DM; Huskins RE; Belton T. (2004). Impacts of atmospheric deposition on New Jersey pine barrens forest soils and communities of ectomycorrhizae. For Ecol Manage, 201, 131-144.

Dijkstra FA; Smits MM. (2002). Tree species effects on calcium cycling: The role of calcium uptake in deep soils. Ecosystems, 5; 385-398.

Dillon PJ; Reid RA; Girard R. (1986). Changes in the chemistry of lakes near Sudbury, Ontario, following reduction of SO_2 emissions. Water Air Soil Pollut, 31, 59-65.

Dillon PJ; LaZerte BD. (1992). Response of Plastic Lake catchment, Ontario, to reduced sulphur deposition. Environ. Pollut, 77, 211-217.

Dillon PJ; Molot LA; Futter M. (1997). The effect of El Niño-related drought on the recovery of acidified lakes. Environ Monit Assess, 46, 105-111.

Dise NB; Wright RF. (1995). Nitrogen leaching from European forests in relation to nitrogen deposition. For Ecol Manage, 71, 153-161.

Dise NB; Matzner E; Gundersen P. (1998). Synthesis of nitrogen pools and fluxes from European forest ecosystems. Water Air Soil Pollut, 105, 143-154.

Dise NB; Verry ES. (2001). Suppression of peatland methane emission by cumulative sulfate deposition in simulated acid rain. Biogeochemistry, 53, 143-160.

Dixit SS; Keller W; Dixit AS; Smol JP. (2001). Diatom-inferred dissolved organic carbon reconstructions provide assessments of past UV-B penetration in Canadian Shield lakes. Can J Fish Aquat Sci, 58, 543-550.

Dobson JE; Rush RM; Peplies RW. (1990). Forest blowdown and lake acidification. Ann Assoc Amer Geogr, 80, 343-361.

Dodds WK. (2006). Eutrophication and trophic state in rivers and streams. Limnol Oceanogr, 51, 671-680.

Dodge MC. (1977). Combined use of modeling techniques and smog chamber data to derive ozone-precursor relationships. In: Dimitriades B (Ed.). Proceedings from the international conference on photochemical oxidant and its control, Volume II (EPA/600/3/77-001b pp 881-889). Research Triangle Park, NC; Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency.

Domine F; Shepson PB. (2002). Air-snow interactions and atmospheric chemistry. Science, 297, 1506-1510.

Dommen J; Prévôt ASH; Hering AM; Staffelbach T; Kok GL; Schillawski RD. (1999). Photochemical production and aging of an urban air mass. J Geophys Res, 104, 5493-5506.

Donagi AE; Goren AI. (1979). Use of indicator plants to evaluate atmospheric levels of nitrogen dioxide in the vicinity of a chemical plant. Environ Sci Technol, 13, 986-989.

Dortch Q; Whitledge TE. (1992). Does nitrogen or silicon limit phytoplankton production in the Mississippi River plume and nearby regions? Continental Shelf Research, 12, 1293-1309.

Doskey PV; Kotamarthi VR; Fukui Y; Cook DR; Breitbeil FW, III; Wesely ML. (2004). Air-surface exchange of peroxyacetyl nitrate at a grassland site. J Geophys Res, 109, doi 10.1029/2004JD004533

Downing JA; McCauley E. (1992). The nitrogen-phosphorus relationship in lakes. Limnol Oceanogr, 37, 936-945.

Downing JA. (1997). Marine nitrogen: phosphorus stoichiometry and the global N:P cycle. Biogeochemistry, 37, 237-252.

Drake BG; Gonzalez-Meler MA; Long SP. (1997). More efficient plants: a consequence of rising atmospheric CO_2? Ann Rev Plant Physiol Mol Biol, 48, 609-639.

Drenovsky RE; Richards JH. (2005). Nitrogen addition increases fecundity in the desert shrub Sarcobatus *vermiculatus*. Oecologia, 143, 349-356.

Drever JI; Hurcomb DR. (1986). Neutralization of atmospheric acidity by chemical weathering in an alpine drainage basin in the North Cascade Mountains. Geology, 14, 221-224.

Drevnick PE; Canfield DE; Gorski PR; Shinneman ALC; Engstrom DR; Muir DCG; Smith GR; Garrison PJ; Cleckner LB; Hurley JP; Noble RB; Otter RR; Oris JT. (2007). Deposition and cycling of sulfur controls mercury accumulation in Isle Royale fish. Environ Sci Technol, 41, 7266-7272.

Driscoll CT Jr; Baker JP; Bisogni JJ Jr; Schofield CL. (1980). Effect of aluminum speciation on fish in dilute acidified waters. Nature, 284, 161-164.

Driscoll CT. (1984). A procedure for the fractionation of aqueous aluminum in dilute acidic waters. Int J Environ Anal Chem, 16, 267-283.

Driscoll CT; Bisogni JJ. (1984). Weak acid/base systems in dilute acidified lakes and streams of the Adirondack region of New York State. In: Schnoor J.L., ed. Modeling of total acid precipitation. (pp 53-72). Boston, MA: Butterworth Publishers.

Driscoll CT; Newton RM. (1985). Chemical characteristics of Adirondack lakes. Environ Sci Technol, 19, 1018-1024.

Driscoll CT; Van Breemen N; Mulder J. (1985). Aluminum chemistry in a forested spodosol. Soil Sci Soc Am J, 49, 437-444.

Driscoll CT; Yatski CP; Unangst FJ. (1987a). Longitudinal and temporal trends in the water chemistry of the North Branch of the Moose River. Biogeochemistry, 3, 37-61.

Driscoll CT; Wyskowski BJ; Cosentini CC; Smith ME. (1987b). Processes regulating temporal and longitudinal variations in the chemistry of a low-order woodland stream in the Adirondack region of New York. Biogeochemistry, 3, 225-241.

Driscoll CT; Johnson NM; Likens GE; Feller MC. (1988). Effects of acidic deposition on the chemistry of headwater streams: A comparison between Hubbard Brook, New Hampshire, and Jamieson Creek, British Columbia. Water Resour Res, 24, 195-200.

Driscoll CT; Likens GE; Hedin LO; Eaton JS; Bormann FH. (1989). Changes in the chemistry of surface waters. Environ Sci Technol, 23, 137-143.

Driscoll CT; Newton RM; Gubala CP; Baker JP; Christensen SW. (1991). Adirondack Mountains. In: Charles DF; Christie S (Eds.), Acidic deposition and aquatic ecosystems: Regional case studies (pp. 133-202). New York, NY: Springer-Verlag.

Driscoll CT; Van Dreason R. (1993). Seasonal and long-term temporal patterns in the chemistry of Adirondack lakes. Water Air Soil Pollut, 67, 319-344.

Driscoll CT; Yan C; Schofield CL; Munson R; Holsapple J. (1994a). The mercury cycle and fish in the Adirondack lakes. Environ Sci Technol, 28, 136A-143A.

Driscoll CT; Lehtinen MD; Sullivan TJ. (1994b). Modeling the acid-base chemistry of organic solutes in Adirondack, New York, lakes. Water Resour Res, 30, 297-306.

Driscoll CT; Postek KM; Kretser W; Raynal DJ. (1995). Long-term trends in the chemistry of precipitation and lake water in the Adirondack region of New York, USA. Water Air Soil Pollut, 85, 583-588.

Driscoll CT; Postek KM. (1995). The chemistry of aluminum in surface waters. In: Sposito G (Ed.), The environmental chemistry of aluminum (pp. 363-418). Chelsea, MI: Lewis Publishers.

Driscoll CT; Likens GE; Church MR. (1998). Recovery of surface waters in the northeastern U.S. from decreases in atmospheric deposition of sulfur. Water Air Soil Pollut, 105, 319-329.

Driscoll CT; Lawrence GB; Bulger AJ; Butler TJ; Cronan CS; Eagar C; Lambert KF; Likens GE; Stoddard JL; Weather KC. (2001a). Acid rain revisited: Advances in scientific understanding since the passage of the 1970 and 1990 Clean Air Act amendments. (Vol. 1, No. 1). Hanover, NH: Hubbard Brook Research Foundation; Science Links Publication.

Driscoll CT; Lawrence GB; Bulger AJ; Butler TJ; Cronan CS; Eagar C; Lambert KF; Likens GE; Stoddard JL; Weather KC. (2001b). Acidic deposition in the northeastern United States: Sources and inputs, ecosystem effects, and management strategies. Bioscience, 51, 180-198.

Driscoll C; Whitall J; Aber E; Boyer M; Castro C; Cronan C; Goodale P; Groffman C; Hopkinson K; Lambert G; Lawrence G; Ollinger S. (2003a). Nitrogen pollution in the northeastern United States: Sources, effects and management options. BioScience, 53, 357-374.

Driscoll CT; Driscoll KM; Mitchell MJ; Raynal DJ. (2003b). Effects of acidic deposition on forest and aquatic ecosystems in New York State. Environ Pollut, 123, 327-336.

Driscoll CT; Driscoll KM; Roy KM; Mitchell MJ. (2003c). Chemical response of lakes in the Adirondack Region of New York to declines in acidic deposition. Environ Sci Technol, 37, 2036-2042.

Driscoll C; Whitall J; Aber E; Boyer M; Castro C; Cronan C; Goodale P; Groffman C; Hopkinson K; Lambert G; Lawrence G; Ollinger S. (2003d). Nitrogen pollution: Sources and
consequences in the U.S. Northeast. Environ, 45, 8-22.

 Driscoll CT; Driscoll KM; Roy KM; Dukett J. (2007a). Changes in the chemistry of lakes in the Adirondack Region of New York following declines in acidic deposition. Appl Geochem, 22, 1181-1188

Driscoll CT; Han Y-J; Chen CY; Evers DC; Lambert KF; Holsen TM; Kamman NC; Munson RK. (2007b). Mercury contamination in forest and freshwater ecosystems in the northeastern United States. Bioscience, 57, 17-28.

Driscoll CT; Fallon-Lambert K; Chen L. (2007c). Acidic deposition: sources and ecological effects. In: Visgilio GR; Whitelaw DM, (Eds.). Acid in the environment: Lessons learned and future prospects. New York, NY: Springer.

Drohan JR; Sharpe WE. (1997). Long-term changes in forest soil acidity in Pennsylvania, USA. Water Air Soil Pollut, 95, 299-311.

Drohan P; Stout S; Petersen G. (1999). Spatial relationships between sugar maple (*Acer sacharum* Marsh.), sugar maple decline, slope, aspect, and atmospheric deposition in northern Pennsylvania. In: Horsley SB; Long RP, (Eds.). Sugar Maple Ecology and Health: Proceedings of an International Symposium held in Warren, PA in June, 1998. (General technical report NE-261). Radnor, PA; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Drohan PJ; DeWalle DR. (2002). Defoliation and atmospheric deposition influences on spring baseflow chemistry in 56 Pennsylvania mixed land-use watersheds. Water Air Soil Pollut, 133, 31-48.

Drohan PJ; Stout SL; Petersen GW. (2002). Sugar maple (*Acer saccharum* Marsh.) decline during 1979-1989 in northern Pennsylvania. For Ecol Manage, 170, 1-17.

Duan L; Hao JM; Xie SD; Du K. (2000a). Critical loads of acidity for surface waters in China. Sci. Total Environ, 246, 1-10.

Duan L; Xie SD; Zhou ZP; Hao JM. (2000b). Critical loads of acid deposition on soil in China. Water Air Soil Pollut, 118, 35-51.

Duan L; Xie SD; Zhou ZP; Ye XM; Hao JM. (2001). Calculation and mapping of critical loads for S, N and acidity in China. Water Air Soil Pollut, 130, 1199-1204.

Dubowski Y; Sumner AL; Menke EJ; Gaspar DJ; Newberg JT; Hoffman RC; Penner RM; Hemminger JC; Finlayson-Pitts BJ. (2004). Interactions of gaseous nitric acid with surfaces of environmental interest. Phys Chem Chem Phys, 6, 3879-3888.

Duce RA; Liss PS; Merrill JT; Atlans EL; Buat-Menard P; Hicks BB; Miller JM; Prospero JM; Atimoto R; Church TM; Ellis W; Galloway JN; Hansen L; Jickells TD; Knap AH; Reinhardt KH; Schneider B; Soudine A; Tokos JJ; Tsunogai S; Wollast R; Ahou M (1991) The atmospheric input of trace species to the world ocean. Global Biogeochem. Cycles, 5, 193–259

Dudhia J. (1993). A nonhydrostatic version of the Penn State-NCAR mesoscale model: Validation tests and simulation of an Atlantic cyclone and cold front. Monthly Weather Rev, 121, 1493-1513.

Dueck TA; Dorel FG; Ter Horst R; Van de Eerden LJM. (1990). Effects of ammonia, ammonium sulphate and sulpur dioxide on the frost sensitivity of Scots pine (*Pinus sylvestris* L.).Water Air Soil Pollut, 54, 35-49.

Dueck TA; Van der Eerden LJM; Breemsterboer B; Elderson J. (1991). Nitrogen uptake and allocation by *Calluna vulgaris* (L.). Hull and *Deschampsia flexuosa* (L.).Trin. exposed to $^{15}NH_3$. Acta Bot Neerl, 40, 257-267.

Dumont E; Harrison JA; Kroeze C; Bakker EJ; Seitzinger SP. (2005). Global distribution and sources of dissolved inorganic nitrogen export to the coastal zone: Results from a spatially explicit, global model. Glob Biogeochem Cycles, 19, GB4S02, doi:10.1029/2005GB002488.

Dunlea EJ; Herndon SC; Nelson DD; Volkamer RM; San Martini F; Sheehy PM; Zahniser MS; Shorter JH; Wormhoudt JC; Lamb BK; Allwine EJ; Gaffney JS; Marley NA; Grutter M; Marquez, C; Blanco S; Cardenas B; Retama,A; Ramon Villegas CR; Kolb CE; Molina LT; Molina MJ. (2007). Evaluation of nitrogen dioxide chemiluminescence monitors in a polluted urban environment. Atmos Chem Phys, 7, 2691-2704.

Dupont J; Clair TA; Gagnon C; Jeffries DS; Kahl JS; Nelson S; Peckenham J. (2005). Estimation of critical loads of acidity and water sensitivity in New England states and eastern Canadian provinces. Environ Monit Assess, 109, 275-291.

Durant JL; Busby WF Jr; Lafleur AL; Penman BW; Crespi CL. (1996). Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols. Mutat Res, 371, 123-157.

Durham JL; Wilson WE; Bailey EB. (1978). Application of an SO_2-denuder for continuous measurement of sulfur in submicrometric aerosols. Atmos Environ, 12, 883-886.

Duriscoe DM; Stolte KW. (1989). Photochemical oxidant injury to ponderosa pine (*Pinus ponderosa* Laws.).and Jeffrey pine (*Pinus jeffreyi* Grev. and Balf.).in the national parks of the Sierra Nevada of California. In: Olson RK; Lefohn AS, eds. Effects of air pollution on western forests [an A&WMA symposium held in Anaheim, CA; in June 1989; (APCA transactions series: no. 16 pp. 261-278)]. Pittsburgh, PA: Air and Waste Management Asssociation.

Dyrness CT; Van Cleve K; Levison JD. (1989). The effect of wildfire on soil chemisty in four forest types in interior Alaska. Can J For Res, 19, 1389-1396.

Eadie BJ; McKee BA; Lansing MB; Robbins JA; Metz S; Trefry JH. (1994). Records of nutrient-enhanced coastal productivity in sediments from the Louisiana continental shelf. Estuaries, 17, 754-765.

Eagar C; Adams MB. eds. (1992). Ecology and decline of red spruce in the eastern United States. (Ecological studies: Volume 96). New York, NY: Springer-Verlag.

Eagar C; Van Miegroet H; McLaughline SB; Nicholas NS. (1996). Evaluation of effects of acidic deposition to terrestrial ecosystems in class I areas of the Southern Appalachians (No. A technical report to the Southern Appalachian Mountains Initiative (SAMI)). Tennessee Valley Authority (TVA), Asheville, NC; U.S. Forest Service, U.S. Department of Agriculture (USDA).

Eder B; Yu S. (2006). A performance evaluation of the 2004 release of models-3 CMAQ. Atmos Environ, 40, 4811-4824.

Edgerton ES; Hartsell BE; Saylor RD; Jansen JJ; Hansen DA; Hidy GM. (2006). The southeastern aerosol research and characterization study. Part 3: Continuous measurements of fine particulate matter mass and composition. J Air Waste Manage Assoc, 56, 1325-1341.

Edgerton ES; Saylor RD; Hartsell BE; Jansen JJ; Alan Hansen D. (2007). Ammonia and ammonium measurements from the southeastern United States. Atmos Environ, 41, 3339-3351.

Edmondson WT. (1969). Eutrophication in North America. Washington, D.C.: National Academy of Sciences, Printing and Publishing Office.

Edmondson WT. (1991). The uses of ecology: Lake Washington and beyond. Seattle, WA: University of Washington Press.

Edwards D; Brown JA; Whitehead C. (1987). Endocrine and other physiological indicators of acid stress in the brown trout. Ann Soc R Zool Belg, 117, 331-342.

Edwards JH; Horton BD. (1977). Aluminum-induced calcium deficiency in peach seedlings. J Am Soc Hortic Sci, 102, 459-461.

Edwards PJ; Gregory JD; Allen HI. (1999). Seasonal sulfate deposition and export patterns for a small Appalachian watershed. Water Air Soil Pollut, 110, 137-155.

Edwards PJ; Wood F; Kochenderfer JN. (2002a). Baseflow and peakflow chemical responses to experimental applications of ammonium sulphate to forested watersheds in north-central West Virginia, USA. Hydrological Processes, 16, 2287-2310.

Edwards PJ; Kochenderfer JN; Coble DW; Adams MB. (2002b). Soil leachate responses during 10 years of induced whole-watershed acidification. Water Air Soil Pollut, 140, 99-118.

Edwards PM; Helvey JD. (1991). Long-term ionic increases from a central Appalachian forested watershed. J Environ Qual, 20, 250-255.

Egerton-Warburton L; Allen EB. (2000). Shifts in *Arbuscular mycorrhizal* communities along an anthropogenic nitrogen deposition gradient. Ecol Appl, 10, 484-496.

Egerton-Warburton LM; Graham RC; Allen EB; Allen MF. (2001). Reconstruction of the historical changes in mycorrhizal fungal communities under anthropogenic nitrogen deposition. Proc R Soc B, 268, 2479-2484.

Eide I; Neverdal G; Thorvaldsen B; Grung B; Kvalheim OM. (2002). Toxicological evaluation of complex mixtures by pattern recognition: correlating chemical fingerprints to mutagenicity. Environ Health Perspect, 1106, 985-988.

Eilers JM; Glass GE; Webster, KE; Rogalla, JA. (1983). Hydrologic control of lake susceptibility to acidification. Can J Fish Aquat Sci, 40, 1896-1904.

Eilers JM; Kanciruck P; McCord RA; Overton WS; Hook L; Blick DJ; Brakke DF; Kellar PE; DeHaan MS; Silverstein ME; Landers DH. (1987). Characteristics of lakes in the western United States. Volume II. Data compendium for selected physical and chemical variables (No. EPA-600/3-86/054b). Washington, DC: U.S. Environmental Protection Agency.

Eilers JM; Brakke DF; Landers DH. (1988). Chemical and physical characteristics of lakes in the Upper Midwest, United States. Environ Sci Technol, 22, 164-172.

Eimers MC; Dillon PJ. (2002). Climate effects on sulphate flux from forested catchments in south-central Ontario. Biogeochemistry, 61, 337-355.

Eimers MC; Buttle JM; Watmough SA. (2007). The contribution of rain-on-snow events to annual NO_3^--N export from a forested catchment in south-central Ontario, Canada. Appl Geochem, 22, 1105-1110.

Eisele FL; Mauldin L; Cantrell C; Zondlo M; Apel E; Fried A; Walega J; Shetter R; Lefer B; Flocke F; Weinheimer A; Avery M; Vay S; Sachse G; Podolske J; Diskin G; Barrick JD; Singh HB; Brune W; Harder H; Martinez M; Bandy A; Thornton D; Heikes B; Kondo Y; Riemer D; Sandholm S; Tan D; Talbot R; Dibb J. (2003). Summary of measurement intercomparisons during TRACE-P. J Geophys Res, 108, doi: 10.1029/2002JD003167.

Ekstrom EB; Morel FMM; Benoit JM. (2003). Mercury methylation independent of the acetyl-coenzyme a pathway in sulfate-reducing bacteria. Appl Environ Microbiol, 69, 5414-5422.

Ekstrom EB; Morel FMM. (2004). Mercury methylation by sulfate-reducing bacteria independent of vitamin B_{12}. Biogeochemistry, 51, 968-970.

Eldred R. (2001). Sulfur-Sulfate Trends for IMPROVE. University of California-Davis. http://vista.cira.colostate.edu/improve/publications/GrayLit/005_Sulfur-Sulfate_Trends/005_sulfur-sulfate_trends.htm.

Eliason SA; Allen EB. (1997). Exotic grass competition in suppressing native shrubland re-establishment. Restor Ecol, 5, 245-255.

Ellenberg H. (1985). Veränderungen der floa mitteleuropas unter dem einfluss von düngung und immissionen. Schweiz Z Forstwesten, 136, 19-39.

Ellenberg H. (1987). Floristic changes due to eutrophication. In Asman WAH; Diederen HSMA (Eds.). Proceedings of the ammonia and acidification symposium of the European association for the science of air pollution (EURASAP), held in Bilthoven, The Netherlands. April 13 – 15, 1987; (pp 301-308). European Association for the Science of Air Pollution (EURASAP).

Elliott EM; Kendall C; Wankel S; Burns DA; Boyer EW; Harlin K; Bain DJ; Butler TJ. (2007). Nitrogen isotopes as indicators of NO_X source contributions to atmospheric nitrate deposition across the midwestern and northeastern United States. Environ Sci Technol, 41, 7661-7667.

Ellis H; Bowman M. (1994). Critical loads and development of acid rain control options. J Environ Eng, 120, 273-290.

Ellis H; Ringold PL; Holdren GR Jr. (1996). Emissions reductions and ecological response: management models for acid rain control. Socioecon Plann Sci, 30, 15-26.

Ellison AM; Gotelli NJ. (2002). Nitrogen availability alters the expression of carnivory in the northern pitcher plant, *Sarracenia purpurea*. Proc Natl Acad Sci USA, 99, 4409-4412.

Elser JJ; Marzolf ER; Goldman CR. (1990). Phosphorus and nitrogen limitation of phytoplankton growth in the freshwaters of North America: A review and critique of experimental enrichments. Can J Fish Aquat Sci, 47, 1468-1477.

Elser JJ; Hayakawa K; Urabe J. (2001). Nutrient limitation reduces food quality for zooplankton: Daphnia response to seston phosphorus enrichment. Ecology, 82, 898-903.

Elser JJ; Bracken MES; Cleland EE; Gruner DS; Harpole WS; Hillebrand II H; Ngai JT; Seabloom EW; Shurin JB; Smith JE. (2007). Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine, and terrestrial ecosystems. Ecol Lett, 10, 1135-1142.

Elsom DM. (2002). Atmospheric pollution: a global problem, 2nd Edition. Oxford,UK: Blackwell Publishers.

Elvir JA; Wiersma GB; White AS; Fernandez IJ. (2003). Effects of chronic ammonium sulfate treatment on basal area increment in red spruce and sugar maple at the Bear Brook Watershed in Maine. Can J For Res, 33, 862-869.

Elvir JA; Wiersma GB; Day ME; Greenwood MS; Fernandez IJ. (2006). Effects of enhanced nitrogen deposition on foliar chemistry and physiological processes of forest trees at the Bear Brook Watershed in Maine. For Ecol Manage, 221, 207-214.

Elwood JW; Sale MJ; Kaufmann PR; Cada GF. (1991). Southern Blue Ridge Province. In: Charles DF, Christie S (Eds.). Acidic deposition and aquatic ecosystems: Regional case studies. (Chapter 11, pp 319-364). New York, NY: Springer-Verlag.

Emmett BA; Boxman D; Bredemeier M; Gundersen P; Kjonaas OJ; Moldan F; Schleppi P; Tietema A; Wright RF. (1998). Predicting the effects of atmospheric nitrogen deposition in conifer stands: Evidence from the NITREX ecosystem-scale experiments. Ecosystems, 1, 352-360.

Emmett BA. (1999). The impact of nitrogen on forest soils and feedbacks on tree growth. Water Air Soil Pollut, 116, 65-74.

Emmons LK; Hauglustaine DA; Muller J-F; Carroll MA; Brasseur GP; Brunner D; Staehelin J; Thouret V; Marenco A. (2000). Data composites of airborne observations of tropospheric ozone and its precursors. J Geophys Res, 105, 20497-20538.

Engel-Cox JA; Holloman CH; Coutant BW; Hoff RM. (2004). Qualitative and quantitative evaluation of MODIS satellite sensor data for regional and urban scale air quality. Atmos Environ, 38, 2495-2509.

Englin J; Cameron T; Mendelsohn R; Parsons G; Shankle S. (1991). Valuation of damages to recreational trout fishing in the Upper Northeast due to acidic deposition. (Report no PNL-7683). Richland, WA: Pacific Northwest Laboratory. (prepared for National Acidic Precipitation Assessment Program (NAPAP)).

Engstrom DR; Swain EB; Henning TA; Brigham MA; Brezonik PL. (1994). Atmospheric mercury deposition to lakes and watersheds: A quantitative reconstruction from multiple sediment cores. In: Baker LA (Ed.), Environmental chemistry of lakes and reservoirs, Volume 237 in Series - Advances in chemistry (pp. 33-66). Washington, DC: American Chemical Society.

Engstrom P; Dalsgaard T; Hulth S; Aller RC. (2005). Anaerobic ammonium oxidation by nitrate (anammox): Implications for N_2 production in coastal marine sediments. Geochim Cosmochim Acta, 69, 2057-2065.

Epp DJ; Al-Ani KS. (1979). The effect of water quality on rural nonfarm residential property values. Am J Agric Econ, 61, 529-534.

Epstein HE; Burke IC; Lauenroth WK. (2002). Regional patterns of decomposition and primary production rates in the U.S. Great Plains. Ecology, 83, 320-327.

Erickson DJ III; Seuzaret C; Keene WC; Gong SL. (1999). A general circulation model based calculation of HCl and $ClNO_2$ production from sea-salt dechlorination: reactive chlorine emissions inventory. J Geophys Res, 104, 8347-8372.

Erickson H; Keller M; Davidson EA. (2001). Nitrogen oxide fluxes and nitrogen cycling during postagricultural succession and forest fertilization in the humid tropics. Ecosystems, 4, 67-84.

Eriksson E. (1981). Aluminium in groundwater, possible solution equilibria. Nord Hydrol, 12, 43-50.

Eriksson MOG. (1983). The role of fish in the selection of lakes by non-piscivorous ducks: mallard, teal and goldeneye. Wildfowl, 34, 27-32.

Eriksson MOG. (1986). Fish delivery, production of young, and nest density of Osprey (*Pandion haliaetus*).in southwest Sweden. Can J Zool, 64, 1961-1965.

Eriksson MOG. (1987). Some effects of freshwater acidification on birds in Sweden. In: Diamond AW, Filion, FL (Eds.). The value of birds. (ICBP Birdlife International Technical Publication Series No. 6, pp 183-190). Cambridge, UK: International Council for Bird Preservation (ICBP).

Eshleman KN. (1988). Predicting regional episodic acidification of surface waters using empirical techniques. Water Resour Res, 24, 1118-1126.

Eshleman KN; Davies TD; Tranter M; Wigington PJ Jr. (1995). A two-component mixing model for predicting regional episodic acidification of surface waters during spring snowmelt periods. Water Resour Res, 31(4), 1011-1021.

Eshleman KN; Morgan II RP; Webb JR; Deviney FA; Galloway JN. (1998). Temporal patterns of nitrogen leakage from mid-Appalachian forested watersheds: role of insect defoliation. Water Resour Res, 34, 2005-2116.

Eshleman KN; Hyer KE. (2000). Discharge and water chemistry at the three intensive sites. In: Bulger AJ; Cosby BJ; Dolloff CA; Eshelman KN; Webb JR; Galloway JH (Eds.). Shenandoah National Park: Fish in sensitive habitats (SNP: FISH) project: An integrated assessment of fish community responses to stream acidification. Final report (Volumes 1-4); Volume II (Chapter 4, pp 51-92). Charlottesville, VA; Department of Environmental Sciences; University of Virginia.

Eshleman KN; Gardner RH; Seagle SW; Castro NM; Fiscus DA; Webb JR; Galloway JN; Deviney FA; Herlihy AT. (2000). Effects of disturbance on nitrogen export from forested lands of the Chesapeake Bay watershed. Environ Monit Assess, 63, 187-197.

Eshleman KN; Fiscus DA; Castro NM; Webb JR; Herlihy AT. (2004). Regionalization of disturbance-induced nitrogen leakage from mid-Appalachian forests using a linear systems model. Hydrol Process, 18, 2713-2725.

Ettershank G; Ettershank J; Bryant M; Whitford WG. (1978). Effects of nitrogen fertilization on primary production in a Chihuahuan desert ecosystem. J Arid Environ, 1, 135–139.

Evans CD; Monteith DT. (2001). Chemical trends at lakes and streams in the UK acid waters monitoring network, 1988-2000: Evidence for recent recovery at a national scale. Hydrol Earth Sys Sci, 5, 351-366.

Evans CD; Chapman PJ; Clark JM; Monteith D; Cresser MS. (2006). Alternative explanations for rising dissolved organic carbon export from organic soils. Glob Change Biol, 12, 2044-2053.

Everett KR; Brown J. (1982). Some recent trends in the physical and chemical characterization and mapping of tundra soils, arctic slope of Alaska. Soil Sci., 133, 264-280.

Everhart WH; Youngs WD. (1981). Principles of fishery science (2nd edition.). Ithaca, NY: Comstock/Cornell University Press.

Evers DC; Kaplan JD; Meyer MW; Reaman PS; Braselton WE; Major A; Burgess N; Scheuhammer AM. (1998). A geographic trend in mercury measured in common loon feathers and blood. Environ Toxicol Chem, 17, 173-183.

Evers DC; Taylor KM; Major A; Taylor RJ; Poppenga RH; Scheuhammer AM. (2003). Common loon eggs as bioindicators of methylmercury availability in North America. Ecotoxicology, 12, 69-81.

Evers DC; Clair TA. (2005). Mercury in northeastern North America: A synthesis of existing databases Ecotoxicology, 14, 7-14.

Evers DC; Burgess NM; Champoux L; Hoskins B; Major A; Goodale WM; Taylor RJ; Poppenga R. (2005). Patterns and interpretation of mercury exposure in freshwater avian communities in northeastern North America. Ecotoxicology, 14, 193-222.

Evers DC; Han Y; Driscoll CT; Kamman NC; Goodale MW; Lambert KF; Holsen TM; Chen CY; Clair TA; Butler T. (2007). Biological mercury hotspots in the northeastern United States and southeastern Canada. Bioscience, 57, 29-43.

Exley C; Phillips MJ. (1988). Acid rain: Implications for the farming of salmonids. In: Muir JF, Roberts RJ (Eds.). Recent advances in aquaculture (Volume 3, pp. 225-342). London, UK: Croom Helm.

Falkengren-Grerup U. (1986). Soil acidification and vegetation changes in deciduous forest in southern Sweden. Oecologia, 70, 339-347.

Falkengren-Grerup U. (1989). Soil acidification and its impact on ground vegetation. Ambio, 18, 179-183.

Falkengren-Grerup U; Eriksson H. (1990). Changes in soil, vegetation and forest yield between 1947 and 1988 in beech and oak sites of southern Sweden. For Ecol Manage, 38, 37-53.

Falkengren-Grerup U. (1998). Nitrogen response of herbs and graminoids in experiments with simulated acid soil solution. Environ Pollut, 102, 93-99.

Fan Z; Chen D; Birla P; Kamens RM. (1995). Modeling of nitro-polycyclic aromatic hydrocarbon formation and decay in the atmosphere. Atmos Environ, 29, 1171-1181.

Fangmeier A; Hadwiger-Fangmeier A; Van der Eerden L; Jager HJ. (1994a). Effects of atmospheric ammonia on vegetation - A review. Environ Pollut, 86, 43-82.

Fangmeier A; Brockerhoff U; Gruters U; Jager H-J. (1994b). Growth and yield responses of spring wheat (*Triticum aestivum* L. cv. Turbo) grown in open-top chambers to ozone and water stress. Environ Pollut, 83, 317-325.

FAO/IFA. (2001). Global estimates of gaseous emissions of NH_3, NO and N_2O from agricultural land. Rome, Italy: (ftp://ftp.fao.org/agl/agll/docs/globest.pdf).Food and Agriculture Organization of the United Nations (FAO).and International Fertilizer Industry Association (IFA).

Farag AM; Woodward DF; Little EE; Steadman B; Vertucci FA. (1993). The effects of low pH and elevated aluminum on Yellowstone cutthroat trout (*Oncorhynchus clarki bouvieri*). Environ Toxicol Chem, 12, 719-731.

Faraji M; Kimura Y; Allen D. (2005). Comparison of the carbon bond and SAPRC photochemical mechanisms under conditions relevent to southeast Texas. (Project report H12.8HRB). http://files.harc.edu/Projects/AirQuality/Projects/H012.2004/8HRB/H12-8HRBMechanismReport.pdf. Houston, TX: Texas Environmental Research Consortium (TERC).

Farmer AM; Bates JW; Bell JNB. (1992). Ecophysiological effects of acid rain on bryophytes and lichens. In: Bates JW; Farmer AM (Eds.), Bryophytes and lichens in a changing environment. Oxford, UK: Claredon Press.

Farmer DK; Wooldridge PJ; Cohen RC. (2006). Application of thermal-dissociation laser induced fluorescence (TD-LIF).to measurement of HNO_3, Σalkyl nitrates, Σperoxy nitrates, and NO_2 fluxes using eddy covariance. Atmos Chem Phys, 6, 3471-3486.

Farmer GJ; Beamish FWH. (1969). Oxygen consumption of *Tilapia nilotica* in relation to swimming speed and salinity. J Fish Res Bd Can, 26, 2807-2821.

Farwell SO; Rasmussen RA. (1976). Limitations of the FPD and ECD in atmospheric analysis: A review. J Chromatogr Sci, 14, 224-234.

Fast JD; Zaveri RA; Bian RX; Chapman EG; Easter RC. (2002). Effect of regional-scale transport on oxidants in the vicinity of Philadelphia during the 1999 NE-OPS Field Campaign. J Geophys Res (Atmos) 107(D16),m 10.1029/2001JD000980.

Federal Register. (1993). Report of the NOAA Panel on contingent valuation. FR58:4601-4614.

Federal Register. (1995). National ambient air quality standards for nitrogen dioxide: proposed decision. FR60:52874-52889.

Federal Register. (1996). National ambient air quality standards for nitrogen dioxide: final decision. FR61:52852-52856.

Federal Register. (2006). National ambient air quality standards for particulate matter. Final rule. FR71:61144-61233.

Federal Register. (2007). Endangered and threatened wildlife and plants; designation of critical habitat for the bay checkerspot butterfly (*Euphydryas editha* bayensis). FR50:48177-48218.

Federer CA; Hornbeck JW; Tritton LM; Martin CW; Pierce RS. (1989). Long-term depletion of calcium and other nutrients in eastern U.S. forests. Environ Manage, 13, 593-601.

Fehsenfeld FC; Dickerson RR; Hubler G; Luke WT; Nunnermacker LJ; Williams EJ; Roberts JM; Calvert JG; Curran CM; Delany AC; Eubank CS; Fahey DW; Fried A; Gandrud BW; Langford AO; Murphy PC; Norton RB; Pickering KE; Ridley BA. (1987). A ground-based intercomparison of NO, NO_X, and NO_Y measurement techniques. J Geophys Res, 92, 14710-14722.

Fehsenfeld FC; Trainer M; Parrish DD; Volz-Thomas A; Penkett S. (1996a). North Atlantic regional experiment (NARE) 1993 summer intensive: Foreword. J Geophys Res, 101, 28869-28875.

Fehsenfeld FC; Daum P; Leaitch WR; Trainer M; Parrish DD; Hübler, G. (1996b). Transport and processing of O_3 and O_3 precursors over the North Atlantic: An overview of the 1993 North Atlantic Regional Experiment (NARE).summer intensive. J Geophys Res, 101, 28877-28891.

Fehsenfeld FC; Huey LG; Sueper DT; Norton RB; Williams EJ; Eisele FL; Mauldin RL, III; Tanner DJ. (1998). Ground-based intercomparison of nitric acid measurement techniques. J Geophys Res, 103, 3343-3353.

Fehsenfeld FC; Ancellet G; Bates TS; Goldstein AH; Hardesty RM; Honrath R; Law KS; Lewis AC; Leaitch R; McKeen S; Meagher J; Parrish DD; Pszenny AAP; Russell PB; Schlager H; Seinfeld J; Talbot R; Zbinden R. (2006). International consortium for atmospheric research on transport and transformation (ICARTT): North America to Europe -Overview of the 2004 summer field study. J Geophys Res, 111, D23S01, doi:10.1029/2006JD007829

Feilberg A; Kamens RM; Strommen MR; Nielsen T. (1999). Modeling the formation, decay, and partitioning of semivolatile nitro-polycyclic aromatic hydrocarbons (nitronaphthalenes).in the atmosphere. Atmos Environ, 33, 1231-1243.

Fenn ME; Dunn PH. (1989). Litter decomposition across an air-pollution gradient in the San Bernardino Mountains. Soil Sci Soc Am J, 53, 1560-1567.

Fenn ME; Poth MA; Johnson DW. (1996). Evidence for nitrogen saturation in the San Bernardino Mountains in southern California. For Ecol Manage, 82, 211-230.

Fenn ME; Bytnerowicz A. (1997). Summer throughfall and winter deposition in the San Bernardino Mountains in southern California. Atmos Environ, 31, 673-683.

Fenn ME; Poth MA. (1998). Indicators of nitrogen status in California forests. (General technical report PSW-GTR-166). Washington, DC; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Fenn ME; Poth MA; Aber JD; Baron JS; Bormann BT; Johnson DW; Lemly AD; McNulty SG; Ryan DF; Stottlemyer R. (1998). Nitrogen excess in North American ecosystems: Predisposing factors, ecosystem responses, and management strategies. Ecol Appl, 8, 706-733.

Fenn ME; Poth MA. (1999). Temporal and spatial trends in streamwater nitrate concentrations in the San Bernardino Mountains, southern California. J Environ Qual, 28, 822-836.

Fenn ME; Poth MA; Schilling S; Grainger D. (2000). Throughfall and fog deposition of nitrogen and sulfur at an N-limited and N-saturated site in the San Bernardino Mountains, southern California. Can J For Res, 30, 1476-1488.

Fenn ME; Poth MA. (2001). A case study of nitrogen saturation in western U.S. forests. Scientific WorldJournal, 1 433-439.

Fenn ME; De Bauer, LI; Hernández-Tejeda, T. (2002a).Urban air pollution and forests: resources at risk in the Mexico City air basin. (Volume 156, Ecological studies). New York, NY; Springer-Verlag.

Fenn ME., Poth MA; Arbaugh MJ. (2002b). A throughfall collection method using mixed bed ion exchange resin columns. In: Proceedings of the International Symposium on Passive Sampling of Gaseous Air Pollutants in Ecological Effects Research held in Riverside, California; April 9, 2001. Scientific World Journal, 2, 122–130.

Fenn ME; Baron; JS, Allen, EB, Rueth, HM, Nydick KR, Geiser, L, Bowman, WD, Sickman, JO, Meixner, T, Johnson, DW, Neitlich, P. (2003a). Ecological effects of nitrogen deposition in the western United States. Bioscience, 53, 404-420.

Fenn ME; Haeuber R; Tonnesen GS; Baron JS; Grossman-Clark S; Hope D; Jaffe DA; Copeland S; Geiser L; Rueth HM; Sickman JO. (2003b). Nitrogen emissions, deposition, and monitoring in the western United States. Bioscience, 53, 391-403.

Fenn ME; Poth MA; Bytnerowicz A; Sickman JO; Takemoto BK. (2003c). Effects of ozone, nitrogen deposition, and other stressors on montane ecosystems in the Sierra Nevada. In: Bytnerowicz A; Arbaugh MJ; Alonso R (Eds.). Ozone air pollution in the Sierra Nevada: distribution and effects on forests. (Developments in Environmental Science: Volume 2; pp. 111-155). New York, NY: Elsevier.

Fenn ME; Poth MA. (2004). Monitoring nitrogen deposition in throughfall using ion exchange resin columns: a field test in the San Bernarndino Mountains. J Environ Qual, 33, 2007-2014.

Fenn ME; Huntington TG; McLaughlin SB; Eagar C; Gomez A; Cook RB. (2006). Status of soil acidification in North America. J For Sci, 52, 3-13.

Fenn ME; Geiser L; Bachman R; Blubaugh TJ; Bytnerowicz A. (2007). Atmospheric deposition inputs and effects on lichen chemistry and indicator species in the Columbia River Gorge, USA. Environ Pollut, 146, 77-91.

Fenn ME; Jovan S; Yuan F; Geiser L; Meixner T; Gimeno BS. (2008). Empirical and simulated critical loads for nitrogen deposition in California mixed conifer forests. Environ Pollut, 155, 492-511.

Fernandez IJ; Rustad LE; Norton SA; Kahl JS; Cosby BJ. (2003). Experimental acidification causes soil base-cation depletion at the Bear Brook watershed in Maine. Soil Sci Soc Am J, 67, 1909-1919.

Ferrari JB. (1999). Fine-scale patterns of leaf litterfall and nitrogen cycling in an old-growth forest. Can. J Forest Res, 29, 291-302.

Ferrier RC; Helliwell RC; Cosby BJ; Jenkins A; Wright RF. (2001). Recovery from acidification of lochs in Galloway, south-west Scotland, UK: 1979-1998. Hydrol Earth Sys Sci, 5, 421-431.

Field CB; Mooney HA. (1986). The photosynthesis-nitrogen relationship in wild plants. In: Givinish TJ (Ed.), The economy of plant form and function. (pp 25-55). Cambridge, UK: Cambridge University Press.

Field C. B; Mortsch, L. D; Brklacich, M; Forbes, D. L; Kovacs, P; Patz, J. A; Running, S. W; Scott, M. J. (2007).North America. In: Climate change 2007: impacts, adaptation and vulnerability. (Contribution of Working Group II to the fourth assessment report of the Intergovernmental Panel on Climate Change; pp. 617-852).http://www.ipcc.ch/pdf/assessment-report/ar4/wg2/ar4-wg2-chapter14.pdf. Cambridge, UK: Cambridge University Press.

Fields RF. (1988). Physiological responses of lichens to air pollutant fumigations. In: Nash TH III; Wirth V (Eds.), Lichens, bryophytes and air quality. Volume 30; Bibl. Lichenol. (pp 175-200). Berlin/ Stuttgart, Germany: Cramer Publisher.

Findlay DL; Kasian SEM. (1996). The effect of incremental pH recovery on the Lake 223 phytoplankton community. Can J Fish Aquat Sci, 53, 856-864.

Findlay DL; Hecky RE; Kasian SEM; Stainton MP; Hendzel LL; Schindler EU. (1999). Effects on phytoplankton of nutrients added in conjunction with acidification. Freshw Biol, 41, 131-145.

Findlay DL. (2003). Response of phytoplankton communities to acidification and recovery in Killarney Park and the Experimental Lakes Area, Ontario. Ambio, 32, 190-195.

Findlay SEG. (2005). Increased carbon transport in the Hudson River: Unexpected consequence of nitrogen deposition? Front Ecol Environ, 3, 133-137.

Finlayson-Pitts BJ; Ezell MJ; Pitts JN Jr. (1989). Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N_2O_5 and $ClONO_2$. Nature, 337, 241-244.

Finlayson-Pitts BJ; Pitts JN Jr. (2000). Chemistry of the upper and lower atmosphere: theory, experiments and applications. San Diego, CA: Academic Press.

Finlayson-Pitts BJ; Wingen LM; Sumner AL; Syomin D; Ramazan KA. (2003). The heterogeneous hydrolysis of NO_2 in laboratory system and in outdoor and indoor atmospheres: An integrated mechanism. Phys Chem Chem Phys, 5, 223-242.

Finley BD; Saltzman ES. (2006). Measurement of Cl_2 in coastal urban air. Geophys Res Lett, 33, L11809, doi:10.1029/2006GL025799.

Finley MT; Stendell RC. (1978). Survival and reproductive success of black ducks fed methyl mercury. Environ Pollut, 16, 51-64.

Finley MT; Stickel WH; Christensen RE. (1979). Mercury residues in tissues of dead and surviving birds fed methylmercury. Bull Environ Contam Toxicol, 21, 105-110.

Finzi AC; Van Breemen N; Canham CD. (1998). Canopy tree-soil interactions within temperate forests: Species effects on soil carbon and nitrogen. Ecol Appl, 8, 440-446.

Fiore AM; Jacob DJ; Field BD; Streets DG; Fernandes SD; Jang C. (2002). Linking ozone pollution and climate change: the case for controlling methane. Geophys Res Lett, 29(19), 10.1029/2002GL015601.

Fiore A; Jacob DJ; Liu H; Yantosca RM; Fairlie TD; Li Q. (2003). Variability in surface ozone background over the United States: implications for air quality policy. J Geophys Res, 108, 4787, doi:10.1029/2003JD003855 (Correction Published 2004).

Firestone MK; Davidson EA. (1989). Microbiological basis of NO and N_2O production and consumption in soil. In: Andreae MO; Schimel DS (Eds.), Exchange of trace gases between terrestrial ecosystems and the atmosphere: Report of the Dahlem workshop on exchange of trace gases between terrestrial ecosystems and the atmosphere (pp. 7-21). Berlin, New York, NY: Wiley.

Fischer E; Pszenny A; Keene W; Maben J; Smith A; Stohl A; Talbot R. (2006). Nitric acid phase partitioning and cycling in the New England coastal atmosphere. J Geophys Res, 111, D23S09, doi:10.1029/2006JD007328.

Fisher DC; Oppenheimer M. (1991). Atmospheric nitrogen deposition and the Chesapeake Bay estuary. Ambio, 20, 102-108.

Fisher TR; Harding LW Jr; Stanley DW; Ward LG. (1988). Phytoplankton, nutrients, and turbidity in the Chesapeake, Delaware, and Hudson estuaries. Estuarine Coastal Shelf Sci, 27, 61-93.

Fisher TR; Lee K-Y; Berndy H; Benitez JA; Norton MM. (1998). Hydrology and chemistry of the Choptank River basin in the Chesapeake Bay drainage. Water Air Soil Pollut, 105, 387-397.

Fisher TR; Hagy III JD; Boynton WR; Williams MR. (2006). Cultural eutrophication in the Choptank and Patuxent estuaries of Chesapeake Bay. Limnol Oceanogr, 51, 435-447.

Fishman J; Larsen JC. (1987). Distribution of total ozone and stratospheric ozone in the tropics-Implications for the distribution of tropospheric ozone. J Geophys Res, 92, 6627-6634.

Fishman J; Creilson JK; Wozniak AE; Crutzen PJ. (2005).The interannual variability of stratospheric and tropospheric ozone determined from satellite measurements. J Geophys Res, 110, doi: 10.1029/2005JD005868.

Fisk MC; Schmidt SK. (1996). Microbial responses to nitrogen additions in alpine tundra soil. Soil Biol Biogeochem, 28, 751-755.

Fisk MC; Schmidt SK; Seastedt TR. (1998). Topographic patterns of above-and belowground production and nitrogen cycling in alpine tundra. Ecology, 79, 2253-2266.

Fisk MC; Zak DR; Crow TR. (2002). Nitrogen storage and cycling in old- and second-growth northern hardwood forests. Ecology, 83, 73-87.

Fitzhugh RD; Lovett GM; Venterea RT. (2003). Biotic and abiotic immobilization of ammonium, nitrite, and nitrate in soils developed under different tree species in the Catskill Mountains, New York, USA. Glob Chang Biol, 9, 1591-1601.

Fjeld E; Haugen TO; VØllestad LA. (1998). Permanent impairment in the feeding behavior of grayling (*Thymallus thymallus*).exposed to methylmercury during embryogenesis. Sci Total Environ, 213, 247-254.

Fjellheim A; Raddum GG; Sagen T. (1985). Effect of aluminum at low pH on the mortality of elvers (*Anguilla anguilla* L). J Exp Zool, 262, 247-254.

Flower RJ; Battarbee RW. (1983). Diatom evidence for recent acidification of two Scottish Lochs. Nature, 305, 130-133.

Flowers PJ; Vaux HJ; Gardner PD; Mills TJ. (1985). Changes in recreation values after fire in the northern Rocky Mountains (Research note PSW-373). Berkeley, CA; Pacific Southwest Forest and Range Experiment Station; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Flum T; Nodvin SC. (1995). Factors affecting streamwater chemistry in the Great Smoky Mountains, USA. Water Air Soil Pollut, 85, 1707-1712.

Ford J; Stoddard JL; Powers CF. (1993). Perspectives in environmental monitoring: an introduction to the U.S. EPA long-term monitonring (LTM)project. Water Air Soil Pollut, 67, 247-255.

Fore LS; Karr JR; Wisseman RW. (1996). Assessing invertebrate responses to human activities: evaluating alternative approaches. J North Am Benthol Soc, 15, 212-231.

Forkner RE; Hunter MD. (2000). What goes up must come down? Nutrient addition and predation pressure on oak herbivores. Ecology, 81, 1588-1600.

Forster P; Ramaswamy V; Artaxo P; Betss R; Fahey DW; Haywood J; Lean J; Lowe DC; Myhre G; Nganga J; Prinn R; Raga G; Schultz M; Van Dorland R. (2007). Changes in Atmospheric constituents and in radiative Forcing. In: Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M & Miller HL (Eds.). Climate Change 2007: The Physical Science Basis. (Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmetnal Panel on Climate Change (IPCC).

Foster KL; Plastridge RA; Bottenheim JW; Shepson PB; Finlayson-Pitts BJ; Spicer CW. (2001). The role of Br_2 and BrCl in surface ozone destruction at polar sunrise. Science, 291, 471-474.

Foster NW; Nicolson JA; Hazlett PW. (1989). Temporal variation in nitrate and nutrient cations in drainage waters from a deciduous forest. J Environ Qual, 18, 238-244.

Foster NW; Mitchell MJ; Morrison IK; Shepard JP. (1992). Cycling of acid and base cations in deciduous stands of Huntington Forest, New York, and Turkey Lakes, Ontario. Can J For Res, 22, 167-174.

Fowler D; Cape JN; Unsworth MH. (1989). Deposition of atmospheric pollutants on forests. Philosophical Transactions of the Royal Society of London B 324: 247-265.

Fowler D; Duyzer JH; Baldocchi DD. (1991). Inputs of trace gases, particles and cloud droplets to terrestrial surfaces. Proceedings of the Royal Society of Edinburgh Sect B: Biol Sci 97: 35-59.

Fowler D; MacDonald J; Leith ID; Hargreaves J; Martynoga R. (1995). The response of peat wetland methane emissions to temperature, water table and sulphate deposition. In: Heij GJ; Erisman JW (Eds.), Acid rain research: Do we have enough answers? (pp. 485-487). New York: Elsevier Science.

Fox GA. (1991). Practical causal inference for ecoepidemiologists. J Toxicol Environ Health, 33, 359-373.

Fox-Rabinovitz MS; Takacs LL; Govindaraju RC. (2002). A variable-resolution stretched-grid general circulation model and data assimilation system with multiple areas of interest: Studying the anomalous regional climate events of 1998. J Geophys Res, 107, 4768, doi:10.1029/2002JD002177

Fraser MP; Cass GR; Simoneit BRT; Rasmussen RA. (1998). Air quality model evaluation data for organics. 5: C_6-C_{22} nonpolar and semipolar aromatic compounds. Environ Sci Technol, 32, 1760-1770.

Fraterrigo JM; Turner MG; Pearson SM; Dixon P. (2005). Effects of past land use on spatial heterogeneity of soil nutrients in southern Appalachian forests. Ecol Monogr, 75, 215-230.

Freda J; McDonald DG. (1988). Physiologic correlates of interspecific variation in acid tolerance in fish. J Exp Biol, 136, 243-258.

Frederick PC; Spalding MG; Dusek R. (2002). Wading birds as bioindicators of mercury contamination in Florida, USA: Annual and geographic variation. Environ Toxicol Chem, 21, 163-167.

Freeman MA. III (2003). The measurement of environmental and resource values: Theory and methods. 2nd Edition. Washington, D.C: RFF Press.

Fremstad E; Paal J; Möls T. (2005). Impacts of increased nitrogen supply on Norwegian lichen-rich alpine communities: A 10 year experiment. J Ecol, 93, 471-481.

Frenette JJ; Richard Y; Moreau G. (1986). Fish responses to acidity in Québec lakes: A review. Water Air Soil Pollut, 30, 461-475.

Frey SD; Knorr M; Parrent JL; Simpson RT. (2004). Chronic nitrogen enrichment affects the structure and function of the soil microbial community in temperate hardwood and pine forests. For Ecol Manage, 196, 159-171.

Friedmann AS; Watzin MC; Brinck-Johnsen T; Leiter JC. (1996). Low levels of dietary methylmercury inhibit growth and gonadal development in juvenile walleye. Aquat Toxicol, 35, 265-278.

Friend A; Stevens A; Knox R; Cannell M. (1997). A process-based, terrestrial biosphere model of ecosystem dynamics (Hybrid v3.0). Ecol Model, 95, 249-287.

Frost GJ; McKeen SA; Trainer M; Ryerson TB; Neuman JA; Roberts JM; Swanson A; Holloway JS; Sueper DT; Fortin T; Parrish DD; Fehsenfeld FC; Flocke F; Peckham SE; Grell GA; Kowal D; Cartwright J; Auerbach N; Habermann T. (2006a). Effects of changing power plant NO_X emissions on ozone in the eastern United States: Proof of concept. J Geophys Res, 111.

Frost PC; Stelzer RS; Lamberti GA; Elser JJ. (2002). Ecological stoichiometry of trophic interactions in the benthos: Understanding the role of C:N:P ratios in lentic and lotic habitats. J N Am Benthol Soc, 21, 515-528.

Frost TM; Montz PK; Kratz TK; Badillo T; Brezonik PL; Gonzalez MJ; Rada RG; Watras CJ; Webster KE; Wiener JG; Williamson CE; Morris DP. (1999). Multiple stresses from a single agent: Diverse responses to the experimental acidification of Little Rock Lake, Wisconsin. Limnol Oceanogr, 44, 784-794.

Frost TM; Fischer JM; Klug JL; Arnott SE; Montz PK. (2006b). Trajectories of zooplankton recovery in the Little Rock Lake whole-lake acidification experiment. Ecol Appl, 16, 353-367.

Fu T-M; Jacob DJ; Palmer PI; Chance K; Wang YX; Barletta B; Blake DR; Stanton JC; Pilling MJ. (2006). Space-based formaldehyde measurements as constraints on volatile organic compound emissions in east and south Asia, and implications for ozone. J Geophys Res, 112, D06312, doi:10.1029/2006JD007853

Fuentes M; Raftery AE. (2005). Model evaluation and spatial interpolation by Bayesian combination of observations with outputs from numerical models. Biometrics, 61, 36-45.

Fuller RD; Driscoll CT; Lawrence GB; Nodvin SC. (1987). Processes regulating sulphate flux after whole-tree harvesting. Nature, 325, 707-710.

Funk JL; Giardina CP; Knohl A; Lerdau MT. (2006). Influence of nutrient availability, stand age, and canopy structure on isoprene flux in a *Eucalyptus saligna* experimental forest. J Geophys Res, 111, doi:10.1029/2005JG000085.

Furutani H; Akimoto H. (2002). Development and characterization of a fast measurement system for gas-phase nitric acid with a chemical ionization mass spectrometer in the marine boundary layer. J Geophys Res, 107, doi 10.1029/2000JD000269.

Gaffney JS; Bornick RM; Chen Y-H; Marley NA. (1998). Capillary gas chromatographic analysis of nitrogen dioxide and pans with luminol chemiluminescent detection. Atmos Environ, 32, 1445-1454.

Gagen CJ; Sharpe WE; Carline RF. (1993). Mortality of brook trout, mottled sculpins, and slimy sculpins during acidic episodes. Trans Am Fish Soc, 122, 616-628.

Gaio-Oliveira G; Dahlman L; Palmqvist K; Martins-Loução MA; Máguas C. (2005). Nitrogen uptake in relation to excess supply and its effects on the lichens *Evernia prunastri* (L.)Ach and *Xanthoria parietina* (L.). Th. Fr. Planta, 220, 794-803.

Galbally IE; Bentley ST; Meyer CP. (2000). Mid-latitude marine boundary-layer ozone destruction at visible sunrise observed at Cape Grim, Tasmania, 41degrees S. Geophys Res Lett, 27, 3841-3844.

Gallagher J; Baker JL. (1990). Current status of fish communities in Adirondack lakes. In: Adirondack Lakes Survey: An interpretative analysis of fish communities and water chemistry, 1984-87. (pp. 3-48). Ray Brook, NY: Adirondack Lake Survey Corporation.

Galloway JN; Norton SA; Church MR. (1983). Freshwater acidification from atmospheric deposition of sulfuric acid: A conceptual model. Environ Sci Technol, 17, 541A-545A.

Galloway JN; Schlesinger WH; Levy H; Michaels AF; Schnoor JL. (1995). Nitrogen-fixation: anthropogenic enhancement, environmental response. Glob Biogeochem Cycles, 9, 235-252.

Galloway J. (1995). Acid deposition: Perspectives in time and space. Water Air Soil Pollut, 85, 15-24.

Galloway JN. (1996). Anthropogenic mobilization of sulphur and nitrogen: Immediate and delayed consequences. Ann Rev Energy Environ, 21, 261-292.

Galloway JN. (1998). The global nitrogen cycle: Changes and consequences. Environ Pollut, 102, 15-24.

Galloway JN; Cowling EB. (2002). Reactive nitrogen and the world: 200 years of change. Ambio, 31, 64-71.

Galloway JN; Aber JD; Erisman JW; Seitzinger SP; Howarth RW; Cowling EB; Cosby J. (2003). The nitrogen cascade. Bioscience, 53, 341-356.

Gao W; Wesely ML; Lee IY. (1991). A numerical study of the effects of air chemistry on fluxes of NO, NO_2, and O_3 near the surface. J Geophys Res, 96, 18761-18769.

Gao W; Wesely ML; Doskey PV. (1993). Numerical modeling of the turbulent diffusion and chemistry of NO_X, O_3, isoprene, and other reactive trace gases in and above a forest canopy. J Geophys Res, 98, 18339-18353.

Garcia E; Carignan R. (2000).Mercury concentrations in northern pike (*E*SO$_X$ *lucius*).from boreal lakes with logged, burned, or undisturbed catchments. Can J Fish Aquat Sci, 57, 129-135.

Garner JHB; Pagano T; Cowling EB. (1989). An evaluation of the role of ozone, acid deposition, and other airborne pollutants in the forests of eastern North America (No. General Technical Report SE-59). Asheville, NC: U.S. Department of Agriculture, Forest Service, Southeastern Forest Experiment Station.

Garner JHB. (1994). Nitrogen oxides, plant metabolism, and forest ecosystem response. In: Alscher RG; Wellburn A (Eds.). Plant responses to the gaseous environment: Molecular, metabolic, and physiological aspects, (Proceedings from the 3rd International symposium on air pollutants and plant metabolism, held in Blacksburg,VA at Virginia Polytechnic Institute inJune 1992; pp 301-314). Norwell, MA: Kluwer Academic Publishers.

Garten CT, Jr.; Hanson PJ. (1990). Foliar retention of 15N-nitrate and 15N-ammonium by red maple (Acer rubrum) and white oak (Quercus alba) leaves from simulated rain. Environmental and Experimental Botany 30: 333-342.

Gates DM. (1968). Transpiration and leaf temperature. Annu Rev Plant Biol , 19, 211-238.

Gauci V; Dise N; Fowler D. (2002). Controls on suppression of methane flux from a peat bog subjected to simulated acid rain sulfate deposition. Glob Biogeochem Cycles, 16, 4-1 - 4-12. doi: 10.1029/2000GB001370

Gauci V; Fowler D; Chapman SJ; Dise NB. (2004). Sulfate deposition and temperature controls on methane emission and sulfur forms in peat. Biogeochemistry, 71, 141-162.

Gauslaa Y. (1995). Lobarion, an epiphytic community of ancient forests, threatened by acid rain. Lichenologist, 27, 59-76.

Gbondo-Tugbawa SS; Driscoll CT; Aber JD; Likens GE. (2001). Evaluation of an integrated biogeochemical model (PnET-BGC) at a northern hardwood forest ecosystem. Water Resour Res, 37, 1057-1070.

Gbondo-Tugbawa SS; Driscoll CT. (2002a). Evaluation of the effects of future controls on sulfur dioxide and nitrogen oxide emissions on the acid-base status of a northern forest ecosystem. Atmos Environ, 36, 1631-1643.

Gbondo-Tugbawa SS; Driscoll CT; Mitchell MJ; Aber JD; Likens GE. (2002a). A model to simulate the response of a northern hardwood forest ecosystem to changes in S deposition. Ecol Appl, 12, 8-23.

Gbondo-Tugbawa SS; Driscoll CT. (2003). Factors controlling long-term changes in soil pools of exchangeable basic cations and stream acid neutralizing capacity on a northern hardwood forest ecosystem. Biogeochem, 63, 161-185.

Gebauer RLE; Reynolds JF; Tenhunen JD. (1995). Growth and allocation of the arctic sedges *Eriophorum angustifolium* and *E. vaginatum*: effects of variable soil oxygen and nutrient availability. Oecologia, 104, 330-339.

Geiser LH; Neitlich PN. (2007). Air pollution and climate gradients in western Oregon and Washington indicated by epiphytic macrolichens. Environ Pollut, 145, 203-218.

Genfa Z; Dasgupta PK. (1989). Fluorometric measurement of aqueous ammonium ion in a flow injection system. Anal Chem, 61, 408-412.

Gensemer RW; Playle RC. (1999). The bioavailability and toxicity of aluminum in aquatic environments. Crit Rev Environ Sci Technol, 29, 315-450.

George C; Strekowski RS; Kleffmann J; Stemmler K; Ammann M. (2005). Photoenhanced uptake of gaseous NO_2 on solid organic compounds: A photochemical source of HONO? Faraday Discuss, 130, 195-210.

Gerlach TM. (2004).Volcanic sources of tropospheric ozone-depleting trace gases. Geochem Geophys Geosys, 5, doi: 10.1029/2004GC000747.

Gerritsen J; Carlson RE; Dycus DL; Faulkner C; Gibson GR. Harcum J; Markowitz SA. (1998). Lake and reservoir bioassessment and biocriteria: Technical guidance document. (Report no EPA 841-B-98-007). http://www.epa.gov/owow/monitoring/tech/lakes.html. Washington, DC; Office of Water; U.S. Environmental Protection Agency.

Gery MW; Whitten GZ; Killus JP; Dodge MC. (1989). A photochemical kinetics mechanism for urban and regional scale computer modeling. J Geophys Res, 94, 12925-12956.

Geyer A; Alicke B; Konrad S; Schmitz T; Stutz J; Platt U. (2001). Chemistry and oxidation capacity of the nitrate radical in the continental boundary layer near Berlin. J Geophys Res, 106, 8013-8025.

Geyer A; Platt U. (2002). Temperature dependence of the NO_3 loss frequency: A new indicator for the contribution of NO_3 to the oxidation of monoterpenes and NO_X removal in the atmosphere. J Geophys Res, 107, 4431, doi:10.1029/2001JD001215.

Gherini SA; Mok L; Hudson RJ; Davis GF; Chen CW; Goldstein RA. (1985). The ILWAS model: formulation and application. Water Air Soil Pollut, 26, 425-459.

Giardina CP; Binkley D; Ryan MG; Fownes JH; Senock RS. (2004). Belowground carbon cycling in a humid tropical forest decreases with fertilization. Oecologia, 139, 545-550.

Gibson TL. (1983). Sources of direct-acting nitroarene mutagens in airborne particulate matter. Mutat Res, 122, 115-121.

Gidel LT. (1983). Cumulus cloud transport of transient tracers. J Geophys Res, 88, 6587-6599.

Gilliam FS; Adams MB; Yurish BM. (1996). Ecosystem nutrient responses to chronic nutrient inputs at Fernow Experimental Forest, West Virginia. Can J For Res, 26, 196-205.

Gilliam FS; Yurish BM; Adams MB. (2001). Temporal and spatial variation of nitrogen transformations in nitrogen-saturated soils of a central Appalachian hardwood forest. Can J For Res, 31, 1768-1785.

Gilliam FS. (2006). Response of the herbaceous layer of forest ecosystems to excess nitrogen deposition. J Ecol, 94, 1176-1191.

Gilliam FS; Hockenberry AW; Adams MB. (2006). Effects of atmospheric deposition on the herbaceous layer of a central Appalachian hardwood forest. J Torrey Bot Soc, 133, 240-254.

Gilliland A. (2001). A sensitivity study of the discrete Kalman filter (DKF).to initial condition discrepancies. J Geophys Res, 106, 17939-17952.

Gilliland AB; Dennis RL; Roselle SJ; Pierce TE; Bender LE. (2001). Developing seasonal ammonia emission estimates with an inverse modeling technique. Scientific WorldJournal, 1, 356-362.

Gilliland AB; Dennis RL; Roselle SJ; Pierce TE. (2003). Seasonal NH_3 emission estimates for the eastern United States based on ammonium wet concentrations and an inverse modeling method. J Geophys Res, 108, 4477, doi:10.1029/2002JD003063.

Gilmour CC; Henry EA. (1991). Mercury methylation in aquatic systems affected by acid deposition. Environ Pollut, 71, 131-169.

Gilmour CC; Henry EA; Mitchell R. (1992). Sulfate stimulation of mercury methylation in freshwater sediments. Environ Sci Technol, 26, 2281-2287.

Gilmour CC; Riedel GS; Ederington MC; Bell JT; Gill GA; Stordal MC. (1998). Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. Biogeochemistry, 40, 327-345.

Gipson GL. (1999). Process analysis (Chapter 16). In: Byun DW; Ching JKS. (Eds.). Science algorithms in models-3 community multiscale air quality modeling system (CMAQ). (EPA-600/R-99/030, pp 16-1 – 16-20), Research Triangle Park, NC; U.S. Environmental Protection Agency.

Gipson GL; Young JO. (1999). Gas phase chemistry (Chapter 8). In: Byun DW; Ching JKS. (Eds.). Science algorithms in models-3 community multiscale air quality modeling system (CMAQ). (EPA-600/R-99/030, pp 8-1 – 8-99), Research Triangle Park, NC; U.S. Environmental Protection Agency.

Gitay H; Brown S; Easterling W; Jallow B (2001). Ecosystems and their goods and services. http://www.grida.no/publications/other/ipcc_tar/?src=/climate/ipcc_tar/wg2/196.htm In: McCarthy JJ; Osvaldo FC; Leary NA; Dokken DJ; White KS (Eds.). Climate change 2001: Impacts, adaptation, and vulnerability: Contribution of working group II to the third assessment report of the intergovernmental panel on climate change (IPCC). (pp 237-342). New York, NY: Cambridge University Press

Glooschenko V; Blancher P; Herskowitz J; Fulthorpe R; Rang S. (1986). Association of wetland acidity with reproductive parameters and insect prey of the eastern kingbird (*Tyrannus tyrannus*) near Sudbury, Ontario. Water Air Soil Pollut, 30, 553-567.

Gobler CJ; Davis TW; Coyne KJ; Boyer GL. (2007). Interactive influences of nutrient loading, zooplankton grazing, and microcystin synthetase gene expression on cyanobacterial bloom dynamics in a eutrophic New York lake. Harmful Algae, 6,119-133.

Gochfeld M. (1980). Tissue distribution of mercury in normal and abnormal young common terns. Mar Pollut Bull, 11, 362-366.

Godbold DL; Fritz E; Huttermann A. (1988). Aluminum toxicity and forest decline. Proc Natl Acad Sci USA, 85, 3888-3892.

Goebes MD; Strader R; Davidson C. (2006). An ammonia emission inventory for fertilizer application in the United States. Atmos Environ, 37. 2539-2550.

Goede RW; Barton BA. (1990). Organismic indices and an autopsy-based assessment as indicators of health and condition of fish. Am Fish Soc Symp, 8, 80-93.

Goldan PD; Kuster WC; Albritton DL; Fehsenfeld FC; Connell PS; Norton RB; Huebert BJ. (1983). Calibration and tests of the filter-collection method for measuring clean-air, ambient levels of nitric acid. Atmos Environ, 17, 1355-1364.

Goldan PD; Trainer M; Kuster WC; Parrish DD; Carpenter J; Roberts JM; Yee JE; Fehsenfeld FC. (1995). Measurements of hydrocarbons, oxygenated hydrocarbons, carbon monoxide, and nitrogen oxides in an urban basin in Colorado: Implications for emission inventories. J Geophys Res, 100, 22771-22783

Goldan PD; Kuster WC; Fehsenfeld FC. (1997). Nonmethane hydrocarbon measurements during the tropospheric OH photochemistry experiment. J Geophys Res, 102, 6315-6324.

Goldan PD; Parrish DD; Kuster WC; Trainer M; McKeen SA; Holloway J; Jobson BT; Sueper DT; Fehsenfeld FC. (2000). Airborne measurements of isoprene, CO, and anthropogenic hydrocarbons and their implications. J Geophys Res, 105, 9091-9105.

Golden DM; Smith GP. (2000). Reaction of OH + NO_2 + M: A New View. J Phys Chem A, 104, 3991-3997

Goldman CR. (1988). Primary productivity, nutrients, and transparency during the early onset of eutrophication in ultra-oligotrophic Lake Tahoe, California-Nevada. Limnol Oceanogr, 33, 1321-1333.

Goldstein RA; Gherini SA; Chen CW; Mok L; Hudson RJM; Kramer JR; Brown DJA; Chester PF. (1984). Integrated acidification study (ILWAS): A mechanistic ecosystem analysis. Philos Trans R Soc Lond B Biol Sci, 305, 409-425.

Goldstein AH; Schade GW. (2000). Quantifying biogenic and anthropogenic contributions to acetone mixing ratios in a rural environment. Atmos Environ, 34, 4997-5006.

Gondal MA. (1997). Laser photoacoustic spectrometer for remote monitoring of atmospheric pollutants. Laser photoacoustic spectrometer for remote monitoring of atmospheric pollutants. Appl Opt, 36, 3195-3201.

Gondal MA; Mastromarino J. (2001). Pulsed laser photoacoustic detection of SO_2 near 225.7 nm. Appl Opt, 40, 2010-2016.

Goodale CL; Aber JD; McDowell WH. (2000). The long-term effects of disturbance on organic and inorganic nitrogen export in the White Mountains, New Hampshire. Ecosystems, 3, 433-450.

Goodale CL; Aber JD. (2001). The long-term effects of land-use history on nitrogen cycling in northern hardwood forests. Ecol Appl, 11, 253-267.

Goodale C; Lajtha K; Nadelhoffer KJ; Boyer EW; Jaworski NA. (2002). Forest nitrogen sinks in large eastern U.S. watersheds: estimates from forest inventory and an ecosystem model. Biogeochemistry, 57/58, 239-266.

Goodale CL; Aber JD; Vitousek PM. (2003). An unexpected nitrate decline in New Hampshire streams. Ecosystems, 6, 75-86.

Goodale CL; Aber JD; Vitousek PM; McDowell WH. (2005). Long-term decreases in stream nitrate: successional causes unlikely; possible links to DOC? Ecosystems, 8, 334-337.

Göransson A; Eldhuset TD. (1987). Effects of aluminum on growth and nutrient uptake of *Betula pendula* seedlings. Physiol Plant, 69, 193-199.

Gordon C; Wynn JM; Woodin SJ. (2001). Impacts of increased nitrogen supply on high Arctic heath: The importance of bryophytes and phosphorus availability. New Phytol, 149, 461-471.

Gorham E; Janssens JA; Wheeler GA; Glaser PH. (1987). Natural and anthropogenic acidification of peatlands. In: Hutchinson TC; Meema KM (Eds.). Effects of atmospheric pollutants on forests, wetlands, and agricultural ecosystems. (Proceedings from the NATO advanced research workshop on effects of acid deposition of forests, wetlands and agricultural ecosystems (1985, Toronto). (NATO ASI series G: Ecololgical sciences pp. 493-512). New York: Springer-Verlag

Goriup PD. (1989). Acidic air pollution and birds in Europe. Oryx, 23, 82-86.

Gotelli NJ; Ellison AM. (2002). Nitrogen deposition and extinction risk in the northern pitcher plant, *Sarracenia purpurea*. Ecology, 83, 2758-2765.

Gotelli NJ; Ellison AM. (2006). Food-web models predict species abundances in response to habitat change. PLoS Biol, 4, e324, doi:10.1371/journal.pbio.0040324.

Goulder LH; Kennedy D. (1997). Valuing ecosystem services: Philosophical bases and empirical methods. In: Daily GC (Ed.). Nature's services: Societal Ddpendence on natural ecosystems. (pp 23-47). Washington, DC: Island Press.

Graetz DA; Pollman CD; Roof B; Will E. (1985). Effects of acidic treatments on soil chemistry and microbiology. In: Florida acid deposition study. Phase IV report. (Vol. I. ESE No. 83-152-0106/0207/0307; pp. 4-5 - 4-123). Gainesville, FL: Environmental Science and Engineering, Inc

Gramlich FW. (1977). The demand for clean water: The case of the Charles River. Natl Tax J, 30, 183-194.

Gran G. (1952). Determination of the equivalence point in potentiometric titrations. Analyst, 77, 661-671.

Granberg G; Sundh I; Svensson BH; Nilsson M. (2001). Effects of temperature and nitrogen and sulfur deposition, on methane emission from a boreal mire. Ecology, 82, 1982-1998.

Grant EHC; Jung RE; Rice KC. (2005). Stream salamander species richness and abundance in relation to environmental factors in Shenandoah National Park, Virginia. Am Midl Nat, 153, 348-356.

Green PA; Vörösmarty CJ; Meybeck M; Galloway JN; Peterson BJ; Boyer EW. (2004). Pre-industrial and contemporary fluxes of nitrogen through rivers: A global assessment based on typology. Biogeochemistry, 68, 71-105.

Greenhut GK; Ching JKS; Pearson R Jr; Repoff TP. (1984). Transport of ozone by turbulence and clouds in an urban boundary layer. J Geophys Res, 89, 4757-4766.

Greenhut GK. (1986). Transport of ozone between boundary layer and cloud layer by cumulus clouds. J Geophys Res, 91, 8613-8622.

Gregory GL; Hoell JM Jr; Torres AL; Carroll MA; Ridley BA; Rodgers MO; Bradshaw J; Sandholm S; Davis DD. (1990). An intercomparison of airborne nitric oxide measurements: A second opportunity. J Geophys Res, 95, 10129-10138.

Grell GA; Dudhia J; Stauffer DR. (1995). A description of the fifth-generation Penn State/NCAR mesoscale model (MM5). [NCAR technical note NCAR/TN-398 + STR]. Boulder, CO; Mesoscale and Microscale meteorology Division, National Center for Atmospheric Research; and Forcast Systems Laboratory, National Oceanic and Atmospheric Administration (NOAA).

Grell GA; Emeis S; Stockwell WR; Schoenemeyer T; Forkel R; Michalakes J; Knoche R; Seidl W. (2000). Application of a multiscale, coupled MM5/chemistry model to the complex terrain of the VOTALP valley campaign. Atmos Environ, 34, 1435-1453.

Grenon F; Bradley RL; Joanisse G; Titus BD; Prescott CE. (2004). Mineral N availability for conifer growth following clearcutting: responsive versus non-responsive ecosystems. For Ecol Manage, 188, 305-316.

Grieb TM; Driscoll CT; Gloss SP; Schofield CL; Bowie GL; Porcella DB. (1990). Factors affecting mercury accumulation in fish in the Upper Michigan Peninsula. Environ Toxicol Chem, 9, 919-930.

Grier CC (1975). Wildfire effects on nutrient distribution and leaching in a coniferous ecosystem. Can J For Res, 5, 599-607.

Griffin K; Bashkin M; Thomas R; Strain B. (1997). Interactive effects of soil nitrogen and atmospheric carbon dioxide on root/rhizosphere carbon dioxide efflux from loblolly and Ponderosa pine seedlings. Plant Soil, 190, 11-18.

Griffiths RW; Keller W. (1992). Benthic macroinvertebrate changes in lakes near Sudbury, Ontario following a reduction in acid emissions. Can J Fish Aquat Sci, 49, 63-75.

Grill, D. (1971). Pufferkapazitat gesunder und rauchgeschadigter Fichtennadeln. Z. Pflanzenkr Pflanzenschutz, 78, 612-622.

Grimm NB; Fisher SG. (1986). Nitrogen limitation in a Sonoran Desert stream. J North Am Benthol Soc, 5, 2-15.

Grippo MA; Heath AG. (2003). The effect of mercury on the feeding behavior of fathead minnows (*Pimephales promelas*). Ecotoxicol Environ Saf, 55, 187-198.

Groffman PM. (1994). Denitrification in freshwater wetlands. Curr Topics Wetland Biogeochem, 1, 15-35.

Groffman PM; Altabet AM; Böhlke JK; Butterbach-Bahl K; David MB; Firestone MK; Giblin AE; Kana TM; Nielsen LP; Voytek MA. (2006). Methods for measuring denitrification: diverse approaches to a difficult problem. Ecol Appl, 16, 2091-2122.

Grosjean D; Fung K; Harrison J. (1983). Interactions of polycyclic aromatic hydrocarbons with atmospheric pollutants. Environ Sci Technol, 17, 673-679.

Grosjean D; Grosjean E; Williams EL. (1993). Fading of artists' colorants by a mixture of photochemical oxidants. Atmos Environ, 27, 765-772.

Grosjean D; Grosjean E; Williams EL II. (1994). Fading of colorants by atmospheric pollutants: reflectance spectroscopy studies. Sci Total Environ, 151, 213-226.

Grosjean D. (2003). Ambient PAN and PPN in southern California from 1960 to the SCOS97-NARSTO. Proceedings from the SCO-97-NARSTO Data Analysis Conference, February 13-15, 2001; Diamond Bar, CA. Atmos Environ, 37, S221-S238.

Grosovsky AJ; Sasaki JC; Arey J; Eastmond DA; Parks KK; Atkinson R. (1999). Evaluation of the potential health effects of the atmospheric reaction products of polycyclic aromatic hydrocarbons. HEI Research Report #084. Boston, MA: Health Effects Institute (HEI).

Gross A; Stockwell WR. (2003). Comparison of the EMEP, RADM2 and RACM mechanisms. J Atmos Chem , 44, 151-170.

Grossenbacher JW; Couch T; Shepson PB; Thornberry T; Witmer-Rich M; Carroll MA; Faloona I; Tan D; Brune W; Ostling K; Bertman S. (2001). Measurements of isoprene nitrates above a forest canopy. J Geophys Res, 106, 24429-24438.

Grossman GD; Ratajczak RE Jr; Crawford MK; Freeman MC. (1998). Assemblage of organization in stream fishes: effects of environmental variation and interspecific interactions. Ecol Monogr, 68, 395-420.

Grulke NE; Andersen CP; Fenn ME; Miller PR. (1998). Ozone exposure and nitrogen deposition lowers root biomass of ponderosa pine in the San Bernardino Mountains, California. Environ Pollut, 103, 63-73.

Grulke NE; Balduman L. (1999). Deciduous conifers: high N deposition and O_3 exposure effects on growth and biomass allocation in ponderosa pine. Water Air Soil Pollut, 116, 235-248.

Grulke N; Schilling S. (2008). Air Pollution and Climate Change. Washington, DC; Climate Change Resource Center; U.S. Forest Service; U.S. Department of Agriculture (USDA). http://www.fs.fed.us/ccrc/topics/air-pollution.shtml.

Grulke NE; Minnich RA; Paine TD; Seybold SJ; Chavez D; Fenn ME; Riggan PJ; Dunn A. (2008). Air pollution increases forest susceptibility to wildfires: A case study in the San Bernardino Mountains in southern California. (An air pollution and climate change case study). In: Bytnerowicz A; Arbaugh MJ; Riebau AR; Anderson, C (Eds.).Wildland fires and air pollution; Section III: Ecological Impacts of Forest Fires and Air Pollution (Volume 8 in Developments in Environmental Sciences Series, pp 365-403). Amsterdam, The Netherlands: Elsevier Ltd.

Grünhage L; Dämmgen U; Haenel HD; Jäger HJ. (1992). Vertikale flüsse von spurengasen in der bodennahen atmosphäre. Landbauforsch Voelkenrode, 128, 201-245.

Gubala CP; Driscoll CT; Newton RM; Schofield CL. (1991). Chemistry of a near-shore lake region during spring snowmelt. Environ Sci Technol, 25, 2024-2030.

Guderian R; Tingey DT; Rabe R. (1985). Effects of photochemical oxidants on plants. In Guderian R. (Ed.).Air pollution by photochemical oxidants: Formation, transport, control, and effects on plants. (Volume 52 in Series: Billings WD; Golley F; Lange OL; Olson JS; Remmert H (Eds.). Ecological studies: Analysis and synthesis, pp 129-333). Berlin, Germany: Springer-Verlag.

Guenther FR; Dorko WD; Miller WR; Rhoderick GC. (1996). The NIST traceable reference material program for gas standards. (NIST special publication 260-126). Washington, DC; National Institute of Standards and Technology; U.S. Department of Commerce.

Guenther A; Geron C; Pierce T; Lamb B; Harley P; Fall R. (2000). Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America. Atmos Environ, 34, 2205-2230.

Guerold F; Boudot JP; Jacquemin G; Vein D; Merlet D; Rouiller J. (2000). Macroinvertebrate community loss as a result of headwater stream acidification in the Vosges Mountains (N-E France). Biodivers Conserv, 9, 767-783.

Gulledge J; Doyle AP; Schimel JP. (1997). Different NH_4^+-inhibition patterns of soil CH_4 -oxidizer populations across sites. Soil Biol Biochem, 29, 13-21.

Gulledge J; Schimel JP. (2000). Controls on soil carbon dioxide and methane fluxes in a variety of taiga forest stands in interior Alaska. Ecosystems, 3, 269-282.

Gundersen P; Rasmussen L. (1995). Nitrogen mobility in a nitrogen limited forest at Klosterhede, Denmark, examined by NH_4NO_3 addition. For Ecol Manage, 71, 75-88.

Gundersen P; Callesen I; de Vries W. (1998). Nitrate leaching in forest ecosystems is controlled by forested floor C/N ratio. Environ Pollut, 102, 403-407.

Gundersen P; Schmidt IK; Raulund-Rasmussen K. (2006). Leaching of nitrate from temperate forests - Effects of air pollution and forest management. Environ Rev, 14, 1-57.

Gunn JM; Keller W. (1984a). In situ manipulation of water chemistry using crushed limestone and observed effects on fish. Fisheries, 9, 19-24.

Gunn JM; Keller W. (1984b). Spawning site water chemistry and lake trout (*Salvelinus namaycush*).sac fry survival during spring snowmelt. Can J Fish Aquat Sci, 41, 319-329.

Gunn JM; Noakes DLG. (1987). Latent effects of pulse exposure to aluminum and low pH on size, ionic composition and feeding efficiency of lake trout (*Salvelinus fontinalis*).alevins. Can J Fish Aquat Sci, 44, 1418-1424.

Gunn JM; McMurtry MJ; Casselman JM; Keller W; Powell MJ. (1988). Changes in the fish community of a limed lake near sudbury, Ontario: Effects of chemical neutralization or reduced atmospheric deposition of acids? Water Air Soil Pollut, 41, 113-136.

Gunn JM. (1989). Survival of lake charr (*Salvelinus namaycush*) embryos under pules exposure to acidic runoff water. In: Nriagu JO; Lakshminarayana JSS, (Eds.). Aquatic toxicology and water quality management. (Advances in environmental science and technology: Volume 22, pp 23-45).New York, NY: John Wiley & Sons.

Gunn JM; Keller W. (1990). Biological recovery of an acid lake after reductions in industrial emissions of sulphur. Nature, 355, 431-433.

Gunn J; Keller W; Negusanti J; Potvin R; Beckett P; Winterhalder K. (1995). Ecosystem recovery after emission reductions: Sudbury, Canada. Water Air Soil Pollut, 85, 1783-1788.

Gunn JM; Mills KH. (1998).The potential for restoration of acid-damaged lake trout lakes. Restor Ecol, 6, 390-397.

Günthardt-Goerg MS; Schmutz P; Matyssek R; Bucher JB. (1996). Leaf and stem structure of poplar (*Populus x euramericana*) as influenced by O_3, NO_2, their combination, and different soil N supplies. Can J For Res, 26, 649-657.

Günthardt-Goerg MS; McQuattie CJ; Maurer S; Frey B. (2000). Visible and microscopic injury in leaves of five deciduous tree species related to current critical ozone levels. Environ Pollut, 109, 489-500.

Gupta UC; Munro DC. (1969). Influence of sulfur, molybdenum and phosphorus on the chemical composition and yield of brussels sprouts and of molybdenum on sulfur contents of several plant species grown in the greenhouse. Soil Sci, 107, 114-118.

Gupta VK; Mehla DS. (1980). Influence of sulphur on the yield and concentration of copper, manganese, iron and molybdenum in Berseem (*Trifolium alexandrinum*) grown on two different soils. Plant Soil, 56, 229-234.

Gysels K; Delalieux F; Deutsch F; Van Grieken R; Camuffo D; Bernardi A; Sturaro G; Busse HJ; Wieser M. (2004). Indoor environment and conservation in the Royal Museum of Fine Arts, Antwerp, Belgium. Journal of Cultural Heritage, 5, 221-230.

Hachmoller B; Matthews RA; Brakke DF. (1991). Effects of riparian community structure, sediment size, and water-quality on the macroinvertebrate communities in a small, suburban stream. Northwest Science, 65, 125-132.

Haefele M; Kramer RA; Holmes TP. (1992). Estimating the total value of forest quality in high elevation spruce-fir forests. In: Payne C; Bowker JM; Reed PC (Eds.). The economic value of wilderness. Proceedings of the conference held in Jackson, WY May 8-11, 1991; General technical report #SE-78 (pp 91-96). Asheville, NC; Southeastern Forest Experimental Station, U.S. Forest Service, U.S. Department of Agriculture (USDA).

Hagy JD; Boynton WR; Keefe CW; Wood KV. (2004). Hypoxia in Chesapeake Bay, 1950-2001: Long-term change in relation to nutrient loading and river flow. Estuaries, 27, 634-658.

Haines TA; Baker JP. (1986). Evidence of fish population responses to acidification in the eastern United States. Water Air Soil Pollut, 31, 605-629.

Hains JC; Chen LWA; Taubman BF; Doddridge BG; Dickerson RR. (2007). A side-by-side comparison of filter-based $PM_{2.5}$ measurements at a suburban site: A closure study. Atmos Environ, 41, 6167-6184.

Hall SJ; Matson PA. (1999). Nitrogen oxide emissions after nitrogen additions in tropical forests. Nature, 400, 152-155.

Hall SJ; Matson PA. (2003). Nutrient status of tropical rain forests influences soil N dynamics after N additions. Ecol Monogr, 73, 107-129.

Hall LW. (1987). Acidification effects on larval striped bass, *Morone saxatilis*, in Chesapeake Bay tributaries: A review. Water Air Soil Pollut, 35, 87-96.

Hall RI; Leavit PR; Quinlan R; Dixit AS; Smol JP. (1999). Effects of agriculture, urbanization, and climate on water quality in the northern Great Plains. Limnol Oceanogr, 44, 739-756.

Hall RJ; Likens GE; Fiance SB; Hendrey GR. (1980). Experimental acidification of a stream in the Hubbard Brook Experimental Forest, New Hampshire. Ecology, 61, 976-989.

Hall RJ; Ide FP. (1987). Evidence of acidification effects on stream insect communities in central Ontario between 1937 and 1985. Can J Fish Aquat Sci, 44, 1652-1657.

Hallett RA; Bailey SW; Horsley SB; Long RP. (2006). Influence of nutrition and stress on sugar maple at a regional scale. Can J For Res, 36, 2235-2246.

Hallingbäck T. (1991). Blue-green algae and cyanophilic lichens threatened by air pollution and fertilization. Sven Bot Tidskr, 85, 87-104.

Hallingbäck T; Kellner O. (1992). Effects of simulated nitrogen rich and acid rain on the nitrogen-fixing lichen *Peltigera aphthosa* (L.)Willd. New Phytol, 120, 99-103.

Hallock-Waters KA; Doddridge BG; Dickerson RR; Spitzer S; Ray JD. (1999). Carbon monoxide in the U.S. mid-Atlantic troposphere: Evidence for a decreasing trend. Geophys Res Lett, 26, 2861-2864.

Hallquist M; Stewart DJ; Stephenson SK; Cox RA. (2003). Hydrolysis of N_2O_5 on sub-micron sulfate aerosols. Phys Chem Chem Phys, 5, 3453-3463.

Hamburg SP; Yanai RD; Arthur MA; Blum JD; Siccama TG. (2003). Biotic control of calcium cycling in northern hardwood forests: Acid rain and aging forests. Ecosystems, 6, 399-406.

Hameed S; Pinto JP; Stewart RW. (1979). Sensitivity of the predicted CO-OH-CH4 perturbation to tropospheric NO_X concentrations. J Geophys Res, 84, 763-768.

Hames RS; Rosenberg KV; Lowe JD; Barker SE; Dhondt AA. (2002). Adverse effects of acid rain on the distribution of the wood thrush *Hylocichla mustelina* in North America. Proc Natl Acad Sci USA, 99, 11235-11240.

Hammitt WE; Patterson ME; Noe FP. (1994). Identifying and predicting visual preferences of southern Appalachian forest recreation vistas. Landsc Urban Plan, 29 171-183.

Hanemann M. (1991). Willingness to pay and willingness to accept: How much can they differ? Am Econ Rev, 81, 635-647.

Hanke M; Umann B; Uecker J; Arnold F; Bunz H. (2003). Atmospheric measurements of gas-phase HNO_3 and SO_2 using chemical ionization mass spectrometry during the MINATROC field campaign 2000 on Monte Cimone. Atmos Chem Phys, 3, 417-436.

Hanley N; Shogren J; White B. (1997). Environmental economics in theory and practice. New York, NY: Oxford University Press.

Hansen DA; Edgerton ES; Hartsell BE; Jansen JJ; Kandasamy N; Hidy GM; Blanchard CL. (2003). The southeastern aerosol research and characterization study: Part 1 - Overview. J Air Waste Manage Assoc, 53, 1460-1471.

Hansen J; Sato M; Ruedy R; Lo K; Lea DW; Medina-Elizade M. (2006). Global temperature change. Proc Natl Acad Sci, USA, 103, 14288-14293.

Hansen K; Draaijers GPJ; Ivens WPMF; Gundersen P; Van Leeuwen NFM. (1994). Concentration variations in rain and canopy throughfall collected sequentially during individual rain events. Atmos Environ, 28, 3195-3205.

Hanson PJ; Rott K; Taylor GE; Gunderson CA; Lindberg SE; Ross-Todd BM. (1989). NO2 deposition to elements representative of a forest landscape. Atmos Environ, 23, 1783-1794.

Hanson PJ; Lindberg SE. (1991). Dry deposition of reactive nitrogen compounds: A review of leaf, canopy, and non-foliar measurements. Atmos Environ, 25, 1615-1634.

Hanson PJ; Garten CT Jr. (1992). Deposition of $H^{15}NO_3$ vapour to white oak, red maple, and loblolly pine foliage: Experimental observations and a generalized model. New Phytol, 122, 329-337.

Hao JM; Ye XM; Duan L; Zhou ZP. (2001). Calculating critical loads of sulfur deposition for 100 surface waters in China using the MAGIC model. Water Air Soil Pollut, 130, 1157-1162.

Harasmis GM; Chu DS. (1987). Acid rain effects on waterfowl: Use of black duck broods to assess food resources of experimentally acidified wetlands. In: Diamond AW; Filion FL (Eds.), The value of birds. (ICBP technical publication no 6; pp 173-181). Cambridge, United Kingdom: International Council for Bird Preservation (ICBP).

Harder JW; Williams EJ; Baumann K; Fehsenfeld FC. (1997). Ground-based comparison of NO_2, H_2O, and O_3 measured by long-path and in situ techniques during the 1993 tropospheric OH photochemistry experiment. J Geophys Res, 102, 6227-6243.

Harding LW; Perry ES. (1997). Long-term increase of phytoplankton biomass in Chesapeake Bay, 1950-1994. Mar Ecol Prog Ser, 157, 39-52.

Harding, LWJ; Mallonee ME; Perry ES. (2002). Toward a predictive understanding of primary productivity in a temperate, partially stratified estuary. Estuar Coast Shelf Sci, 55, 437-463.

Hari P; Raivonen M; Vesala T; Munger JW; Pilegaard K; Kulmala M. (2003). Atmospheric science: Ultraviolet light and leaf emission of NO_X. Nature, 422, 134.

Harley PC; Litvak ME; Sharkey TD; Monson RK. (1994). Isoprene emission from velvet bean leaves: Interactions among nitrogen availability, growth photon flux density, and leaf development. Plant Physiol, 105, 279-285.

Harmon SM; King JK; Gladden JB; Chandler GT; Newman LA. (2004). Methylmercury formation in a wetland mesocosm amended with sulfate. Environ Sci Technol, 38, 650-656.

Harpole WS; Potts DL; Suding KN. (2007). Ecosystem responses to water and nitrogen amendment in a California grassland. Glob Change Biol, 13, 2341-2348.

Harriman R; Morrison BRS. (1982). Ecology of streams draining forested and non-forested catchments in an area of central Scotland subject to acid precipitation. Hydrobiologia, 88, 251-263.

Harris GW; Carter WPL; Winer AM; Pitts JN Jr; Platt U; Perner D. (1982). Observations of nitrous acid in the Los Angeles atmosphere and implications for predictions of ozone-precursor relationships. Environ Sci Technol, 16, 414-419.

Harris HH; Pickering IJ; George GN. (2003). The chemical form of mercury in fish. Science, 301, 1203.

Harris RC; Rudd JWM. (2007). Whole-ecosystem study shows rapid fish-mercury response to changes in mercury deposition. Proc Natl Acad Sci USA, 104, 16586-16591.

Harrison RM; Kitto A-MN. (1994). Evidence for a surface source of atmospheric nitrous acid. Atmos Environ, 28, 1089-1094.

Harrison RM; Peak JD; Collins GM. (1996). Tropospheric cycle of nitrous acid. J Geophys Res, 101, 14429-14439.

Hartman MD; Baron JS; Ojima DS. (2005a). Calculating pre-measurement atmospheric deposition, stream chemistry, and soil chemistry for an alpine watershed in Rocky Mountain National Park, Colorado. In: Abstracts of the Ecological Society of America 90th annual meeting; held in Montreal, Canada; Aug 7-12, 2005.

Hartman MD; Baron JS; Ojima DS; Parton WJ. (2005b). Modeling the timeline for surface water acidification from excess nitrogen deposition for Rocky Mountain National Park. In: Abstracts of the George Wright Society biennial conference; Philadelphia, PA.

Hartman MD; Baron JS; Ojima DS. (2007). Application of a coupled ecosystem-chemical equilibrium model, DayCent-Chem, to stream and soil chemistry in a Rocky Mountain watershed. Ecol Modell, 200, 493-510.

Harvey H; Lee C. (1982). Historical fisheries changes related to surface water pH changes in Canada. In: Johnson RE (Ed.), Acid rain/ fisheries (pp. 44-55). Bethesda, MD: American Fisheries Society.

Harwell MA; Myers V; Young T; Bartuska A; Gassman N; Gentile JH; Harwell CC; Appelbaum S; Barko J; Causey B; Johnson C; McLean A; Smola R; Templet P; Tosini S. (1999). A framework for an ecosystem integrity report card. BioScience, 49, 543-556.

Hasler AD. (1947). Eutrophication of lakes by domestic drainage. Ecology, 28, 383-395.

Hassan R; Scholes R; Ash N. (2005). Ecosystem change and human well-being. In: Hassan R; Scholes R. (Eds). Current state and trends assessment: Volume 1: Findings of the condition and trends working group (Chapter 5; http://www.millenniumassessment.org/en/Condition.aspx). Nairobi, Kenya; Millennium Ecosystem Assessment; United Nations Environment Programme (UNEP): Island Press.

Hauer FR; Spencer CN. (1998). Phosphorous and nitrogen dynamics in streams associated with wildfire: A study of immediate and longterm effects. Int J Wildland Fire, 8, 183-198.

Havas M; Hutchinson TC; Likens GE. (1984). Red herrings in acid rain research. Environ Sci Technol, 18, 176A-186A.

Havas, M. (1985). Aluminum bioaccumulation and toxicity to Daphnia magna in soft water at low pH. Can J Fish Aquat Sci, 42, 1741-1748.

Havas M. (1986). Effects of acid deposition on aquatic ecosystems. In Stern A (Ed.), Air pollution (Vol. VI, pp. 351-389). New York, NY: Academic Press.

Havas M; Woodfine DG; Lutz P; Yung K; MacIsaac HJ; Hutchinson TC. (1995). Biological recovery of two previously acidified, metal-contaminated lakes near Sudbury, Ontario, Canada. Water Air Soil Pollut, 85, 791-796.

Havens KE; Yan ND; Keller W. (1993). Lake acidification: effects on crustacean zooplankton populations. Environ Sci Technol, 27, 1621-1624.

Havens KE; Carlson RE. (1998). Functional complementarity in plankton communities along a gradient of acid stress. Environ Pollut, 101, 427-436.

Hawksworth DL. (2002). Bioindication calibrated scales and their utility. In: Nimis PL; Scheidegger C; Wolseley PA (Eds.), Monitoring with lichens-monitoring lichens: Proceedings of the NATO Advanced Research Workshop on Lichen Monitoring (pp. 11-20). Netherlands: Kluwer Academic Publishers.

Hawley GJ; Schaberg PG; Eagar C; Borer CH. (2006). Calcium addition at the Hubbard Brook Experimental Forest reduced winter injury to red spruce in a high-injury year. Can J Forest Res, 36, 2544-2549.

Haya K; Waiwood BA. (1981). Acid pH and chorionase activity of Atlantic salmon (*Salmo salar*) eggs. Bull Environ Contam Toxicol, 27, 7-12.

Hayden KL; Anlauf KG; Hastie DR; Bottenheim JW. (2003). Partitioning of reactive atmospheric nitrogen oxides at an elevated site in southern Quebec, Canada. J Geophys Res, 108, doi: 10.1029/2002JD003188.

Hayden MJ; Ross DS. (2005). Denitrification as a nitrogen removal mechanism in a Vermont peatland. J Environ Qual, 34, 2052-2061.

Haynes RW; Adams DM. (1992). Assessing economic impacts of air pollution damage to U.S. forests. In: de Steiguer JE (Ed.),The economic impact of air pollution on timber markets: Studies from North America and Europe. (General technical report no. SE-75). Asheville, NC; Southeastern Forest Experiment Station ; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Hazlett PW; Gordon AM; Voroney RP; Sibley PK. (2007). Impact of harvesting and logging slash on nitrogen and carbon dynamics in soils from upland spruce forests in northeastern Ontario. Soil Biol Biogeochem, 39, 43-57.

He Y; Zhou X; Hou J; Gao H; Bertman SB. (2006). Importance of dew in controlling the air-surface exchange of HONO in rural forested environments. Geophys Res Lett, 33, L02813, doi:10.1029/2005GL024348.

Heal GM; Barbier EB; Boyle KJ. (2005). Valuing Ecosystem Services: Toward Better Environmental Decision Making. http://www.nap.edu/openbook.php?isbn=030909318X. Washington, DC: The National Academies Press.

Heber AJ; Ni JQ; Haymore BL; Duggirala RK; Keener KM. (2001). Air quality and emission measurement methodology at swine finishing buildings. Trans of the ASAE, 44, 1765-1778.

Hebestreit K; Stutz J; Rosen D; Matveiv V; Peleg M; Luria M; Platt U. (1999). DOAS measurements of tropospheric bromine oxide in mid-latitudes. Science, 283, 55-57.

Heck WW; Adams RM; Cure WW; Heagle AS; Heggestad HE; Kohut RJ; Kress LW; Rawlings JO; Taylor OC. (1983). A reassessment of crop loss from ozone. Environ Sci Technol, 17, 573A-581A.

Hecnar SJ. (1995). Acute and chronic toxicity of ammonium-nitrate fertilizer to amphibians from southern Ontario. Environ Toxicol Chem, 14, 2131-2137.

Hedin LO; Likens GE; Postek KM; Driscoll CT. (1990). A field experiment to test whether organic acids buffer acid deposition. Nature, 345, 798-800.

Hedin LO; Granat L; Likens GE; Buishand TA; Galloway JN; Butler TJ; Rodhe H. (1994). Steep declines in atmospheric base cations in regions of Europe and North America. Nature, 367, 351-354.

Hedin LO; Armesto JJ; Johnson AH. (1995). Patterns of nutrient loss from unpolluted, old-growth temperate forests: evaluation of biogeochemical theory. Ecology, 76, 493-509.

Hedin LO; von Fischer JC; Ostrom NE; Kennedy BP; Brown MG; Robertson GP. (1998). Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. Ecology, 79, 684-703.

Heeb NV; Schmid P; Kohler M; Gujer E; Zennegg M; Wenger D; Wichser A; Ulrich A; Gfeller U; Honegger P; Zeyer K; Emmenegger L; Petermann JL; Czerwinski J; Mosimann T; Kasper M; Mayer A. (2008). Secondary effects of catalytic diesel particulate filters: conversion of PAHs versus formation of nitro-PAHs. Environ Sci Technol, 42, 3773-3779.

Hefting MM; Bobbink R; De Caluwe H. (2003). Nitrous oxide emission and denitrification in chronically nitrate-loaded riparian buffer zones. J Environ Qual, 32, 1194-1203.

Heil GW; Diemont WH. (1983). Raised nutrient levels change heathland in grassland. Vegetation, 53, 113-120.

Heil GW; Bruggink M. (1987). Competition for nutrients between *Calluna vulgaris* (L.) Hull and *Molinia caerulea* (L.) Moench. Oecologia, 73, 105-107.

Heinz G. (1974). Effects of low dietary levels of methyl mercury on mallard reproduction. Bull Environ Contam Toxicol, 11, 386-392.

Heinz GH. (1979). Methylmercury: reproductive and behavioral effects on three generations of mallard ducks. J Wildl Manage, 43, 394-401.

Hemond HF. (1980). Biogeochemistry of Thoreau's Bog, Concord, Massachusetts. Ecol Monogr, 50, 507-526.

Hemond HF. (1990). Wetlands as the source of dissolved organic carbon to surface waters. In: Perdue M; Gjessing ET (Eds.), Organic acids in aquatic ecosystems (pp. 301-313). New York, NY: Wiley & Sons.

Hemond HF. (1994). Role of organic acids in acidification of fresh waters. In Steinberg C; Wright R (Eds.), Acidification of freshwaters: Implications for the future. (Report of the Dahlem workshop on acidification of freshwater ecosystems; held in Berlin, Germany; September-October 1992 (pp. 103–116). New York, NY: John Wiley & Sons.

Hendrickson OQ. (1990). Asymbiotic nitrogen fixation and soil metabolism in three Ontario forests. Soil Biol Biochem, 22, 967-971.

Hendry CD; Brezonik PL. (1984). Chemical composition of softwater Florida lakes and their sensitivity to acid precipitation. JAWRA, 20, 75-86.

Hennigan CJ; Sandholm S; Kim S; Stickel RE; Huey LG; Weber RJ. (2006). Influence of Ohio River valley emissions on fine particle sulfate measured from aircraft over large regions of the eastern United States and Canada during INTEX-NA. J Geophys Res, 111, doi:10.1029/2006JD007282.

Henriksen A. (1980).Acidification of freshwaters - a large scale titration. In: Drablos D; Tollan A, (Eds.), Ecological impact of acid precipitation: Proceedings of an international conference; held in Sandefjord, Norway in March 1980. (SNSF Project; pp 68-74). Oslo, Norway; The Norwegian Interdisciplinary Research Programme.

Henriksen A. (1984). Changes in base cation concentrations due to freshwater acidification. Verh Internat Verein Limnol, 22, 692-698.

Henriksen A; Skogheim OK; Rosseland BO. (1984). Episodic changes in pH and aluminium-speciation kill fish in a Norwegian salmon river. Vatten, 40, 255-260.

Henriksen A; Kamari J; Posch M; Wilander A. (1992). Critical loads of acidity: Nordic surface waters. Ambio, 356-363.

Henriksen, A; Dillon PJ. (2001). Critical load of acidity to surface waters in south-central Ontario, Canada. I: Application of the Steady-State Water Chemistry SSWC model. (Acid Rain Research Report no 2001:52). Oslo, Norway; Norwegian Institute for Water Research (NIVA).

Henriksen A; Posch M. (2001). Steady-state models for calculating critical loads of acidity for surface waters. Water Air Soil Pollut: Focus, 1, 375-398.

Henriksen A; Dillon PJ; Aherne J. (2002). Critical loads of acidity to surface waters in south-central Ontario, Canada: Regional application of the steady-state water chemistry model. Can J Fish Aquat Sci, 59, 1287-1295.

Hering SV; Lawson DR; Allegrini I; Febo A; Perrino C; Possanzini M; Sickles JE, II; Anlauf KG; Wiebe A; Appel BR; John W; Ondo J; Wall S; Braman RS; Sutton R; Cass GR; Solomon PA; Eatough DJ; Eatough NL; Ellis EC; Grosjean D; Hicks BB; Womack JD; Horrocks J; Knapp KT; Ellestad TG; Paur RJ; Mitchell WJ; Pleasant M; Peake E; MacLean A; Pierson WR; Brachaczek W; Schiff HI; Mackay GI; Spicer CW. (1988). The nitric acid shootout: Field comparison of measurement methods. Atmos Environ, 22, 1519-1539.

Hering S; Cass G. (1999). The magnitude of bias in the measurement of PM$_{2.5}$ arising from volatilization of particulate nitrate from Teflon filters. J Air Waste Manage Assoc, 49, 725-733.

Herlihy AT; Kaufman PR; Mitch ME. (1991). Stream chemistry in the eastern United States 2. Current sources of acidity in acidic and low acid-neutralizing capacity streams. Water Resour Res, 27, 629-642.

Herlihy AT; Kaufmann PR; Church MR; Wigington PJ Jr; Webb JR; Sale MJ. (1993). The effects of acidic deposition on streams in the Appalachian Mountain and Piedmont region of the mid-Atlantic United States. Water Resour Res, 29, 2687-2703.

Herlihy AT; Larsen DP; Paulsen SG; Urquhart NS; Rosenbaum BJ. (2000). Designing a spatially balanced, randomized site selection process for regional stream surveys: The EMAP mid-Atlantic pilot study. Environ Monit Assess, 63, 95-113.

Hess PG. (2001). Model and measurement analysis of springtime transport and chemistry of the Pacific Basin. J Geophys Res, 106, 12689-12717.

Hicke JA; Asner GA; Randerson JT; Tucker CJ; Los S; Birdsey RA; Jenkins JC; Field CB. (2002). Trends in North American net primary productivity derived from satellite observations, 1982-1998. Glob Biogeochem Cycles, 16, 2-1 – 2-15, doi: 10.1029/2001GB001550.

Hicks BB; Baldocchi DD; Meyers TP; Hosker RP Jr; Matt DR. (1987). A preliminary multiple resistance routine for deriving dry deposition velocities from measured quantities. Water Air Soil Pollut, 36, 311-330.

Hicks BB; McMillen RT; Turner RS; Holdren J; Strickland TC. (1993). A national critical loads framework for atmospheric deposition effects assessment: III: Deposition characterization. Environ, Manage, 17, 343-353.

Higley B; Carrick HJ; Brett MT; Luecke C; Goldman, CR. (2001). The effects of ultraviolet radiation and nutrient additions on periphyton biomass and composition in a sub-alpine lake (Castle Lake, USA). Int Rev Hydrobiol, 86, 147-163.

Hill AB. (1965). The Environment and Disease: Association or Causation? Proc R Soc Med, 58, 295-300.

Hill AR. (1996). Nitrate removal in stream riparian zones. J Environ Qual, 25, 743-755.

Hill BH; Elonen CM; Jicha TM; Cotter AM; Trebitz AS; Danz NP. (2006). Sediment microbial enzyme activity as an indicator of nutrient limitation in Great Lakes coastal wetlands. Fresh Biol, 51, 1670-1683.

Hill WR; Knight AW. (1988). Nutrient and light limitation of algae in 2 northern California streams. J Phycol, 24, 125-132.

Hilliard JC; Wheeler RW. (1979). Nitrogen dioxide in engine exhaust. Paper presented at the SAE Passenger Car Meeting; Dearborn, MI, June 11-15, 1979. (Paper #790691). SAE Trans, 88, 790691.

Hindar A; Posch M; Henriksen A; Gunn J; Snucins E. (2000). Development and application of the FAB model to calculate critical loads of S and N for lakes in the Killarney Provincial Park (Ontario, Canada). (NIVA report SNO 4202-2000). Oslo, Norway: Norwegian Institute for Water Research (NIVA).

Hindar A; Posch M; Henriksen A. (2001). Effects of in-lake retention of nitrogen on critical load calculations. Water Air Soil Pollut, 130, 1403-1408.

Hinga KR; Keller AA; Oviatt CA. (1991). Atmospheric deposition and nitrogen inputs to coastal waters. Ambio, 20, 256-260.

Hintelmann H; Evans RD. (1997). Application of stable isotopes in environmental tracer studies – measurement of monomethylmercury ($CH3Hg^+$) by isotope dilution ICP-MS and detection of species transformation. Fresenius J Anal Chem, 358, 378-385.

Hobbie SE. (1996). Temperature and plant species control over litter decomposition in Alaskan tundra. Ecol Monogr, 66, 503-522.

Hoell JM; Davis DD; Liu SC; Newell RE; Akimoto H; McNeal RJ; Bendura RJ. (1997). The Pacific exploratory mission-west phase B: February-March, 1994. J Geophys Res, 102, 28223-28239.

Hoell JM; Davis DD; Jacob DJ; Rodgers MO; Newell RE; Fuelberg HE; McNeal RJ; Raper JL; Bendura RJ. (1999). Pacific exploratory mission in the tropical Pacific: PEM-Tropics A, August-September 1996. J Geophys Res, 104, 5567-5583.

Hoffman DJ; Moore JM. (1979). Teratogenic effects of external egg applications of methyl mercury in the mallard, *Anas platyrynchos*. Teratology, 20, 453-461.

Hofmann D; Butler J; Dutton E; Elkins J; Ogren J; Oltmans S; Tans P; Schnell R. (2004). Variation in the direct radiative climate forcing by well-mixed greenhouse gases over the past 25 years. Geophys Res Abstr, 6, 00545, doi: 1607-7962/gra/EGU04-A-00545.

Hogan GD; Rennenberg H; Fink S. (1998a). Role and effect of sulfur in tree biology. In Maynard DG (Ed.), Sulfur in the environment (pp. 173-217). New York, NY: Marcel Dekker.

Hogan K; Marcus A; Smith R; White P. (1998b). Integrated exposure uptake biokinetic model for lead in children: Empirical comparisons with epidemiologic data. Environ Health Perspect, 106, 1557-1567.

Högberg P; Fan H; Quist M; Binkleys D; Oloftamm C. (2006). Tree growth and soil acidification in response to 30 years of experimental nitrogen loading on boreal forest. Glob Chang Biol, 12, 489-499.

Högbom L; Högberg P. (1991). Dynamics of soil nitrate after forest fertilization as monitored by the plant nitrate reductase assay. Forest Ecol Manage, 44, 223–238.

Holdren GR Jr; Strickland TC; Cosby BJ; Marmorek D; Bernard D; Santore R; Driscoll CT; Pardo L; Hunsaker C; Turner RS; Aber J. (1993a). A national critical loads framework for atmospheric deposition effects assessment: IV. Model selection, applications and critical loads mapping. Environ Manage, 17, 355-363.

Holdren GR; Strickland TC; Rosenbaum BJ; Turner RE; Ryan PF; McDowell MK; Bishop GD. (1993b). Comparison of selected critical loads estimation approaches for assessing the effects of sulfate deposition on lakes in the northeastern United States. (Report no EPA/600/R93/074). Washington, D.C; U.S. Environmental Protection Agency.

Holdren GR; Strickland TC; Shaffer PW; Ryan PF; Ringold PL; Turner RS. (1993c). Sensitivity of critical load estimates for surface waters to model selection and regionalization schemes. J Environ Qual, 22, 279-289.

Holland EA; Lamarque JF. (1997). Modeling bio-atmospheric coupling of the nitrogen cycle through NO_X emissions and NO_Y deposition. Nutr Cycling Agroecosyst, 48, 7-24.

Holland EA; Braswell BH; Lamarque JF; Townsend A; Sulzman JM; Muller JF; Dentener F; Brasseur G; Levy H; Penner JE; Roelofs GJ. (1997). Variations in the predicted spatial distribution of atmospheric nitrogen deposition and their impact on carbon uptake by terrestrial ecosystems. J Geophys Res, 102, 15849-15866.

Holland EA; Dentener FJ; Braswell BH; Sulzman JM. (1999). Contemporary and pre-industrial global reactive nitrogen budgets. Biogeochemistry, 46, 7-43.

Holland EA; Braswell BH; Sulzman J; Lamarque JF. (2005). Nitrogen deposition onto the United States and western Europe: Synthesis of observations and models. Ecol Appl, 15, 38-57.

Holland HD. (1978). The chemistry of the atmosphere and oceans. New York, NY: John Wiley & Sons.

Hollenhorst SJ; Brock SM; Freimund WA; Twery MJ. (1993). Predicting the effects of gypsy moth on near-view aesthetic preferences and recreation appeal. For Sci, 39, 28-40.

Hollwedel J; Wenig M; Beirle S; Kraus S; Kühl S; Wilms-Grabe W; Platt U; Wagner T. (2004). Year-to-year variations of spring time polar tropospheric BrO as seen by GOME. Adv Space Res, 34, 804-808.

Holmes RW; Whiting MC; Stoddard JL. (1989). Changes in diatom-inferred pH and add neutralizing capacity in a dilute, high elevation, Sierra Nevada lake since AD 1825. Freshw Biol, 21, 295-310.

Holmes TP. (1992). Economic welfare impacts of air pollution damage to forests in the southern United States. In: de Steiguer JE (Ed.), The economic impact of air pollution on timber markets: Studies from North America and Europe. (General Technical Report SE-75; pp. 19-26). Asheville, NC; Southeastern Forest Experiment Station; U.S. Forest Service; U.S. Department. of Agriculture (USDA).

Holmes TP; Kramer RA. (1996). Contingent valuation of ecosystem health. Ecosystem Health, 2, 56-60.

Holmes TP; Murphy EA; Bell KP. (2006). Exotic forest insects and residential property values. Agricultural and Resource Economics Review, 35, 155-166.

Holt CA; Yan N D; Somers KM. (2003). pH 6 as the threshold to use in critical load modeling for zooplankton community change with acidification in lakes of south-central Ontario: accounting for morphometry and geography. Can J Fish Aquat Sci, 60, 151-158.

Holt C; Yan ND. (2003). Recovery of crustacean zooplankton communities from acidification in Killarney Park, Ontario, 1971-2000: pH 6 as a recovery goal. R Swed Acad Sci, 32, 203-207.

Holtze KE; Hutchinson NJ. (1989). Lethality of low pH and Al to early life stages of six fish species inhabiting precambrian shield waters in Ontario. Can J Fish Aquat Sci, 46, 1188-1202.

Holzmueller E; Jose S; Jenkins M; Camp A; Long A. (2006). Dogwood anthracnose in eastern hardwood forests: What is known and what can be done? Journal of Forestry, 104, 21-26.

Holzmueller EJ; Jose S; Jenkins MA. (2007). Influence of calcium, potassium, and magnesium on Cornus florida L. density and resistance to dogwood anthracnose. Plant Soil, 290, 189-199.

Honrath RE; Guo S; Peterson MC; Dziobak MP; Dibb JE; Arsenault MA. (2000). Photochemical production of gas phase NO_X from ice crystal NO_3^-. J Geophys Res, 105, 24183-24190.

Honrath RE; Lu Y; Peterson MC; Dibb JE; Arsenault MA; Cullen NJ; Steffen K. (2002). Vertical fluxes of NO_X, HONO, and HNO_3 above the snowpack at Summit, Greenland. Atmos Environ, 36, 2629-2640.

Hooper DU; Vitousek PM. (1997). The effects of plant composition and diversity on ecosystem processes. Science, 277, 1302-1305.

Hooper DU, Johnson L. (1999). Nitrogen limitation in dryland ecosystems: responses to geographical and temporal variation in precipitation. Biogeochemistry, 46, 247–293.

Hoppel WA; Caffrey PF. (2005). Oxidation of S(IV).in sea-salt aerosol at high pH: ozone versus aerobic reaction. J Geophys Res, 110, D23202, doi:10.1029/2005JD006239.

Horii CV. (2002). Tropospheric reactive nitrogen speciation, deposition, and chemistry at Harvard Forest [dissertation]. Cambridge, MA: Harvard University.

Horii CV; Munger JW; Wofsy SC; Zahniser M; Nelson D; McManus JB. (2004). Fluxes of nitrogen oxides over a temperate deciduous forest. J Geophys Res, 109, D08305: doi: 10.1029/2003JD004326.

Horii C; Munger JW; Wofsy S; Zahniser M; Nelson D; McManus JB. (2006). Atmospheric reactive nitrogen concentrations and flux budgets at a northeastern U.S forest site. Ag For Meteor, 136, 159-174.

Hornbeck JW; Bailey SW; Buso DC; Shanley JB. (1997). Streamwater chemistry and nutrient budgets for forested watersheds in New England" variability and management implications. For Ecol Manage, 93, 73-89.

Hornberger GM; Cosby BJ; Wright RF. (1989). Historical reconstructions and future forecasts of regional surface water acidification in southernmost Norway. Water Resource Research, 25, 2009-2018.

Hornung M; Bull KR; Cresser M; Hall J; Langan SJ; Loveland P; Smith C. (1995). An empirical map of critical loads of acidity for soils in Great Britain. Environ Pollut, 90, 301-310.

Horowitz LW; Liang J; Gardner GM; Jacob DJ (1998). Export of reactive nitrogen from North America during summertime: Sensitivity to hydrocarbon chemistry. J Geophys Res, 103, 13451–13476

Horowitz LW; Walters S; Mauzerall DL; Emmons LK; Rasch PJ; Granier C; Tie X; Lamarque J-F; Schultz MG; Tyndall GS; Orlando JJ; Brasseur GP. (2003). A global simulation of tropospheric ozone and related tracers: description and evaluation of MOZART, version 2. J Geophys Res, 108, 4784, doi:10.1029/2002JD002853.

Horowitz LW; Fiore AM; Milly GP; Cohen RC; Perring A; Wooldridge PJ; Hess PG; Emmons LK; Lamarque JF. (2007). Observational constraints on the chemistry of isoprene nitrates over the eastern United States. J Geophys Res, 112, 10.1029/2006JD007747.

Horsley SB; Long RP; Bailey SW; Hallet RA; Hall TJ. (1999). Factors contributing to sugar maple decline along topographic gradients on the glaciated and unglaciated Allegheny Plateau. In: Horsely SB; Long RP, (Eds.), Sugar maple ecology and health: proceedings of an international symposium; June 1998; (General technical report NE-261, pp 60-62). Warren, PA. Radnor, PA; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Horsley SB; Long RP; Bailey SW; Hallett RA; Hall TJ. (2000). Factors associated with the decline disease of sugar maple on the Allegheny Plateau. Can J For Res, 30, 1365-1378.

Hosker RP; Lindberg SE. (1982). Review Article: Atmospheric deposition and plant assimilation of airborne gases and particles. Atmos Environ, 16, 889-910.

Houdijk A; Verbeek PJM; Van Dijk HFG; Roelofs JGM. (1993). Distribution and decline of endangered herbaceous heathland species in relation to the chemical composition of the soil. Plant Soil, 148, 137-143.

Houghton RA. (2003). Why are estimates of the terrestrial carbon balance so different? Glob Chang Biol, 9, 500-509.

Houle D; Carignan R; Ouimet R. (2001). Soil organic sulfur dynamics in a coniferous forest. Biogeochemistry, 53, 105-124.

Houlton BZ; Driscoll CT; Fahey TJ; Likens GE; Groffman PM; Bernhardt ES; Buso DC. (2003). Nitrogen dynamics in ice storm-damaged forest ecosystems: Implications for nitrogen limitation theory. Ecosystems, 6, 431-443.

Houston DR. (1994). Major new tree epidemics: beech bark disease. Annu Rev Phytopathol, 32, 75-87.

Howarth RW; Billen G; Swaney D; Townsend A; Jaworski N; Lajtha K; Downing JA; Elmgren R; Caraco N; Jordan T; Berendse F; Freney J; Kudeyarov V; Murdoch PS; Zhao-Liang Z. (1996). Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: natural and human influences. Biogeochemistry, 35, 75-139.

Howarth RW; Anderson D; Cloern J; Elfring C; Hopkinson C; Lapointe B; Malone T; Marcus N; McGlathery K; Sharpley A; Walker D. (2000). Nutrient pollution of coastal rivers, bays, and seas. Iss Ecol, 1-15.

Howarth RW, Sharpley A; Walker D. (2002a). Sources of Nutrient Pollution to Coastal Waters in the United States: Implications for Achieving Coastal Water Quality Goals. Estuaries, 25: 656-676.

Howarth RW; Boyer EW; Pabich WJ; Galloway JN. (2002b). Nitrogen use in the United States from 1961-2000 and potential future trends. Ambio, 31, 88-96.

Howarth RW; Marino R. (2006). Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: evolving views over three decades. Limnol Oceanogr, 51, 364-376.

Howarth RW; Swaney DP; Boyer EW; Marino R; Jaworski N; Goodale C. (2006). The influence of climate on average nitrogen export from large watersheds in the Northeastern United States. Biogeochemistry, 79, 163-186.

Howarth RW. (2007). Atmospheric deposition and nitrogen pollution in coastal marine ecosystems. In: Visgilio GR, Whitelaw DM (Eds.), Acid in the Environment. New York, NY: Springer.

Howes BL; Dacey JWH; Goehringer DD. (1986). Factors controlling the growth form of *Spartina alterniflora*: feedbacks between above-ground production, sediment oxidation, nitrogen and salinity. J Ecol, 74, 881-898.

Hrabik TR; Watras CJ. (2002). Recent declines in mercury concentration in a freshwater fishery: isolating the effects of de-acidification and decreased atmospheric mercury deposition in Little Rock Lake. Sci Total Environ, 297, 229-237.

Huberty LE; Gross KL; Miller CJ. (1998). Effects of nitrogen addition on successional dynamics and species diversity in Michigan old-fields. J Ecol, 86, 794-803.

Hübler G; Alvarez R II; Daum P; Dennis R; Gillani N; Kleinman L; Luke W; Meagher J; Rider D; Trainer M; Valente R. (1998). An overview of the airborne activities during the Southern Oxidants Study (SOS) 1995 Nashville/Middle Tennessee ozone study. J Geophys Res, 103, 22245-22259.

Hudman RC; Jacob DJ; Cooper OR; Evans MJ; Heald CL; Park RJ; Fehsenfeld F; Flocke F; Holloway J; Hubler G; Kita K; Koike M; Kondo Y; Neuman A; Nowak J; Oltmans S; Parrish D; Roberts JM; Ryerson T. (2004). Ozone production in transpacific Asian pollution plumes and implications for ozone air quality in California. J Geophys Res, 109, doi:10.1029/2004JD004974.

Hudman RC; Jacob DJ; Turquety S; Leibensperger EM; Murray LT; Wu S; Gilliland AB; Avery M; Bertram TH; Brune W; Cohen RC; Dibb JE; Flocke FM; Fried A; Holloway J; Neuman JA; Orville R; Perring A; Ren X; Sachse GW; Singh HB; Swanson A; Wooldridge PJ. (2007). Surface and lightning sources of nitrogen oxides over the United States: magnitudes, chemical evolution, and outflow. J Geophys Res, 112, doi:10.1029/2006JD007912.

Huebert DB; L'Hirondelle SJ; Addison PA. (1985). The effects of sulfur dioxide on net CO_2 assimilation in the lichen *Evernia mesomorpha* Nyl. New Phytol, 100, 643-651.

Huebert BJ; Zhuang L; Howell S; Noone K; Noone B. (1996). Sulfate, nitrate, methanesulfonate, chloride, ammonium, and sodium measurements from ship, island, and aircraft during the Atlantic Stratocumulus Transition Experiment/Marine Aerosol Gas Exchange. J Geophys Res, 101, 4413-4423.

Huey LG; Dunlea EJ; Lovejoy ER; Hanson DR; Norton RB; Fehsenfeld FC; Howard CJ. (1998). Fast time response measurements of HNO_3 in air with a chemical ionization mass spectrometer. J Geophys Res, 103, 3355-3360.

Huey LG; Tanner DJ; Slusher DL; Dibb JE; Arimoto R; Chen G; Davis D; Buhr MP; Nowak JB; Mauldin RL. (2004). CIMS measurements of HNO_3 and SO2 at the South Pole during ISCAT 2000. Atmos Environ, 38, 5411-5421.

Hulsman PF; Powles PM; Gunn JM. (1983). Mortality of walleye eggs and rainbow trout yolk-sac larvae in low-pH waters of the LaCloche Mountain area, Ontario. Trans Am Fish Soc, 112, 680-683.

Hultberg H; Andersson I. (1982). Liming of acidified lakes: induced long-term changes. Water Air Soil Pollut, 18, 311-331.

Humphreys FR; Lambert MJ; Kelly J. (1975). The occurrence of sulphur deficiency in forests. In: McLachlan, K. D., ed. Sulphur in Australasian agriculture. (pp. 154-162.). Sydney, Australia: Sydney University Press.

Hungate BA; Lund CP; Pearson HL; Chapin FS. (1997). Elevated CO_2 and nutrient addition alter soil N cycling and N trace gas fluxes with early season wet-up in a California annual grassland. Biogeochem, 37, 89-109.

Hunsaker C; Graham R; Turner RS; Ringold PL; Holdren GR Jr; Strickland TC. (1993). A national critical loads framework for atmospheric deposition effects assessment: II. Defining assessment end points, indicators, and functional subregions. Environ Manage, 17, 335-341.

Hunter MD; Schultz JC. (1995). Fertilization mitigates chemical induction and herbivore responses within damaged oak trees. Ecology, 76, 1226-1232.

Hunter ML; Jones JJ; Gibbs KE; Moring JR. (1986). Duckling responses to lake acidification: do black ducks and fish compete? Oikos, 47, 26-32.

Huntington TG. (2000). The potential for calcium depletion in forest ecosystems of southeastern United States: review and analysis. Glob Biogeochem Cycles, 14, 623-638.

Huntington TG; Hooper RP; Johnson CE; Aulenbach BT; Cappellato R; Blum AE. (2000). Calcium Depletion in a Southeastern United States Forest Ecosystem. Soil Sci Soc Am J, 64, 1845-1858.

Huntrieser H; Feigl C; Schlager H; Schroder F; Gerbig C; Van Velthoven P; Flatoy F; Thery C; Petzold A; Holler H; Schumann U. (2002). Airborne measurements of NO_X, tracer species, and small particles during the European Lightning Nitrogen Oxides Experiment. J Geophys Res, 107, 4113, doi:10.1029/2000JD000209.

Huntrieser H; Schlager H; Roiger A; Lichtenstern M; Schumann U; Kurz C; Brunner D; Schwierz C; Richter A; Stohl A. (2007). Lightning-produced NO_X over Brazil during TROCCINO$_X$: airborne measurements in tropical and subtropical thunderstorms and the importance of mesoscale convective systems. Atmos Chem Phys, 7, 2987-3013.

Huntzicker JJ; Hoffman RS; Ling C-S. (1978). Continuous measurement and speciation of sulfur-containing aerosols by flame photometry. Atmos Environ, 12, 83-88.

Hurd TM; Brach AR; Raynal DJ. (1998). Response of understory vegetation of Adirondack forests to nitrogen additions. Can J For Res, 28, 799-807.

Hurd TM; Raynal DJ; Schwintzer CR. (2001). Symbiotic N2 fixation of Alnus incana ssp. rugosa in shrub wetlands of the Adirondack Mountains, New York, USA. Oecologia, 126, 94-103.

Hurrell JW. (1995). Decadal trends in the North Atlantic Oscillation: regional temperatures and precipitation. Science, 269, 676-679.

Husar RB; Sullivan TJ. (1991). Historical trends in atmospheric sulfur deposition and methods for assessing long-term trends in surface water chemistry. In: Charles DF; Christie S (Eds.), Acidic deposition and aquatic ecosystems: regional case studies (pp. 65-82). New York: Springer-Verlag.

Husar RB; Poirot RL. (2005). DataFed and Fastnet: Tools for agile air quality analysis. http://datafedwiki.wustl.edu/images/c/c4/EM_DataFed_FASTNET_050720.pdf. Environ Manager, 39-41.

Hutchinson J; Maynard D; Geiser L. (1996). Air quality and lichens - a literature review emphasizing the Pacific Northwest, USA. Pacific Northwest Region Air Resource Management Program; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Hutchinson NJ; Holtze KE; Munro JR; Pawson TW. (1989). Modifying effects of life stage, ionic strength and post-exposure mortality n lethality of H+ and Al to lake trout and brook trout. Aquat Toxicol, 15, 1-26.

Hutchinson TC; Bozic L; Munoz-Vega G. (1986). Responses of five species of conifer seedlings to aluminum stress. Water Air Soil Pollut, 31, 283-294.

Hyer KE; Webb JR; Eshleman KN. (1995). Episodic acidification of three streams in Shenandoah National Park, Virginia, USA. Water Air Soil Pollut, 85, 523-528.

Hyvarinen M; Crittenden PD. (1998). Relationships between atmospheric nitrogen inputs and the vertical nitrogen and phosphorus concentration gradients in the lichen Cladonia portentosa. New Phytol, 140, 519-530.

Hyvönen R; Ågren GI; Linder S; Persson T; Cotrufo MF; Ekblad A; Freeman M; Grelle A; Janssens IA; Jarvis PG. (2007). The likely impact of elevated CO_2, nitrogen deposition, increased temperature and management on carbon sequestration in temperate and boreal forest ecosystems: a literature review. New Phytol, 173, 463-480.

IARC. (1989). Diesel and gasoline engine exhausts and some nitroarenes: Summary of data reported and evaluation. Volume 46 of IARC Monographs on the evaluation of carcinogenic risks to humans. Lyons, France: International Agency for Research on Cancer (IARC); World Health Organization (WHO).

IARC. (2006). Preamble to the IARC monographs on the evaluation of carcinogenic risks to humans: http://monographs.iarc.fr/ENG/Preamble/CurrentPreamble.pdf. Lyon, France: International Agency for Research on Cancer (IARC), World Health Organization (WHO).

ICP. (2007a). Developments in deriving critical limits and modeling critical loads of nitrogen for terrestrial ecosystems in Europe. (Alterra report no 1382). The International Cooperative Programme (ICP) on Modelling and Mapping of Critical Loads & Levels and Air Pollution Effects, Risks and Trends works under the Convention on Long-range Transboundary Air Pollution of the United Nations Economic Commission for Europe (UNECE).

ICP. (2007b). CCE Progress Report 2007: Critical loads of nitrogen and dynamic modeling - Status of European critical loads with focus on nitrogen. The International Cooperative Programme (ICP) on Modelling and Mapping of Critical Loads & Levels and Air Pollution Effects, Risks and Trends works under the Convention on Long-range Transboundary Air Pollution of the United Nations Economic Commission for Europe (UNECE).

IEc. (1999a). Benefits Assessment of Decreased Nitrogen Deposition to Estuaries in the United States Attributable to the 1990 Clean Air Act Amendments, 1990-2010. Referenced in: Economic benefits of decreasing atmospheric deposition of nitrogen, in Appendix E (Ecological Effects of Criteria Pollutants). In: The benefits and costs of the Clean Air Act 1990 to 2010: A report to Congress. (Report # EPA-410-R-99-001). Prepared by Industrial Economics, Inc (IEc) for Office of Air and Radiation; Office of Policy; U.S. Environmental Protection Agency.

IEc. (1999b). Characterizing the Commercial Timber Benefits from Tropospheric Ozone Reduction Attributable to the 1990 Clean Air Act Amendments, 1990-2010: Referenced in: Timber production impacts from tropospheric ozone, in Appendix E (Ecological effects of criteria pollutants). In: The benefits and costs of the Clean Air Act 1990 to 2010: A report to Congress. (Report # EPA-410-R-99-001). Prepared by Industrial Economics (IEc) Inc, for Office of Air and Radiation; Office of Policy; U.S. Environmental Protection Agency.

IEc. (1999c).Characterizing the forest aesthetics benefits attributable to the 1990 Clean Air Act Amendments, 1990-2010. Referenced in: Timber production impacts from tropospheric ozone, in Appendix E (Ecological effects of criteria pollutants). In: The benefits and costs of the Clean Air Act 1990 to 2010: A report to Congress. (Report # EPA-410-R-99-001). Prepared by Industrial Economics (IEc), Inc, for Office of Air and Radiation; Office of Policy; U.S. Environmental Protection Agency.

Ilvesniemi H. (1992). The combined effect of mineral nutrition and soluble aluminum on *Pinus sylvestris* and *Picea abies* seedlings. For Ecol Manage, 51, 227-238.

Ineson P; Coward P; Benham DG; Robertson SMC. (1998). Coniferous forests as "secondary agricultural" sources of nitrous oxide. Atmos Environ, 32, 3321-3330.

Ingersoll CG. (1986). The effects of pH, aluminum, and calcium on survival and growth of brook trout (*Salvelinus fontinalis*).early life stages [dissertation]. Laramie, WY; University of Wyoming; Department of Zoology and Physiology. Ann Arbor, MI: ProQuest; publication no. AAD86-23090.

Ingersoll CG; Gulley DD; Mount DR; Mueller ME; Fernandez JD; Hockett JR; Bergman HL. (1990a). Aluminum and acid toxicity to two strains of brook trout (*Salvelinus fontinalis*). Can J Fish Aquat Sci, 47, 1641-1648.

Ingersoll CG; Mount DR; Gulley DD; La Point TW; Bergman HL. (1990b). Effects of pH, aluminum, and calcium on survival and growth of eggs and fry of brook trout (*Salvelinus fontinalis*). Can J Fish Aquat Sci, 47, 1580-1592.

Inouye RS. (2006). Effects of shrub removal and nitrogen addition on soil moisture in sagebrush steppe. J Arid Environ, 65, 604-618.

Interlandi SJ; Kilham SS. (1998). Assessing the effects of nitrogen deposition on mountain waters: a study of phytoplankton community dynamics. Water Science and Technology, 38, 139-146.

Interlandi SJ; Kilham SS; Theriot EC. (1999). Responses of phytoplankton to varied resource availability in large lakes of the Greater Yellowstone ecosystem. Limnol Oceanogr; 44; 668-682.

Interlandi SJ; Kilham SS. (2001). Limiting resources and the regulation of diversity in phytoplankton communities. Ecology, 82, 1270-1282.

IPCC. (1996). Climate Change 1995: The Science of Climate Change. In: Houghton JT (Ed.), Working Group I of the Intergovernmental Panel on Climate Change (IPCC): Climate Change 1995: The Science of Climate Change. New York, NY: Cambridge University Press.

IPCC. (1999).Aviation and the global atmosphere. Cambridge, United Kingdom: Cambridge University Press. Available: http://www.ipcc.ch/ipccreports/sres/aviation/index.htm.

IPCC. (2000). Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories: http://www.ipcc-nggip.iges.or.jp/public/gp/english/. Intergovernmental Panel on Climate Change (IPCC), in response to a request from the United Nations Framework Convention on Climate Change (UNFCCC). New York, NY: Cambridge University Press.

IPCC. (2001a). Climate change 2001: The scientific basis. In: Houghton JT; Ding Y; Griggs DJ; Noguer M; van der Linden PJ; Dai X; Maskell K; Johnson CA (Eds.), Working Group I of the intergovernmental panel on climate change (IPCC): Climate change 2001: The scientific basis. New York, NY: Cambridge University Press.

IPCC. (2001b). Climate change 2001: Impacts, adaptation, and vulnerability. Contribution of working group II to the third assessment report of the Intergovernmental Panel on Climate Change. Cambridge, United Kingdom: Cambridge University Press.

IPCC. (2007a).Summary for policymakers. In: Solomon S; Qin D; Manning M; Solomon S; Chen Z; Marquis M; Averyt KB; Tignor M; Miller HL Eds. Climate Change 2007: The physical science basis. Contribution of Working Group I to the fourth assessment report of the Intergovernmental Panel on Climate Change (IPCC). . http://www.ipcc.ch/ipccreports/ar4-wg1.htm New York, NY: Cambridge Unviersity Press.

IPCC. (2007b).Climate change 2007: Impacts, adaptation and vulnerability. Contribution of Working Group II to the fourth assessment report of the Intergovernmental Panel on Climate Change. http://www.ipcc.ch/ipccreports/assessments-reports.htm Cambridge, United Kingdom: Cambridge University Press.IPCC (2007). Climate change impacts, adaptation and vulnerability. Working group II: Contribution to the intergovernmental panel on climate change (IPCC): Fourth assessment Report. New York, NY: Cambridge University Press.

IPCS. (2003). Nitrogenated polycyclic aromatic hydrocarbons. (Environmenal Health Criteria no 229). Geneva, Switzerland; International Programme on Chemical Safety (IPCS); World Health Organization (WHO).

Irving PM; Miller JE; Xerikos PB. (1982). The effect of NO_2 and SO_2 alone and in combination on the productivity of field-grown soybeans. In: Schneider T; Grant L (Eds.), Air Pollution by Nitrogen Oxides (pp. 521-531). Amsterdam, The Netherlands: Elsevier Scientific Publishing Company.

Isopp H; Frehner M; Almeida JPF; Blum H; Daepp M; Hartwig UA; Luscher A; Suter S; Nosberger J. (2000). Nitrogen plays a major role in leaves when source-sink relations change: C and N metabolism in Lolium perenne growing under free air CO_2 enrichment. Aust J Plant Physiol; 27; 851-858.

Ito M; Mitchell MJ; Driscoll CT. (2002). Spatial patterns of precipitation quantity and chemistry and air temperature in the Adirondack region of New York. Atmos Environ, 36, 1051-1062.

Ito M; Mitchell MJ; Driscoll CT; Roy KM. (2005a). Factors affecting acid neutralizing capacity in the Adirondack region of New York: a solute mass balance approach. Environ Sci Technol; 39; 4076-4081.

Ito M; Mitchell MJ; Driscoll CT; Roy KM. (2005b). Nitrogen input-output budgets for lake-containing watersheds in the Adirondack region of New York. Biogeochemistry, 72, 283-314.

Ito M; Mitchell MJ; Driscoll CT; Newton RM; Johnson CE; Roy KM. (2007). Controls on surface water chemistry in two lake-watersheds in the Adirondack region of New York: differences in nitrogen solute sources and sinks. Hydrological Processes, 21, 1249-1264.

Ittekot V. (2003). Carbon-silicon interactions. In: Melillo JM; Field CB; Moldan B. Eds. Interactions of the major biogeochemical cycles: global change and human impacts. Washington, D.C.: Island Press; pp. 311-322.

Izuta TM, H; Ohashi, T; Miyake, H; Totsuka, T. (1993). Effects of peroxyacetyl nitrate on the growth of petunia, kidney bean and radish plants. Environmental Sciences, 2, 63-75.

Izuta, T. (1998). Ecopysiological responses of Japanese forest tree species to ozone, simulated acid rain and soil acidification. J Plant Res, 111, 471-480.

Jackson DA; Harvey HH. (1995). Gradual reduction and extinction of fish populations in acid lakes. Water Air Soil Pollut, 85, 389-394.

Jackson JBC; Kirby MX; Berger WH; Bjorndal KA; Botsford LW; Bourque BJ; Bradbury RH; Cooke R; Erlandson J; Estes JA; Hughes TP; Kidwell S; Lange CB; Lenihan HS; Pandolfi JM; Peterson CH; Steneck RS; Tegner, MJ; Warner RR. (2001). Historical overfishing and recent collapse of coastal ecosystems. Science, 293, 629-637.

Jacob DJ; Bakwin PS. (1991). Cycling of NO_X in tropical forest canopies. In: Rogers JE; Whitman WB. Eds. Microbial production and consumption of greenhouse gases. Washington, DC: American Society of Microbiology; pp. 237-253.

Jacob DJ; Horowitz LW; Munger JW; Heikes BG; Dickerson RR; Artz RS; Keene WC. (1995). Seasonal transition from NO_X- to hydrocarbon-limited conditions for ozone production over the eastern United States in September. J Geophys Res, 100, 9315-9324.

Jacob DJ. (1999). Introduction to atmospheric chemistry. Princeton, NJ: Princeton University Press.

Jacob DJ. (2000). Heterogeneous chemistry and tropospheric ozone. Atmos Environ, 34, 2131-2159.

Jacobs TC; Gilliam JW. (1985). Riparian losses of nitrate from agricultural drainage waters. J Environ Qual, 14, 472-478.

Jacobson MZ; Lu R; Turco RP; Toon OP. (1996). Development and application of a new air pollution modeling system-Part I: gas-phase simulations. Atmos Environ, 30, 1939-1963.

Jacobson MZ. (1999). Isolating nitrated and aromatic aerosols and nitrated aromatic gases as sources of ultraviolet light absorption. J Geophys Res, 104, 3527-3542.

Jacobson MZ. (2002). Atmospheric pollution: history, science, and regulation. Cambridge, UK: Cambridge University Press.

Jaeglé L; Jacob DJ; Wennberg PO; Spivakovsky CM; Hanisco TF; Lanzendorf EJ; Hintsa EJ; Fahey DW; Keim ER; Proffitt MH; Atlas EL; Flocke F; Schauffler S; McElroy CT; Midwinter C; Pfister L; Wilson JC. (1997). Observed OH and HO_2 in the upper troposphere suggests a major source from convective injection of peroxides. Geophys Res Lett, 24, 3181-3184.

Jaeglé L; Jacob DJ; Brune WH; Wennberg PO. (2001). Chemistry of HOx radicals in the upper troposphere. Atmos Environ, 35, 469-489.

Jaeglé L; Martin RV; Chance K; Steinberger L; Kurosu TP; Jacob DJ; Modi AI; Yoboue V; Sigha-Nkamdjou L; Galy-Lacaux C. (2004). Satellite mapping of rain-induced nitric oxide emissions from soils. J Geophys Res, 109, doi:10.1029/2004JD004787.

Jaeglé L; Steinberger L; Martin RV; Chance K. (2005). Global partitioning of NOx sources using satellite observations: Relative roles of fossil fuel combustion, biomass burning and soil emissions. Faraday Discuss,130, 407-423.

Jager HJ; Klein H. (1977). Biochemical and physiological detection of sulfur dioxide injury to pea plants (Pisum sativum). Journal of Air and Waste Management Association, 27, 464-466.

Jager H-J; Klein H. (1980). Biochemical and physiological effects of SO_2 on plants. Angewandte Botanik, 54, 337-348.

Jagoe CH; Haines TA; Kircheis FW. (1984). Effects of reduced pH on three life stages of Sunapee char *Salvelinus alpinus*. Bull Environ Contam Toxicol, 33, 430-438.

Jaklevic JM; Loo BW; Fujita TY. (1981). Automatic particulate sulfur measurements with a dichotomous sampler and on-line x-ray fluorescence analysis. Environ Sci Technol, 15, 687-690.

Jakus PM; Smith VK. (1991). Measuring use and nonuse values for landscape amenities: A contingent behavior analysis of gypsy moth control (RFF Discussion Paper #QE92-07). Washington DC: Resources for the Future (RFF).

Jansson M; Bergstrom AK; Drakare S; Blomquist P. (2001). Nutrient limitation of bacterioplankton and phytoplankton in humic lakes in northern Sweden. Freshw Biol, 46, 653-666.

Jassby AD; Reuter JE; Axler RP; Goldman CR; Hackley SH. (1994). Atmospheric deposition of N and phosphorus in the annual nutrient load of Lake Tahoe (California-Nevada). Water Resour Res, 30, 2207-2216.

Jaworski NA; Howarth RS; Hetling LJ. (1997). Atmospheric deposition of nitrogen oxides onto the landscape contributes to coastal eutrophication in the northeast United States. Environ Sci Technol, 31, 1995-2004.

Jayanty RKM. (2003). Overview of $PM_{2.5}$ chemical speciation nationwide network program. Presented at the american association for aerosol research (AAAR) conference: Particulate matter: Atmospheric sciences, exposure and the fourth colloquium on PM and human health, held in Pittsburgh, PA; March 31 – April 4, 2003 Mt Laurel, NJ; American Association for Aerosol Research (AAAR). http://www.rti.org/pubs/PM25_Overview_Jay_Apr2003.pdf

Jeffries DS; Lam CCL. (1993). Assessment of the effect of acidic deposition on Canadian lakes: determination of critical loads for sulphate deposition. Water Science and Technology, 28, 183-187.

Jeffries DS; Clair TA; Dillon PJ; Papineau M; Stainton MP. (1995). Trends in surface water acidification at ecological monitoring sites in southeastern Canada (1981-1993). Water Air Soil Pollut, 85, 577-582.

Jeffries DS. (1997). Canadian acid rain assessment: The effects on Canada's lakes, rivers and wetlands (Volume 3, pp. 224). Burlington, Ontario: Environment Canada.

Jeffries DS; Semkin RG; Beall FD; Franklyn J. (2002).Temporal trends in water chemistry in the Turkey Lakes watershed, Ontario, Canada, 1982-1999. Water Air Soil Pollut, 2, 5-22.

Jeffries DS; Clair TA; Couture S; Dillon PJ; Dupont J; Keller W; McNicol DK; Turner MA; Vet R; Weeber R. (2003). Assessing the recovery of lakes in southeastern Canada from the effects of acidic deposition. Royal Swedish Academy of Sciences, 32, 176-182.

Jeffries DS; Ouimet R; Aherne J; Arp PA; Balland V; Demerchant I; Dupont J; Franklyn J; Lam CCL; Norouzian F; Watmough SA; Wong I. (2005). Critical load values and exceedances (Chapter 8.4). In: 2004 Canadian acid deposition science assessment. Ottawa, Ontario; Meteorological Service of Canada; Environment Canada.

Jenkin ME; Cox RA; Williams DJ. (1988). Laboratory studies of the kinetics of formation of nitrous acid from the thermal reaction of nitrogen dioxide and water vapour. Atmos Environ, 22, 487-498.

Jenkins A; Cosby BJ; Ferrier RC; Walker TAB; Miller JD. (1990). Modelling stream acidification in afforested catchments: an assessment of the relative effects of acid deposition and afforestation. J Hydrol, 120, 163–181.

Jenkins A; Cosby BJ; Ferrier RC; Larssen T; Posch M. (2003). Assessing emission reduction targets with dynamic models: deriving target load functions for use in integrated assessment. Hydrol Earth Syst Sci, 7, 609-617.

Jenkins DH; Sullivan J; Amacher GS. (2002). Valuing high altitude spruce-fir forest improvements: Importance of forest condition and recreation activity. J For Econ, 8, 77-99.

Jenkins DH; Sullivan J; Amacher G S; Nicholas NS; Reaves DW. (2002). Valuing high altitude spruce-fir forest improvements: importance of forest condition and recreation activity. J For Econ, 8, 77-99.

Jenkinson DS; Goulding K; Powlson DS. (1999). Nitrogen deposition and carbon sequestration. Nature, 400, 629-629.

Jeremiason JD; Engstrom DR; Swain EB; Nater EA; Johnson BM; Almendinger JE; Monson BA; Kolka RK. (2006). Sulfate Addition Increases Methylmercury Production in an Experimental Wetland. Environ Sci Technol, 40, 3800-3806.

Jetten MSM; Sliekers O; Kuypers MMM; Dalsgaard T; Van Niftrik L; Cirpus I; Van de Pas-Schoonen KT; Lavik G; Thamdrup B; Le Paslier D; Op Den Camp HJM; Hulth S; Nielsen LP; Abma W; Third K; Engstrom P; Kuenen JG; Jorgensen BB; Canfield DE; Damste JSS; Revsbech NP; Fuerst J; Weissenbach J; Wagner M; Schmidt I; Schmid M; Strous M. (2003). Anaerobic ammonium oxidation by marine and freshwater planctomycete-like bacteria. Applied Microbiology and Biotechnology, 63, 107-114.

Jetten MSM; Cirpus I; Kartal B; van Niftrik L; van de Pas-Schoonen KT; Sliekers O; Haaijer SCM; Van der Star WRL; Schmid M; Van de Vossenberg J; Schmidt I; Harhangi HR; van Loosdrecht M; Gijs Kuenen J; Op den Camp H; Strous M. (2005). 1994-2004: 10 years of research on the anaerobic oxidation of ammonium. Biochemical Society Transactions, 33, 119-123.

Jimenez P; Baldasano JM; Dabdub D. (2003). Comparison of photochemical mechanisms for air quality modeling. Atmos Environ, 37, 4179-4194.

Jobson BT; Niki H; Yokouchi Y; Bottenheim J; Hopper F; Leaitch R. (1994). Measurements of C2-C6 hydrocarbons during the Polar Sunrise 1992 Experiment: evidence for Cl atom and Br atom chemistry. J Geophys Res, 99, 25355-25368.

Johannessen M; Henriksen A. (1978). Chemistry of snow meltwater: Changes in concentrations during melting. Water Resour Res, 14, 615-619.

Johansson A; Lennholm H. (2000). Influences of SO_2 and O_3 on the ageing of paper investigated by in situ diffuse reflectance FTIR and time-resolved trace gas analysis. Appl Surf Sci, 161, 163-169.

Johansson M; Rasanen K; Merila J. (2001). Comparison of nitrate tolerance between different populations of the common frog, *Rana temporaria*. Aquat Toxicol, 54, 1-14.

Johansson N; Kihlström JE. (1975). Pikes (*ESOₓ lucius* L.) shown to be affected by low pH values during first weeks after hatching. Environ Res, 9, 12-17.

Johansson N; Milbrink G. (1976). Some effects of acidified water on the early development of roach (*Rutilus rutilus* L.) and perch (*Perca fluviatilis* L.). Water Resour Bull, 12, 39-48.

Johansson N; Runn P; Milbrink G. (1977). Early development of three salmonid species in acidified water. Zoon, 5, 127-132.

John W; Wall SM; Ondo JL. (1988). A new method for nitric acid and nitrate aerosol measurement using the dichotomous sampler. Atmos Environ, 22, 1627-1635.

Johnson AH; Andersen SB; Siccama TG. (1994a). Acid rain and soils of the Adirondacks. I. Changes in pH and available calcium, 1930-1984. Can J For Res, 24, 39-45.

Johnson AH; Friedland AJ; Miller EK; Siccama TG. (1994b). Acid rain and soils of the Adirondacks. III. Rates of soil acidification in a montane spruce-fir forest at Whiteface Mountain, New York. Can J For Res, 24, 663-669.

Johnson CE; Johnson AH; Siccama TG. (1991a). Whole-tree clear-cutting effects on exchangeable cations and soil acidity. Soil Sci Soc Am J, 55, 502-508.

Johnson CE. (1995). Soil nitrogen status 8 years after whole-tree clear-cutting. Can J Forest. Res, 25, 1346-1355.

Johnson DW; Cole DW. (1980). Mobility in soils: Relevance to nutrient transport from forest ecosystems. Environ Int, 3, 79-90.

Johnson, DW; Cole DW; Bledsoe CS; Cromack K; Edmonds RL; Gessel SP; Grier CC; Richards BN; Vogt KA. (1982a). Nutrient cycling in forests of the Pacific Northwest. In: Edmonds RL (Ed.), Analysis of coniferous forest ecosystems in the Western United States. (U.S./IBP synthesis series: Volume 14, pp 186-232). Stroudsburg, PA: Hutchinson Ross Publishing Company.

Johnson DW; Henderson GS; Huff DD; Lindberg SE; Richter DD; Shriner DS; Todd DE; Turner J. (1982b). Cycling of organic and inorganic sulphur in a chestnut oak forest. Oecologia, 54, 141-148.

Johnson DW; Turner J; Kelly JM. (1982c). The effects of acid rain on forest nutrient status. Water Resour Res, 18, 449-461.

Johnson DW. (1984). Sulfur cycling in forests. Biogeochem, 1, 29-43.

Johnson DW; Simonin HA; Colquhoun JR; Flack FM. (1987). In situ toxity tests of fishes in acid waters. Biogeochem, 3, 181-208.

Johnson DW; Kelly JM; Swank WT; Cole DW; Van Miegroet H; Hornbeck JW; Pierce RS; Van Lear D. (1988). The effects of leaching and whole-tree harvesting on cation budgets of several forests. J Environ Qual, 17, 418-424.

Johnson DW; Todd DE. (1990). Nutrient cycling in forests of Walker Branch Watershed Tennessee: roles of uptake and leaching in causing soil changes. J Environ Qual, 19, 97-104.

Johnson DW; Cresser MS; Milsson SI; Turner J; Ulrich B; Binkley D; Cole DW. (1991b). Soil changes in forest ecosystems: evidence for and probable causes. Proceedings of the Royal Society of Edinburg Section B: Biol Sci, 97B, 81-116.

Johnson DW; Van Miegroet H; Lindberg SE; Todd DE; Harrison RB. (1991c). Nutrient cycling in red spruce forests of the Great Smoky Mountains. Can J For Res, 21, 769-787.

Johnson DW; Fernandez IJ. (1992). Soil-mediated effects of atmospheric deposition on eastern U.S. spruce-fir forests. In: Eagar C; Adams MB (Eds.), Ecology and decline of red spruce in the eastern United States. (Series Volume 96 of: Ecology studies; pp 235-270). New York, NY: Springer-Verlag.

Johnson DW; Lindberg SE. (1992a). Atmospheric deposition and forest nutrient cycling: A synthesis of the integrated forest study. (Series: Billings WD; Golley F; Lange OL; Olson JS; Remmert H (Eds.), Ecological Studies: Analysis and Synthesis, Volume 91). New York, NY: Springer-Verlag.

Johnson DW; Lindberg SE. (1992b). Nitrogen chemistry, deposition, and cycling in forests. In: Johnson DW; Lindberg SE (Eds.), Atmospheric deposition and forest nutrient cycling: A synthesis of the integrated forest study. (Series: Billings WD; Golley F; Lange OL; Olson JS; Remmert H (Eds.), Ecological Studies: Analysis and Synthesis, Volume 91; pp. 150-213). New York, NY: Springer-Verlag, Inc

Johnson DW; Swank WT; Vose JM. (1993). Simulated effects of atmospheric sulfur deposition on nutrient cycling in a mixed deciduous forest. Biogeochemistry, 23, 169-196

Johnson DW; Binkley D; Conklin P. (1995). Simulated effects of atmospheric deposition, harvesting, and species change on nutrient cycling in a loblolly pine forest. For Ecol Manage, 76, 29-45.

Johnson DW; Susfalk RB; Brewer PF. (1996). Simulated responses of red spruce forest soils to reduced sulfur and nitrogen deposition. J Environ Qual, 25, 1300-1309.

Johnson DW; Mitchell MJ. (1998). Responses of forest ecosystems to changing sulfur inputs. In: Maynard DG (Ed.), Sulfur in the environment (pp. 219-262). New York, NY: Marcel Dekker, Inc.

Johnson DW; Curtis PS. (2001). Effects of forest management on soil C and N storage: Meta analysis. For Ecol Manage, 140, 227-238.

Johnson DW; Susfalk RB; Caldwell TG; Murphy JD; Miller WW; Walker RF. (2004). Fire effects on carbon and nitrogen budgets in forests. Water Air Soil Pollut, 4, 263-275.

Johnson DW. (2005). Comments on "Thirty years of change in forest soils of the Allegheny Plateau, Pennsylvania." Soil Sci. Soc. Amer. J. 69: 2077, doi: 10.2136/sssaj2005.0197l.

Johnson DW; Murphy JF; Susfalk RB; Caldwell TG; Miller WW; Walker RF; Powers RF. (2005a). The effects of wildfire, salvage logging, and post-fire N-fixation on the nutrient budgets of a Sierran forest. For Ecol Manage, 220, 155-165.

Johnson DW; Hoylman AM; Ball JT; Walker RF. (2006). Ponderosa pine responses to elevated CO_2 and nitrogen fertilization. Biogeochem, 77, 157-175.

Johnson DW; Todd DE; Trettin CF; Mulholland PJ. (2008). Changes in soil exchangeable K+, Ca2+, and Mg2+ in forests of Walker Branch Watershed, 1972-2004. Soil Sci Soc Am J, (In press).

Johnson GV. (1991). General Model for Predicting Crop Response to Fertilizer. Agron J, 83, 367-373.

Johnson LB; Richards C; Host GE; Arthur JW. (1997). Landscape influences on water chemistry in Midwestern stream ecosystems. Freshw Biol, 37, 193-208.

Johnson MG; Phillips DL; Tingey DT; Storm MJ. (2000). Effects of elevated CO2, N-fertilization, and season on survival of ponderosa pine fine roots. Can J For Res, 30, 220-228.

Johnson NM; Driscoll CT; Eaton JS; Likens GE; McDowell WH. (1981). "Acid Rain", dissolved aluminum and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire. Geochim Cosmochim Acta, 45, 1421-1437.

Johnston RJ; Besedin EY; Ranson MH; Helm EC. (2005b). What determines willingness to pay per fish? A meta-analysis of recreational fishing values. Mar Resource Econ, 21, 1–32.

Johnson T. (2002). A guide to selected algorithms, distributions, and databases used in exposure models developed by the Office of Air Quality Planning and Standards [revised draft]. http://www.epa.gov/ttn/fera/data/human/report052202.pdf. Chapel Hill, NC Piscataway, New Jersey: TRJ Environmental, Inc & Environmental and Occupational Health Sciences Institute. prepared for Office of Air Quality Planning and Standards (OAQPS); U.S. Environmental Protection Agency.

Jones JA; Swanson FJ; Wemple BC; Snyder KU. (2000). Effects of roads on hydrology, geomorphology, and disturbances patches in stream networks. Conserv Biol, 14, 76-85.

Jones ME; Paine TD; Fenn ME; Poth MA. (2004). Influence of ozone and nitrogen deposition on bark beetle activity under drought conditions. For Ecol Manage, 200, 67-76.

Joos F; Prentice IC; House JI. (2002). Growth enhancement due to global atmospheric change as predicted by terrestrial ecosystem models: consistent with U.S. forest inventory data. Glob Change Biol, 8, 299-303.

Jordan TE; Correll DL; Weller DE. (1993). Nutrient interception by a riparian forest receiving inputs from adjacent cropland. J Environ Qual, 22, 467-473.

Jordan TE; Weller DE. (1996). Human contributions to terrestrial nitrogen flux. Bioscience, 46, 655-664.

Joseph DW; Spicer CW. (1978). Chemiluminescence method for atmospheric monitoring of nitric acid and nitrogen oxides. Anal Chem, 50, 1400-1403.

Joslin JD; Mays PA; Wolfe MH; Kelly JM; Garber RW; Brewer PF. (1987). Chemistry of tension lysimeter water and lateral flow in spruce and hardwood stands. J Environ Qual, 16, 152-160.

Joslin JD; Wolfe MH. (1988). Responses of red spruce seedlings to changes in soil aluminum in six amended forest soil horizons. Can J For Res, 18, 1614-1623.

Joslin JD; Wolfe MH. (1989). Aluminum effects on northern red oak seedling growth in six forest soil horizons. Soil Sci Soc Am J, 53, 274-281.

Joslin JD; Wolfe MH. (1992a). Red spruce soil solution chemistry and root distribution across a cloud water deposition gradient. Can J For Res, 22, 893-904.

Joslin JD; Wolfe MH. (1992b). Tests of the use of net throughfall sulfate to estimate dry and occult sulfur deposition. Atmos Environ, 63-72.

Joslin JD; Kelly JM; van Miegroet H. (1992). Soil chemistry and nutrition of North American spruce-fir stands: evidence for recent change. J Environ Qual, 21, 12-30.

Joslin JD; Wolfe MH. (1994). Foliar deficiencies of mature Southern Appalachian red spruce determined from fertilizer trials. Soil Sci Soc Am J, 58, 1572-1579.

Jouen S; Jean M; Hannover B. (2004). Atmospheric corrosion of nickel in various outdoor environments. Corros Sci, 46, 499-514.

Jovan S; McCune B. (2005). Air-quality bioindication in the greater central valley of California, with epiphytic macrolichen communities. Ecol Appl, 15, 1712-1726.

Jovan S; McCune B. (2006). Using epiphytic macrolichen communities for biomonitoring ammonia in forests of the greater Sierra Nevada, California. Water Air Soil Pollut, 170, 69-93.

JPL. (2003). Chemical kinetics and photochemical data for use in atmospheric studies. (No. Evaluation number 15. JPL publication 06-2). Pasadena, CA; Jet Propulsion Laboratory (JPL); National Aeronautics and Space Administration (NASA).

Juggins S; Omerod SJ; Harriman R. (1995). Relating critical loads to aquatic biota. In: Critical loads of acid deposition for UK freshwaters (pp 9-13). London UK: Department of the Environment.

Juice SM; Fahey TJ; Siccama TG; Driscoll CT; Denny EG; Eagar C; Cleavitt NL; Minocha R; Richardson AD. (2006). Response of sugar maple to calcium addition to Northern Hardwood Forest. Ecology, 87, 1267-1280.

Junge CE; Chagnon CW; Manson JE. (1961). Stratospheric aerosols. Journal of Meteorol, 18, 81-108.

Justic D; Rabalais NN; Turner RE; Wiseman WJ Jr. (1993). Seasonal coupling between riverborne nutrients, net productivity and hypoxia. Mar Pollut Bull, 26, 184-189.

Justic D; Rabalais NN; Turner RE; Dortch Q. (1995a). Changes in nutrient structure of river-dominated coastal waters: Stoichiometric nutrient balance and its conseqeuences. Estuarine Coastal & Shelf Science, 40, 339-356.

Justic D; Rabalais NN; Turner RE. (1995b). Stoichiometric nutrient balance and origin of coastal eutrophication. Marine Pollution Bulletin, 30, 41-46.

Justic D; Rabalais NN; Turner RE. (1997). Impacts of climate change on net productivity of coastal waters: implications for carbon budget and hypoxia. Climate Research, 8, 225-237.

Kahl JS; Norton SA; Cronan CS; Fernandez IJ; Bacon LC; Haines TA. (1991). Maine. In: Charles DF, Christie S (Eds.), Acidic deposition and aquatic ecosystems: regional case studies (pp. 203-235). New York, NY: Springer-Verlag.

Kahl JS; Norton SA; Haines TA; Rochette EA; Heath RH; Nodvin SC. (1992). Mechanisms of episodic acidification in low-order streams in Maine, USA. Environ Pollut (1987), 78, 37-44.

Kahl JS; Norton SA; Fernandez IJ; Nadelhoffer KJ; Driscoll CT; Aber JD. (1993a). Experimental inducement of nitrogen saturation at the watershed scale. Environ Sci Technol, 27, 565-568.

Kahl JS; Haines TA; Norton SA; Davis RB. (1993b). Recent trends in the acid-base status of surface waters in Maine, USA. Water Air Soil Pollut, 67, 281-300.

Kahl JS; Scott M. (1994). High elevation lake monitoring in Maine: 1986-1989. August, ME: Maine Department of Environmental Protection.

Kahl J; Norton S; Fernandez I; Rustad L; Handley M. (1999). Nitrogen and sulfur input-output budgets in the experimental and reference watersheds, Bear Brook Watershed in Maine (BBWM). Environ Monit Assess, 55, 113-131

Kahl S. (1999). Responses of Maine surface waters to the Clean Air Act Amendments of 1990. Final report; EPA project CX826563-01-0. Orono, ME; Gulf of Maine Council on the Marine Environment; Water Research Institute; University of Maine-Orono.

Kain JS; Fritsch JM. (1993). Convective parameterization in mesoscale models: The Kain-Fritsch scheme. In: Emanuel KA; Raymond DJ (Eds.),The representation of cumulus convection in numerical models. Meteorological Monographs, (Volume 24, pp 165-170). Boston, MA: American Meteorological Society.

Kainulainen P; Holopainen JK; Oksanen J. (1995). Effects of SO2 on the concentrations of carbohydrates and secondary compounds in Scots Pine (pinus-sylvestris L) and Norway Spruce (picea-abies(L) karst) seedlings. New Phytol, 130, 231-238.

Kaiser EW; Wu CH. (1977). A kinetic study of the gas phase formation and decomposition reactions of nitrous acid. J Phys Chem, 81, 1701-1706.

Kalbitz K; Solinger S; Park JH; Michalzik B; Matzner E. (2000). Controls on the dynamics of dissolved organic matter in soils: A review. Soil Sci, 165, 277-304.

Kameda T; Inazu K; Bandow H; Sanukida S; Maeda Y. (2004). Diurnal change of direct-acting mutagenicity of soluble organic fraction of airborne particles collected at Southern Osaka: Correlation between the mutagenicity, particles-associated nitroarenes, and gaseous emission. Atmos Environ, 38, 1903-1912.

Kamman NC; Lorey PM; Driscoll CT; Estabrook R; Major A; Pientka B; Glassford E. (2004). Assessment of mercury in waters, sediments and biota of New Hampshire and Vermont lakes sampled using a geographically randomized design. Environ Toxicol Chem, 23(5), 1172-1186.

Kana TM; Sullivan MB; Cornwell JC; Groszkowski. (1998). Denitrification in estuarine sediments determined by membrane inlet mass spectrometry. Limnol Oceanogr, 43, 334-339.

Kane DA; Rabeni CF. (1987). Effects of aluminum and pH on the early life stages of smallmouth bass (*Micropterus dolemieui*). Water Res, 21, 633-639.

Kane SM; Caloz F; Leu M-T. (2001). Heterogeneous uptake of gaseous N_2O_5 by $(NH_4)_2SO_4$, NH_4HSO_4, and H_2SO_4 aerosols. J Phys Chem, 105, 6465-6470.

Kaoru Y. (1995). Measuring marine recreation benefits of water quality improvements by the nested random utility model. Resource and Energy Economics, 17, 119-136.

Kaoru Y; Smith VK; Liu JL. (1995). Using random utility models to estimate the recreational value of estuarine resources. Am J Agric Econ, 77, 141-151.

Karnosky DF. (2003). Impacts of elevated atmospheric CO_2 on forest trees and forest ecosystems: Knowledge gaps. Environ Int, 29, 161-169.

Karr JR; Chu LW. (1999). Restoring life in running rivers: better biological monitoring. Washington, DC: Island Press.

Kasibhatla P; Chameides WL. (2000).Seasonal modeling of regional ozone pollution in the eastern United States. Geophys Res Lett, 27, 1415-1418.

Kaufmann PR; Herlihy AT; Elwood JW; Mitch ME; Overton WS; Sale MJ; Messer JJ; Cougan KA; Peck DV; Reckhow KH; Kinney AJ; Christie SJ; Brown DD; Hagley CA; Jager HI. (1988). Chemical characteristics of streams in the Mid-Atlantic and Southeastern United States. Volume I: Population descriptions and physico-chemical relationships (No. EPA/600/3-88/021a). Washington, DC: U.S. Environmental Protection Agency.

Kaufmann PR; Herlihy AT; Mitch ME; Messer JJ; Overton WS. (1991). Stream chemistry in the eastern United States 1. synoptic survey design, acid-base status, and regional patterns. Water Resour Res, 27, 611-627.

Kauppi PE; Mielikäinen K; Kuusela K. (1992). Biomass and carbon budget of European forests, 1971 to 1990. Science, 256, 70-74.

Kebabian PL; Robinson WA; Freedman A. (2007). Optical extinction monitor using cw cavity enhanced detection. Rev Sci Instrum, 78, 063102.

Keck L; Wittmaack K. (2005). Effect of filter type and temperature on volatilisation losses from ammonium salts in aerosol matter. Atmos Environ, 39, 4093-4100.

Keck L; Wittmaack K. (2006). Simplified approach to measuring semivolatile inorganic particulate matter using a denuded cellulose filter without backup filters. Atmos Environ, 40, 7106-7114.

Keene WC; Jacob DJ; Fan S-M. (1996). Reactive chlorine: a potential sink for dimethylsulfide and hydrocarbons in the marine boundary layer. Atmos Environ, 306, i-iii.

Keene WC; Savoie DL. (1998). The pH of deliquesced sea-salt aerosol in polluted marine air. Geophys Res Lett, 25, 2181-2194.

Keene WC; Sander R; Pszenny AAP; Vogt R; Crutzen PJ; Galloway JN. (1998). Aerosol pH in the marine boundary layer: a review and model evaluation. Journal of Aerosol Science, 29, 339-356.

Keene WC; Khalil MAK; Erickson DJ III; McCulloch A; Graedel TE; Lobert JM; Aucott ML; Gong SL; Harper DB; Kleiman G; Midgley P; Moore RM; Seuzaret C; Sturges WT; Benkovitz CM; Koropalov V; Barrie LA; Li YF. (1999). Composite global emissions of reactive chlorine from anthropogenic and natural sources: reactive chlorine emissions inventory. J Geophys Res, 104. 8429-8440.

Keene WC; Pszenny AAP; Maben JR; Sander R. (2002). Variation of marine aerosol acidity with particle size. Geophys Res Lett, 29, 1101, doi:10.1029/2001GL013881.

Keene WC; Pszenny AAP; Maben JR; Stevenson E; Wall A. (2004). Closure evaluation of size-resolved aerosol pH in the New England coastal atmosphere during summer. J Geophys Res, 109, doi:10.1029/2004JD004801.

Keene WC; Lobert RM; Crutzen PJ; Maben JR; Scharffe DH; Landmann T; Hély C; Brain C. (2006). Emissions of major gaseous and particulate species during experimental burns of southern African biomass. J Geophys Res, 111, doi: 10.1029/2005JD006319.

Keene WC; Stutz J; Pszenny AAP; Maben JR; Fischer EV; Smith AM; Von Glasow R; Pechtl S; Sive BC; Varner RK. (2007). Inorganic chlorine and bromine in coastal New England air during summer. J Geophys Res, 112, doi:10.1029/2006JD007689.

Keller JK; Bridgham SD; Chapin CT; Iversen CM. (2005). Limited effects of six years of fertilization on carbon mineralization dynamics in a Minnesota fen. Soil Biol Biochem, 37, 1197-1204.

Keller M; Kaplan WA; Wofsy SC; da Costa JM. (1988). Emissions of N_2O from tropical forest soils: Response to fertilization with NH_4, NO_3^-, and PO_4^{3-}. J Geophys Res, 93, 1600-1604.

Keller W; Pitblado JR. (1986). Water quality changes in Sudbury area lakes: a comparison of synoptic surveys in 1974-1976 and 1981-1983. Water Air Soil Pollut, 29, 285-296.

Keller W; Pitblado JR; Conroy NI. (1986). Water quality improvements in the Sudbury, Ontario, Canada area related to reduced smelter emissions. Water Air Soil Pollut, 31, 765-774.

Keller W; Yan D. (1991). Recovery of crustacean zooplankton species richness in Sudbury area lakes following water quality improvements. Can J Fish Aquat Sci, 48, 1635-1644.

Keller W. (1992). Introduction and overview to aquatic acidificaiton studies in the Sudbury, Ontario, Canada, area. Can J Fish Aquat Sci, 49, 3-7.

Keller W; Gunn JM. (1995). Lake water quality improvements and recovering aquatic communities. In: Gunn JM (Ed.), Restoration and recovery of an industrial region: progress in restoring the smelter-damaged landscape near Sudbury, Canada (pp. 67-80). New York, NY: Springer-Verlag.

Kellman M; Carty A. (1986). Magnitude of nutrient influxes from atmospheric sources to a central american Pinus caribaea woodland. J Appl Ecol, 23, 211-226.

Kelly CA; Rudd JWM; Hesslein RH; Schindler DW; Dillon PJ; Driscoll CT; Gherini SA; Hecky RE. (1987). Prediction of biological acid neutralization in acid sensitive lakes. Biogeochem, 3, 129-140.

Kelly CA; Rudd JW; Holoka MH. (2003). Effect of pH on mercury uptake by an aquatic bacterium: implications for Hg cycling. Environ Sci Technol, 37, 2941-2946.

Kelly J; Lambert M. (1972). The relationship between sulphur and nitrogen in the foliage of *Pinus radiata*. Plant Soil, 37, 395-407.

Kelly RH; Parton WJ; Hartman MD; Stretch LK; Ojima DS; Schimel DS. (2000). Intra- and interannual variability of ecosystem processes in shortgrass steppe. J Geophys Res, 105, 20093–20100.

Kelly TJ; Spicer CW; Ward GF. (1990). An assessment of the luminol chemiluminescence technique for measurement of NO_2 in ambient air. Atmos Environ, 24, 2397-2403.

Kelso JRM; Jeffries DS. (1988). Response of headwater lakes to varying atmospheric deposition in north-central Ontario. Can J Fish Aquat Sci, 45, 1905-1911.

Keltjens WG; Van Loenen E. (1989). Effects of aluminum and mineral nutrition on growth and chemical composition of hydroponically grown seedlings of five different forest tree species. Plant Soil, 119, 39-40.

Kemp WM; Twilley RR; Stevenson JC; Boynton WR; Means JC. (1983). The decline of submerged vascular plants in upper Chesapeake Bay: summary of results concerning possible causes. Marine Technology Society Journal, 17, 78-89.

Kemp WM; Sampou P; Caffrey J; Mayer M; Henriksen K; Boynton WR. (1990). Ammonium recycling versus denitrification in Cheasapeake Bay sediments. Limnol Oceanogr, 35, 1545-1563.

Kendall C; Silva SR; Chang CC; Campbell DH; Burns DA; Shanley JB. (1995). Use of oxygen and nitrogen isotopes to trace sources of nitrate during snowmelt in forested catchments. In: Tonnessen KA, Williams MW, Tranter M (Eds.), Biogeochemistry of Seasonally Snow-Covered Catchments (Vol. Publication no. 228, pp. 339-347): International Association of Hydrologic Sciences.

Kenk G; Fischer H. (1988). Evidence from nitrogen fertilisation in the forests of Germany. Environ Pollut, 54, 199-218.

Kesik M; Ambus P; Baritz R. (2005). Inventory of N_2O and NO emissions from European forest soils. Biogeosciences, 2, 353-375.

Kesik M; Brüggemann N; Forkel R; Kiese R; Knoche R; Li C; Seufert G; Simpson D; Butterbach-Bahl K. (2006). Future scenarios of N_2O and NO emissions from European forest soils. J Geophys Res, 111, doi:10.1029/2005JG000115.

Kessler C; Niederau A; Scholz W. (2006). Estimation of NO_2/NO_X relations of traffic emissions in Baden-Württemberg from 1995 to 2005. Paper presented at the 2nd conference of Environment & Transport, (Joint with 15th conference of Transport and air pollution). Held in Reims, France; June 12-14, 2006. Atmospheric Compositon Change: The European Network of Excellence (ACCENT).

Khan MA; Hany O; Azeem M; Hasan SA; Jabeen S; Khan MA. (2007). Pollution Profile of Malir River. Pak J Sci Ind Res, 50, 96-100.

Khanna PK; Raison RJ. (1986). Effect of fire intensity on solution chemistry of surface soil under a *Eucalyptus pauciflora* forest. Aust J Soil Res, 24, 423-434.

Khanna PK; Raison RJ; Falkiner RA (1994). Chemical properties of ash derived from Eucalyptus litter and its effects on forest soils. For Ecol Manage, 66, 107-125.

Kieft T; Soroker LE; Firestone MK. (1987). Microbial biomass response to a rapid increase in water potential when dry soil is wetted. Soil Biol Biochem, 19, 119-126.

Kielland, K. (1994). Amino acid absorption by arctic plants: Implications for plant nutrition and nitrogen cycling. Ecology, 75, 2373-2383.

Kielland, K. (1995). Landscape patterns of free amino acids in arctic tundra soils. Biogeochem, 31, 85-98.

Killingbeck KT. (1996). Nutrients in senesced leaves: keys to the search for potential resorption and resorption proficiency. Ecology, 77, 1716-1727.

Kim BM; Lester J; Tisopulos L; Zeldin MD. (1999). Nitrate artifacts during $PM_{2.5}$ sampling in the South Coast Air Basin of California. J Air Waste Manage Assoc, 49(special issue), PM142-153.

Kim EY; Murakami T; Saeki K; Tatsukawa R. (1996). Mercury levels and its chemical form in tissues and organs of seabirds. Arch Environ Contam Toxicol, 30, 259-266.

Kim HJ; Helfand GE; Howitt RE. (1998). An economic analysis of ozone control in California's San Joaquin Valley. J Agric Resource Econ, 23, 55-70.

Kim H; Lee J-T; Hong Y-C; Yi S-M; Kim Y. (2004). Evaluating the effect of daily PM10 variation on mortality. Inhalation Toxicology, 1, 55-58.

Kim K-H; Kim M-Y. (2001). Comparison of an open path differential optical absorption spectroscopy system and a conventional in situ monitoring system on the basis of long-term measurements of SO_2, NO_2, and O_3. Atmos Environ, 35, 4059-4072.

Kim S-T; Maedab Y; Tsujino Y. (2004). Assessment of the effect of air pollution on material damages in northeast Asia. Atmos Environ, 38, 37-48.

Kim S-W; Heckel A; McKeen SA; Frost GJ; Hsie EY; Trainer MK; Richter A; Burrows JP; Peckham SE; Grell GA. (2006). Satellite-observed U.S. power plant NO_X emission reductions and their impact on air quality. Geophys Res Lett, 33, doi:10.1029/2006GL027749.

Kimmel WG; Murphey DJ; Sharpe WE; DeWalle DR. (1985). Macroinvetebrate community structure and detritus processing rates in two southwestern Pennsylvania streams acidified by atmospheric deposition. Hydrobiologia, 124, 97-102.

Kincheloe JW; Wedemeyer GA; Koch DL. (1979). Tolerance of developing salmonid eggs and fry to nitrate exposure. Bull Environ Contam Toxicol, 23, 575-578.

King GM; Schnell S. (1994). Ammonium and nitraite inhibition of methane oxidation by *Methylobacter albus* BG8 and *Methylosinus trichosporium* OB3b at Low Methane Concentrations. Appl Environ Microbiol, 60, 3508-3513.

King GM; Schnell S. (1998). Effects of ammonium and non-ammonium salt additions on methane oxidation by *Methylosinus trichosporium* OB3b and Maine forest soils. Appl Environ Microbiol, 64, 253-257.

King JK; Kostka JE; Frischer ME; Saunders FM. (2000). Sulfate-Reducing Bacteria Methylate Mercury at Variable Rates in Pure Culture and in Marine Sediments. Appl Environ Microbiol, 66, 2430-2437.

King JK; Kostka JE; Frischer ME; Saunders FM; Jahnke RA. (2001a). A Quantitative Relationship that Demonstrates Mercury Methylation Rates in Marine Sediments Are Based on the Community Composition and Activity of Sulfate-Reducing Bacteria. Environ Sci Technol, 35, 2491-2496.

King JS; Pregitzer KS; Zak DR; Kubiske ME; Holmes WE. (2001b). Correlation of foliage and litter chemistry of sugar maple, *Acer saccharum*, as affected by elevated CO_2 and varying N availability, and effects on decomposition. Oikos, 94, 403-416.

Kingston JC; Birks HJB. (1990). Dissolved organic carbon reconstruction from diatom assemblages in PIRLA project lakes, North America. Philosophical Transactions of the Royal Society of London, 327, 279-288.

Kingston JC; Cook RB; Kreis RG Jr; Camburn KE; Norton SA; Sweets PR; Binford MW; Mitchell MJ; Schindler SC; Shane LCK; King GA. (1990). Paleoecological investigation of recent lake acidification in the northern Great Lakes states. J Paleolimnol, 4, 153-201.

Kinney KK; Lindroth RL; Jung SM; Nordheim EV. (1997). Effects of CO_2 and NO_3^- availability on deciduous trees: Phytochemistry and insect performance. Ecology, 78, 215-230.

Kirchner JW; Lydersen E. (1995). Base Cation Depletion and Potential Long-Term Acidification of Norwegian Catchments. Environ Sci Technol, 29, 1953-1960.

Kirchstetter TW; Harley RA. (1996). Measurement of nitrous acid in motor vehicle exhaust. Environ Sci Technol, 30, 2843-2849.

Kireev SV; Shnyrev SL; Zhiganov AA. (1999). A laser fluorimeter for NO and NO_2 in atmosphere. Instruments and Experimental Techniques, 42, 701-703.

Kirschbaum MUF. (1994). THe temperature dependence of soil organic matter decomposition, and the effect of global warming on soil organic C storage. Soil Biol Biochem, 27, 753-760.

Kittelson DB; McKenzie R; Vermeersch M; Dorman F; Pui D; Linne M; Liu B; Whitby K. (1978). Total sulfur aerosol concentration with an electrostatically pulsed flame photometric detector system. Atmos Environ, 12, 105-111.

Kittelson DB; Watts WF; Johnson JP; Rowntree C; Payne M; Goodier S; Warrens C; Preston H; Zink U; Ortiz M. (2006). On-road evaluation of two Diesel exhaust aftertreatment devices. Journal of Aerosol Science, 37, 1140-1151.

Kitzler B; Zechmeister-Boltenstern S; Holtermann C; Skiba U; Butterbach-Bahl K. (2006). Nitrogen oxides emission from two beech forests subjected to different nitrogen loads. Biogeosciences, 3, 293-310.

Kjonaas OJ; Wright RF. (1998). Nitrogen leaching from N limited forest ecosystems: The MERLIN model applied to Gardsjon, Sweden. Hydrol Earth Syst Sci, 2, 415-429.

Klauda RJ; Palmer RE. (1987). Responses of blueback herring eggs and larvae to pulses of acid and aluminum. Trans Am Fish Soc, 116, 561-569.

Klauda RJ; Palmer RE; Lenkevich MJ. (1987). Sensitivity of early life stages of blueback herring to moderate acidity and aluminum in soft freshwater. Estuaries, 10, 44-53.

Kleb HR; Wilson SD. (1997). Vegetation effects on soil resource heterogeneity in prairie and forest. American Naturalist, 150, 283-298.

Kleeman MJ; Hughes LS; Allen JO; Cass GR. (1999). Source contributions to the size and composition distribution of atmospheric particles: Southern California in September 1996. Environ Sci Tech, 33, 4331-4341.

Kleffmann J; Becker KH; Wiesen P. (1998). Heterogeneous NO_2 conversion processes on acid surfaces: possible atmospheric implications. Atmos Environ, 32, 2721-2729.

Kleindienst TE. (1994). Recent developments in the chemistry and biology of peroxyacetyl nitrate. Res Chem Intermed, 20, 335-384.

Kleinman LI. (1991). Seasonal dependence of boundary-layer peroxide concentration: the low and high NO_X regimes. J Geophys Res, 96, 20721-20733.

Kleinman LI; Daum PH; Imre DG; Lee JH; Lee Y-N; Nunnermacker LJ; Springston SR; Weinstein-Lloyd J; Newman L. (2000). Ozone production in the New York City urban plume. J Geophys Res, 105, 14495-14511.

Kleinman LI; Daum PH; Lee Y-N; Nunnermacker LJ; Springston SR; Weinstein-Lloyd J; Rudolph J. (2001). Sensitivity of ozone production rate to ozone precursors. Geophys Res Lett, 28, 2903-2906.

Klemedtsson L; Klemedtsson AK; Moldan F; Weslien P. (1997). Nitrous oxide emission from Swedish forest soils in relation to liming and simulated increased N-deposition. Biol Fertil Soils, 25, 290-295.

Kley D; Crutzen PJ; Smit HGJ; Vomel H; Oltmans SJ; Grassl H; Ramanathan V. (1996). Observations of near-zero ozone concentrations over the convective Pacific: effects on air chemistry. Science, 274, 230-233.

Klironomos JN; Rillig MC; Allen MF; Zak DR; Kubiske M; Pregitzer KS. (1997). Soil fungal-arthropod responses to *Populus tremuloides* grown under enriched atmospheric CO_2 under field conditions. Glob Change Biol, 3, 473-478.

Klopatek JM; Barry MJ; Johnson DW. (2006). Potential canopy interception of nitrogen in the Pacific Northwest, USA. For Ecol Manage, 234, 344-354.

Knapp AK; Smith MD (2001). Variation among biomes in temporal dynamics of aboveground primary production. Science, 291, 481–484.

Knight H. (1966). Loss of nitrogen from the forest floor by burning. For Chron, 42. 149-152.

Knights JS; Zhao FJ; Spiro B; McGrath SP. (2000). Long-term effects of land use and fertilizer treatments on sulfur cycling. J Environ Qual, 29, 1867-1874.

Knoepp JD; Swank WT. (1994). Long-term soil chemistry changes in aggrading forest ecosystems. Soil Sci Soc Am J, 58, 325-331.

Knorr M; Frey SD; Curtis PS. (2005). Nitrogen additions and litter decomposition: A meta-analysis. Ecology, 86, 3252-3257.

Kobe RK; Likens GE; Eagar C. (2002). Tree seedling growth and mortality responses to manipulations of calcium and aluminum in a northern hardwood forest. Can J Forest Res, 32, 954-966.

Koch MS; Mendelssohn IA; McKee KL. (1990). Mechanism for the hydrogen sulfide-induced growth limitation in wetland macrophytes. Limnol Oceanogr, 35, 399-408.

Kochy M; Wilson SD. (2001). Nitrogen deposition and forest expansion in the northern Great Plains. J Ecol, 89, 807-817.

Koerselman W. (1989). Groundwater and surface water hydrology of a small groundwater-fed fen. Wetlands Ecol Manag, 1, 31-43

Koerselman W; Van Kerkhoven MB; Verhoeven JTA. (1993). Release of inorganic N, P, and K in peat soils; effect of temperature, water chemistry and water level. Biogeochemistry, 20, 63-81.

Kooijman AM; Bakker C. (1994). The acidification capacity of wetland bryophytes as influenced by simulated clean and polluted rain. Aquatic Botany, 48, 133-144.

Kopp RJ; Vaughn WJ; Hazilla M; Carson R. (1985). Implications of environmental policy for U.S. agriculture: The case of ambient ozone standards. J Environ Manage, 20, 321-331.

Korb JE; Ranker TA. (2001). Changes in stand composition and structure between 1981 and 1996 in four Front Range plant communities in Colorado. Plant Ecology, 157, 1-11.

Korhonen P; Kulmala M; Laaksonen A; Viisanen Y; McGraw R; Seinfeld JH. (1999). Ternary nucleation of H_2SO_4, NH3, and H2O in the atmosphere. J Geophys Res, 104, 26349-26353.

Kotchenruther RA; Jaffe DA; Jaegle L. (2001). Ozone photochemistry and the role of peroxyacetyl nitrate in the springtime northeastern Pacific troposphere: results from the Photochemical Ozone Budget of the Eastern North Pacific Atmosphere (PHOBEA).campaign. J Geophys Res, 106, 28731-28742.

Koutrakis P; Wolfson JM; Slater JL; Brauer M; Spengler JD; Stevens RK; Stone CL. (1988a). Evaluation of an annular denuder/filter pack system to collect acidic aerosols and gases. Environ Sci Technol, 22, 1463-1468.

Koutrakis P; Wolfson JM; Spengler JD. (1988b). An improved method for measuring aerosol strong acidity: results from a nine-month study in St. Louis, Missouri and Kingston, Tennessee. Atmos Environ, 22, 157-162.

Koutrakis P; Thompson KM; Wolfson JM; Spengler JD; Keeler GJ; Slater JL. (1992). Determination of aerosol strong acidity losses due to interactions of collected particles: results from laboratory and field studies. Atmos Environ, 26, 987-995.

Kozlowski TT. (1985). SO_2 effects on plant community structure. In: Winner WE; Mooney HA; Goldstein RA (Eds.), Sulfur dioxide and vegetation: physiology, ecology, and policy issues. (pp 431-453). Stanford, CA: Stanford University Press.

Krabbenhoft DP; Wiener JG; Brumbaugh WG; Olson ML; DeWild JF; Sabin TJ. (1999). A National Plot Study of Mercury Contamination of Aquatic Ecosystems along Multiple Gradients In Morganwalp DW, Buxton HT (Eds.), U.S. Geological Survey Toxic Substances Hydrology Program: Proceedings of the technical meeting; held in Charleston, SC March 8-12, 1999. (Volume 2 of 3: Contamination of hydrologic systems and related ecosystems. (U.S. Geological Survey Water resources investigations report #99-4018-B, pp. 147-160). West Trenton, NJ; U.S. Geological Survey.

Krabbenhoft DP; Olson ML; Dewild JF; Clow DW; Striegel RG; Dornblaser MM; VanMetre P. (2002). Mercury loading and methylmercury production and cycling in high-altitude lakes from the western United States. Water Air Soil Pollut Focus, 2, 233-249.

Kramar D; Goodale WM; Kennedy LM; Carstensen LW; Kaur T. (2005). Relating land cover characteristics and common loon mercury levels using geographic information systems. Ecotoxicology, 14, 253-262.

Kramer A; Holmes TP; Haefel M. (2003). Contingent valuation of forest ecosystem protection. In: Sills EO; Abt KL (Eds.), Forests in a Market Economy (pp. 303-320). Dordrecht, The Netherlands: Kluwer Academic Publishers.

Kramer R; Mercer E. (1997). Valuing a global environmental good: U.S. residents willingness to pay to protect tropical rain forests. Land Econ, 73, 196-210.

Kramer RA; Eisen-Hecht JI. (2002). Estimating the economic value of water quality protection in the Catawba River basin. Water Resour Res, 38, 1183-1191.

Kratz KW; Cooper SD; Melack JM. (1994). Effects of single and repeated experimental acid pulses on invertebrates in a high altitude Sierra Nevada stream. Freshw Biol, 32, 161-183.

Kress LW; Skelly JM. (1982). Response of several eastern forest tree species to chronic doses of ozone and nitrogen dioxide. Plant Dis, 66, 1149-1152.

Kretser W; Gallagher J; Nicolette J. (1989). Adirondack Lakes Study, 1984-1987: An Evaluation of Fish Communities and Water Chemistry: Ray Brook, NY; prepared for: Adirondack Lakes Survey (ALS) Corporation.

Kristensen HL; Gundersen P; Callesen I; Reinds G-J. (2004). Throughfall nitrogen deposition has different impacts on soil solution nitrate concentration in European coniferous and deciduous forests. Ecosystems, 7, 180-192.

Kristensen HL; Thorup-Kristensen K. (2006). Roots Below One Meters Depth Are Important for Nitrate Uptake by Annual Crops. Paper presented at the American society of agronomy - Crop science society of America - Soil science society of America international annual meetings, held in Indianapolis, IN, November 12-16, 2006. (CD-rom no. 205-9). Published in CD-rom by The American Society of Agronomy; Crop Science Society of America; Soil Science Society of America.

Kropff MJ. (1990). The effects of long-term open-air fumigation with SO_2 on a field crop of braod bean (*Vicia faba* L.); III. Quantitative analysis of damage components. New Phytol, 115, 357-365.

Kropff MJ. (1991). Long-term effects of SO_2 on plants, SO_2 metabolism and regulation of intracellular pH. Plant Soil, 131, 235-245.

Kros J; Reinds GJ; de Vries W; Latour JB; Bollen MJS. (1995). Modelling abiotic site factors in response to atmospheric deposition and upward seepage. In: Schoute JFT; Finke PA; Veeneklaas FR; Wolfert HP (Eds.), Scenario studies for the rural environment (pp. 445-448): Kluwer, Dordrecht.

Krug EC; Frink CR. (1983). Acid rain on acid soil: a new perspective. Science, 221, 520-525.

Krug EC; Isaacson PJ; Frink CR. (1985). Appraisal of some current hypotheses describing acidification of watersheds. Journal of the Air Pollution Control Association, 35, 109-114.

Krug EC. (1989). Assessment of the theory and hypotheses of the acidification of watersheds. Champaign, IL: Illinois State water Survey.

Krug EC. (1991). Review of acid-deposition-catchment interaction and comments on future research needs. J Hydrol, 128, 1-27.

Krupa SV; Legge AH. (1986). Single or joint effects of coarse and fine particulate sulfur aerosols and ozone on vegetation. In: Lee SD; Schneider T; Grant LD; Verkerk PJ (Eds.), Aerosols: research, risk assessment and control strategies: Proceedings of the second U.S.-Dutch international symposium, held in Williamsburg, VA, May 19-25, 1985. Organized by the U.S. Environmental Protection Agency and the Ministry of Housing, Physical Planning, and the Environment of The Netherlands. (pp 879-887). Chelsea, MI: Lewis Publishers.

Krupa SV; Legge AH. (1998). Sulphur dioxide, particulate sulphur and its impacts on a boreal forest ecosystem. In: Ambasht RD (Ed.), Modern trends in ecology and environment (pp. 285-306). Leiden, The Netherlands: Backhuys Publishers.

Krupa SV; Legge AH. (1999). Foliar injury symptoms of Saskatoon serviceberry (*Amelanchier alnifolia* Nutt.) as a biological indicator of ambient sulfur dioxide exposures. Environ Pollut, 106, 449-454.

Krupa SV. (2003). Effects of atmospheric ammonia (NH3).on terrestrial vegetation: A review. Environ Pollut, 124, 179-221.

Krywult M; Bytnerowicz A. (1997). Induction of nitrate reductase activity by nitric acid vapor in California black oak (Quercus kelloggii), canyon live oak (Quercus chrysolepis), and ponderosa pine (Pinus ponderosa).seedlings. Can J For Res, 27, 2101-2104.

Kubiske M; Godbold DL. (2001). Influence of carbon dioxide on the growth and function of roots and roots systems. In: Karnosky DF, Scarascia-Mungozza GE, Ceulemans R, Innes JL (Eds.), The impacts of carbon dioxide and other greenhouse gases on forest ecosystems (Research Series Report No. 3 of the IUFRO Task Force on Environmental Change, IUFRO Series #08, pp. 147-192). Wallingford, Oxfordshire, UK: CABI Publishing.

Kuik OJ; Helming JFM; Dorland C; Spaninks FA. (2000). The economic benefits to agriculture of a reduction of low-level ozone pollution in The Netherlands. Eur Rev Agric Econ, 27, 75-90.

Kulmala M; Pirjola L; Makela JM. (2000). Stable sulphate clusters as a source of new atmospheric particles. Nature, 404, 66-69.

Kulmala M; Riipinen I; Sipila M; Manninen HE; Petaja T; Junninen H; Maso MD; Mordas G; Mirme A; Vana M; Hirsikko A; Laakso L; Harrison RM; Hanson I; Leung C; Lehtinen KE; Kerminen VM. (2007). Toward direct measurement of atmospheric nucleation. Science, 318, 89-92.

Kumar N; Russell AG. (1996). Development of a computationally efficient, reactive subgrid-scale plume model and the impact in the northeastern United States using increasing levels of chemical detail. J Geophys Res, 101, 16737-16744.

Kurz D; Alveteg M; Sverdrup H. (1998). Integrated assessment of soil chemical status. 2. Application of a regionalized model to 622 forested sites in Switzerland. Water Air Soil Pollut, 105, 11-20.

Kuypers MMM; Lavik G; Woebken D; Schmid M; Fuchs B; Amann R; Jorgensen BB; Jetten MSM. (2005). Massive nitrogen loss from the Benguela upwelling system through anaerobic ammonium oxidation. Proc Natl Acad Sci USA, 102, 6478-3483.

Lacroix GL. (1985a). Plasma ionic composition of the Atlantic salmon (*Salmo salar*), white sucker (*Catostomus commersoni*), and alewife (*Alosa pseudoharengus*) in some acidic rivers of Nova Scotia. Can J Zool, 63, 2254-2261.

Lacroix GL. (1985b). Survival of eggs and alevins of Atlantic salmon (*Salmo salar*) in relation to the chemistry of interstitial water in redds in some acidic streams of Atlantic Canada. Can J Fish Aquat Sci, 42, 292-299.

Lacroix GL; Townsend DR. (1987). Responses of juvenile Atlantic salmon (*Salmo salar*) to episodic increases in acidity of Nova Scotia rivers. Can J Fish Aquat Sci, 44, 1475-1484.

Lafrancois BM; Carlisle DM; Nydick KR; Johnson BM; Baron JS. (2003a). Environmental characteristics and benthic invertebrate assemblages in Colorado mountain lakes. Western North American Naturalist, 63, 137-154.

Lafrancois BM; Nydick KR; Caruso B. (2003b). Influence of nitrogen on phytoplankton biomass and community composition in fifteen Snowy Range lakes (Wyoming, USA). Arct Antarct Alp Res, 35, 499-508.

Lafrancois BM; Nydick KR; Johnson BM; Baron JS. (2004). Cumulative effects of nutrients and pH on the plankton of two mountain lakes. Can J Fish Aquat Sci, 61, 1153-1165.

Lamers LPM; Tomassen HBM; Roelofs JGM. (1998). Sulfate-induced eutrophication and phytotoxicity in freshwater wetlands. Environ Sci Technol, 32, 199-205.

Lamers LPM; Falla SJ; Samborska EM; van Dulken IAR; van Hengstum G; Roelofs JGM. (2002). Factors controlling the extent of eutrophication and toxicity in sulfate-polluted freshwater wetlands. Limnol Oceanogr, 47, 585-593.

Lammel G; Perner D. (1988). The atmospheric aerosol as a source of nitrous acid in the polluted atmosphere. Journal of Aerosol Science, 19, 1199-1202.

Lammel G; Cape JN. (1996). Nitrous acid and nitrite in the atmosphere. Chem Soc Rev, 25, 361-369.

Lamsal LN; Martin RV; van Donkelaar A; Steinbacher M. (2008). Ground-level nitrogen dioxide concentrations inferred. J Geophys Res, 113, doi:10.1029/2007JD009235.

Lan T; Wu S-P; Xu F-L; Wang X-J; Tao S. (2005). DDTs in Airborne Particles with Different Sizes in Tianjin During Winter. Journal of Agro-Environment Science, 24, 1182-1185.

Lan TTN; Thoa NTP; Nishimura R; Tsujino Y; Yokoi M; Maeda Y. (2005). New model for the sulfation of marble by dry deposition sheltered marble: The indicator of air pollution by sulfur dioxide. Atmos Environ, 39, 913-920.

Lancaster J; Real M; Juggins S; Monteith DT; Flower RJ; Beaumont WRC. (1996). Monitoring temporal changes in the biology of acid waters. Freshwater Biol, 36, 179-201.

Landers DH; Eilers JM; Brakke DF; Overton WS; Kellar PE; Silverstein WE; Schonbrod RD; Crowe RE; Linthurst RA; Omernik JM; Teague SA; Meier EP. (1987). Western lake survey phase I: Characteristics of lakes in the western United States. Volume I: Population descriptions and physico-chemical relationships. (Report # EPA/600/3-86/054a). Washington, D.C.: U.S. Environmental Protection Agency.

Landers DH; Overton WS; Linthurst RA; Brakke DF. (1988). Eastern lake survey: regional estimates of lake chemistry. Environ Sci Technol, 22, 128-135.

Lane DR; BassiriRad H. (2002). Differential responses of tallgrass prairie species to nitrogen loading and varying ratios of NO_3^- to NH_4^+. Functional Plant Biology, 29, 1227-1235.

Langford AO; Fehsenfeld FC. (1992). Natural Vegetation as a Source or Sink for Atmospheric Ammonia: A Case Study. Science, 255, 581-583.

Langford AO; Fehsenfeld FC; Zachariassen J; Schimel DS. (1992). Gaseous Ammonia Fluxes and Background Concentrations in Terrestrial Ecosystems of the United States. Glob Biogeochem Cycles, 6, 459-459.

Lapenis AG; Lawrence GB; Andreev AA; Bobroc AA; Torn MS; Harden JW. (2004). Acidification of forest soil in Russia: from 1893 to present. Glob Biogeochem Cycles, 18, 1-13.

Laposata MM; Dunson WA. (1998). Effects of boron and nitrate on hatching success of amphibian eggs. Arch Environ Contam Toxicol, 35, 615-619.

Larsen DP; Urquhart NS. (1993). A framework for assessing the sensitivity of the EMAP design. In: Larsen DP, Christie SJ; Paulson, SG; Hughes RM; Johnson CB (Eds.), EMAP-Surface Waters 1991 Pilot Report (EPA--620/R-93/003, pp. 4.1-4.37). Corvallis, OR; Environmental Research Laboratory; U.S. Environmental Protection Agency.

Larsen DP; Thornton KW; Urquhart NS; Paulsen SG. (1994). The role of sample surveys for monitoring the condition of the nation's lakes. Environ Monit Assess, 32, 101-134.

Larson GL; Moore SE. (1985). Encroachment of exotic rainbow trout into stream populations of native brook trout in the Southern Appalachian Mountains. Trans Am Fish Soc, 114, 195-203.

Latty EF; Canham CD; Marks PL. (2004). The Effects of Land-use History on Soil Properties and Nutrient Dynamics in Northern Hardwood Forests of the Adirondack Mountains. Ecosystems, 7, 193-207.

Laudon H; Clair TA; Hemond HF. (2002). Long-term response in episodic acidification to declining SO_4^{2-} deposition in two streams in Nova Scotia. Hydrol Earth Sys Sci, 6, 773-782.

Laudon H; Dillon PJ; Eimers MC; Semkin RG; Jeffries DS. (2004). Climate-Induced Episodic Acidification of Streams in Central Ontario. Environ Sci Technol, 38, 6009-6015.

Laurence JA; Amundson RG; Friend AL; Pell EJ; Temple PJ. (1994). Allocation of carbon in plants under stress: an analysis of the ROPIS experiments. J Environ Qual, 23, 412-417.

Laurenroth WK; Milchunas DG. (1985). SO_2 effects on plant community function. In: Winter WE; Mooney HA; Goldstein RA (Eds.), Sulfur dioxide and vegetation: Physiology, ecology, and policy issues. (pp. 454-477). Sanford, CA: Sanford University Press.

Lawrence GB; David MB. (1977). Response of aluminum solubility to elevated nitrification in soil of a red spruce stand in eastern Maine. Environ Sci Technol, 31, 825-830.

Lawrence GB; Fuller RD; Driscoll CT. (1987). Release of aluminum following whole-tree harvesting at the Hubbard Brook Experimental Forest, New Hampshire. J Environ Qual, 16, 383-390.

Lawrence GB; David MB; Shortle WC. (1995). A New Mechanism for Calcium Loss in Forest-Floor Soils. Nature, 378, 162-165.

Lawrence GB; David MB. (1997). Response of aluminum solubility to elevated nitrification in soil of a red spruce stand in eastern Maine. Environ Sci Technol, 31, 825-830.

Lawrence GB; David MB; Bailey SW; Shortle WC. (1997). Assessment of soil calcium status in red spruce forests in the northeastern United States. Biogeochemistry, 38, 19-39.

Lawrence GB; David MB; Shortle WC; Bailey SW; Lovett GM. (1998). Mechanisms of base-cation depletion by acid deposition in forest soils of the northeastern U.S. In: Sugar Maple Ecology and Health: Proceedings of an International Symposium held in Warren, PA; June, 2–4, 1998. (Pages 75–87).

Lawrence GB; Huntington TG. (1999). Soil-Calcium Depletion Linked to Acid Rain and Forest Growth in the Eastern United States. (Report no WRIR 98-4267). Reston, VA: U.S. Geological Survey.

Lawrence GB; David MB; Shortel WS; Bailey SW; Lovett GM. (1999a). Mechanisms of base-cation depletion by acid deposition in forest soils of the northeastern U.S. In:Horsely, SB; Long RP (Eds.) Sugar maple ecology and health: Proceedings of an international symposium held in Radner, PA June 2-4, 1998. (pp 75-87). U.S. Forest Service; U.S. Department of Agriculture (USDA).

Lawrence GB; David MB; Lovett GM; Murdoch PS; Burns DA; Stoddard JL; Baldigo B; Porter JH; Thompson AW. (1999b). Soil calcium status and the response of stream chemistry to changing acidic deposition rates. Ecol Appl, 9, 1059-1072.

Lawrence GB. (2002). Persistent episodic acidification of streams linked to acid rain effects on soil. Atmos Environ, 36, 1589-1598.

Lawrence GB; Momen B; Roy KM. (2004). Use of stream chemistry for monitoring acidic deposition effects in the Adirondack Region of New York. J Environ Qual, 33, 1002-1009.

Lawrence GB; Sutherland JW; Boylen CW; Nierzwicki-Bauer SA; Momen B; Baldigo BP; Simonin HA. (2007). Acid rain effects on aluminum mobilization clarified by inclusion of strong organic acids. Environ Sci Technol, 41, 93-98.

Lawrence GB; Lapenis AG; Berggren D; Aparin BF; Smith KT; Shortle WC; Bailey SW; Varlyguin DL; Babikov B. (2005). Climate dependency of tree growth suppressed by acid deposition effects on soils in northwest Russia. Environ Sci Technol, 39, 2004-2010.

Lawrence GB; Roy KM; Baldigo BP; Simonin HA; Capone SB; Sutherland JW; Nierzwicki-Bauer SA; Boylen CW. (2008). Chronic and episodic acidification of adirondack streams from Acid rain in 2003–2005 . J Environ Qual, 37, 2264-2274.

Lawson DR. (1990). The Southern California Air Quality Study. J Air Waste Manage Assoc, 40, 156-165.

Le Mer J; Roger P. (2001). Production, oxidation, emission and consumption of methane by soils: A review. European Journal of Soil Biology, 37, 25-50.

Leaderer BP; Naeher L; Jankun T; Balenger K; Holford TR; Toth C; Sullivan J; Wolfson JM; Koutrakis P. (1999). Indoor, outdoor, and regional summer and winter concentrations of PM_{10}, $PM_{2.5}$, SO_4^{2-}, H^+, NH_4^+, NO_3^-, NH_3, and nitrous acid in homes with and without kerosene space heaters. Environ Health Perspect, 107, 223-231.

Leavitt PR; Findlay DL; Hall RI; Smol JP. (1999). Algal responses to dissolved organic carbon loss and pH decline during whole-lake acidification: evidence from paleolimnology. Limnol Oceanogr, 44, 757-773.

LeBauer DS; Treseder KK. (2008). Nitrogen limitation of net primary productivity in terrestrial ecosystems is globally distributed. Ecology, 89, 371-379.

Lee EH; Tingey DT. (2003). History of tropospheric ozone for the San Bernardino Mountains of Southern California, 1963-1999. Atmos Environ, 37, 2705-2717.

Lefer BL; Shetter RE; Hall SR; Crawford JH; Olson JR. (2003). Impact of clouds and aerosols on photolysis frequencies and photochemistry during TRACE-P: 1. Analysis using radiative transfer and photochemical box models. J Geophys Res, 108,, 8821, doi:10.1029/2002JD003171.

Lefohn A; Husar J; Husar R. (1999). Estimating historical anthropogenic global sulfur emissions patterns for the period 1850—1990. Atmos Environ, 33, 3435-3444.

Lefohn AS; Oltmans SJ; Dann T; Singh HB. (2001). Present-day variability of background ozone in the lower troposphere. J Geophys Res, 106, 9945-9958.

Leggett ZH; Kelting DL. (2006). Fertilization effects on carbon pools in loblolly pine plantations on two upland sites. Soil Sci Soc Am J, 70, 279-286.

Leigh RJ; Corlett GK; Friess U; Monks PS. (2006). Concurrent multiaxis differential optical absorption spectroscopy system for the measurement of tropospheric nitrogen dioxide. Appl Opt, 45, 7504-7518.

Leino RL; Wilkinson P; Anderson JG. (1987). Histopathlogical changes in the gills of pearl dace, *Semotilus margarita*, and fathead minnows, *Pimephales promleas*, from experimentally acidified Canadian lakes. Can J Fish Aquat Sci, 44, 126-134.

Leivestad H. (1982). Physiological effects of acid stress on fish. In Haines TA, Johnson E (Eds.), Acid rain/fisheries (pp. 157-164). Bethesda, MD: American Fisheries Society.

Lendzian KJ; Kerstiens G. (1988). Interactions between plant cuticles and gaseous air pollutants. Aspects of Applied Biology, 17, 97-104.

Lenner M. (1987). Nitrogen dioxide in exhaust emissions from motor vehicles. Atmos Environ, 21, 37-43.

Lerdau MT; Munger JW; Jacob DJ. (2000). The NO_2 flux conundrum. Science, 289, 2293.

Lesack LFW; Melack JM. (1996). Mass balance of major solutes in a rainforest catchment in the central Amazon: Implications for nutrient budgets in tropical rainforests. Biogeochemistry, 32, 115-142.

Leue C; Wenig M; Wagner T; Klimm O; Platt U; Jahne B. (2001). Quantitative analysis of NO_X emissions from Global Ozone Monitoring Experiment satellite image sequences. J Geophys Res, 106, 5493-5505.

Leuenberger-Minger AU; Faller M; Richner P. (2002). Runoff of copper and zinc caused by atmospheric corrosion. Mater Corros, 53, 157-164.

Leung F-YT; Colussi AJ; Hoffmann MR; Toon GC. (2002). Isotopic fractionation of carbonyl sulfide in the atmosphere: implications for the source of background stratospheric sulfate aerosol. Geophys Res Lett, 29, doi: 10.1029/2001GL013955.

Leuschner WA; Young RL. (1978). Estimating the southern pine beetle's impact on reservoir campsites. For Sci, 24, 527-537.

Levelt PF; Ven Den Oord GHJ; Dobber MR; Mälkki A; Visser H; de Vries J; Stammes P; Lundell JOV; Saari H. (2006). The ozone monitoring instrument. IEEE Trans Geosci Remote Sens, 44, 1093-1101.

Levin SA. (1998). Ecosystems and the Biosphere as Complex Adaptive Systems. Ecosystems, 1, 431-436.

Levine, J. S; Bobbe, T; Ray, N; Witt, R. G; Singh, A. (1999).Wildland fires and the environment: A global synthesis. (Report no. UNEP/DEIAEW/TR.99.1). http://www.na.unep.net/publications/wildfire.pdf. Nairobi, Kenya: Division of Environmental Information; Assessment an Early Warning (DEIA&EW); United Nations Environment Programme (UNEP).

Levine MA; Whalen SC. (2001). Nutrient limitation of phytoplankton production in Alaskan arctic foothill lakes. Hydrobiologia, 455, 189-201.

Levine SN; Shambaugh AD; Pomeroy SE; Braner M. (1997). Phosphorus, nitrogen, and silica as controls on phytoplankton biomass and species composition in Lake Champlain (USA-Canada). Intern Assoc for Great Lakes Res, 23, 131-148.

Levlin SA. (1998). Ecosystems and the biosphere as complex adaptive systems. Ecosystems, 1, 431-436.

Lewis GP; Likens GE. (2007). Changes in stream chemistry associated with insect defoliation in a Pennsylvania hemlock-hardwoods forest. For Ecol Manage, 238, 199-211.

Ley RE; Williams MW; Schmidt SK. (2004). Microbial population dynamics in an extreme environment: Controlling factors in talus soils at 3750 m in the Colorado Rocky Mountains. Biogeochemistry, 68, 297-311.

Li C; Frolking S; Frolking TA. (1992). A model of nitrous-oxide evolution from soil driven by rainfall events. 1: Model structure and sensitivity. J Geophys Res, 97, 9759–9776.

Li C; Narayanan V; Harriss RC. (1996). Model estimates of nitrous oxide emissions from agricultural lands in the United States. Glob Biogeochem Cycles, 10, 297-306.

Li CS. (2000). Modeling trace gas emissions from agricultural ecosystems. Nutr Cycling Agroecosyst, 58, 259-276.

Li C; Aber J; Stange F; Butterbach-Bahl K; Papen H. (2000). A process-oriented model of N_2O and NO emissions from forest soils: 1. Model development. J Geophys Res [Atmos.], 105, 4369-4384.

Li JH; Tang HX; Bai QZ; Nie YF; Luan ZK. (2000). Aquatic acidification sensitivity for regional environment: a multi-indicator evaluation approach. Water Air Soil Pollut, 11. 251-261.

Liang J; Horowitz LW; Jacob DJ; Wang Y; Fiore AM; Logan JA; Gardner GM; Munger JW. (1998). Seasonal budgets of reactive nitrogen species and ozone over the United States, and export fluxes to the global atmosphere. J Geophys Res, 103, 13435-13450.

Lien L; Raddum GG; Fjellheim A. (1992). Critical loads for surface waters: invertebrates and fish. (Acid rain research report no 21). Oslo, Norway: Norwegian Institute for Water Research.

Lien L; Raddum GG; Fjellheim A; Henriksen A. (1996). A critical limit for acid neutralizing capacity in Norwegian surface waters, based on new analyses of fish and invertebrate responses. Sci Total Environ, 177, 173-193.

Likens GE; Bormann FH; Johnson NM; Fisher DW; Pierce RS. (1970). Effects of forest cutting and herbicide treatment on nutrient budgets in the Hubbard Brook watershed-ecosystem. Ecol Monogr, 40, 23-47.

Likens GE; Bormann FH; Pierce RS; Eaton JS; Johnson NM. (1977). Biogeochemistry of a Forested Ecosystem. New York, NY: Springer Verlag.

Likens GE; Bormann FH; Pierce RS; Reiners WA. (1978). Recovery of a deforested ecosystem. Science, 199, 492-496.

Likens GE. (1985). An ecosystem approach to aquatic ecology: Mirror Lake and its environment: New York, NY: Springer-Verlag.

Likens GE; Bormann FH; Hedin LO; Driscoll CT; Eaton JS. (1990). Dry deposition of sulfur: A 23 year record for the Hubbard Brook Forest ecosystem. Tellus B, 42, 319-329.

Likens GE. (1992). The ecosystem approach: Its use and abuse. Volume 3 of Series: Excellence in ecology. Oldendorf/Luhe, Germany: Ecology Institute.

Likens GE; Bormann FH. (1995). Biogeochemistry of a forested ecosystem. 2nd Edition. New York, NY: Springer-Verlag.

Likens GE; Driscoll CT; Buso DC. (1996). Long-term effects of acid rain: Response and recovery of a forest ecosystem. Science, 272, 244-246.

Likens GE; Driscoll CT; Buso DC; Siccama TG; Johnson CE; Lovett GM; Fahey TJ; Reiners WA; Ryan DF; Martin CW; Bailey SW. (1998). The biogeochemistry of calcium at Hubbard Brook. Biogeochemistry, 41, 89-173.

Likens GE; Butler TJ; Buso DC. (2001). Long- and short-term changes in sulfate deposition: Effects of the 1990 Clean Air Act Amendments. Biogeochemistry, 52, 1-11.

Likens GE; Driscoll CT; Buso DC; Mitchell MJ; Lovett GM; Bailey SW; Siccama TG; Reiners WA; Alewell C. (2002). The biogeochemistry of sulfur at Hubbard Brook. Biogeochemistry, 60, 235-316.

Lilleskov EA; Fahey TJ; Lovett GM. (2001). Ectomycorrhizal Fungal Aboveground Community Change over an Atmospheric Nitrogen Deposition Gradient. Ecol Appl, 11, 397-410.

Lilleskov EA; Fahey TJ; Horton TR; Lovett GM. (2002). Belowground ectomycorrhizal fungal community change over a nitrogen deposition gradient in Alaska. Ecology, 83, 104-115.

Lind CJ; Hem JD. (1975). Effects of organic solutes on chemical reactions of aluminum. Chemistry of aluminum in natural water. (Geological Survey Water Supply Paper No. 1827). Reston, VA; U.S. Geological Survey.

Lindau CW; Delaune RD; Pardue JH. (1994). Inorganic nitrogen processing and assimilation in a forested wetland. Hydrobiologia, 277, 171-178.

Lindberg SE; Lovett GM. (1985). Field measurements of particle dry deposition rates to foliage and inert surfaces in a forest canopy. Environmental Science and Technology 19: 238-244.

Lindberg SE; Bredemeir M; Schaefer DA; Qi L. (1990). Atmospheric concentrations and deposition during the growing season in conifer forests in the United States and West Germany. Atmos Environ, 24A, 2207-2220.

Lindberg SE. (1992). Atmospheric deposition and canopy interactions of sulfur. In: Johnson DW; Lindberg SE (Eds.), Atmospheric deposition and forest nutrient cycling: A synthesis of the integrated forest study. (Series: Billings WD; Golley F; Lange OL; Olson JS; Remmert H (Eds.), Ecological studies: Analysis and synthesis; Volume. 91, pp. 74-90). New York, NY: Springer-Verlag.

Lindroth, RL; Roth S; Kruger EL; Volin JC; Koss PA. (1997). CO_2-mediated changes in aspen chemistry: Effects on gypsy moth performance and susceptibility to virus. Glob Change Biol, 3, 279-289.

Linthurst RA; Landers DH; Eilers JM; Brakke DF; Overton WS; Meier EP; Crowe RE. (1986a). Characteristics of Lakes in the easten United States. Volume I. Population descriptions and physico-chemical relationships. (EPA-600/4-86-007A). Washington, DC; Office of Acid Deposition; Environmental Monitoring, and Quality Assurance; U.S. Environmental Protection Agency.

Linthurst RA; Landers DH; Eilers JM; Kellar PE; Brakke DF; Overton WS; Crowe R; Meier EP; Kanciruk P; Jeffries DS. (1986b). Regional chemical characteristics of lakes in North America Part II: eastern United States. Water Air Soil Pollut, 31, 577-591.

Lipton D. (2003). The value of improved water quality to Chesapeake Bay boaters. (Working Paper # 03-16). College Park, MD; Department of Agricultural and Resource Economics, University of Maryland–College Park.

Lipton D. (2004). The value of improved water quality to Chesapeake Bay boaters. Mar Resour Econ, 19, 265-270.

Little EL Jr. (1971). Atlas of United States trees. Vol. 1: Conifers and important hardwoods (USDA. Misc. Publ., no. 1146).Washington, DC; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Little P; Wiffen RD. (1977). Emission and deposition of petrol engine exhaust Pb—Deposition of exhaust Pb to plant and soil surfaces, Atmos Environ, 11, 437–447

Litvak ME; Loreto F; Harley PC; Sharkey TD; Monson RK. (1996). The response of isoprene emission rate and photosynthetic rate to photon flux and nitrogen supply in aspen and white oak trees. Plant Cell and Environment, 19, 549-559.

Liu H; Jacob DJ; Bey I; Yantosca RM. (2001a). Constraints from ^{210}Pb and ^{7}Be on wet deposition and transport in a global three-dimensional chemical tracer model driven by assimilated meteorological fields. J Geophys Res, 106, 12109-12128.

Liu S; Munson R; Johnson D; Gherini S; Summers K; Hudson R; Wilkinson K; Pitelka L. (1991). Application of a nutrient cycling model (NuCM).to a northern mixed hardwood and a southern coniferous forest. Tree Physiology, 9, 173-184.

Liu X; Hegg DA; Stoelinga MT. (2001b). Numerical simulation of new particle formation the Northwest Atlantic using the M5 mesoscale model coupled with sulfur chemistry. J Geophys Res, 106, 9697-9715.

Liu X; Chance K; Sioris CE; Kurosu TP; Spurr RJD; Martin RV; Fu T-M; Logan JA; Jacob DJ; Palmer PI; Newchurch MJ; Megretskaia IA; Chatfield RB. (2006). First directly retrieved global distribution of tropospheric column ozone from GOME: Comparison with the GEOS-CHEM model. J Geophys Res, 111, doi: 10.1029/2005JD006564.

Lobert JM; Scharffe DH; Hao W-M; Kuhlbusch TA; Seuwen R; Warneck P; Crutzen PJ. (1991). Experimental evaluation of biomass burning emissions: nitrogen and carbon containing compounds. In: Levine, JS (Ed.), Global biomass burning. (pp 289-304). Cambridge, MA: MIT Press.

Lobert JM; Keene WC; Logan JA; Yevich R. (1999). Global chlorine emissions from biomass burning: Reactive Chlorine Emissions Inventory. J Geophys Res, 104, 8373-8389.

Locke A; Sprules WG. (1994). Effects of lake acidification and recovery on the stability of zooplankton food webs. Ecology, 75,: 498-506.

Lofts S; Woof C; Tipping E; Clarke N; Mulder J. (2001). Modelling pH buffering and aluminium solubility in European forest soils. European Journal of Soil Sci, 52, 189-204.

Lohman K; Jones JR; Baysinger-Daniel C. (1991). Experimental evidence for nitrogen limitation in a northern Ozark stream. J North Am Benthol Soc, 10, 14-23.

Lohman K; Priscu JC. (1992). Physiological indicators of nutrient deficiency in cladophora (chlorophyta) in the Clark Fork of the Columbia River, Montana. J Phycol, 28, 443-448.

Lohrenz SE; Fahnenstiel GL; Redakje DG; Lang GA; Chen X; Dagg MJ. (1997). Variations in primary production of northern Gulf of Mexico continental shelf waters linked to nutrient inputs from the Mississippi River. Marine Ecology Progress Series, 155, 445-454.

Løkke H; Bak J; Falkengren-Grerup U; Finlay RD; Ilvesniemi H; Nygaard PH; Starr M. (1996). Critical loads of acidic deposition for forest soils: Is the current approach adequate. Ambio, 25, 510-516.

Longcore JR; Gill JD (Eds.), (1993). Acidic depositions: effects on wildlife and habitats. (Wildlife Society technical review no 93-1). Bethesda, MD: The Wildlife Society.

Longfellow CA; Ravishankara AR; Hanson DR. (1999). Reactive uptake on hydrocarbon soot: focus on NO$_2$. J Geophys Res, 104, 13833-13840.

Loomis JB; González-Cabán A; Gregory R. (1996). A contingent valuation study of the value of reducing fire hazards to old-growth forests in the Pacific Northwest. (Research paper no. PSW-RP-229). Portland, OR; Pacific Southwest Research Station; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Lotter AF. (1998). The recent eutrophication of Baldeggersee (Switzerland).as assessed by fossil diatom assemblages. Holocene, 8, 395-405.

Lovett GM. (1992). Atmospheric deposition and canopy interactions of nitrogen. In: Johnson DW, Lindberg SE (Eds.), Atmospheric deposition and forest nutrient cycling: A systhesis of the integrated forest study. (Series: Billings WD; Golley F; Lange OL; Olson JS; Remmert H (Eds.), Ecological studies: Analysis and synthesis; Volume 91; pp. 152-166). New York, NY: Springer-Verlag.

Lovett GM. (1994). Atmospheric deposition of nutrients and pollutants in North America: an ecological perspective. Ecological Applications 4(4): 629-650.

Lovett GM; Ruesink AE. (1995). Carbon and nitrogen assimilation in red oaks *(Quercus rubra* L.) subject to defoliation and nitrogen stress. Tree Physiol, 12, 259-269.

Lovett GM; Rueth H. (1999). Soil nitrogen transformations in beech and maple stands along a nitrogen deposition gradient. Ecol Appl, 9, 1330-1344.

Lovett GM; Traynor MM; Pouyat RV; Carreiro MM; Zhu W-X; Baxter JW. (2000a). Atmospheric deposition to oak forest along an urban-rural gradient. Environ Sci Technol, 34, 4294-4300.

Lovett GM; Weathers KC; Sobczak WV. (2000b). Nitrogen saturation and retention in forested watersheds of the Catskill Mountains, New York. Ecol Appl, 10, 73-84.

Lovett GM; Christenson LM; Groffman PM; Jones CG; Hart JE; Mitchell MJ. (2002a). Insect defoliation and nitrogen cycling in forests. BioScience, 52, 335-341.

Lovett GM; Weathers KC; Arthur MA. (2002b). Control of nitrogen loss from forested watersheds by soil C:N ratio and tree species composition. Ecosystems, 5, 712-718.

Lovett GM; Burns DA; Driscoll CT; Jenkins JC; Mitchell MJ; Rustad L; Shanley JB; Likens GE; Haeuber R. (2007). Who needs environmental monitoring? Front Ecol Environ, 5, 253-260.

Lowe PN; Lauenroth WK; Burke IC. (2002). Effects of nitrogen availability on the growth of native grasses exotic weeds. Journal of Range Management, 55, 94-98.

Lowrance RR; Todd RL; Asmussen LE. (1983). Waterborne nutrient budgets for the riparian zone of an agricultural watershed. Agric Ecosyst Environ, 10, 371-384.

Lowrance R. (1992). Groundwater nitrate and denitrification in a coastal plain riparian forest. J Environ Qual, 21, 401-405.

Lu R; Turco RP; Jacobson MZ. (1997). An integrated air pollution modeling system for urban and regional scales: 1. Structure and performance. J Geophys Res, 102, 6063-6079.

Lu S; Mattson KG; Zaerr JB; Marshall JD. (1998). Root respiration of Douglas-fir seedlings: effects of N concentration. Soil Biol Biochem, 30, 331-336.

Lucassen E; Smolders AJP; van der Salm AL; Roelofs JGM. (2004). High groundwater nitrate concentrations inhibit eutrophication of sulphate-rich freshwater wetlands. Biogeochemistry, 67, 249-267.

Lukac M; Calfapietra C; Godbold DL. (2003). Production, turnover and mycorrhizal colonization of root systems of three Populus species grown under elevated CO_2 (POPFACE). Glob Change Biol, 9, 838-848.

Luke WT; Dickerson RR; Ryan WF; Pickering KE; Nunnermacker LJ. (1992). Tropospheric chemistry over the lower Great Plains of the United States. 2. Trace gas profiles and distributions. J Geophys Res, 97, 20647-20670.

Luke WT. (1997). Evaluation of a commercial pulsed fluorescence detector for the measurement of low-level SO2 concentrations during the Gas-Phase Sulfur Intercomparison Experiment. J Geophys Res, 102, 16255-16265.

Luke WT; Watson TB; Olszyna KJ; Gunter RL; McMillen RT; Wellman DL; Wilkison SW. (1998). A comparison of airborne and surface trace gas measurements during the Southern Oxidants Study (SOS). J Geophys Res, 103, 22317-22337.

Luo C; Zender CS; Bian H; Metzger S. (2007). Role of ammonia chemistry and coarse mode aerosols in global climatological inorganic aerosol distributions. Atmospheric Environment 41: 2510-2533.

Lussenhop J; Treonis A; Curtis PS; Teeri JA; Vogel CS. (1998). Response of soil biota to elevated atmospheric CO_2 in poplar model systems. Oecologia, 113, 247-251.

Luterbacher J; Dietrich D; Xoplaki E; Grosjean M; Wanner H. (2004). European seasonal and annual temperature variability, trends, and extremes since 1500. Science, 303, 1499-1503.

Lydersen E; Fjeld E; Gjessing ET. (1996). The Humic Lake Acidification Experiment (HUMEX): Main physico-chemical results after five years of artificial acidification. Environ Int, 22, 591-604.

Lynch JA; Corbett ES. (1989). Hydrologic control of sulfate mobility in a forested watershed. Water Resour Res, 25(7), 1695-1703.

Ma J; Richter A; Burrows JP; Nüß H; Van Aardenne JA. (2006). Comparison of model-simulated tropospheric NO_2 over China with GOME-satellite data. Atmos Environ, 40, 593-604.

Maag M; Malinovsky M; Nielson SM. (1997). Kinetics and temperature dependence of potential denitrification in riparian soils. Journal of Environmental Sciences, 26, 215-223.

MacAvoy SW; Bulger AJ. (1995). Survival of brook trout (*Salvelinus fontinalis*) embryos and fry in streams of different acid sensitivity in Shenandoah National Park, USA. Water Air Soil Pollut, 85, 445-450.

MacDonald JA; Skiba U; Sheppard LJ; Ball B; Roberts JD; Smith KA; Fowler D. (1997). The effect of nitrogen deposition and seasonal variability on methane oxidation and nitrous oxide emission rates in an upland spruce plantation and moorland. Atmos Environ, 31, 3693-3706.

MacDonald JA; Dise NB; Matzner E; Arbruster M; Gundersen P; Forsius M. (2002). Nitrogen input together with ecosystem nitrogen enrichment predict nitrate leaching from European forests. Glob Chang Biol, 8, 1028-1033.

Mack MC; Schuur EAG; Bret-Harte MS; Shaver GR; Chapin FS. (2004). Ecosystem carbon storage in arctic tundra reduced by long-term nutrient fertilization. Nature, 431, 440-443.

MacLean DC; McCune DC; Weinstein LH; Mandl RH; Woodruff GN. (1968). Effects of acute hydrogen fluoride and nitrogen dioxide exposures on citrus and ornamental plants of central Florida. Environ Sci Technol, 2, 444-449.

MacMillan D; Ferrier B; Hanley N. (2001). Valuation of air pollution effects on ecosystems: A scoping study. (A report to the Department for Environment, Food and Rural Affairs). Aberdeen, Scotland: University of Aberdeen.

Madronich S. (1987). Photodissociation in the atmosphere. 1. Actinic flux and the effects of ground reflections and clouds. J Geophys Res, 92, 9740-9752.

Magill AH; Aber JD; Berntson GM; McDowell WH; Nadelhoffer KJ; Melillo JM; Steudler P. (2000). Long-term nitrogen additions and nitrogen saturation in two temperate forests. Ecosystems, 3, 238-253.

Magill AH; Aber JD; Currie WS; Nadelhoffer KJ; Martin ME; McDowell WH; Melillo JM; Steudler P. (2004). Ecosystem response to 15 years of chronic nitrogen additions at the Harvard Forest LTER, Massachusetts, USA. For Ecol Manage, 196, 7-28.

Magill AH; Aber JD; Hendricks JJ; Bowden RD; Melillo JM; Steudler PA. (1997). Biogeochemical response of forest ecosystms to simulated chronic nitrogen dispositon. Ecol Appl, 7, 402-415.

Magnani F; Mencuccini M; Borghetti M; Berbigier P; Berninger F; Delzon S; Grelle A; Hari P; Jarvis PG; Kolari P; Kowalski AS; Lankreijer H; Law BE; Lindroth A; Loustau D; Manca G; Moncrieff JB; Rayment M; Tedeschi V; Valentini R; Grace J. (2007). The human footprint in the carbon cycle of temperate and boreal forests. Nature, 447, 848-850.

Magnani F; Mencuccini M; Borghetti M; Berninger F; Delzon S; Grelle A; Hari P; Jarvis PG; Kolari P; Kowalski AS. (2008). Magnani et al. reply. Nature, 451, 3.Mahrt L. (1998). Stratified atmospheric boundary layers and breakdown of models. Theor Comput Fluid Dyn, 11, 263-279.

Makipaa R; Karjalainen T; Pussinen A; Kellomaki S. (1999). Effects of climate change and nitrogen deposition on the carbon sequestration of a forest ecosystem in the boreal zone. Can J For Res-Revue Canadienne De Recherche Forestiere, 29, 1490-1501.

Mäler K-G; Vincent JR. (Eds.). (2005). Handbook of Environmental Economics. Vol. 2. Valuation of Environmental Changes. Amsterdam, The Netherlands: Elsevier.

Malhi Y; Baldocchi DD; Jarvis PG. (1999). The carbon balance of tropical, temperate and boreal forests. Plant Cell and Environment, 22, 715-740.

Maljanen M; Jokinen H; Saari A; Strommer R; Martikainen PJ. (2006). Methane and nitrous oxide fluxes, and carbon dioxide production in boreal forest soil fertilized with wood ash and nitrogen. Soil Use Manage, 22, 151-157.

Malley DF; Chang PS. (1995). Assessing the health of a zooplankton community in a small Precambrian Shield lake during recovery from experimental acidification. Journal of Aquatic Ecosystem Health, 3, 273-286.

Malm WC; Hand JL. (2007). An examination of the physical and optical properties of aerosols collected in the IMPROVE program. Atmos Environ, 41:3,407-3,427, 2007.

Malone DJ; Conley TR; Fisher PM; Gilbert LW; Harding J; Dellner KG. (1996). Scales of nutrient-limited phytoplankton productivity in Chesapeake Bay. Estuaries, 19, 371-385.

Malone TC; Crocker LH; Pike SE; Wendler BW. (1988). Influence of river flow on the dynamics of phytoplankton in a partially stratified estuary. Mar Ecol Progr Ser, 48, 235-249.

Malone TC. (1991). River flow, phytoplankton production and oxygen depletion in Chesapeake Bay. In: Tyson RV, Peason TH (Eds.), Modern and ancient continentintal shelf aNO$_X$ia. Geological Society special publication no. 58 (pp. 83-93). London: The Geological Society.

Malone TC. (1992). Effects of water column processes on dissolved oxygen, nutrients, phytoplankton and zooplankton. In: Smith DE, Leffler M, Makiernan G (Eds.), Oxygen dynamics in Chesapeake Bay: a synthesis of recent research (pp. 61-112). College Park, MD: Maryland Sea Grant College Program.

Mann LK; Johnson DW; West DC; Cole DW; Hornbeck JW; Martin CW; Riekerk H; Smith CT; Swank WT; Tritton LM; Van Lear DH. (1988). Effects on whole-tree and stem-only clearcutting on post harvest hydrologic losses, nutrient capital, and regrowth. For Sci, 34, 412-428.

Manninen S; Huttunen S. (2000). Response of needle sulphur and nitrogen concentrations of Scots pine versus Norway spruce to SO2 and NO$_2$. Environ Pollut, 107, 421-436.

Mansfield TA; Jones T. (1985). Growth environment interactions in SO$_2$ responses of grasses. In: Winter WE, Mooney HA, Goldstein RA (Eds.), Sulfur dioxide and vegetation: physiology, ecology, and policy issues. (pp. 332-345). Stanford, CA: Stanford University Press.

Marco A; Blaustein AR. (1999). The effects of nitrite on behavior and metamorphosis in cascades frogs (*Rana cascadae*). Environ Toxicol Chem, 18, 949-949.

Margitan JJ; Watson RT. (1982). Kinetics of the reaction of hydroxyl radicals with nitric acid. The J Phys Chem, 86, 3819-3824.

Marinoni N; Birelli MP; Rostagno C; Pavese A. (2003). The effects of atmospheric multipollutants on modern concrete. Atmos Environ, 37, 4701-4712.

Markewitz D; Richter DD; Allen HL; Urrego J. (1998). Three decades of observed soil acidification in the Calhoun experimental forest: Has acid rain made a difference?. So/7. Science Society of America Journal, 62, 1428-1439.

Marler RJ; Stromberg JC; Pattern DT. (2001). Growth response of *Populus fremontii*, *Salix gooddingii*, and *Tamarix ramosissimi* seedlings under different nitrogen and phosphorus concentrations. J Arid Environ, 49, 133-146.

Marley NA; Gaffney JS; White RV; Rodriguez-Cuadra L; Herndon SE; Dunlea E; Volkamer RM; Molina LT; Molina MJ. (2004). Fast gas chromatography with luminol chemiluminescence detection for the simultaneous determination of nitrogen dioxide and peroxyacetyl nitrate in the atmosphere. Rev Sci Instrum, 75, 4595-4605.

Marschner H. (1995). Sulfur. In Mineral nutrition of higher plants (pp. 255-265). London, UK: Academic Press.

Marshall HG; Lacouture R. (1986). Seasonal patterns of growth and composition of phytoplankton in the lower Chesapeake Bay and vicinity. Estuar Coast Shelf Sci, 23, 115-130.

Martilli A; Neftel A; Favaro G; Kirchner F; Sillman S; Clappier A. (2002). Simulation of the ozone formation in the northern part of the Po Valley. J Geophys Res, 107, doi: 10.1029/2001JD000534.

Martin CW; Noel DS; Federer CA. (1984). Effects of forest clearcutting in New England on stream chemistry. J Environ Qual, 13, 204-210.

Martin D; Tsivou M; Bonsang B; Abonnel C; Carsey T; Springer-Young M; Pszenny A; Suhre K. (1997). Hydrogen peroxide in the marine atmospheric boundary layer during the Atlantic Stratocumulus Transition Experiment/Marine Aerosol and Gas Exchange experiment in the eastern subtropical North Atlantic. J Geophys Res, 102, 6003-6015.

Martin RV; Chance K; Jacob DJ; Kurosu TP; Spurr RJD; Bucsela E; Gleason JF; Palmer PI; Bey I; Fiore AM; Li Q; Yantosca RM; Koelemeijer RBA. (2002). An improved retrieval of tropospheric nitrogen dioxide from GOME. J Geophys Res, 107, doi: 10.1029/2001JD001027.

Martin RV; Jacob DJ; Chance KV; Kurosu TP; Palmer PI; Evans MJ. (2003). Global inventory of nitrogen oxide emissions constrained by space-based observations of NO$_2$ columns. J Geophys Res, 108, 10.1029/2003JD003453.

Martin RV; Fiore AM; Van Donkelaar A. (2004a). Space-based diagnosis of surface ozone sensitivity to anthropogenic emissions. Geophys Res Lett, 31, doi: 10.1029/2004GL019416.

Martin RV; Parrish DD; Ryerson TB; Nicks DK Jr; Chance K; Kurosu TP; Jacob DJ; Sturges ED; Fried A; Wert BP. (2004b). Evaluation of GOME satellite measurements of trophospheric NO$_2$ and HCHO using regional data from aircraft campaigns in the southeastern United States. J Geophys Res, 109, doi: 10.1029/2004JD004869.

Martin RV; Sioris CE; Chance K; Ryerson TB; Bertram TH; Wooldridge PJ; Cohen RC; Neuman JA; Swanson A; Flocke FM. (2006). Evaluation of space-based constraints on nitrogen oxide emissions with regional aircraft measurements over and downwind of eastern North America. J Geophys Res, 111, doi:10.1029/2005JD006680.

Martinez M; Arnold T; Perner D. (1999). The role of bromine and chlorine chemistry for arctic ozone depletion events in Ny-Alesund and comparison with model calculations. Annales Geophysicae, 17, 941-956.

Martinez-Arkarazo I; Angulo M; Bartolome L; Etxebarria N; Olazabal MA; Madariaga JM. (2007). An integrated analytical approach to diagnose the conservation state of building materials of a palace house in the metropolitan Bilbao (Basque Country, North of Spain). Analytica Chimica Acta, 584, 350-359.

Martinson L; Alveteg M; Warfvinge P. (2003). Parameterization and evaluation of sulfate adsorption in a dynamic soil chemistry model. Environ Pollut, 124, 119-125.

Martinson L; Lamersdorf N; Warfvinge P. (2005). The Solling roof revisited - Slow recovery from acidification observed and modeled despite a decade of "clean-rain" treatment. Environ Pollut, 135, 293-302.

Mason BJ. (1992). Acid rain: its causes and its effects on inland waters. Science Technology and Society Series No 8 1992:i-x, 1-126.

Mason J; Seip HM. (1985). The current state of knowledge on acidification of surface waters and guidelines for further research. Ambio, 14, 45-51.

Mason RR; Wickman BE; Beckwith RC; Paul HG. (1992). Thinning and nitrogen fertilization in a grand fir stand infested with spruce budworm. part I: insect response. For Sci, 38, 235-251.

Massman WJ; Pederson J; Delany A; Grantz D; Denhartog G; Neumann HH; Oncley SP; Pearson R; Shaw RH. (1994). An evaluation of the regional acid deposition model surface module for ozone uptake at 3 sites in the San-Joaquin valley of California. J Geophys Res, 99, 8281-8294.

Matamala R; Gonzalez-Meler MA; Jastrow JD; Norby RJ; Schlesinger WH. (2003). Impacts of fine root turnover on forest NPP and soil C sequestration potential. Science, 302, 1385-1387.

Matamala R; Schlesinger WH. (2000). Effects of elevated atmospheric CO_2 on fine root production and activity in an intact temperate forest ecosystem. Glob Change Biol, 6, 967-979.

MathTech. (1994). The regional model farm (RMF): An agricultural sector benefits assessment model: Version 3.0 for personal computers. (Mathech, Inc; Princeton, NJ; Report to the Office of Air Quality Planning and Standards pp 1-83). Research Triangle Park, NC; U.S. Environmental Protection Agency.

Mathur R; Dennis RL. (2000). A regional modeling analysis of reduced nitrogen cycling in the eastern United States. In: Preprints of the symposium on atmospheric chemistry: Issues in the 21st century - held in Long Beach, CA. in January 2000 (p. 85-88). Boston, MA: American Meteorological Society.

Mathur R; Dennis RL. (2003). Seasonal and annual modeling of reduced nitrogen compounds over the eastern United States: Emissions, ambient levels, and deposition amounts. J Geophys Res-Atmos, 108.

Matson PA; Volkmann C; Grier CC; Gower ST; Billow C. (1992). Soil nitrogen cycling and nitrous oxide flux in a Rocky Mountain Douglas-fir forest: effects of fertilization, irrigation and carbon addition. Biogeochemistry, 18, 101-117.

Matsumi Y; Murakami S-I; Kono M; Takahashi K; Koike M; Kondo Y. (2001). High-sensitivity instrument for measuring atmospheric NO_2. Anal Chem, 73, 5485-5493.

Matsumi Y; Shigemori H; Takahashi K. (2005). Laser-induced fluorescence instrument for measuring atmospheric SO 2. Atmos Environ, 39, 3177-3185.

Mattson WJ Jr. (1980). Herbivory in relation to plant nitrogen content. Annu Rev Ecol Syst, 11, 119-161.

Matuszek JE; Beggs GL. (1988). Fish species richness in relation to lake area, pH, and other abiotic factors in Ontario lakes. Can J Fish Aquat Sci, 45, 1931-1941.

Matzner E; Blanck K; Hartmann G; Stock R. (1989). Needle chlorosis pattern in relation to soil chemical properties in two Norway spruce (*Picea abies*, Karst) forests of the German Harz Mountains. In: Bucher JB; Bucher-Wallin I, (Eds.), Air pollution and forest decline: Proceedings of the 14th international meeting for specialists in air pollution effects of forest ecosystems; held in Interlaken, Switzerland in October 1988. (pp. 195-199). Birmensdorf, Switzerland: International Union of Forestry Research Organizations.

Mauldin RL III; Tanner DJ; Eisele FL. (1998). A new chemical ionization mass spectrometer technique for the fast measurement of gas phase nitric acid in the atmosphere. J Geophys Res, 103, 3361-3367.

May JD; Burdette SB; Gilliam FS; Adams MBeth. (2005). Interspecific divergence in foliar nutrient dynamics and stem growth in a temperate forest in response to chronic nitrogen inputs. Can J For Res, 35, 1023-1030.

May PF; Till AR; Cumming MJ. (1972). Systems analysis of [35]sulphur kinetics in pastures grazed by sheep. J Appl Ecol, 9, 25-49.

McAuley DG; Longcore JR. (1988a). Foods of juvenile ring-necked ducks: Relationship to wetland pH. J Wildlife Management, 52, 177-185.

McAuley DG; Longcore JR. (1988b). Survivial of juvenile ring-necked ducks on wetlands of different pH. J Wildlife Management, 52, 169-176.

McClain ME; Boyer EW; Dent CL; Gergel SE; Grimm NB; Goffman PM; Hart SC; Harvey JW; Johnston CA; Mayorga E; McDowell WH; Pinay G. (2003). Biogeochemical hot spots and hot moments at the interface of aquatic and terrestrial ecosystems. Ecosystems, 6, 301-312.

McClenahen JR. (1987). Effects of simulated throughfall pH and sulfate concentration on a deciduous forest soil. Water Air Soil Pollut, 35, 319-333.

McClenny WA. (Ed.), (2000). Recommended methods for ambient air monitoring of NO, NO_2, NO_Y, and individual NO_Z species. (Report no. EPA/600/R-01/005). Research Triangle Park, NC; National Exposure Research Laboratory; U.S. Environmental Protection Agency.

McClenny WA; Williams EJ; Cohen RC; Stutz J. (2002). Preparing to measure the effects of the NO_X SIP Call--methods for ambient air monitoring of NO, NO_2, NO_Y, and individual NO_Z species. J Air Waste Manage Assoc, 52, 542-562.

McConnell V; Walls M. (2005). The value of open space: Evidence from studies of nonmarket benefits. Washington, DC; Resources for the Future (RFF).

McCormick JH; Jensen KM; Anderson LE. (1989). Chronic effects of low pH and elevated aluminum on survival, maturation, spawning, and embryo-larval development of the fathead minnow in soft water. Water Air Soil Pollut, 43, 293-307.

McCormick LH; Steiner KC. (1978). Variation in aluminum tolerance among six genera of trees. For Sci, 24, 565-568.

McCulloch RB; Few GS; Murray GC Jr; Aneja VP. (1998). Analysis of ammonia, ammonium aerosols and acid gases in the atmosphere at a commercial hog farm in eastern North Carolina, USA. Environ Pollut,102, 263–268

McCune B. (1988). Lichen communities along O_3 and SO_2 gradients in Indianapolis. Bryologist, 91, 223-228.

McCune B; Geiser L. (1997). Macrolichens of the Pacific Northwest. Corvallis, OR: Oregon State University Press.

McCurdy T; Zelenka MP; Lawrence PM; Houston RM; Burton R. (1999). Acid aerosols in the Pittsburgh Metropolitan area. Atmos Environ, 33, 5133–5145.

McDonald DG. (1983). The effects of H^+ upon the gills of freshwater fish. Canadian Journal of Zoology, 61, 691-703.

McDonald DG; Milligan CL. (1988). Sodium transport in the brook trout, *Salvelinus fontinalis*: effects of prolonged low pH exposure in the presence and absence of aluminum. Can J Fish Aquat Sci, 45, 1606-1613.

McDowell WH; Magill AH; Aitkenhead-Peterson JA; Aber JD; Merriam JL; Kaushal SS. (2004). Effects of chronic nitrogen amendment on dissolved organic matter and inorganic nitrogen in soil solution. For Ecol Manage, 196, 29-41.

McFiggans G; Plane JMC; Allan B; Carpenter LJ; Coe H; O'Dowd C. (2000). A modeling study of iodine chemistry in the marine boundary layer. J Geophys Res, 105, 14371-14385.

McFiggans G; Coe H; Burgess R; Allan J; Cubison M; Alfarra MR; Saunders R; Saiz-Lopez A; Plane JMC; Wevill D; Carpenter LJ; Rickard AR; Monks PS. (2004). Direct evidence for coastal iodine particles from Laminaria macroalgae: Linkage to emissions of molecular iodine. Atmos Chem Phys, 4, 701-713.

McFiggans G. (2005). Marine aerosols and iodine emissions. (Arising from O'Dowd et al. (2002) Nature 417, 632-636). Nature, 433, e13, doi: 10.1038/nature03372.

McFrederick QS; Kathilankal JC; Fuentes JD. (2008). Air pollution modifies floral scent trails. Atmos Environ, 42, 2336-2348.

McGurk MD; Landry F; Tang A; Hanks CC. (2006). Acute and chronic toxicity of nitrate to early life stages of lake trout (*Salvelinus namaycush*).and lake whitefish (*Coregonus clupeaformis*). Environ Toxicol Chem, 25, 2187-2196.

McHale MR; Cirmo CP; Mitchell MJ; McDonnell JJ. (2004). Wetland nitrogen dynamics in an Adirondack forested watershed. Hydrological Processes, 18, 1853-1870.

McKane RB; Johnson LC; Shaver GR; Nadelhoffer KJ; Rastetter EB; Fry B; Giblin AE; Kielland K; Kwiatkowski BL; Laundre JA; Murray G. (2002). Resource-based niches provide a basis for plant species diversity and dominance in arctic tundra. Nature, 415, 68-72.

McKeen SA; Liu SC. (1993). Hydrocarbon ratios and photochemical history of air masses. Geophys Res Lett, 20, 2363-2366.

McKeen SA; Liu SC; Hsie E-Y; Lin X; Bradshaw JD; Smyth S; Gregory GL; Blake DR. (1996). Hydrocarbon ratios during PEM-WEST A: a model perspective. J Geophys Res, 101, 2087-2109.

McKenna DS; Konopka P; Grooß J-U; Günther G; Müller R; Spang R; Offermann D; Orsolini Y. (2002). A new chemical Lagrangian model of the stratosphere (CLaMS). 1. Formulation of advection and mixing. J Geophys Res, 107, doi: 10.1029/2000JD000114.

McKnight DM; Smith RL; Bradbury JP; Baron JS; Spaulding S. (1990). Phytoplankton dynamics in 3 Rocky Mountain Lakes, Colorado USA. Arct Antarct Alp Res, 22, 264-274.

McLain JET; Martens DA. (2006). Moisture controls on trace gas fluxes in semiarid riparian soils. Soil Sci Soc Am J, 70, 367–377.

McLaughlin SB; Tjoelker MJ. (1992). Growth and physiological changes in red spruce saplings associated with acidic deposition at high elevations in the southern Appalachians, USA. For Ecol Manage, 51, 43-51.

McLaughlin S; Percy K. (1999). Forest health in North America: some perspectives on actual and potential roles of climate and air pollution. Water Air Soil Pollut, 116, 151-197.

McLaughlin SB; Wimmer R. (1999). Tansley review no.104: Calcium physiology and terrestrial ecosystem processes. New Phytol, 142, 373-417.

McNeil BE; Read JM; Driscoll CT. (2007). Foliar nitrogen responses to elevated atmospheric nitrogen deposition in nine temperate forest canopy species. Environ Sci Technol, 41, 5191-5197.

McNeil BE; Read JM; Sullivan TJ; McDonnell TC; Fernandez IJ; Driscoll CT. (2008). The spatial pattern of nitrogen cycling in the Adirondack Park, New York. Ecol Appl, 18, 438-452.

McNicol DK; Bendell BE; McAuley D. (1987). Avain Trophic Relationships and Wetland Acidity. Transcr N Amer Wildlife Natural Resources Conference, 52, 619-627.

McNicol DK; Mallory ML; Wedeles CHR. (1995). Assessing biological recovery of acid-sensitive lakes in Ontario, Canada. Water Air Soil Pollut, 85, 457-462.

McNicol DK. (2002). Relation of lake acidification and recovery to fish, common loon and common merganser occurrence in Algoma Lakes. Water Air Soil Pollut: Focus, 2, 151-168.

McNulty SG; Aber JD. (1993). Effects of chronic nitrogen additions on nitrogen cycling in a high-elevation spruce–fir stand. Can J For Res, 23, 1252-1263.

McNulty SG; Aber JD; Newman SD. (1996). Nitrogen saturation in a high elevation New England spruce-fir stand. For Ecol Manage, 84, 109-121.

McNulty SG; Boggs J; Aber JD; Rustad L; Magill A. (2005). Red spruce ecosystem level changes following 14 years of chronic N fertilization. For Ecol Manage, 219, 279-291.

McNulty SG; Cohen EC; Myers JAM; Sullivan TJ; Li H. (2007). Estimates of critical acid loads and exceedances for forest soils across the conterminous United States. Environ Pollut, 149, 281-292.

McPhaden MJ; Zebiak SE; Glantz MH. (2006). ENSO as an integrating concept in earth science. Science, 314, 1740-1745.

McRoberts RE; McWilliams WH; Reams GA; Schmidt TL; Jenkins JC; O'Neill KP; Miles PD; Brand GJ. (2004). Assessing sustainability using data from the Forest Inventory and Analysis program of the United States Forest Service. J Sustain For, 18, 23-46.

McWilliams PG; Potts WTW. (1978). The effects of pH and calcium concentrations on gill potentials in the brown trout, *Salmo trutta*. Journal of Comparative Physiology, 126, 277-286.

Meagher JF; Cowling EB; Fehsenfeld FC; Parkhurst WJ. (1998). Ozone formation and transport in southeastern United States: overview of the SOS Nashville/Middle Tennessee Ozone Study. J Geophys Res, 103, 22213-22223.

Mebust MR; Eder BK; Binkowski FS; Roselle SJ. (2003). Models-3 community multiscale air quality (CMAQ).model aerosol component. 2. Model evaluation. J Geophys Res, 108, doi: 10.1029/2001JD001410.

Meehl GA; Washington WM; Collins WD; Arblaster JM; Hu A; Buja LE; Strand WG; Teng H. (2005). How much more global warming and sea level rise? Science, 307, 1769-1772.

Meili M. (1991). Fluxes, pools and turnover of mercury in Swedish forest lakes Water Air Soil Pollut, 56, 719-727.

Meiwes KJ; Khanna PK. (1981). Distribution and cycling of sulphur in the vegetation of two forest ecosystems in an acid rain environment. Plant Soil, 60, 369-375.

Meixner T; Fenn M. (2004). Biogeochemical budgets in a Mediterranean catchment with high rates of atmospheric N deposition - importance of scale and temporal asynchrony. Biogeochemistry, 70, 331-356.

Meixner T; Fenn ME; Wohlgemuth P; Oxford M; Riggan P. (2006). N Saturate symptoms in chaparral catchments are not reversed by prescribed fire. Environ Sci Technol, 40, 2887-2894.

Melack JM; Stoddard JL; Ochs CA. (1985). Major ion chemistry and sensitivity to acid precipitation of Sierra Nevada lakes. Water Resour Res, 21, 27-32.

Melack JM; Sickman JO; Leydecker A. (1988). Comparative analyses of high-altitude lakes and catchments in the Sierra Nevada: susceptibility to acidification. (Final report). Sacramento, CA: California Air Resources Board.

Melack JM; Cooper SC; Jenkins TM; Barmuta L Jr; Hamilton S; Kratz K; Sickman J; Soiseth C. (1989). Chemical and biological characteristics of Emerald Lake and the streams in its watershed, and the response of the lake and streams to acidic deposition. (Final report). Sacramento, CA: California Air Resources Board.

Melack JM; Stoddard JL. (1991). Sierra Nevada: Unacidified, very dilute waters and mildly acidic atmospheric deposition. In: Charles DF, Christie S (Eds.), Acidic deposition and aquatic ecosystems: regional case studies (pp. 503-530). New York: Springer-Verlag.

Melillo JM; Aber JD; Muratore JM. (1982). Nitrogen and lignin control of hardwood leaf litter decomposition dynamics. Ecology, 63, 621-662.

Melillo JM; Steudler PA; Aber JD; Newkirk K; Lux H; Bowles FP; Catricala C; Magill A; Ahrens T; Morrisseau S. (2002). Soil Warming and Carbon-Cycle Feedbacks to the Climate System (Vol. 298, pp. 2173-2176).

Mendelssohn IA. (1979). Nitrogen Metabolism in the Height Forms of Spartina Alterniflora in North Carolina. Ecology, 60, 574-584.

Mendoza-Dominguez A; Russell AG. (2000). Iterative inverse modeling and direct sensitivity analysis of a photochemical air quality model. Environ Sci Technol, 3, 4974-4981.

Mendoza-Dominguez A; Russell AG. (2001a). Emission strength validation using four-dimensional data assimilation: application to primary aerosol and precursors to ozone and secondary aerosol. J Air Waste Manage Assoc, 51, 1538-1550.

Mendoza-Dominguez A; Russell AG. (2001b). Estimation of emission adjustments from the application of four-dimensional data assimilation to photochemical air quality modeling. Atmos Environ, 35, 2879-2894.

Meng F-R; Cox RM; Arp PA. (1994). Fumigating mature spruce branches with SO_2 – Effects on net photosynthesis and stomatal conductance. Can J For Res, 24, 1464-1471.

Meng Z; Seinfeld JH. (1996). Time scales to achieve atmospheric gas-aerosol equilibrium for volatile species. Atmos Environ, 30, 2889-2900.

Mennen MG; Van Elzakker BG; Van Putten EM; Uiterwijk JW; Regts TA; Van Hellemond J; Wyers GP; Otjes RP; Verhage AJL; Wouters LW. (1996). Evaluation of automatic ammonia monitors for application in an air quality monitoring network. Atmos Environ, 30, 3239-3256.

Meyer MW; Evers DC; Daulton T; Braselton WE. (1995). Common loons (*Gavia immer*) nesting on low pH lakes in nothern Wisconsin have elevated blood mercury content. Water Air Soil Pollut, 80, 871-880.

Meyer JL; Swank WT. (1996). Ecosystem management challenges ecologists. Ecol Appl, 6, 738-740.

Meyers TP; Sickles JE; Dennis R; Russell K; Galloway J; Church T. (2001). Atmospheric nitrogen deposition to coastal estuaries and their watersheds. In: Valigura RM, Alexander RB, Castro MS, Greening H, Meyers T, Paerl H, Turner RE (Eds.), Nitrogen loading in coastal water bodies: An atmospheric perspective. (Series: Coastal and Estuarine Studies, Volume 57; pp 53-76). Washington, DC: American Geophysical Union.

Michalski G; Meixner T; Fenn M; Hernandez L; Sirulnik A; Allen E; Thiemens M. (2004). Tracing Atmospheric Nitrate Deposition in a Complex Semiarid Ecosystem Using Δ17O. Environ Sci Technol, 38, 2175-2181.

Michel TJ; Saros JE; Interlandi SJ; Wolfe AP. (2006). Resource requirements of four freshwater diatom taxa determined by in situ growth bioassays using natural populations from alpine lakes. Hydrobiologia, 568, 235-243.

Mierle G. (1990). Aqueous inputs of mercury to Precambrian Shield Lakes in Ontario. Environ Toxicol Chem, 9, 843-851.

Mierle G; Ingram R. (1991). The role of humic substances in the mobilization of mercury from watersheds. Water Air Soil Pollut, 56, 349-357.

Mikan CJ; Zak DR; Kubiske ME; Pregitzer KS. (2000). Combined effects of atmospheric CO_2 and N availability on the belowground carbon and nitrogen dynamics of aspen mesocosms. Oecologia, 124, 432-445.

Milberg P; Lamont BB; Pérez-Fernández MA. (1999). Survival and growth of native and exotic composites in response to a nutrient gradient. Plant Ecology, 145, 125-132.

Milchunas DG; Lauenroth WK. (1995). Inertia in plant community structure: State changes after cessation of nutrient-enrichment stress. Ecol Appl, 5, 452-458.

Milford JB; Gao D; Sillman S. (1994). Total reactive nitrogen (NO{sub y}).as an indicator of the sensitivity of ozone to reductions in hydrocarbon and NO{sub x} emissions. J Geophys Res ; VOL 99 ; ISSUE: D2 ; PBD: 20 Feb 1994, pp. 3533-3542 ; PL:.

Milindalekha J; Vashkin VN; Towpprayoon S. (2001). Calculation and mapping of sulfur critical loads for terrestrial ecosystems of Thailand. Water Air Soil Pollut, 130, 1265-1270.

Millennium Ecosystem Assessment. (2003). Ecosystems and Human Well-being: A Framework for Assessment. Washington, DC: Island Press.

Miller AE; Bowman WD. (2002). Variation in nitrogen-15 natural abundance and nitrogen uptake traits among co-occuring alpine species: Do species partition by nitrogen form? Oecologia, 130, 609-616.

Miller EK; Blum JD; Friedland AJ. (1993). Determination of soil exchangeable-cation loss and weatheirng rates using Sr isotopes. Nature, 362, 438-441.

Miller EK; McDonald K. (2006). Assessment of forest sensitivity to nitrogen and sulfur deposition in Maine. (Report to the Maine Department of Environmental Protection). http://www.maine.gov/dep/air/acidrain/ME-Forest-Mapping-Report-2007-01-26.pdf. Augusta, ME; Conference of New England Governors and Eastern Canadian Premiers, Forest Mapping Group ; Bureau of Air Quality; Maine Department of Environmental Protection.

Miller PR; Longbotham GJ; Longbotham CR. (1983). Sensitivity of selected western conifers to ozone. Plant Dis, 67, 1113-1115.

Miller JD; Lindsay BE. (1993). Willingness to pay for a state gypsy moth control program in New Hampshire: A contingent valuation case study. J Econ Entomol, 86, 828-837.

Miller PR; McBride JR., (Eds.), (1999). Oxidant air pollution impacts in the Montane forests of southern California: A case study of the San Bernardino Mountains. (Series: Ecological Studies: Volume 134) New York, NY: Springer-Verlag.

Miller WW, Johnson DW; Loupe TM; Sedinger JS; Carroll EM; Murphy JD; Walker RF; Glass D. (2006). Nutrients Flow from Runoff at Burned Forest Site in Lake Tahoe Basin. California Agriculture, 60, 65-71.

Mills KH; Chalanchuk SM; Mohr LC; Davies IJ. (1987). Responses of fish populations in Lake 223 to 8 years of experimental acidification. Can J Fish Aquat Sci, 44, 114-125.

Minnich RA; Barbour MG; Burk JH; Fernau RF. (1995). Sixty Years of Change in Californian Conifer Forests of the San Bernardino Mountains. Conserv Biol, 9, 902-914.

Minnich RA; Dezzani RJ. (1998). Historical decline of coastal sage scrub in the Riverside-Perris Plain, California. Western Birds, 29, 366-391.

Minocha R; Shortle WC; Lawrence GB; David MB; Minocha SC. (1997). Relationships among foliar chemistry, foliar polyamines, and soil chemistry in red spruce trees growing across the northeastern United States. Plant Soil, 191, 109-122.

Mitchell MJ; Harrison RB; Fitzgerald JW; Johnson DW; Lindberg SE; Zhang Y; Autry A. (1992a). Sulfur distribution and cycling in forest ecosystems. In: Johnson DW, Lindberg SE (Eds.), Atmospheric deposition and forest nutrient cycling: A synthesis of the integrated forest study. (Series: Billings WD; Golley F; Lange OL; Olson JS; Remmert H (Eds.) Ecological studies: Analysis and synthesis, Volume 91; pp. 90-129). New York, NY: Springer-Verlag.

Mitchell, M. J; Lindberg, S. E; Johnson, D. W; Lindberg, S. E. (1992b). Sulfur, chemistry, deposition, and cycling in forests. In: Johnson DW, Lindberg SE (Eds.) Atmospheric deposition and forest nutrient cycling: A synthesis of the integrated forest study. (Series: Billings WD; Golley F; Lange OL; Olson JS; Remmert H (Eds.) Ecological studies: Analysis and synthesis, Volume 91; pp. 72-149). New York, NY: Springer-Verlag.

Mitchell MJ; Driscoll CT; Kahl JS; Likens GE; Murdoch PS; Pardo LH. (1996). Climatic control of nitrate loss from forested watersheds in the northeast United States. Environ Sci Technol, 30, 2609-2612.

Mitchell MJ; Piatek KB; Christopher S; Mayer B; Kendall C; McHale PJ. (2006). Solute sources in stream water during consecutive fall storms in a northern hardwood forest watershed: a combined hydrological, chemical and isotopic approach. Biogeochemistry, 78, 217-246.

Mitchell PJ; Branfireun BA; Kolka, RK. (2008). Assessing sulfate and carbon controls on net methylmercury production in peatlands: An in situ mesocosm approach. Appl Geochem, 23, 503-518.

Mitchell RJ; Sutton MA; Truscott A-M; Leith ID; Cape JN; Pitcairn CER; Van Dijk N. (2004). Growth and tissue nitrogen of epiphytic Atlantic bryophytes: effects of increased and decreased atmospheric N deposition. Functional Ecology, 18, 322-329.

Mitchell RJ; Truscot AM; Leith ID; Cape JN; Dijk NV; Tang YS; Fowler D; Sutton MA. (2005). A study of the epiphytic communities of Atlantic oak woods along an atmospheric nitrogen deposition gradient. J Ecol, 93, 482-492.

Mitsch W; Gosselink J. (1986). Wetlands, (1st Edition). New York, NY: Van Nostrand Reinhold International.

Mitsch W; Gosselink J. (2000). Wetlands, (3rd Edition). New York, NY: John Wiley & Sons.

Mitsch W; Gosselink J. (2007). Wetlands, (4th Edition). New York, NY: John Wiley & Sons.

Moayeri M; Meng FR; Arp PA; Foster NW. (2001). Evaluating critical soil acidification loads and exceedances for a deciduous forest at the Turkey Lakes Watershed. Ecosystems, 4, 555-567.

Mocker D; Jung K; Forstel H; Schuurmann G. (1998). Isotopic and enzymatic investigations into the assimilation and effect of NO_2 on C3 and C4 plants. Journal of Appl Bot, 72, 186-190.

Mohn J; Schurmann A; Hagedorn F; Schleppi P; Bachofen R. (2000). Increased rates of denitrification in nitrogen-treated forest soils. For Ecol Manage, 137, 113-119.

Moldan F; Wright RF; Ferrier RC; Andersson BI; Hultberg H. (1998). Simulating the Gårdsjön covered catchment experiment with the MAGIC model. In: Hultberg H, Skeffington RA (Eds.), Experimental Reversal of Acid Rain Effects. The Gårdsjön Roof Project, 466 pp. (pp. p.351-362). Chichester, UK: Wiley and Sons.

Molot LA; Dillon PJ; LaZerte BD. (1989). Changes in ionic composition of streamwater during snowmelt in central Ontario. Can J Fish Aquat Sci, 46, 1658-1666.

Momen B; Lawrence GB; Nierzwicki-Bauer SA; Sutherland JW; Eichler L; Harrison JP; Boylen CW. (2006). Trends in summer chemistry linked to productivity in lakes recovering from acid deposition in the Adirondack Region of New York. Ecosystems, 9, 1306-1317.

Moncoulon D; Probst A; Party J. (2004). Weathering, atmospheric deposition and vegetation uptake: role for ecosystem sensitivity to acid deposition and critical load. Comptes Rendus Geoscience, 336, 1417-1426.

Monteith DT; Stoddard JL; Evans CD; de Wit HA; Forsius M; Hogasen T; Wilander A; Skjelkvale BL; Jeffries DS; Vuorenmaa J; Keller B; Kopacek J; Vesely J. (2007). Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature, 450, 537-540.

Montgomery DR; Buffington JM. (1998). Channel processes, classification, and response. In: Naiman, R. J; Bilby, R., eds. River ecology and management: Lessons from the Pacific coastal ecoregion. (pp. 13-42). New York: Springer-Verlag.

Moore DRJ; Keddy PA; Gaudet CL; Wisheu IC. (1989). Conservation of wetlands: Do infertile wetlands deserve a higher priority? Biological Conservation, 47, 203-217.

Moore JC; McCann K; Setala H; De Ruiter PC. (2003). Top-down is bottom-up: does predation in the rhizosphere regulate aboveground dynamics? Ecology, 84, 846-857.

Moore JD; Ouimet R. (2006). Ten-year effect of dolomitic lime on the nutrition, crown vigor, and growth of sugar maple. Can J For Res, 36, 1834-1841.

Moore MT; Lizotte JRE; Cooper CM; Smith JS; Knight SS. (2004a). Survival and growth of *Hyalella azteca* exposed to three Mississippi Oxbow Lake sediments. Bull Environ Contam Toxicol, 72, 777-783.

Moore TR; Trofymow JA; Taylor B; Prescott C; Camire C; Duschene L; Fyles J; Kozak L; Kranabetter M; Morrison I; Siltanen M; Smith S; Titus B; Visser S; Wein R; Zoltai S. (1999). Litter decomposition rates in Canadian forests. Glob Change Biol, 5, 75-82.

Moore T; Blodau C; Turunen J; Roulet N; Richard PJH. (2004b). Patterns of nitrogen and sulfur accumulation and retention in ombrotrophic bogs, eastern Canada. Glob Change Biol, 11, 356-367

Moorthi S; Suarez MJ. (1992). Relaxed Arakawa-Schubert: a parameterization of moist convection for general circulation models. Mon Weather Rev, 120, 978-1002.

Morel FMM; Hering JG. (1993). Principles and Applications of Aquatic Chemistry. New York, NY: Wiley-Interscience.

Morey ER; Shaw WD. (1990). An economic model to assess the impact of acid rain: A characteristics approach to estimating the demand for and benefits from recreational fishing. In: Link AN; Smith VK (Eds.), Advances in Applied Micro-Economics, Volume 5; Recent developments in the modeling of technical change, and modeling demand for and valuation of recreations resources. (pp 195-216). Greenwich, CT: JAI Press, Inc.

Morgan C; Owens N. (2001). Benefits of water quality policies: the Chesapeake Bay. Ecol Econ, 39, 271-284.

Morley SA; Karr JR. (2002). Assessing and restoring the health of urban streams in the Puget Sound Basin. Conserv Biol, 16, 1498-1509.

Morris DP; Lewis WM Jr. (1988). Phytoplankton nutrient limitation in Colorado mountain lakes. Freshw Biol, 20, 315-327.

Morris JT. (1991). Effects of nitrogen loading on wetland ecosystems with particular reference to atmospheric deposition. Annual Review of Ecological Systems, 22, 257-279.

Mörth CM; Torssander P; Kjønaas OJ; Stuanes AO; Moldan F; Giesler R. (2005). Mineralization of organic sulfur delays recovery from anthropogenic acidification. Environ Sci Technol, 39, 5234-5240.

Mosier A; Schimel D; Valentine D; Bronson K; Parton W. 1991. Methane and nitrous-oxide fluxes in native, fertilized and cultivated grasslands. Nature, 350, 330-332.

Moss MR. (1978). Sources of sulfur in the environment; the global sulfur cycle. In Nriagu JO (Ed.), Sulfur in the environment, Part 1: The atmospheric cycle (pp. 23-50). New York: Wiley.

Mount DR; Hockett JR; Gern WA. (1988). Effect of long-term exposure to acid, aluminum, and low calcium on adult brook trout(Salvelinus fontinalis). 2. Vitellogenesis and osmoregulation. Can J Fish Aquat Sci, 45, 1633-1642.

Mudd JB; Kozlowski TT., (Eds.) (1975). Responses of plants to air pollution. (Physiological ecology, A series of monographs, texts, and treatises). New York, NY: Academic Press.

Mueller DK; Ruddy BC; Battaglin WA. (1997). Logistic model of nitrate in streams of the upper-midwestern United States. J Environ Qual, 26, 1223-1230.

Mueller PK; Collins JF. (1980). Development of a particulate sulfate analyzer. (Report no. P-1382F, NTIS no EPRI-EA-1492). Palo Alto, CA: Electric Power Research Institute.

Muir PS; McCune B. (1988). Lichens, tree growth, and foliar symptoms of air pollution: are the stories consistent? J Environ Qual, 17, 361-370.

Mulder J; Stein A. (1994). The solubility of aluminum in acidic forest soils: Long-term changes due to acid deposition. Geochim Cosmochim Acta, 58, 85-94.

Mulder J; van Breemen N; Eijck HC. (1989). Depletion of soil aluminium by acid deposition and implications for acid neutralization. Nature, 337, 247-249.

Mulholland PJ; Valett HM; Webster JR; Thomas SA; Cooper LW; Hamilton SK; Peterson B. (2004). Stream denitrification and total nitrate uptake rates measured using a field ^{15}N tracer addition approach. Limnol Oceanogr, 49, 809-820.

Mulholland PJ; Helton AM; Poole GC; Hall RO Jr; Hamilton SK; Peterson BJ; Tank JL; Ashkenas LR; Cooper LW; Dahm CN; Dodds WK; Findlay SEG; Gregory SV; Grimm NB; Johnson SL; McDowell WH; Meyer JL; Valett HM; Webster JR; Arango CP; BeaulieuJJ; Bernot MJ; Burgin AJ; Crenshaw CL; Johnson LT; Niederlehner BR; O'Brien JM; Potter JD; Sheibley RW; Sobota DJ; Thomas SM. (2008). Stream denitrification across biomes and its response to anthropogenic nitrate loading. Nature, 452, 202-206.

Mullen JK; Menz FC. (1985). The effect of acidification damages on the economic value of the Adirondack fishery to New York anglers. Am J Agric Econ, 67, 112-119.

Muller BT, B;Rennenberg, H. (1996). Interaction between atmospheric and pedospheric nitrogen nutrition in spruce (Picea abies L. Karst) seedlings. Plant, Cell, and Environment, 19, 345-355.

Munger JW; Wofsy SC; Bakwin PS; Fan S-M; Goulden ML; Daube BC; Goldstein AH. (1996). Atmospheric deposition of reactive nitrogen oxides and ozone in a temperate deciduous forest and a subarctic woodland. 1. Measurements and mechanisms. J Geophys Res, 101, 12639-12657.

Munger JW; Fan S-M; Bakwin PS; Goulden ML; Goldstein AH; Colman AS; Wofsy SC. (1998). Regional budgets of nitrogen oxides from continental sources: Variations of rates for oxidation and deposition with season and distance from source regions. J Geophys Res, 103, 8355-8368.

Muniz IP. (1991). Freshwater acidification: its effects on species and communities of freshwater microbes, plants and animals. 97B, 227-254.

Munoz MSS; Rossi MJ. (2002). Heterogeneous reactions of HNO_3 with flame soot generated under different combustion conditions. Reaction mechanism and kinetics. Phys Chem Chem Phys, 4, 5110-5118.

Munoz-Hincapie MJ; Morell JM; Corredor JE. (2002). Increase of nitrous oxide flux to the atmosphere upon nitrogen addition to red mangroves sediments. Mar Pollut Bull, 44, 992-996.

Munro DC; Gupta UC. (1969). Influence of sulfur, molybdenum and phosphorus on chemical composition and yields of Brussels sprouts and of molybdenum on sulfur contents of several plant species grown in the greenhouse. Soil Sci, 107, 114-118.

Munson RK; Gherini SA. (1991). Processes influencing the acid-base chemistry of surface waters. In: Charles DF; Christie S (Eds.), Acidic deposition and aquatic ecosystems: Regional case studies. (pp 9-34). New York: Springer-Verlag.

Munson RK; Gherini SA. (1993a). Analysis of the mineral acid-base components of acid-neutralizing capacity in Adirondack Lakes. Water Resour Res, 29, 881-890.

Munthe J; Bodaly RAD; Branfireun BA; Driscoll CT; Gilmour CC; Harris R; Horvat M; Lucotte M; Malm O.(2007). Recovery of Mercury-Contaminated Fisheries. AMBIO: A Journal of the Human Environment, 36, 33-44.

Murdoch PS; Burns DA; Lawrence GB. (1998). Relation of climate change to the acidification of surface waters by nitrogen deposition. Environ Sci Technol, 32, 1642-1647.

Murdoch PS; Stoddard JL. (1992). The role of nitrate in the acidification of streams in the Catskill Mountains of New York. Water Resour Res, 28, 2707-2720.

Murdoch PS; Stoddard JL. (1993). Chemical characteristics and temporal trends in eight streams of the Catskill Mountains. Water Air Soil Pollut, 67, 367-395.

Murdoch PS; Shanley JB. (2006a). Detection of water quality trends at high, median, and low flow in a Catskill Mountain stream, New York, through a new statistical method. Water Resour Res, 42, doi: 10.1029/2004WR003892.

Murdoch PS; Shanley JB. (2006b). Flow-specific trends in river-water quality resulting from the effects of the Clean Air Act in three mesoscale, forested river basins in the northeastern United States through 2002. Environ Monit Assess, 120, 1-25.

Murphy JD, Johnson DW; Miller WW; Walker RF; Blank RR. (2006). Prescribed fire effects on forest floor and soil nutrients in a Sierra Nevada ecosystem. Soil Sci, 171, 181-199.

Murphy JD; Johnson DW; Miller WW; Walker RF; Carroll EF; Blank RR. (2006). Wildfire Effects on Soil Nutrients and Leaching in a Tahoe Basin Watershed. J Environ Qual, 35, 479-489.

Murphy JJ; Delucchi MA; McCubbin DR; Kim HJ. (1999). The cost of crop damage caused by ozone air pollution from motor vehicles. J Environ Manage, 55, 273-289.

Musselman RC; Hudnell L; Williams MW; Sommerfeld RA. (1996). Water chemistry of Rocky Mountain Front Range aquatic ecosystems (No. Research Paper RM-RP-325). Ft. Collins, CO: Rocky Mountain Forest and Range Experiment Station; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Myhre G; Berglen TF; Myhre CE; Isaksen ISA. (2004). The radiative effect of the anthropogenic influence on the stratospheric sulfate aerosol layer. Tellus Ser B, 56, 294-299.

Mylonda S. (1996). Sulphur dioxide emissions in Europe 1880—1991 and their effect on sulphur concentrations and depositions. Tellus, 48, 662-689.

Myneni RB; Keeling CD; Tucker CJ; Asrar G; Nemani RR. (1997). Increased plant growth in the northern high latitudes from 1981 to 1991. Nature, 386, 698-702.

Nadelhoffer K; Downs M; Fry B; Magill A; Aber J. (1999a). Controls on N retention and exports in a forested watershed. Environ Monit Assess, 55(1), 187-210.

Nadelhoffer KJ; Emmett BA; Gundersen P; Kjonaas OJ; Koopmans CJ; Schleppi P; Tietema A; Wright RF. (1999b). Nitrogen deposition makes a minor contribution to carbon sequestration in temperate forests. Nature, 398, 145-148.

Nadelhoffer KJ. (2000). The potential effects of nitrogen deposition on fine-root production in forest ecosystems. New Phytol, 147, 131-139.

Nadelhoffer KJ; Colman BP; Currie WS; Magill AH; Aber JD. (2004). Decadal-scale fates of 15N tracers to oak and pine stands under ambient and elevated N inputs at the Harvard Forest (USA). For Ecol Manage, 196, 89-107.

NADP/NTN (2004). http://nadp.sws.uiuc.edu. Annual 2004 isopleth maps. http://nadp.sws.uiuc.edu/isopleths/maps2004/2004Maps.pdf. http://nadp.sws.uiuc.edu/isopleths/annualmaps.asp. Champaign, IL; Program Office, National Atmospheric Deposition Program (NADP) / National Trends Network (NTN).

Nagao I; Matsumoto K; Tanaka H. (1999). Sunrise ozone destruction found in the sub-tropical marine boundary layer. Geophys Res Lett, 26, 3377-3380.

Nagase H; Ose Y; Sato T; Ishikawa T. (1984). Mercury methylation by compounds in humic material. Sci Total Environ, 32, 147-156.

Nagy KA; Henen BT; Vyas DB. (1998). Nutritional quality of native and introduced food plants of wild desert tortoises. J Herpetol, 32, 260-267.

Najjar RG; Walker HA; Anderson PJ; Barron EJ; Bord RJ; Gibson JR; Kennedy VS; Knight CG; Megonigal JP; O'Connor RE; Polsky CD; Psuty NP; Richards BA; Sorenson LG; Steele EM; Swanson RS. (2000). The potential impacts of climate change on the mid-Atlantic coastal region. Clim Res, 14, 219-233.

Nakamura K; Kondo Y; Chen G; Crawford JH; Takegawa N; Koike M; Kita K; Miyazaki Y; Shetter RE; Lefer BL; Avery M; Matsumoto J. (2003). Measurement of NO_2 by the photolysis conversion technique during the Transport and Chemical Evolution Over the Pacific (TRACE-P) campaign. J Geophys Res, 108D24.

NAPAP. (1990). 1990 integrated assessment report. Washington, DC: National Acid Precipitation Assessment Program (NAPAP).

NAPAP. (1991). Experience and legacy of NAPAP. Report of the Oversight Review Board of the National Acid Precipitation Assessment Program (No. PB-92-128230/XAB). Washington, DC: National Acid Precipitation Assessment Program (NAPAP); Council on Environmental Quality.

NAPAP. (1998). NAPAP biennial report to Congress: An integrated assessment. Silver Spring, MD: National Acid Precipitation Assessment Program (NAPAP); Committee on Environment and Natural Resources (CENR) of the National Science and Technology Council (NSTC).

NAPAP. (2005). National acid precipitation assessment program report to Congress: An integrated assessment. http://www.esrl.noaa.gov/csd/aqrs/reports/napapreport05.pdf. Silver Spring, MD: National Acid Precipitation Assessment Program (NAPAP); Committee on Environment and Natural Resources (CENR) of the National Science and Technology Council (NSTC).

NARSTO. (2005). Improving emission inventories for effective air quality management across North America. A NARSTO assessment. (Report no. NARSTO-05-001). http://www.narsto.org/Section.src?SID=8. Pasco, WA: The NARSTO Emission Inventory Assessment Team

Nash TH; Sigal LL. (1999). Epiphytic lichens in the San Bernardino mountains in relation to oxidant gradients. In: Miller PR, McBride JR (Eds.), Oxidant air pollution impacts on the montane forests of southern California: A case study of the San Bernardino mountains. Ecological Studies, 134, (pp. 223-234). New York, NY: Springer-Verlag.

Näsholm T; Ekblad A; Nordin A; Giesler R; Hogberg M; Högberg P. (1998). Boreal forest plants take up organic nitrogen. Nature, 392: 914-916.

Naumova YY; Offenberg JH; Eisenreich SJ; Meng QY; Polidori A; Turpin BJ; Weisel CP; Morandi MT; Colome SD; Stock TH; Winer AM; Alimokhtari S; Kwon J; Maberti S; Shendell D; Jones J; Farrar C. (2003). Gas/particle distribution of polycyclic aromatic hydrocarbons in coupled outdoor/indoor atmospheres. Atmos Environ, 37, 703-719.

Neary AJ; Mistry E; Vanderstar L. (1987). Sulphate relationships in some central Ontario forest soils. Can J Soil Sci, 67, 341-352.

Neary BP; Dillon PJ. (1988). Effects of sulphur deposition on lake-water chemistry in Ontario, Canada. Nature, 333, 340-343.

Neary DG; Klopatek CC; DeBano LF; Ffolliot PF. (1999). Fire effects on belowground sustainability: A review and synthesis. For Ecol Manage, 122, 51-71.

Needelman M; Kealy MJ. (1995). Recreational swimming benefits of New Hampshire lake water quality policies: An application of a repeated discrete choice model. Agricultural and Resource Economics Review, 24, 78-87.

Neff JS; Bowman WD; Holland EA; Fisk MC; Schmidt SK. (1994). Fluxes of nitrous oxide and methane from nitrogen-amended soils in a Colorado alpine ecosystem. Biogeochemistry, 27, 23-33.

Neff JC; Townsend AR; Gleixner G; Lehman SJ; Turnbull J; Bowman WD. (2002). Variable effects of nitrogen additions on the stability and turnover of soil carbon. Nature, 419, 915-917.

NEG/ECP Forest Mapping Group. (2001). Protocol for assessment and mapping of forest sensitivity to atmospheric S and N deposition. Acid rain action plan. (Action item 4: forest mapping research project). http://www.ecosystems-research.com/fmi/Protocol.pdf. Paper presented at the The Conference of the New England Governors (NEG) and Eastern Canadian Premiers (ECP). Boston, MA: New England Governors/Eastern Canadian Premiers.

Nellemann C; Thomsen MG. (2001). Long-term changes in forest growth: potential effects of nitrogen depsoition and acidification. Water Air Soil Pollut, 128, 197-205.

Nelson PO. (1991). Cascade Mountains: Lake chemistry and sensitivity of acid deposition. In: Charles DF, Christie S (Eds.), Acidic deposition and aquatic ecosystems: regional case studies (pp. 531-563). New York: Springer-Verlag.

Neuman JA; Huey LG; Dissly RW; Fehsenfeld FC; Flocke F; Holecek JC; Holloway JS; Hubler G; Jakoubek R; Nicks DK Jr; Parrish DD; Ryerson TB; Sueper DT; Weinheimer AJ. (2002). Fast-response airborne in-situ measurements of HNO_3 during the Texas 2000 Air Quality Study. J Geophys Res, 107, 10.1029/2001JD001437.

Newman DH. (1987). An econometric analysis of the southern softwood stumpage market:1950-l980. For Sci,33, 932-945.

Newton I; Hass MB. (1988). Pollutants in Merlin eggs and their effects on breeding. Br Birds, 81, 258-269.

Nicholls KH; Hopkins GJ; Standke SJ; Nakamoto L. (2001). Trends in total phosphorus in Canadian nearshore waters of Laurentian Great Lakes: 1976-1999. Great Lakes Res, 27, 402-422.

Nicks DK; Benner RL. (2001). Subminute measurements of SO_2 and low parts per trillion by volume mixing ratios in the atmosphere. J Geophys Res, 106, 27769-27776.

Nieboer E; Richardson DHS; Puckett KJ; Tomassini FD. (1976). The phytotoxicity of sulphur dioxide in relation to measurable responses in lichens. In: Mansfield T (Ed.), Effects of Air Pollutions on Plants (pp 61). Cambridge, U.K: Cambridge University Press.

Niering WA. (1998). Forces that shaped the forests of the northeastern United States. Northeast Nat, 5, 99-110.

Nikitas C; Clemitshaw KC; Oram DE; Penkett SA. (1997). Measurements of PAN in the polluted boundary layer and free troposphere using a luminol-NO_2 detector combined with a thermal converter. J Atmos Chem, 28, 339-359.

Nilles MA; Conley BE. (2001). Changes in the chemistry of precipitation in the United States, 1981-1998. Water Air Soil Pollut, 130, 409-414.

Nilsson J. (Ed.) (1986). Critical loads of nitrogen and sulphur. Environmental report 1986:11). Copenhagen, Denmark: Council of Ministers.

Nilsson J; Grennfelt P. (1988). Critical loads for sulphur and nitrogen. In: Nilsson J; Grennfelt P (Eds.), Report from UNECE/Nordic Council workshop held in Skokloster, Sweden; March 19-24, 1988. (Miljorapport: 1988: 15; pp 225-268). Copenhagen, Denmark: Published by Nordic Council of Ministers.

Nilsson LO; Wiklund K. (1995). Indirect effects of N and S deposition on a Norway spruce ecosystem. An update of findings within the Skogaby project. Water Air Soil Pollut, 85, 1613-1622.

Nilsson L; Giesler R; Bååth E; Wallander H. (2004). Growth and biomass of mycorrhizal mycelia in coniferous forests along short natural nutrient gradients. New Phytol, 165, 613-622.

Nilsson SI; Miller JG; Miller JD. (1982). Forest growth as a possible cause of soil and water acidification: an examination of the concepts. Oikos, 39, 40-49.

Nilsson SI. (1993). Acidification of Swedish ologotrophic lakes - interactions between deposition, forest growth and effects on lake-water quality. Ambio, 22, 272-276.

Nixon S. W. (1995). Coastal marine eutrophication: a definition, social causes, and future concerns. Ophelia, 41, 199-219.

Nodvin SC; Miegroet H; Lindberg SE; Nicholas NS; Johnson DW. (1995). Acidic deposition, ecosystem processes, and nitrogen saturation in a high elevation Southern Appalachian watershed. Water Air Soil Pollut, 85, 1647-1652.

Nolin MP; Stewart HT; Currier PN; Estabrook RH. (2004). Total Maximum Daily Load (TMDL) for 65 Acid Impaired New Hampshire Ponds (Final). New Hampshire Department of Environmental Services Document Number: R-WD-0417.

Norby RJ; Weerasuriya Y; Hanson PJ. (1989). Induction of nitrate reductase activity in red spruce needles by NO_2 and HNO_3 vapor. Can J For Res, 19, 889-896.

Norby RJ. (1998). Nitrogen deposition: a component of global change analyses. New Phytol, 139, 189-200.

Norby RJ; Cotrufo MF. (1998). Global change - a question of litter quality. Nature, 396, 17-18.

Norby RJ; Cotrufo MF; Ineson P; O'Neill EG; Canadell JG. (2001). Elevated CO_2, litter chemistry, and decomposition: a synthesis. Oecologia, 127, 153-165.

Nordin A; Nasholm T; Ericson L. (1998). Effects of simulated N deposition on understorey vegetation of a boreal coniferous forest. Functional Ecology, 12, 691-699.

Nordin A; Strengbom J; Witzell J; Nasholm T; Ericson L. (2005). Nitrogen depositon and the biodiversity of boreal forests: implications for the nitrogen critical load. Ambio, 34, 20-24.

Norton SA; Akielaszek JJ; Haines TA; Stromborg KL; Longcore JR. (1982). Bedrock geologic control of sensitivity of aquatic ecosystems in the United States to acidic deposition, Report no NP-4901887; pp 1-13). Fort Collins, CO; National Atmospheric Deposition Program (NADP).

Norton SA; Wright RF; Kahl JS; Scofield JP. (1992). The MAGIC simulation of surface water acidification at, and first year results from, the Bear Brook Watershed Manipulation, Maine, USA. Environ. Pollut, 77, 279-286.

Norton SA; Kahl JS; Fernandez IJ; Rustad LE; Scofield JP; Haines TA. (1994). Response of the West Bear Brook watershed, Maine, USA, to the addition of $(NH_4)_2SO_4$: 3 year results. For Ecol Manage, 68, 61-73.

Norton S; Kahl J; Fernandez I. (1999a). Altered soil-soil water interactions inferred from stream water chemistry at an artificially acidified watershed at Bear Brook Watershed, Maine USA. Environ Monit Assess, 55, 97-111.

Norton S; Kahl J; Fernandez I; Haines T; Rustad L; Nodvin S; Schofield J; Strickland T; Erickson J; Wignington P Jr; Lee J. (1999b). The Bear Brook Watershed, Maine (BBWM), USA. Environ Monitor Assess, 55, 7-51.

Nosko P; Brassard P; Kramer JR; Kershaw KA. (1988). The effect of aluminum on seed germination and early seedling establishment, growth, and respiration of white spruce (*Picea glauca*). Can J Bot, 66, 2305-2310.

Notholt J; Hjorth J; Raes F. (1992a). Formation of HNO_2 on aerosol surfaces during foggy periods in the presence of NO and NO_2. Atmos Environ, 26, 211-217.

Notholt J; Hjorth J; Raes F; Schrems O. (1992b). Simultaneous long path field measurements of HNO_2, CH2O and aerosol. Ber Bunsen Ges Phys Chem, 96, 290-293.

Nouchi I; Mayumi H; Yamazoe F. (1984). Foliar injury response of petunia and kidney bean to simultaneous and alternate exposures to ozone and PAN. Atmos Environ, 18, 453-460.

Novák M; Bottrell SH; Prechová E. (2001). Sulfur isotope inventories of atmospheric deposition, spruce forest floor and living Sphagnum along a NW–SE transect across Europe. Biogeochemistry, 53, 23-50.

Novák M; Kirchner JW; Fottová D; Prechová E; Jăcková I; Krám P; Hruska J. (2005). Isotopic evidence for processes of sulfur retention/release in 13 forested catchments spanning a strong pollution gradient (Czech Republic, central Europe). Glob Biogeochem Cycles, 19, doi: 10.1029/2004GB002396.

Novák M; Mitchell MJ; Jăcková I; Buzek F; Schweigstillova J; Erbanova L; Prikryl R; Fottová D. (2007). Processes Affecting Oxygen Isotope Ratios of Atmospheric and Ecosystem Sulfate in Two Contrasting Forest Catchments in Central Europe. Environ Sci Technol, 41, 703-709.

Nowak RS; Ellsworth DS; Smith SD. (2004). Functional responses of plants to elevated atmospheric CO_2-do photosynthetic and productivity data from FACE experiments support early predictions? New Phytol, 162, 253-280.

NPS. (2000). Federal land manager's air quality related values workgroup (FLAG) phase I report. Lakewood, CO; Air Resources Division; National Park Service (NPS), U.S. Department of the Interior.

NPS. (2004). Federal land manager's critical loads for sulfur and nitrogen workshop. Denver, CO; Air Quality Branch; U.S. Fish and Wildlife Service; U.S. Forest Service, U.S. Department of Agriculture (USDA). Lakewood, CO; Air Resource Management Program. Air Resources Division; National Park Service (NPS); U.S. Department of the Interior.

NRC. (1992). Rethinking the ozone problem in urban and regional air pollution. Washington, DC: National Research Council (NRC); The National Academies Press.

NRC. (1998). Research priorities for airborne particulate matter. I. Immediate priorities and a long-range research portfolio. Washington, DC: National Research Council (NRC); The National Academies Press.

NRC. (2000). Clean coastal waters: Understanding and reducing the effects of nutrient pollution. Washington, DC: National Research Council (NRC); The National Academies Press.

NRC. (2002). Estimating the public health benefits of proposed air pollution regulations. Washington, DC: National Research Council (NRC); The National Academies Press.

NRC. (2004). Air quality management in the United States. Washington, DC: National Research Council (NRC); The National Academies Press.

Nriagu JO. (1978). Production and uses of sulfur. In: Nriagu JO (Ed.), Sulfur in the environment, Part 1: The atmospheric cycle (pp. 1-21). New York: Wiley.

Nriagu JO; Holdway DA; Corker RD. (1987). Biogenic sulfur and the acidity of rainfall in remote areas of Canada. Science, 237, 1189-1192.

NSTC. (2000). Integrated assessment of hypoxia in the northern Gulf of Mexico. Washington, DC; Committee on Environment and Natural Resources; U.S. National Science and Technology Council (NSTC).

Nunnermacker LJ; Imre D; Daum PH; Kleinman L; Lee Y-N; Lee JH; Springston SR; Newman L; Weinstein-Lloyd J; Luke WT; Banta R; Alvarez R; Senff C; Sillman S; Holdren M; Keigley GW; Zhou X. (1998). Characterization of the Nashville urban plume on July 3 and July 18, 1995. J Geophys Res, 103, 28129-28148.

Nussbaum S; Vonballmoos P; Gfeller H; Schluneggerz UP; Fuhrer J; Rhodes D; Brunold C. (1993). Incorporation of atmospheric (NO_2)-N-15-nitrogen into free amino-acids by Norway spruce *picea-abies* (l) karst. Oecologia, 94, 408-414.

Nydick KR; Lafrancois BM; Baron JS; Johnson BM. (2003). Lake-specific responses to elevated atmospheric nitrogen deposition in the Colorado Rocky Mountains, USA. Hydrobiologia, 510, 103-114.

Nydick KR; Lafrancois BM; Baron JS; Johnson BM. (2004a). Nitrogen regulation of algal biomass, productivity, and composition in shallow mountain lakes, Snowy Range, Wyoming, USA. Can J Fish Aquat Sci, 61, 1256-1268.

Nydick KR; Lafrancois BM; Baron JS. (2004b). NO_3 uptake in shallow, oligotrophic, mountain lakes: the influence of elevated NO_3 concentrations. J North Am Benthol Soc, 23, 397-415.

Nykanen H; Vasander H; Huttunen JT; Martikainen PJ. (2002). Effect of experimental nitrogen load on methane and nitrous oxide fluxes on ombrotrophic boreal peatland. Plant Soil, 242, 147-155.

Odman MT; Ingram CI (1996). Multiscale air quality simulation platform (MAQSIP): Source code documentation and validation. (MCNC Technical report ENV-96TR002-v1.0). Research Triangle Park, NC; MCNC Environmental Modeling Center @ the North Carolina Supercomputing Center.

Odman MT; Russell AG. (1999). Mass conservative coupling of non-hydrostatic meteorological models with air quality models. In: Grying S-E; Batchvarova E (Eds.), Air pollution modeling and its application XIII. New York, NY: Plenum Press.

Odman MT; Boylan JW; Wilkinson JG; Russell AG; Mueller SF; Imhoff RE; Doty KG; Norris WB; McNider RT. (2002). SAMI air quality modeling. (Final report). Asheville, NC; Southern Appalachian Mountains Initiative (SAMI).

O'Dowd C; McFiggans G; Creasey DJ; Pirjola L; Hoell C; Smith MH; Allan BJ; Plane JMC; Heard DE; Lee JD; Pilling MJ; Kulmala M. (1999). On the photochemical production of new particles in the coastal boundary layer. Geophys Res Lett, 26, 1707-1710.

O'Dowd CD; Jimenez JL; Bahreini R; Flagan RC; Seinfeld JH; Hamerl K; Pirjola L; Kulmala M; Jennings SG; Hoffmann T. (2002). Marine aerosol formation from biogenic iodine emissions. Nature, 417, 632-636.

Odum EP. (1989). Ecology and our endangered life-support systems. (pp 58-66, 108-118). Sunderland, MA: Sinauer Associates, Inc.

Oesch S; Faller M. (1997). Environmental effects on materials: The effect of the air pollutants SO_2, NO_2, NO and O-3 on the corrosion of copper, zinc and aluminium. A short literature survey and results of laboratory exposures. Corros Sci, 39, 1505-1530.

Officer CB; Biggs RB; Taft JL; Cronin LE; Tyler MA; Boynton WR. (1984). Chesapeake Bay anoxa. Origin, development and significance. Science, 223, 22-27.

Officer CB; Ryther JH. (1980). The possible importance of silicon in marine eutrophication. Marine Ecology Progress Series, 3, 83-91.

Ohno T; Sucoff EI; Erich MS; Bloom PR; Buschena CA; Dixon RK. (1988). Growth and nutrient content of red spruce seedlings in soil amended with aluminum. J Environ Qual, 17, 666-672.

Økland J; Økland KA. (1986). The effects of acid deposition on benthic animals in lakes and streams. Experientia, 42, 471-486.

Oliver BG; Thurman EM; Malcolm RL. (1983). The contribution of humic substances to the acidity of colored natural waters. Geochim Cosmochim Acta, 47, 2031-2035.

Ollinger SV; Lathrop RG; Ellis JM; Aber JD; Lovett GM; Millham SE. (1993). A spatial model of atmospheric deposition for the northeastern U.S. Ecol Appl, 3, 459-472.

Ollinger SV; Aber JD; Reich PB. (1997). Simulating ozone effects on forest productivity: Interactions among leaf-, canopy-, and stand-level processes. Ecol Appl, 7, 1237-1251.

Ollinger SV; Smith ML; Martin ME; Hallett RA; Goodale CL; Aber JD. (2002). Regional variation in foliar chemistry and N cycling among forests of diverse history and composition. Ecology, 83, 339-355.

Olsen Y; Agustí S; Andersen T; Duarte CM; Gasol JM; Gismervik I; Heiskanen AS; Hoell E; Kuuppo P; Lignell R; Reinertsen H; Sommer U; Stibor H; Tamminen T; Vadstein O; Vaqué D; Vidal M. (2006). A comparative study of responses in planktonic food web structure and function in contrasting European coastal waters exposed to experimental nutrient addition. Limnol Oceanogr, 51, 488-503.

Omernik JM; Powers CF. (1983). Map Supplement: Total Alkalinity of Surface Waters-A National Map. Annals of the Association of American Geographers, 73, 133-136.

Op Den Camp HJM; Kartal B; Guven D; van Niftrik LAMP; Haaijer SCM; van der Star WRL; Pas-Schoonen KTvd; Cabezas A; Ying Z; Schmid MC; Kuypers MMM; van de Vossenberg J; Harhangi HR; Picioreanu C; van Loosdrecht MCM; Kuenen JG; Strous M; Jetten MS. (2006). Global impact and application of the anaerobic ammonium-oxidizing (anammox).bacteria. Biochemical Society Transactions, 34, 174-178.

Ordóñez C; Richter A; Steinbacher M; Zellweger C; Nüß H; Burrows JP; Prévôt ASH. (2006). Comparison of 7 years of satellite-borne and ground-based tropospheric NO_2 measurements around Milan, Italy. J Geophys Res, 111, doi: 10.1029/2005JD006305.

Oren R; Ellsworth DS; Johnsen KH; Phillips N; Ewers BE; Maier C; Schäfer KVR; McCarthy H; Hendrey G; McNulty SG; Katul GG. (2001). Soil fertility limits carbon sequestration by forest ecosystems in a CO_2-enriched atmosphere. Nature, 411, 469-472.

Oreskes N; Shrader-Frechette K; Belitz K. (1994). Verification, validation, and confirmation of numerical models in the earth sciences. Science, 263, 641-646.

Ormerod SJ; Tyler SJ; Lewis JMS. (1985). Is the breeding distribution of dippers influenced by stream acidity. Bird Study, 32, 32-39.

Ormerod SJ; Allinson N; Hudson D; Tyler SJ. (1986). The distribution of breeding dippers (Cinclus cinclus) [L.]; Aves) in relation to stream acidity in upland Wales. Freshw Biol, 16, 501-507.

Ormerod SJ; Tyler SJ. (1987). Dippers (*Cinclus cinclus*) and grey wagtails (*Motacilla cinerea*) as indicators of stream acidity in upland Wales. In: Diamond AW; Filion FL (Eds.), The value of birds. (ICBP technical publication no. 6 pp 191-208). Cambridge, UK: International Council for Bird Preservation (ICBP).

Ormerod SJ; Boole P; McCahon CP; Weatherley NS; Pascoe D; Edwards RW. (1987). Short-term experimental acidification of a Welsh UK stream comparing the biological effects of hydrogen ions and aluminum. Freshwater Biol, 17, 341-356.

Ormerod SJ; Tyler SJ. (1991). Exploitation of prey by a river bird, the dipper *Cinclus cinclus* (L.), along acidic and circumneutral streams in upland Wales. Freshwater Biol, 25, 105-116.

Orth RJ; Moore KA. (1984). Distribution and abundance of submerged aquatic vegetation in Chesapeake Bay: an historical prespective. Estuaries, 7, 531-540.

Osthoff HD; Brown SS; Ryerson TB; Fortin TJ; Lerner BM; Williams EJ; Pettersson A; Baynard T; Dubé WP; Ciciora SJ; Ravishankara AR. (2006). Measurement of atmospheric NO_2 by pulsed cavity ring-down spectroscopy. J Geophys Res, 111, doi: 10.1029/2005JD006942.

Ott LE; Pickering KE; Stenchikov GL; Huntrieser H; Schumann U. (2007). Effects of lightning NO_X production during the July 21 European Lightning Nitrogen Oxides Project storm studied with a three-dimensional cloud-scale chemical transport model. J Geophys Res, 112, doi: 10.1029/2006JD007365.

Ouimet R; Arp PA; Watmough SA; Aherne J; Demerchant I. (2006). Determination and mapping critical loads of acidity and exceedances for upland forest soils in Eastern Canada. Water Air Soil Pollut, 172, 57-66.

Padgett P; Allen EB. (1999). Differential responses to nitrogen fertilization in native shrubs and exotic annuals common to Mediterranean coastal sage scrub of California. Plant Ecology, 144, 93-101.

Padgett PE; Allen EB; Bytnerowicz A; Minnich RA. (1999). Changes in soil inorganic nitrogen as related to atmospheric nitrogenous pollutants in southern California. Atmos Environ, 33, 769-781.

Padro J. (1996). Summary of ozone dry deposition velocity measurements and model estimates over vineyard, cotton, grass and deciduous forest in summer. Atmos Environ, 30, 2363-2369.

Paerl HW. (1985). Enhancement of marine primary production by nitrogen-enriched acid rain. Nature, 315, 747-749.

Paerl H. (1995). Coastal eutrophication in relation to atmospheric nitrogen deposition: current perspectives. Ophelia, 41, 237-259.

Paerl H. (1997). Coastal eutrophication and harmful algal blooms: importance of atmospheric deposition and groundwater as "new" nitrogen and other nutrient sources. Limnol Oceanogr, 42, 1154-1162.

Paerl H; Pinckney J; Fear J; Peierls B. (1998). Ecosystem responses to internal and watershed organic matter loading: Consequences for hypoxia in the eutrophying Neusse River Estuary, NC, USA. Mar Ecol Prog Ser, 166, 17-25.

Paerl HW; Pinckney JL; Steppe TF. (2000). Cyanobacterial-bacterial mat consortia: examining the functional unit of microbial survival and growth in extreme environments. Environmental Microbiology, 2, 11-26.

Paerl HW; Boynton WR; Dennis RL; Driscoll CT; Greening HS; Kremer JN; Rabalais NN; Seitzinger SP. (2001a). Atmospheric deposition of nitrogen in coastal waters: Biogeochemical and ecological implications. In: Valigura RW; Alexander RB; Castro MS; Meyers TP; Paerl HW; Stacey PE; Turner RE (Eds.), Nitrogen loading in coastal water bodies: an atmospheric perspective. (Coastal and estuarine series; Volume 57, pp 11-52). Washington, DC: American Geophysical Union.

Paerl HW; Bales JD; Ausley LW; Buzzelli CP; Crowder LB; Eby LA; Go M; Peierls BL; Richardson TL; Ramus JS. (2001b). Ecosystem impacts of three sequential hurricanes (Dennis, Floyd, and Irene) on the United States' largest lagoonal estuary, Pamlico Sound, NC. Proc Natl Acad Sci USA, 98, 5655-5611.

Paerl HW. (2002). Connecting atmospheric deposition to coastal eutrophication. Environ Sci Technol, 36, 323A-326A.

Paerl HW; Dennis RL; Whitall DR. (2002). Atmospheric deposition of nitrogen: Implications for nutrient over-enrichment of coastal waters. Estuaries, 25, 677–693

Paerl HW; Valdes LM; Pinckney JL; Piehler MF; Dyble J; Moisander PH. (2003). Phytoplankton photopigments as indicators of estuarine and coastal eutrophication. Bioscience, 53, 953-964.

Paerl HW; Valdes LM; Peierls BL; Adolf JE; Harding LW. (2006). Anthropogenic and climatic influences on the eutrophication of large estuarine ecosystems. Limnol Oceanogr, 51, 448-462.

Palmer PI; Abbot DS; Fu T-M; Jacob DJ; Chance K; Kurosu TP; Guenther A; Wiedinmyer C; Stanton JC; Pilling MJ; Pressley SN; Lamb B; Sumner AL. (2006). Quantifying the seasonal and interannual variability of North American isoprene emissions using satellite observations of the formaldehyde column. J Geophys Res, 111, 10.1029/2005JD006689.

Palmer RE; Klauda RJ; Lewis TE. (1988). Comparative sensitivities of bluegill, channel catfish and fathead minnow to pH and aluminum. Environ Toxicol Chem, 7, 505-516.

Palmer SM; Driscoll CT; Johnson CE. (2004). Long-term trends in soil solution and stream water chemistry at the Hubbard Brook Experimental Forest: relationship with landscape position. Biogeochemistry, 68, 51-70.

Palmqvist K. (2000). Carbon economy in lichens. New Phytol, 148, 11-36.

Palmqvist K; Campbell D; Ekblad A; Johansson H. (1998). Photosynthetic capacity in relation to nitrogen content and its partitioning in lichens with different photobionts. Plant, Cell and Environment, 21, 361-372.

Palmqvist K; Dahlman L. (2006). Responses of the green algal foliose lichen Platismatia glauca to increased nitrogen supply. New Phytol, 171, 343-356.

Pandis SN. (2004). Atmospheric aerosol processes. In: McMurry PH; Shepard M; Vickery JS (Ed.), Particulate Matter Science for Policy Makers: A NARSTO Assessment (Chapter 3). Cambridge, UK: Cambridge University Press.

Papen H; Daum M; Steinkamp R; Butterbach-Bahl K. (2001). N_2O- and CH_4-fluxes from soils of a N-limited and N-fertilized spruce forest ecosystem of the temperate zone. J Appl Bot, 75, 159-163.

Paquet J; Belanger L. (1997). Public acceptability thresholds of clearcutting to maintain visual quality of boreal balsam fir landscapes. For Sci, 43, 46-55.

Pardo LH; Driscoll CT. (1993). A critical review of mass balance methods for calculating critical loads of nitrogen for forest ecosystems. Environmental Review, 1, 145-156.

Pardo LH; Driscoll CT; Likens GE. (1995). Patterns of nitrate loss from a chronosequence of clear-cut watersheds. Water Air Soil Pollut, 85, 1659-1664.

Pardo LH; Driscoll CT. (1996). Critical loads for nitrogen deposition: case studies at two northern hardwood forests. Water Air Soil Pollut, 89, 105-128.

Pardo LH; Kendall C; Pett-Ridge JP; Change CCY. (2004). Evaluating the source of streamwater nitrate using $\delta^{15}N$ and $\delta^{18}O$ in nitrate in two watersheds in New Hampshire, USA. Hydrological Processes, 18, 2699-2712.

Pardo LH; Duarte N. (2007). Assessment of effects of acidic deposition on forested ecosystems in Great Smoky Mountains National Park using critical loads for sulfur and nitrogen. http://www2.nature.nps.gov/air/Pubs/pdf/GSMN_CL_Report_080830.pdf. Lakewood, CO; Air Resources Division; National Park Service; U.S. Department of the Interior.

Park J; Mitchell MJ; McHale PJ; Christopher SF; Myers TP. (2003). Interactive effects of changing climate and atmospheric deposition on N and S biogeochemistry in forested watershed of the Adirondack Mountains, New York State. Glob Chang Biol, 9, 1602-1619.

Park RJ; Stenchikov GL; Pickering; Dickerson RR; Allen DJ; Kondragunta S. (2001). Regional air pollution and its radiative forcing: studies with a single column chemical and radiation transport model. J Geophys Res, 106, 28751-28770.

Park TA; Bowker JM; Leeworthy VR. (2002). Valuing Snorkeling Visits to the Florida Keys With Stated and Revealed Preference Models. J Environ Manage, 65, 301-312.

Parker DR; Zelazny LW; Kinraide TB. (1989). Chemical speciation and plant toxicity of aqueous aluminum. In: Lewis TE (Ed.), Environmental chemistry and toxicology of aluminum (pp. 117-145). American Chemical Society.

Parker JL; Fernandez IJ; Rustad LE; Norton SA. (2001). Effects of nitrogen enrichment, wildfire, and harvesting on forest-soil carbon and nitrogen. Soil Sci Soc Am J, 65, 1248-1255.

Parker KE. (1988). Common loon reproduction and chick feeding on acidified lakes in the Adirondack Park, New York. Canadian Journal of Zoology, 66, 804-810.

Parkhurst DL; Appelo CAJ. (1999). User's Guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. (Water-Resources Investigations Report). Denver, CO: U.S. Geological Survey.

Parrish DD; Trainer M; Buhr MP; Watkins BA; Fehsenfeld FC. (1991). Carbon monoxide concentrations and their relation to concentrations of total reactive oxidized nitrogen at two rural U.S. sites. J Geophys Res, 96, 9309-9320.

Parrish DD; Trainer M; Young V; Goldan PD; Kuster WC; Jobson BT; Fehsenfeld FC; Lonneman WA; Zika RD; Farmer CT; Riemer DD; Rodgers MO. (1998). Internal consistency tests for evaluation of measurements of anthropogenic hydrocarbons in the troposphere. J Geophys Res, 103, 22339-22359.

Parrish DD; Fehsenfeld FC. (2000). Methods for gas-phase measurements of ozone, ozone precursors and aerosol precursors. Atmos Environ, 34, 1921-1957.

Parrish DD; Trainer M; Hereid D; Williams EJ; Olszyna KJ; Harley RA; Meagher JF; Fehsenfeld FC. (2002). Decadal change in carbon monoxide to nitrogen oxide ratio in U.S. vehicular emissions. J Geophys Res, 107, doi: 10.1029/2001JD000720.

Parton WJ; Schimel DS; Ojima DS; Cole CV. (1994). A general model for soil organic matter dynamics: sensitivity to litter chemistry, texture and management. In: Bryant RB; Arnold RW (Eds.), Quantitative Modeling of Soil Forming Processes (pp. 147-167). Madison, WI: Soil Sci Society of America.

Parton WJ; Hartman M; Ojima D; Schimel D. (1998). DAYCENT and its land surface submodel: Description and testing. Global Planet Change, 19, 35-48.

Parton W; Silver WL; Burke IC; Grassens L; Harmon ME; Currie WS; King JY; Adair EC; Brandt LA; Hart SC; Fasth B. (2007). Global-scale similarities in nitrogen release patterns during long-term decomposition. Science, 315, 361-364.

Paschke MW; McLendon T; Redente EF. (2000). Nitrogen availability and old-field succession in a shortgrass steppe. Ecosystems, 3, 144-158.

Paul AJ; Leavitt PR; Schindler DW; Hardie AK. (1995). Direct and indirect effects of predation by a calanoid copepod (subgenus: *Hesperodiaptomus*) and of nutrients in a fishless alpine lake. Can J Fish Aquat Sci, 52, 2628-2638.

Pauli D; Peintinger M; Schmid B. (2002). Nutrient enrichment in calcareous fens: effects on plant species and community structure. Basic and Applied Ecology, 3, 255-266.

Paulsen SG; Larsen DP; Kaufmann PR; Whittier TR; Baker JR; Peck D; McGue J; Hughes RM; McMullen D; Stevens D; Stoddard JL; Lazorchak J; Kinney W; Selle AR; Hjort R. (1991). EMAP: Surface waters monitoring and research strategy, fiscal year. Corvallis, OR; Environmental Research Laboratory; Office of Research and Development; U.S. Environmental Protection Agency.

Paz-Gonzalez A; Taboada MT. (2000). Nutrient variability from point sampling on 2 meter grid in cultivated and adjacent forest land. Comm. Soil Sci Plant Anal, 31, 2135-2146.

Pearcy RW; Björkman O; Caldwell MM; Keeley JE; Monson RK; Strain BR. (1987). Carbon gain by plants in natural environments. BioScience 37: 21-29.

Pearson J; Stewart RG. (1993). Atmospheric ammonia deposition and its effects on plants. Tansley Review No 56, New Phytol, 283-305.

Peierls BL; Caraco NF; Pace ML; Cole JJ. (1991). Human influence on river nitrogen. Nature 350, 386-387.

Peierls BL; Paerl HW. (1997). The bioavailability of atmospheric organic nitrogen deposition to coastal phytoplankton. Limnol Oceanogr, 42, 1819-1823.

Pembrook H. (2004). 2004 update: Calculating critical loads of acidity and exceedances for acid-impaired lakes in Vermont using the steady-state water chemistry (SSWC).model: Water Quality Division of the DEC; Vermont Agency of Natural Resources.

Perdue EM; Reuter JH; Parrish RS. (1984). A statistical model of proton binding by humus. Geochim Cosmochim Acta, 48, 1257-1263.

Pérez I; Wooldridge PJ; Cohen RC. (2007). Laboratory evaluation of a novel thermal dissociation chemiluminescence method for in situ detection of nitrous acid. Atmos Environ, 41, 3993-4001.

Perrini G; Tomasello M; Librando V; Minniti Z. (2005). Nitrated polycyclic aromatic hydrocarbons in the environment: formation, occurrences and analysis. Annales de Chimie: Science des Materiaux, 95, 567-577.

Peterjohn WT; Adams MB; Gilliam FS. (1996). Symptoms of nitrogen saturation in two central Appalachian hardwood forest ecosystems. Biogeochemistry, 35, 507-522.

Peterjohn WT; Correll DL. (1984). Nutrient dynamics in an agricultural watershed: Observation on the role of a riparian forest. Ecology, 65, 1466-1475.

Peters K; Eiden R. (1992). Modelling the dry deposition velocity of aerosol particles to a spruce forest. Atmospheric Environment 26A: 2555-2564.

Peterson BJ; Wollheim WM; Mulholland PJ; Webster JW; Meyer JL; Tank JL; Marti E; Bowden WB; Valett HM; Hershey AE; McDowell WH; Dodds WK; Hamilton SK; Gregory SV; Morrall DD. (2001). Control of nitrogen export from watersheds by headwater streams. Science, 292, 86-89.

Peterson DG; Rowe RD; Schulze WD; Russell GW; Boyce RR; Elliott SR; Hurd B. (1987a). Valuation of Visual Forest Damages from Ozone. In: Improving Accuracy and Reducing Costs of Environmental Benefit Assessments. (Energy & Resource Consultants report to U.S. Environmental Protection Agency). Boulder, CO; Center for Economic Analysis, University of Colorado.

Peterson DL; Arbaugh MJ; Wakefield VA; Miller PR. (1987b). Evidence for growth reduction in ozone injured Jeffrey pine (*Pinus jeffreyi* Grev. and Balf.). in Sequoia and Kings Canyon National Parks. J Air Pollut Control Assoc, 37, 908-912.

Peterson DL; Arbaugh MJ; Robinson LJ. (1991). Regional growth changes in ozone-stressed ponderosa pine (*Pinus ponderosa*).in the Sierra Nevada, California, USA. Holocene, 1, 50-61.

Peterson DL; Sullivan TJ; Eilers JM; Brace S; Horner D; Savig K; Morse D. (1998a). Assessment of air quality and air pollutant impacts in national parks of the Rocky Mountains and northern Great Plains. (Report NPS/CCSOUW/NRTR-98/19). http://www2.nature.nps.gov/air/Pubs/regionPark.cfm. Denver, CO; Air Resources Division; National Park Service, U.S. Department of the Interior.

Peterson EB; Neitlich P. (2001). Impacts of two coal-fired power plants on lichen communities of northwestern Colorado. Washington, DC: Forest Health Monitoring Program; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Peterson G; Allen CR; Holling CS. (1998b). Ecological resilience, biodiversity, and scale. Ecosystems,1, 6-18.

Peterson RH; Daye PG; Metcalfe JL. (1980). Inhibition of Atlantic salmon (*Salmo salar*) hatching at low pH. Can J Fish Aquat Sci, 37, 770-774.

Peterson RH; Martin-Robichaud DJ. (1986). Growth and major inorganic cation budgets of Atlantic salmon alevins at three ambient acidities. Trans Am Fish Soc, 115, 220-226.

Peterson RH; Van Eechhaute L. (1992). Distributions of Ephemeroptera, Plecoptera, and Trichoptera of three maritime catchments differing in pH. Freshwater Biol, 27, 65-78.

Peterson SA; Van Sickle J; Herlihy AT; Hughes GH. (2007). Mercury concentration in fish from streams and rivers throughout the western United States. Environ Sci Technol, 41, 58-65.

Petriconi GL; Papee HM. (1972). On the photolytic separation of halogens from sea water concentrates. Water Air Soil Pollut, 1, 117-131.

Pfister GG; Emmons LK; Hess PG; Honrath R; Lamarque J-F; Val Martin M; Owen RC; Avery MA; Browell EV; Holloway JS; Nedelec P; Purvis R; Ryerson TB; Sachse GW; Schlager H. (2006). Ozone production from the 2004 North American boreal fires. J Geophys Res, 111, doi: 10.1029/2006JD007695.

Phillips K. (1990). Where have all the frogs and toads gone? BioScience, 40, 422-424.

Phillips RL; Whalen SC; Schlesinger WH. (2001). Influence of atmospheric CO_2 enrichment on nitrous oxide flux in a temperate forest ecosystem. Glob BiogeochemCycles, 15, 741-752.

Phillips RL; Zak DR; Holmes WE; White DC. (2002). Microbial community composition and function beneath temperate trees exposed to elevated atmospheric carbon dioxide and ozone. Oecologia, 131, 236-244.

Phillips RP; Yanai RD. (2004). The effects of $AlCl_3$ additions on rhizosphere soil and fine root chemistry of sugar maple (*Acer saccharum*). Water Air Soil Pollut, 159, 339-356.

Piao S; Ciais P; Friedlingstein P; Peylin P; Reichstein M; Luyssaert S; Margolis H; Fang J; Barr A; Chen,A; Grelle A; Hollinger DY; Laurila T; Lindroth A; Richardson AD; Vesala T. (2008). Net carbon dioxide losses of northern ecosystems in response to autumn warming. Nature, 451, 49-52.

Pickering KE; Thompson AM; Dickerson RR; Luke WT; McNamara DP; Greenberg JP; Zimmerman PR. (1990). Model calculations of tropospheric ozone production potential following observed convective events. J Geophys Res, 95, 14049-14062.

Pickering KE; Thompson AM; Scala JR; Tao W-K; Simpson J; Garstang M. (1991). Photochemical ozone production in tropical squall line convection during NASA Global Tropospheric Experiment/Amazon Boundary Layer Experiment 2A. J Geophys Res, 96, 3099-3114.

Pickering KE; Thompson AM; Scala JR; Tao W-K; Dickerson RR; Simpson J. (1992a). Free tropospheric ozone production following entrainment of urban plumes into deep convection. J Geophys Res, 97, 17985-18000.

Pickering KE; Thompson AM; Scala JR; Tao W-K; Simpson J. (1992b). Ozone production potential following convective redistribution of biomass burning emissions. J Atmos Chem , 14, 297-313.

Pickering KE; Thompson AM; Tao W-K; Kucsera TL. (1993). Upper tropospheric ozone production following mesoscale convection during STEP/EMEX. J Geophys Res, 98, 8737-8749.

Pickering KE; Thompson AM; Tao W-K; Rood RB; McNamara DP; Molod AM. (1995). Vertical transport by convective clouds: comparisons of three modeling approaches. Geophys Res Lett, 22, 1089-1092.

Pickering KE; Thompson AM; Wang Y; Tao W-K; McNamara DP; Kirchhoff WJH; Heikes BG; Sachse GW; Bradshaw JD; Gregory GL; Blake DR. (1996). Convective transport of biomass burning emissions over Brazil during TRACE A. J Geophys Res, 101, 23993-24012.

Pickering KE; Wang Y; Tao W-K; Price C; Müller J-F. (1998). Vertical distributions of lightning NO_X for use in regional and global chemical transport models. J Geophys Res, 103, 31203-31216.

Pickering KE; Thompson AM; Kim H; DeCaria AJ; Pfister L; Kucsera TL; Witte JC; Avery MA; Blake DR; Crawford JH; Heikers BG; Sachse GW; Sandholm ST; Talbot RW. (2001). Trace gas transport and scavenging in PEM-Tropics B South Pacific Convergence Zone convection. J Geophys Res, 106, 32591-32602.

Pike LH. (1978). The importance of epiphytic lichens in mineral cycling. Bryologist, 81, 247-257.

Pikelnaya, O; Hurlock, S. C; Trick, S; Stutz, J. (2005). Measurements of reactive iodine species on the Isles of Shoals, Gulf of Maine. EOS Trans. Am. Geophys. Union 86, A14A-06. http://www.agu.org/meetings/fm05/fm05-sessions/fm05_A14A.html.

Pikelnaya O; Hurlock SC; Trick S; Stutz J. (2007). Intercomparison of multiaxis and long-path differential optical absorption spectroscopy measurements in the marine boundary layer. J Geophys Res, 112, doi: 10.1029/2006JD007727.

Pilcher H. (2005). Pipe Dreams. Nature, 437, 1227-1228.

Pilegaard K; Skiba U; Ambus P; Beier C; Bruggemann N; Butterbach-Bahl K; Dick J; Dorsey J; Duyzer J; Gallagher M; Gasche R; Horvath L; Kitzler B; Leip A; Pihlatie MK; Rosenkranz P; Seufert G; Vesala T; Westrate H; Zechmeister-Boltenstern S. (2006). Factors controlling regional differences in forest soil emission of nitrogen oxides (NO and N_2O). Biogeosciences, 3, 651-661.

Pimentel AS; Arbilla G. (1997). Simulation of the urban atmosphere chemistry polluted by alcohol fueled automobiles. Química Nova, 20, 252-260.

Pimentel D; Wilson C; McCullum C; Huang R; Dwen P; Flack J; Tran Q; Saltman T; Cliff B. (1997). Economic and environmental benefits of biodiversity. Bioscience, 47, 747-757.

Pimm SL. (1984). The complexity and stability of ecosystems. Nature, 307, 321-326

Pinay G; Black VJ; Planty-Tabacchi AM; Gumiero B; Décamps H. (2000). Geomorphic control of denitrification in large river floodplain soils. Biogeochemistry, 50, 163-182.

Pinay G; Roques L; Fabre A. (1993). Spatial and temporal patterns of denitrification in a riparian forest. J Appl Ecol, 30, 581-591.

Pinckney JL; Richardson TL; Millie DF; Paerl HW. (2001). Application of photopigment biomarkers for quantifying microalgal community composition and in situ growth rates. Organic Geochemistry, 32, 585-595.

Pinder RW; Strader R; Davidson CI; Adams PJ. (2004). A temporally and spatially resolved ammonia emission inventory for dairy cows in the United States. Atmos Environ, 38, 3747-3756.

Pinder RW; Adams PJ; Pandis SN; Gilliland AB. (2006). Temporally resolved ammonia emission inventories: current estimates, evaluation tools, and measurement needs. J Geophys Res, 111, D16310, doi:10.1029/2005JD006603.

Pinder RW; Adams PJ; Pandis SN. (2007). Ammonia emission controls as a cost-effective strategy for reducing atmospheric particulate matter in the Eastern United States. Environ Sci Technol, 41, 380-386.

Pinto JP; Turco RP; Toon OB. (1989). Self-limiting physical and chemical effects in volcanic eruption clouds. J Geophys Res, 94, 11165-11174.

Pinto JP; Bruhl C; Thompson AM. (1993). The current and future enviorionmental role of atmospheric methane: model studies and uncertainties, pp. 514-551. In: Khalil MAK (Ed.), Atmospheric methane sources, sinks, and role in global change (Vol. 13, NATO ASI Series): NATO.

Pippin M; Bertman S; Thornberry T; Town M; Carroll MA; Sillman S. (2001). Seasonal variations of PAN, PPN, and O_3 at the upper Midwest PROPHET site [O_3]. J Geophys Res, 106, 24457-24463.

Pitcairn CER; Fowler D; Leith ID; Sheppard LJ; Sutton MA; Kennedy V; Okello E. (2003). Bioindicators of enhanced nitrogen deposition. Environ Pollut, 126, 353-361.

Pitchford M. (2008). Carbon analysis workshop summary. Presented at the 2008 IMPROVE Steering Committee Meeting, held in Okefenokke NWR, GA; October 28 - 29, 2008

Pitts JN Jr; Biermann HW; Atkinson R; Winer AM. (1984). Atmospheric implications of simultaneous nighttime measurements of NO3 radicals and HONO. Geophys Res Lett, 11, 557-560.

Pitts JN Jr. (1987). Nitration of gaseous polycyclic aromatic hydrocarbons in simulated and ambient urban atmospheres: a source of mutagenic nitroarenes. Atmos Environ, 21, 2531-2547.

Plafkin JL; Barbour MT; Porter KD; Gross SK; Hughes RM. (1989). Rapid bioassessment protocols for use in streams and rivers: benthic macroinvertebrates and fish. (Report no. EPA 440-89-001). Washington, DC; Office of Water Regulations and Standards; U.S. Environmental Protection Agency.

Poe GL; Boyle KJ; Bergstrom JC. (2000). A meta-analysis of contingent values for groundwater quality in the United States. Paper presented at the American Agricultural Economics Association Conference held in Tampa, FL; July 30-August2, 2000. (No 21871). http://ageconsearch.umn.edu/bitstream/21871/1/sp00po03.pdf

Poff NL; Allan JD; Bain MB; Karr JR; Prestegaard KL; Richter BD; Sparks RE; Stromberg JC. (1997). The natural flow regime: a paradigm for river conservation and restoration. BioScience, 47, 769-784.

Pokharel SS; Bishop GA; Stedman DH. (2002). An on-road motor vehicle emissions inventory for Denver: An efficient alternative to modeling. Atmos Environ, 36, 5177-5184.

Polasky S; Costello C; Solow A. (2005). Economics of Biodiversity. In: Mäler K-G, Vincent JR (Eds.), Handbook of Environmental Economics (Vol. 3, pp. 1517-1560). Amsterdam, The Netherlands: Elsvier Publishing.

Pollman CD; Sweets PR. (1990). Hindcasting of pre-cultural ANC and pH of seepage lakes in the Adirondacks, Upper Midwest, and Florida. (Report no. EPA 89007B1/RES-1). Corvallis, OR; U.S. Environmental Protection Agency.

Pollman CD; Canfield DE. (1991). Florida, hydrologic and biogeochemical controls on seepage lake chemistry. In: Charles DF; Christie S (Eds.), Acidic deposition and aquatic ecosystems: Regional case studies. (pp 367-416). New York: Springer-Verlag,.

Ponnamperuma FN. (1972). The chemistry of submerged soils. Adv Agron, 24, 29-96.

Poor JP; Pessagno KL; Paul RW. (2006). Exploring the hedonic value of ambient water quality: A local watershed-based study. Ecol Econ, 60, 797-806.

Poppe D; Wallasch M; Zimmermann J. (1993). The dependence of the concentration of OH on its precursors under moderately polluted conditions: a model study. J Atmos Chem, 16, 61-78.

Porter E; Blett T; Potter DU; Huber C. (2003). Protecting resources on federal lands: Implications of critical loads for atmospheric deposition of nitrogen and sulfur. Bioscience, 55, 603-612.

Posch M; Reinds GJ; de Vries W. (1993). SMART – A simulation model for acidification's regional trends: Model description and user manual. (Report no 477). Helsinki, Finland: Mimeograph Series of the National Board of Waters and the Environment.

Posch M; De Smet PAM; Hettelingh J-P; Downing RJ (Eds.) (1995a). Calculation and mapping of critical thresholds in Europe. (Status report 1995; Coordination Center for Effects; RIVM report no. 259101004). Bilthoven, The Netherlands: National Institute of Public Health and the Environment (RIVM). http://www.mnp.nl/bibliotheek/rapporten/259101004.pdf.

Posch M; de Vries W; Hettelingh JP. (1995b). Critical loads of sulfur and nitrogen. Calculation and mapping of critical loads in Europe, Status Report, 31–41.

Posch M; Kämäri J; Forsius M; Henriksen A; Wilander A. (1997). Environmental auditing: Exceedance of critical loads for lakes in Finland, Norway and Sweden: reduction requirements for acidifying nitrogen and sulfur deposition. Environ Manage, 21, 291-304.

Posch M; DeSmet PAM; Hettelingh JP; Downing RJ. (2001). Calculation and mapping of critical thresholds in Europe. (Status report 2001; RIVM report no. 259101010). http://www.mnp.nl/cce/Images/SR01_tcm42-16441.pdf. Bilthoven, The Netherlands: Coordination Center for Effects, National Institute of Public Health and the Environment (RIVM).

Posch M; Reinds GJ. (2003). VSD - User Manual of the Very Simple Dynamic soil acidification model. Bilthoven, The Netherlands: Coordination Center for Effects, RIVM.

Posch M; Hettelingh J-P; Slootweg J (Eds.). (2003). Manual for dynamic modelling of soil response to atmospheric deposition. (Working Group on Effects of the Convention on Long-range Transboundary Air Pollution; report 259101012). http://www.mnp.nl/cce/Images/ModMan1_tcm42-16497.pdf. Bilthoven, The Netherlands: National Institute for Public Health and the Environment (RIVM).

Possanzini M; De Santis F; Di Palo V. (1999). Measurements of nitric acid and ammonium salts in lower Bavaria. Atmos Environ, 33, 3597-3602.

Poth MA; Fenn ME. (1998). Mature ponderosa pine nutrient use and allocation responses to air pollution. Riverside, CA; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Powell JFF; McKeown BA. (1986). The effects of acid exposure on the ion regulation and seawater adaptation of Coho salmon (*Oncorhynchus kisutch*) parrs and smolts. Comp Biochem Physiol C: Comp Pharmacol, 83, 45-52.

Power SA; Green ER; Barker CG; Bell JNB; Ashmore MR. (2006). Ecosystem recovery: heathland response to a reduction in nitrogen deposition. Glob Chang Biol, 12, 1241-1252.

Prather MJ; Jacob DJ. (1997). A persistent imbalance in HOx and NO_X photochemistry in the upper troposphere driven by deep tropical convection. Geophys Res Lett, 24, 3189-3192.

Pregitzer KS; Burton AJ; Mroz GD; Liechty HO; Macdonald NW. (1992). Foliar sulfur and nitrogen along an 800-km pollution gradient. Can J For Res, 22, 1761-1769.

Pregitzer KS; Zak DR; Maziasz J; DeForest J; Curtis PS; Lussenhop J. (2000). Interactive effects of atmospheric CO_2 and soil-N availability on fine roots of *Populus tremuloides*. Ecol Appl, 10, 18-33.

Pregitzer KS; Zak DR; Burton AJ; Ashby JA; MacDonald NW. (2004). Chronic nitrate additions dramatically increase the export of carbon and nitrogen from northern hardwood ecosystems. Biogeochemistry, 68, 179-197.

Pregitzer KS; Burton AJ; Zak DR; Talhelm AF. (2008). Simulated chronic nitrogen deposition increases carbon storage in Northern Temperate forests. Glob Chang Biol, 14, 142-153.

Preston SD; Brakebill JW. (1999). Application of spatially reference regression modeling for the evaluation of total nitrogen loading in the Chesapeake Bay Watershed: U.S. Geological Survey.

Prévôt ASH; Staehelin J; Kok GL; Schillawski RD; Neininger B; Staffelbach T; Neftel A; Wernli H; Dommen J. (1997). The Milan photooxidant plume. J Geophys Res, 102: 23375-23388.

Price C; Penner J; and Prather M. (1997). NO_X from lightning. 1. Global distribution based on lightning physics, J Geophys Res, 102, 5929–5941.

Priscu JC; Axler RP; Goldman CR. (1985). Nitrogen metabolism of the shallow and deep water phytoplankton in a subalpine lake. Oikos, 45, 137-147.

Probert ME; Samosir SSR. (1983). Sulfur in non-flooded tropical soils. In: Blair GJ, Till AR (Eds.), Sulfur in south-east Asian and South Pacific agriculture (pp. 15-27). Armidal, N.S.W. Australia: The University of New England; The Australian Development Association Bureau and the Sulphur Institute.

Providoli I; Bugmann H; Siegwolf R; Buchmann N; Schleppi P. (2005). Flow of deposited inorganic N in two Gleysol-dominated mountain catchments traced with $^{15}NO_3^-$ and $^{15}NH_4^+$. Biogeochemistry, 76, 453-475.

Pryor SC; Sørensen LL. (2000). Nitric Acid–Sea Salt Reactions: Implications for Nitrogen Deposition to Water Surfaces. Journal of Applied Meteorology, 39, 725-731.

Pryor SC; Barthelmie RJ; Sorensen LL; Jensen B. (2001). Ammonia concentrations and fluxes over a forest in the midwestern USA. Atmos Environ, 35, 5645-5656.

Pszenny AAP; Keene WC; Jacob DJ; Fan S; Maben JR; Zetwo MP; Springer-Young M; Galloway JN. (1993). Evidence of inorganic chlorine gases other than hydrogen chloride in marine surface air. Geophys Res Lett, 20, 699-702.

Pszenny AAP; Moldanova J; Keene WC; Sander R; Maben JR; Martinez M; Crutzen PJ; Perner D; Prinn RG. (2004). Halogen cycling and aerosol pH in the Hawaiian marine boundary layer. Atmos Chem Phys, 4, 147-168.

Pszenny AAP; Fischer EV; Russo RS; Sive BC; Varner RK. (2007). Estimates of Cl atom concentrations and hydrocarbon kinetic reactivity in surface air at Appledore Island, Maine (USA), during International Consortium for Atmospheric Research on Transport and Transformation/Chemistry of Halogens at the Isles of Shoals. J Geophys Res, 112, D10S13, doi:10.1029/2006JD007725.

Puhe J. (2003). Growth and development of the root system of Norway spruce (*Picea abies*) in forest stands—A review. For Ecol Manage, 175, 253-273.

Pun BK; Wu SY; Seigneur C; Seinfeld JH; Griffin RJ; Pandis SN. (2003). Uncertainties in Modeling Secondary Organic Aerosols: Three-Dimensional Modeling Studies in Nashville/Western Tennessee. Environ Sci Technol, 37, 3647-3661.

Pyzik L; Caddick J; Marx P. (2004). Chesapeake Bay: Introduction to an ecosystem. (Report no EPA-903-R-04-003 // CBP/TRS 232/00). Annapolis, MD: Chesapeake Bay Program (CBP). & Philadelphia, PA; Region III; Regional Center for Environmental Information; U.S. Environmental Protection Agency (EPA).

Qiao Z, Murray, F. (1998). Improvement of the $15 N Dilution Method for Estimation of Absorption of NO_X by Plants Supplied with $15 N-Labelled Fertilizer. New Phytol, 138, 13-18.

Quist ME; Nasholm T; Lindeberg J; Johannisson C; Hogbom L; Hogberg P. (1999). Responses of a nitrogen-saturated forest to a sharp decrease in nitrogen input. J Environ Qual, 28, 1970-1977.

Rabalais NN; Turner RE; Justic D; Dortch Q; Wiseman WJ; Gupta BKS. (1996). Nutrient changes in the Mississippi River and system responses on the adjacent continental shelf. Estuaries, 19, 386-407.

Rabalais NN. (1998). Oxygen depletion in coastal waters. (NOAA state of the coast report). http://oceanservice.noaa.gov/websites/retiredsites/sotc_pdf/HYP.PDF. Silver Springs, MD: National Oceanic and Atmospheric Administration (NOAA).

Rabalais NN. (2002). Nitrogen in aquatic ecosystems. Ambio, 31, 102-112.

Raddum GG; Fjellheim A. (1984). Acidification and early warning organisms in freshwater in western Norway. Verh Int Ver Theor Angew Limnol, 22, 1973-1980.

Raddum GG; Brettum P; Matzow D; Nilssen JP; Skov A; Svealy T; Wright RF. (1986). Liming the acid lake Hovvatn, Norway: a whole lake study. Water Air Soil Pollut, 31, 721-763.

Raddum GG; Skjelvåle BL. (2001). Critical limit of acidifying compounds to invertebrates in different regions of Europe. Water Air Soil Pollut, 130, 825-830.

Radke LF; Hegg DA; Hobbs PV; Nance JD; Lyons JH; Laursen KK; Weiss RE; Riggan PJ; Ward DE. (1991). Particulate and trace gas emissions from large biomass fires in North America. In: Levine JS (Ed.) Global biomass burning: atmospheric, climatic, and biospheric implications. (pp 209-224.). Cambridge, MA: MIT Press.

Rago PJ; Wiener JG. (1986). Does pH affect fish species richness when lake area is considered? Trans Am Fish Soc, 115, 438-447.

Rainey SM; Nadelhoffer KJ; Silver WL; Downs MR. (1999). Effects of chronic nitrogen additions on understory species in a red pine planation. Ecol Appl, 9, 949-957.

Raison RJ; McGarity JW. (1980). Some effects of plant ash on the chemical properties of soils and aqueous suspensions. Plant Soil, 55, 339-352.

Raivonen M; Keronen P; Vesala T; Kulmala M; Hari P. (2003). Measuring shoot-level NO_X flux in field conditions: The role of blank chambers. Boreal Environment Research, 8, 445-455.

Ramazan KA; Syomin D; Finlayson-Pitts BJ. (2004). The photochemical production of HONO during the heterogeneous hydrolysis of NO_2. Phys Chem Chem Phys, 6, 3836-3843.

Ramdahl T; Zielinska B; Arey J; Atkinson R; Winer AM; Pitts JN Jr. (1986). Ubiquitous occurrence of 2-nitrofluoranthene and 2-nitropyrene in air. Nature, 321, 425-427.

Randall A; Kriesel W. (1990). Evaluating national policy proposals by contingent valuation. In Johnson RL; Johnson GV (Eds.), Economic valuation of natural resources: Issues, theory, and applications. (pp 153-178). Boulder, CO: Westview Press.

Rapport DJ; Whitford WG. (1999). How Ecosystems Respond to Stress. Bioscience, 49, 193-203.

Rashid GH. (1987). Effects of fire on soil carbon and nitrogen in a Mediterranean oak forest of Algeria. Plant Soil, 103, 89-93.

Rattner BA; Haramis GM; Chu DS; Bunck CM; Scanes CG. (1987). Growth and physiological condition of black ducks reared on acidified wetlands. Can J Zool, 65, 2953-2958.

Rattray G; Sievering H. (2001). Dry deposition of ammonia, nitric acid, ammonium, and nitrate to alpine tundra at Niwot Ridge, Colorado. Atmos Environ, 35, 1085-1109.

Ravishankara AR. (1997). Heterogeneous and multiphase chemistry in the troposphere. Science, 276, 1058-1065.

Reader JP; Dalziel TRK; Morris R. (1988). Growth, mineral uptake and skeletal calcium deposition in brown trout, *Salmo trutta* L., yolk-sac fry exposed to aluminum and manganese in soft acid water. Journal of Fish Biology, 32, 607-624.

Reavie ED; Smol JP. (2001). Diatom-environmental relationships in 64 alkaline southwestern Ontario (Canada).lakes: a diatom-based model for water quality reconstructions. J Paleolimnol, 25, 27-44.

Reckhow KH; Black RW; Stockton TB Jr; Vogt JD; Wood JG. (1987). Empirical models of fish response to lake acidification. Can J Fish Aquat Sci, 44, 1432-1442.

Redbo-Torstensson P. (1994). The demographic consequences of nitrogen fertilization of a population of sundew, *Drosera rotundifolia*. Acta Botanica Neerlandica, 43, 175-188.

Redfield AC. (1958). The biological control of chemical factors in the environment. Am Sci, 46, 205-221.

Regina K; Nykanen H; Maljanen M; Silvola J; Martikainen PJ. (1998). Emissions of N_2O and NO and net nitrogen mineralization in a boreal forested peatland treated with different nitrogen compounds. Can J For Res, 28, 132-140.

Rehfuess K-E; Ågren GI; Andersson F; Cannell MGR; Friend A; Hunter I; Kahle H-P; Prietzel J; Spiecker H. (1999). Relationships between recent changes of growth and nutrition of Norway spruce, Scots pine, and European beech forests in Europe. (EFI working paper 19). Joensuu, Finland: European Forest Institute.

Reich PB. (1987). Quantifying plant response to ozone: a unifying theory. Tree Physiol, 3, 63-91.

Reich PB; Grigal DF; Aber JD; Gower ST. (1997a). Nitrogen mineralization and productivity in 50 hardwood and conifer stands on diverse soils. Ecology, 78, 335-347.

Reich PB; Walters MB; Ellsworth DS. (1997b). From tropics to tundra: global convergence in plant functioning. Proc Natl Acad Sci USA, 94, 13730-13734.

Reiners WA. (1986). Complementary models in ecology. The American Naturalist, 27, 59-73.

Reisen F; Arey J. (2005). Atmospheric reactions influence seasonal PAH and nitro-PAH concentrations in the Los Angeles basin. Environ Sci Technol, 39, 64-73.

Reithmeier C; Sausen R. (2002). ATTILA: atmospheric tracer transport in a Lagrangian model. Tellus, 54B, 278-299.

Renberg I, Korsman T; Anderson NJ. (1993). A temporal perspective of lake acidification in Sweden. Ambio, 22, 264-271.

Rennenberg H. (1984). The fate of excess sulfur in higher plants. Annual Review of Plant Physiology, 35, 121-153.

Resh VH; Norris, RH; Barbour MT. (1995). Design and implementation of rapid assessment approaches for water resource monitoring using benthic macroinvertebrates. Aust J Ecol, 20, 108-121.

Restrepo C; Zimmerman R; Thurston G; Clemente J; Gorczynski J; Zhong M; Blaustein M; Chen LC. (2004). A comparison of ground-level air quality data with New York State Department of Environmental Conservation monitoring stations data in South Bronx, New York. Atmos Environ, 38, 5295-5304.

Reuss JO. (1980). Simulation of soil nutrient losses due to rainfall acidity. Ecol Modell, 11, 15-38.

Reuss JO. (1983). Implications of the calcium-aluminum exchange system for the effect of acid precipitation on soils. J Environ Qual, 12, 591-595.

Reuss JO; Johnson DW. (1985). Effect of soil processes on the acidification of water by acid deposition. J Environ Qual, 14, 26-31.

Reuss JO; Johnson DW. (1986). Acid deposition and the acidification of soils and waters. (Series: Billings WD; Golley F; Lange OL; Olson JS; Remmert H (Eds.), Ecological studies: Analysis and synthesis; Volume 59). New York, NY: Springer-Verlag.

Reuss JO; Vertucci FA; Musselman RC; Sommerfeld RA. (1995). Chemical fluxes and sensitivity to acidification of two high-elevation catchments in southern Wyoming. J Hydrol, 173, 165-189.

Reuter JE; Loeb SL; Axler RP; Carlton RG; Goldman CR. (1985). Transformation of nitrogen following an epilimnetic nitrogen fertilization in Castle Lake, CA. 1. epilithic periphyton responses. Arch Hydrobiol, 102, 425-433.

Reuter JE; Loeb SL; Goldman CR. (1986). Inorganic nitrogen uptake by epilithic periphyton in a N-deficient lake. Limnol Oceanogr, 31, 149-160.

Reuter JE; Axler RP. (1992). Physiological characterisisics of inorganic nitrogen uptake by spatially separate algal communities in a nitrogen-deficient lake. Freshwater Biol, 27, 227-236.

Richardson DHS; Cameron RP. (2004). Cyanolichens: their response to pollution and possible management strategies for their conservation in notheastern North America. Northeastern Naturalist, 11, 1-22.

Richardson TL; Pinckney JL; Paerl HW. (2001). Responses of estuarine phytoplankton communities to nitrogen form and mixing using microcosm bioassays. Estuaries, 24, 828-839.

Richter A; Burrows JP; Nuss H; Granier C; Niemeier U. (2005). Increase in tropospheric nitrogen dioxide over China observed from space. Nature, 437, 129-132.

Richter DD; Markewitz D; Wells CG; Allen HL; April R; Heine PR; Urrego B. (1994). Soil Chemical Change during Three Decades in an Old-Field Loblolly Pine (*Pinus taeda* L.) Ecosystem. Ecology, 75, 1463-1473.

Richter DD; Markewitz D; Heine PR; Jin V; Raikes J; Tian K; Wells CG. (2000). Legacies of agriculture and forest regrowth in the nitrogen of old-field soils. For Ecol Manage, 138, 233-248.

Richter DD Jr; Markewitz D. (2001). Understanding soil change: Soil sustainability over millennia, centuries, and decades. Cambridge, UK: Cambridge University Press.

Riddell J; Nash Iii TH; Padgett P. (2008). The effect of HNO_3 gas on the lichen Ramalina menziesii. Flora - Morphology, Distribution, Functional Ecology of Plants, 203, 47-54.

Ridley BA; Dye JE; Walega JG; Zheng J; Grahek FE; Rison W. (1996). On the production of active nitrogen by thunderstorms over New Mexico. J Geophys Res, 101, 20985-21005.

Riegman R. (1992). *Phaeocystis* blooms and eutrophication of the continental coastal zones of the North Sea. Marine Biology, 112, 479-484.

Riggan PJ; Lockwood RN; Lopez EN. (1985). Deposition and processing of airborne nitrogen pollutants in Mediterranean-type ecosystems of southern California. Environ Sci Technol, 19, 781-789.

Riggan PJ; Lockwood RN; Jacks PM; Colver CG; Weirich F; DeBano LF; Brass JA. (1994). Effects of fire severity on nitrate mobilization in watersheds subject to chronic atmospheric deposition. Environ Sci Technol, 28, 369-375.

Rillig MC; Allen MF. (1998). Arbuscular mycorrhizae of Gutierrezia sarothrae and elevated carbon dioxide: evidence for shifts in C allocation to and within the mycobiont. Soil Biol. Biochem, 30, 2001-2008.

Rimmer CC; McFarland KP. (2005). Part I. Demographic monitoring of montane forest birds on Mt. Mansfield. In: Faccio SD; Rimmer CC (Eds.), 2004-2005 report to the Vermont monitoring cooperative. (VINS Technical Report 05-02). Woodstock, VT; Conservation Biology Department; Vermont Institute of Natural Science (VINS).

Rimmer CC; McFarland KP; Evers DC; Miller EK; Aubry Y; Busby D; Taylor RJ. (2005). Mercury concentrations in Bicknell's thrush and other insectivorous passerines in montane forests of northeastern North America. Ecotoxicology, 14, 223-240.

RMCC. (1990).The 1990 Canadian long-range transport of air pollutants and acid deposition assessment report, Part 4: Aquatic effects. Ottawa, Ontario, Canada: Federal/Provincial Research and Monitoring Coordinating Committee (RMCC).

Roberts BJ; Howarth RW. (2006). Nutrient and light availability regulate the relative contribution of autotrophs and heterotrophs to respiration in freshwater pelagic ecosystems. Limnol Oceanogr, 51, 288-298.

Roberts JM; Williams J; Baumann K; Buhr MP; Goldan PD; Holloway J; Hubler G; Kuster WC; McKeen SA; Ryerson TB; Trainer M; Williams EJ; Fehsenfeld FC; Bertman SB; Nouaime G; Seaver C; Grodzinsky G; Rodgers M; Young VL. (1998). Measurements of PAN, PPN, and MPAN made during the 1994 and 1995 Nashville Intensives of the Southern Oxidant Study: Implications for regional ozone production from biogenic hydrocarbons. J Geophys Res, 103, 22473-22490.

Roberts JM; Flocke F; Stroud CA; Hereid D; Williams E; Fehsenfeld F; Brune W; Martinez M; Harder H. (2002). Ground-based measurements of peroxycarboxylic nitric anhydrides (PANs) during the 1999 Southern Oxidants Study Nashville Intensive. J Geophys Res, 107.

Roberts JM; Jobson BT; Kuster W; Goldan P; Murphy P; Williams E; Frost G; Riemer D; Apel E; Stroud C. (2003). An examination of the chemistry of peroxycarboxylic nitric anhydrides and related volatile organic compounds during Texas Air Quality Study 2000 using ground-based measurements. J Geophys Res, 108, 4495.

Roberts JM; Flocke F; Chen G; Gouw J; Holloway JS; Hubler G; Neuman JA; Nicks DK; Nowak JB; Parrish DD. (2004). Measurement of peroxycarboxylic nitric anhydrides (PANs).during the ITCT 2K2 aircraft intensive experiment. J Geophys Res, 109.

Robertson GP; Crum JR; Ellis BG. (1993). The spatial variability of soil resources following long-term disturbance. Oecologia, 96, 451-456.

Rochelle BP; Church MR. (1987). Regional patterns of sulphur retention in watersheds of the eastern U.S. Water Air Soil Pollut, 36, 61-73.

Rochelle BP; Church MR; David MB. (1987). Sulfur retention at intensively studied sites in the U.S. and Canada. Water Air Soil Pollut, 33, 73-83.

Rodgers MO; Davis DD. (1989). A UV-photofragmentation/laser-induced fluorescence sensor for the atmospheric detection of HONO. Environ Sci Technol, 23, 1106-1112.

Rodriguez L; Macias F. (2006). Eutrophication trends in forest soils in Galicia (NW Spain).caused by the atmospheric deposition of nitrogen compounds. Chemosphere, 63, 1598-1609.

Roelofs JGM. (1986). The effect of airborne sulphur and nitrogen deposition on aquatic and terrestrial heathland vegetation. Experientia, 42, 372-377.

Roelofs JGM. (1991). Inlet of alkaline river water into peaty lowlands: effects on water quality and *Stratiotes aloides* L. stands. Aquatic Botany, 39, 267-293.

Roem WJ; Berendse F. (2000). Soil acidity and nutrient supply ratio as possible factors determining changes in plant species diversity in grassland and heathland communities. Biological Conservation, 92, 151-161.

Romansic JM; Diez KA; Higashi EM; Blaustein AR. (2006). Effects of nitrate and the pathogenic water mold Saprolegnia on survival of amphibian larvae. Dis Aquat.Org, 68, 235-243.

Rose C; Axler RP. (1998). Uses of alkaline phosphatase activity in evaluating phytoplankton community phosphorous deficiency. Hydrobiologia, 361, 145-156.

Rosemond AD; Reice SR; Elwood JW; Mulholland PJ. (1992). The effects of stream acidity on benthic invertebrate communities in the south-eastern United States. Freshwater Biol, 27, 193-209.

Rosenberger RS; Loomis JB. (2001). Benefit transfer of outdoor recreation use values: A technical document supporting the Forest Service Strategic Plan (2000 revision). (General technical report RMRS-GTR-72). Fort Collins, CO; Rocky Mountain Research Station; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Rosenqvist IT. (1978). Acid precipitation and other possible sources for acidification of rivers and lakes. Sci Total Environ, 10, 271-272.

Ross DS; Lawrence GB; Fredriksen G. (2004). Mineralization and nitrification patterns at eight northeastern USA forested research sites. For Ecol Manage, 188, 317-335.

Rosseland BO; Skogheim OK. (1984). A comparative study on salmonid fish species in acid aluminum-rich water. II. Physiological stress and mortality of one- and two-year-old fish. (Report no. 61; pp. 186-194). Drottningholm, Sweden: Institute of Freshwater Research.

Rosseland BO. (1986). Ecological effects of acidification on tertiary consumers: fish population response. Water Air Soil Pollut, 30, 451-460.

Rosseland BO; Eldhuset TD; Staurnes M. (1990). Environmental effects of aluminum. Environ Geochem Health, 12, 17-27.

Rosseland BO; Staurnes M. (1994). Physiological Mechanisms for Toxic Effects and Resistance to Acidic Water: An Ecophysiological and Ecotoxicological Approach. Acidification of Freshwater Ecosystem: Implications for the Future, 227-245.

Roth PM; Blumenthal DL; Roberts PT; Watson JG; Yocke M; Souten D; Ireson RG; Chinkin LR; Whitten GZ; Daly C; Smith TB. (1988). A proposed concept and scope for the San Joaquin Valley Air Quality Study. (Report no. STI 96040-710FR1). Santa Rosa, CA: Sonoma Technology, Inc.

Roulet N; Moore TR. (2006). Environmental chemistry - Browning the waters. Nature, 444, 283-284.

Rouse JD., Bishop CA., Struger J. (1999). Nitrogen pollution: an assessment of its threat to amphibian survival. Environ Health Perspect, 107, 799-803.

Rouss E; Ahti T. (1989). Systematics of some reindeer lichens (Cladonia subg. Cladina) in the Southern Hemisphere. - Lichenologist 21: 29-44.

Rowe EC; Moldan F; Emmett BA; Evans CD; Hellsten S. (2005). Model chains for assessing impacts of nitrogen on soils, waters and biodiversity: A review. (Report no C02887). Brighton, UK: Centre for Ecology and Hydrology, Natural Environment Research Council.

RTI International. (2001). Evaluation of Waquoit Bay models to estimate the water quality and ecological improvements resulting from atmospheric nitrogen reduction regulatory scenarios. Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, contract no. 68-D-99-024.

Rückert GV; Giani A. (2004). Effect of nitrate and ammonium on the growth and protein concentration of Microcystis viridis Lemmermann (Cyanobacteria). Revista Brasileira de Botânica, 27, 325-331.

Ruddell EJ; Gramann JH. (1989). The psychological utility of visual penetration in near-view forest scenic-beauty models. Environment and Behavior, 21, 393-412.

Rudek J; Paerl HW; Mallin MA; Bates PW. (1991). Seasonal and hydrological control of phytoplankton nutrient limitation in the lower Neuse River Estuary, North Carolina. Mar Ecol Prog Ser, 75, 133-142.

Rueth HM; Baron JS. (2001). Englemann spruce nitrogen dynamics across a nitrogen deposition gradient in Colorado, USA. Ekologia, 20, 43-49.

Rueth HM; Baron JS. (2002). Differences in Englemann Spruce Forest Biogeochemistry East and West of the Continental Divide in Colorado, USA. Ecosystems, 5, 45-57.

Rueth HM; Baron JS; Allstott EJ. (2003). Responses of Engelmann spruce forests to nitrogen fertilization in the Colorado Rocky Mountains. Ecol Appl, 13, 664-673.

Rundle SD; Hildrew AG. (1990). The distribution of micro-anthropods in some southern English streams: The influence of physicochemistry. Freshwater Biol, 23, 411-431.

Runn P; Johansson N; Milbrink G. (1977). Some effects of low pH on the hatchability of eggs of perch, *Perca fluviatilis* L. Zoon, 5, 115-125.

Russell A; Dennis R. (2000). NARSTO critical review of photochemical models and modeling. Atmos Environ, 34, 2283-2324.

Russell CA; Kosola KR; Paul EA; Robertson GP. (2004). Nitrogen cycling in poplar stands defoliated by insects. Biogeochem, 68, 365-381.

Russell KM; Keene WC; Maben JR; Galloway JN; Moody JL. (2003). Phase-partitioning and dry deposition of atmospheric nitrogen at the mid-Atlantic U.S. coast. J Geophys Res, 108, doi: 10.1029/2003JD003736.

Russell LM; Mensah AA; Fischer EV; Sive BC; Varner RK; Keene WC; Stutz J; Pszenny AAP. (2006). Nanoparticle growth following photochemical α- and β-pinene oxidation at Appledore Island during International Consortium for Research on Transport and Transformation/Chemistry of Halogens at the Isles of Shoals 2004. J Geophys Res, 112, doi: 10.1029/2006JD007736.

Russow R; Spott O; Stange CF. (2008). Evaluation of nitrate and ammonium as sources of NO and N_2O emissions from black earth soils (Haplic CherNO$_Z$em) based on N-15 field experiments. Soil Biol Biochem, 40, 380-391.

Rustad LE; Kahl JS; Norton SA; Fernandez IJ. (1994). Underestimation of dry deposition by throughfall in mixed northern hardwood forests. J Hydrol, 162, 319-336.

Ryerson TB; Buhr MP; Frost GJ; Goldan PD; Holloway JS; Hubler G; Jobson BT; Kuster WC; McKeen SA; Parrish DD; Roberts JM; Sueper DT; Trainer M; Williams J; Fehsenfeld FC. (1998). Emissions lifetimes and ozone formation in power plant plumes. J Geophys Res, 103, 22569-22583.

Ryerson TB; Trainer M; Holloway JS; Parrish DD; Huey LG; Sueper DT; Frost GJ; Donnelly SG; Schauffler S; Atlas EL; Kuster WC; Goldan PD; Hubler G; Meagher JF; Fehsenfeld FC. (2001). Observations of ozone formation in power plant plumes and implications for ozone control strategies. Science, 292, 719-723.

Ryerson TB; Williams EJ; Fehsenfeld FC. (2000). An efficient photolysis system for fast-response NO_2 measurements. J Geophys Res, 105, 26447-26461.

Rysgaard S; Glud RN; Risgaard-Petersen N; Dalsgaard T. (2004). Denitrification and anammox activity in Arctic marine sediments. Limnol Oceanogr, 49, 1493-1502.

Rysgaard S; Risgaard-Petersen N; Sloth NP; Jensen K; Nielsen LP. (1994). Oxygen regulation of nitrification and denitrification in sediments. Limnol Oceanogr, 39, 1643-1652.

Saarnio S; Silvola J. (1999). Effects of increased CO_2 and N on CH_4 efflux from a boreal mire: a growth chamber experiment. Oecologia, 119, 349-356.

Saarnio S; Saarinen T; Vasander H; Silvola J. (2000). A moderate increase in the annual CH_4 efflux by raised CO_2 or NH_4NO_3 supply in a boreal oligotrophic mire. Glob Chang Biol, 6, 137-144.

Saarnio S; Jarvio S; Saarinen T; Vasander H; Silvola J. (2003). Minor changes in vegetation and carbon gas balance in a boreal mire under a raised CO_2 or NH_4NO_3 supply. Ecosystems, 6, 46-60.

Saathoff H; Naumann KH; Riemer N; Kamm S; Mohler O; Schurath U; Vogel H; Vogel B. (2001). The loss of NO_2, HNO_3, NO3/N_2O5, and HO_2/$HOONO_2$ on soot aerosol: A chamber and modeling study. Geophys Res Lett, 28, 1957-1960.

Sabaratnam S; Gupta G; Mulchi C. (1988). Nitrogen dioxide effects on photosynthesis in soybean. J Environ Qual, 17, 143-146.

Sabbioni C; Bonazza A; Zappia G. (2002). Damage on hydraulic mortars: The Venice Arsenal. Journal of Cultural Heritage, 3, 83-88.

Sabbioni C; Zappia G; Riontinoa C; Blanco-Varela MT; Aguilerac J; Puertasc F; Van Balen K; Toumbakari EE. (2001). Atmospheric deterioration of ancient and modern hydraulic mortars. Atmos Environ, 35, 539-548.

Sadler K; Lynam S. (1988). The influence of calcium on aluminium-induced changes in the growth rate and mortality of brown trout. Salmo trutta, 171–179.

Saiz-Lopez A; Plane JMC. (2004). Novel iodine chemistry in the marine boundary layer. Geophys Res Lett, 31, doi: 10.1029/2003GL019215.

Saiz-Lopez A; Plane JMC; Shillito JA. (2004). Bromine oxide in the mid-latitude marine boundary layer. Geophys Res Lett, 31, doi: 10.1029/2003GL018956.

Sakamaki F; Hatakeyama S; Akimoto H. (1983). Formation of nitrous acid and nitric oxide in the heterogeneous dark reaction of nitrogen dioxide and water vapor in a smog chamber. Int J Chem Kinetics, 15, 1013-1029.

Sakugawa H; Kaplan IR. (1989). H_2O_2 and O_3 in the atmosphere of Los Angeles and its vicinity: factors controlling their formation and their role as oxidants of SO2. J Geophys Res, 94, 12957-12973.

Salmeen I; Durisin AM; Prater TJ; Riley T; Schuetzle D. (1982). Contribution of 1-nitropyrene to direct-acting Ames assay mutagenicities of diesel particulate extracts. Mutation Research / DNA Repair, 104, 17-23.

SAMAB. (1996). The Southern Appalachian Assessment. Aquatics technical report. KNO$_X$ville, TN; Southern Appalachian Man and the Biosphere (SAMAB) Cooperative. http://samab.org/saa/reports/aquatic/aquatic.html.

Samet JM; Bodurow CC (Eds.). (2008). Improving the presumptive disability decision-making process for veterans. Washington, DC: Institute of Medicine of the National Academies, National Academics Press.

Samie F; Tidblad J; Kucera V; Leygraf C. (2007). Atmospheric corrosion effects of HNO$_3$—Comparison of laboratory-exposed copper, zinc and carbon steel. Atmos Environ, 41, 4888-4896.

Samson JC; Shenker J. (2000). The teratogenic effects of methylmercury on early development of the zebrafish, *Danio Rerio*. Aquat Toxicol, 48, 343-354.

Sander R; Rudich Y; Von Glasow R; Crutzen PJ. (1999). The role of BrNO$_3$ in marine tropospheric chemistry: A model study. Geophys Res Lett, 26, 2858-2860.

Sander R; Keene WC; Pszenny A. AP; Arimoto R. Ayers GP; Chainey JM; Crutzen PJ; Duce RA; Huebert BJ; Maenhaut W; Turekian VC; Van Dingenan, R. (2003). Inorganic bromine in the marine boundary layer: a critical review. Atmos Chem Phys, 3, 1301-1336.

Sanz MJ; Gries C; Nash TH III. (1992). Dose-response relationships for SO$_2$ fumigations in the lichens *Ebernia prunastri* (L.).Ach, *Ramalina fraxinea* (L.). Ach New Phytol, 122, 313-319.

Sarmiento JL; Gruber N. (2006). Ocean Biogeochemical Dynamics. Princeton, NJ: Princeton University Press.

Saros JE; Interlandi SJ; Wolfe AP; Engstrom DR. (2003). Recent changes in the diatom community structure of lakes in the Beartooth Mountain Range, USA. Arct Antarct Alp Res, 35, 18-23.

Saros JE; Michel TJ; Interlandi SJ; Wolfe AP. (2005). Resource requirements of *Asterionella formosa* and *Fragilaria crotonensis* in oligotrophic alpine lakes: implications for recent phytoplankton community reorganizations. Can J Fish Aquat Sci, 62, 1681-1689.

Sasaki JC; Arey J; Eastmond DA; Parks KK; Grosovsky AJ. (1997). Genotoxicity induced in human lymphoblasts by atmospheric reaction products of naphthalene and phenanthrene. Mutation Research / DNA Repair, 393, 23-35.

Sawyer RF; Harley RA; Cadle SH; Norbeck JM; Slott R; Bravo HA. (2000). Mobile sources critical review: 1998 NARSTO assessment. Atmos Environ, 34, 2161-2181.

Saxe H. (1986). Effects of NO, NO$_2$, and CO$_2$ on net photosynthesis, dark respiration, and transpiration of pot plants. New Phytol, 103, 185-197.

Saxe H. (1986). Stomatal-dependent and stomatal-independent uptake of NO$_X$. New Phytol, 103: 199-205.

Scala JM; Garstang M; Tao W-K; Pickering KE; Thompson AM; Simpson J; Kirchhoff VWJH; Browell EV; Sachse GW; L. TA; Gregory GL; Rasmussen RW; Khalil MAK. (1990). Cloud draft structure and trace gas transport. J Geophys Res, 95, 17015-17030.

Schaberg PG; DeHayes DH; Hawley GJ; Strimbeck GR; Cumming JR; Murakami PF; Borer CH. (2000). Acid mist, soil Ca and Al alter the mineral nutrition and physiology of red spruce. Tree Physiol, 20, 73-85.

Schaberg PG; DeHayes DH; Hawley GJ; Murakami PF; Strimbeck GR; McNulty SG. (2002). Effects of chronic N fertilization on foliar membranes, cold tolerance, and carbon storage in montane red spruce. Can J Forest Res, 32, 1351-1359.

Schaeffer SM; Billings SA; Evans RD. (2003). Responses of soil nitrogen dynamics in a Mojave Desert ecosystem to manipulations in soil carbon and nitrogen availability. Oecologia, 134, 547-553.

Schauer C; Niessner R; Poschl U. (2004). Analysis of nitrated polycyclic aromatic hydrocarbons by liquid chromatography with fluorescence and mass spectrometry detection: air particulate matter, soot, and reaction product studies. Anal Bioanal Chem, 378, 725-736.

Schelske CL. (1991). Historical nutrient enrichment of Lake Ontario: paleolimnological evidence. Can J Fish Aquat Sci, 48, 1529-1538.

Scheuhammer AM. (1988). Chronic dietary toxicity of methylmercury in the zebra finch, *Poephila guttata*. Bull Environ Contam Toxicol, 40, 123-130.

Scheuhammer AM; Blancher PJ. (1994). Potential risk to common loons (*Gavia immer*).from methylmercury exposure in acidified lakes. Hydrobiologia, 279/280, 445-455.

Scheuhammer AM; Meyer MW; Sandheinrich MB; Murray MW. (2007). Effects of environmental methylmercury on the health of wild birds, mammals, and fish. Ambio, 36, 12-18.

Schichtel BA; Gebhart KA; Barna MG; Malm WC; Green MC. (2004). Big Bend regional aerosol and visibility observational (BRAVO).study results: Air quality data and source attribution analyses results from the National Park Service. Ft Collins, CO; Cooperative Institute for Research in the Atmosphere (CIRA); Colorado State University.

Schichtel BA; Gebhart KA; Malm WC; Barna MG; Pitchford ML; Knipping EM; Tombach IH. (2005). Reconciliation and interpretation of Big Bend National Park particulate sulfur source apportionment: Results from the Big Bend regional aerosol and visibility observational study-part I. J Air Waste Manage Assoc: 55, 1709-1725.

Schier GA. (1985). Response of red spruce and balsam fir seedlings to aluminum toxicity in nutrient solutions. Can J For Res, 15, 29-33.

Schimel DS; House JI; Hibbard KA; Bousquet P; Ciais P; Peylin P; Braswell BH; Apps MJ; Baker D; Bondeau A; Canadell J; Churkina G; Cramer W; Denning AS; Field CB; Friedlingstein P; Goodale C; Heimann M; Houghton RA; Melillo JM; Moore B III; Murdiyarso D; Noble I; Pacala SW; Prentice IC; Raupach MR; Rayner PJ; Scholes RJ; Steffen WL; Wirth C. (2001). Recent patterns and mechanisms of carbon exchange by terrestrial ecosystems. Nature, 414, 169-172.

Schimel JP; Bennett J. (2004). Nitrogen mineralization: challenges of a changing paradigm. Ecology, 85, 597-602.

Schindler DW; Armstrong FAJ; Brunskill GJ; Holmgren SK. (1971). Eutrophication of Lake 227, Experimental Lakes Area, northwestern Ontario, by addition of phosphate and nitrate. J Fish Res Board Can, 28, 1763-1782.

Schindler DW. (1974). Eutrophication and recovery in experimental lakes: implications for lake management. Science, 184, 897-899.

Schindler DW. (1980). The effect of fertilization with phosphorous and nitrogen versus phosphorus alone on eutrophication of experimental lakes. Limnol Oceanogr, 25, 1149-1152.

Schindler DW; Mills KH; Malley DF; Findlay MS; Schearer JA; Davies IJ; Turner MA; Lindsey GA; Cruikshank DR. (1985). Long-term ecosystem stress: Effects of years of experimental acidification. Science, 228, 1395-1401.

Schindler DW. (1986). The significance of in-lake production of alkalinity. Water Air Soil Pollut, 30, 931-944.

Schindler DW. (1988). Effects of acid rain on freshwater ecosystems. Science, 239, 149-157.

Schindler DW. (1990). Experimental perturbations of whole lakes as tests of hypotheses concerning ecosystem structure and function. Oikos, 57, 25-41.

Schindler DW; Bayley SE. (1993). The biosphere as in increasing sink for atmospheric carbon: Estimates from increased nitrogen deposition. Glob Biogeochem Cycles, 7, 717-733.

Schlegel H; Amundson RG; Hüttermann A. (1992). Element distribution in red spruce (Picea rubens).fine roots; evidence for aluminum toxicity at Whiteface Mountain. Can J For Res, 22, 1132-1138.

Schlesinger WH; Andrews JA. (2000). Soil respiration and the global carbon cycle. Biogeochemistry, 48, 7-20.

Schlesinger WH; Ward TJ; Anderson J. (2000). Nutrient losses in runoff from grassland and shrubland habitats in southern New Mexico: II. Field plots. Biogeochem, 49, 69-86.

Schlesinger WH; Lichter J. (2001). Limited carbon storage in soil and litter of experimental forest plots under increased atmospheric CO_2. Nature, 411, 466-469.

Schlesinger WL; Hartley AE. (1992). A global budget for atmospheric NH3. Biogeochemistry, 15, 191-211.

Schnell S; King GM. (1994). Mechanistic analysis of ammonium inhibition of atmospheric methane consumption in forest soils. Appl Environ Microbiol, 60, 3514-3521.

Schnitzer M; Skinner SIM. (1963). Organo-metallic interactions in soils: 2. Reactions between different forms of iron and aluminum and the organic matter of a podzol Bh horizon. Soil Sci, 96, 181-186.

Schnoor JL; Nikolaidis NP; Glass GE. (1986). Lake resources at risk to acidic deposition in the Upper Midwest. J WATER POLLUT CONTROL FED, 58, 139-148.

Schnug E. (1997). Significance of sulphur for the quality of domesticated plants. Sulphur Metabolism in Higher Plants, 3, 109–130.

Schofield CL; Trojnar JR. (1980). Aluminum toxicity to brook trout (*Salvelinus fontinalis*) in acidified waters. In: Toribara TY; Miller MW; Morrow PE (Eds.), Polluted rain: Proceedings of the 12th Rochester international conference on environmental toxicity held in Rochester, NY; May 1979. (Series: Hollaender A; Probstein RF; Welch BL (Eds.), Environmental science research; Volume 17, pp 341-66). New York, NY: Plenum Press.

Schofield CL; Driscoll CT. (1987). Fish species distribution in relation to water quality gradients in the North Branch of the Moose River Basin. Biogeochemistry, 3, 63-85.

Schofield CL. (1993). Habitat suitability for Brook Trout (*Salvelinus fontinalis*) reproduction in Adirondack lakes. Water Resour Res, 29, 875-879.

Schofield CL; Keleher C. (1996). Comparison of brook trout reproductive success and recruitment in an acidic Adirondack lake following whole lake liming and watershed liming. Biogeochem, 32, 323-337.

Schofield KA; Pringle CM; Meyer JL; Sutherland AB. (2001). The importance of crayfish in the breakdown of rhododendron leaf litter. Freshw Biol, 46, 1-14.

Scholes RJ; Noble IR. (2001). Climate change - Storing carbon on land. Science, 294, 1012-1013.

Schopp W; Posch M; Mylonda S; Johansson M. (2003). Long-term development of acid deposition (1880—2030) in sensitive freshwater regions in Europe. Hydrol Earth Syst Sci, 7, 436-446.

Schreck CB. (1981). Stress and rearing of salmonids. Aquaculture, 28, 241-249.

Schreck CB. (1982). Stress and compensation in teleostean fishes: response to social and physical factors. In: Pickering AD (Ed.), Stress and fish (pp. 295-321). London: Academic Press.

Schrimpf W; Lienaerts K; Müller KP; Rudolph J; Neubert R; Schüßler W; Levin I. (1996). Dry deposition of peroxyacetyl nitrate (PAN): Determination of its deposition velocity at night from measurements of the atmospheric PAN and 222 Radon concentration gradient. Geophys Res Lett, 23, 3599-3602.

Schröder WH; Bauch J; Endeward R. (1988). Microbeam analysis of Ca exchange and uptake in the fine roots of spruce: influence of pH and aluminum. Trees, 2, 96-103.

Schubert SD; Rood RB; Pfaendtner J. (1993). An assimilated dataset for earth science applications. Bulletin of the American Meteorological Society, 74, 2331-2342.

Schuetzle D. (1983). Sampling of vehicle emissions for chemical analysis and biological testing. Environ Health Perspect, 47, 65-80.

Schultz MG; Jacob DJ; Bradshaw JD; Sandholm ST; Dibb JE; Talbot RW; Singh HB. (2000). Chemical NO_X budget in the upper troposphere over the tropical South Pacific. J Geophys Res, 105, 6669-6679.

Schulze ED; Hogbberg L; van Oene H. (2000). Interactions between the carbon and nitrogen cycle and the role of biodiversity: A synopsis of a study along a north-south transect through Europe. In: Schultze ED (Ed.), Carbon and Nitrogen Cycling in European Forest Ecosystems (Vol. 142, pp. 468-492). Berlin: Springer.

Schwab JJ; Li Y; Bae MS; Demerjian KL; Hou J; Zhou X; Jensen B; Pryor SC. (2007). A laboratory intercomparison of real-time gaseous ammonia measurement methods. Environ Sci Technol, 41, 8412-8419.

Schweizer B; Arndt U. (1990). CO_2/H2O gas exchange parameters of one- and two-year-old needles of spruce and fir. Environ Pollut, 68, 275-292.

Schwinning S; Starr BI; Wojcik NJ; Miller ME; Ehleringer JE; Sanford RL Jr. (2005). Effects of nitrogen deposition on an arid grassland in the Colorado Plateau cold desert. Journal of Rangeland Ecology and Management, 58, 565-574.

Scott G; Crunkilton RL. (2000). Acute and chronic toxicity of nitrate to fathead minnows (*Pimephales promelas*), *Ceriodaphnia dubia*, and *Daphnia magna*. Environ Toxicol Chem, 19, 2918-2922.

Scott MG; Hutchinson TC; Feth MJ. (1989a). A comparison of the effects on Canadian boreal forest lichens of nitric and sulphuric acids as sources of rain acidity. New Phytol, 111, 663-671.

Scott MG; Hutchinson TC; Feth MJ. (1989b). Contrasting responses of lichens and *Vaccinium angustifolium* to long-term acidification of a boreal forest ecosystem. Can J Bot, 67, 579-588.

Scott MC; Helfman GS. (2001). Native invasions, homogenization, and the mismeasure of integrity of fish assemblages. Fisheries, 26, 6-15.

Scudlark JR; Church TM. (1993). Atmospheric input of inorganic nitrogen to Delaware Bay. Estuaries, 16, 747-759.

Seaman NL. (2000). Meteorological modeling for air quality assessments. Atmos Environ, 34, 2231-2259.

Seastedt TR; Vaccaro L. (2001). Plant species richness, productivity, and nitrogen and phosphorus limitations across a snowpack gradient in alpine tundra, Colorado, USA. Arct Antarct Alp Res, 33, 100-106.

Seastedt TR; Bowman WD; Caine TN; McKnight D; Townsend A; Williams MW. (2004). The landscape continuum: a model for high elevation ecosystems. BioScience, 54, 111-121.

Seely B; Lajtha K. (1997). Application of a ^{15}N tracer to simulate and track the fate of atmospherically deposited N in the coastal forests of the Waquoit Bay watershed, Cape Cod, Massachusetts. Oecologia, 112, 393-402.

Segschneider HJ; Hutzen H; Forstel H; Rockel P; Wildt J. (1993). Uptake of (NO_2)-N-15 and metabolic transfer of the (NO_2)-N-15 nitrogen to various nitrogen fractions of sunflowers. Isotopenpraxis Environ Health Stud, 29, 51-57.

Segschneider H-J; Wildt J; Forstel H. (1995). Uptake of $15NO_2$ by sunflower (Helianthus-annuus).during exposures in light and darkness: quantities, relationship to stomatal aperture and incorporation into different nitrogen pools within the plant. New Phytol, 131, 109-119.

Seinfeld JH; Pandis SN. (1998). Atmos Chem Phys: From Air Pollution to Climate Change. New York, NY: John Wiley-Interscience Publishers.

Seip HM. (1980). Acidification of freshwater - sources and mechanisms. Paper presented at the Ecological impact of acid precipitation. Proceedings of an International Conference, SNSF Project, Sandefjord, Norway, Oslo, Norway.

Seitzinger SP. (1988). Denitrification in freshwater and coastal marine ecosystems: ecological and geochemical significance. Limnol Oceanogr, 33, 702-724.

Seitzinger SP; Nielsen LP; Caffrey J; Christensen PB. (1993). Denitrification measurements in aquatic sediments: a comparison of three methods. Biogeochemistry, 23, 147-167.

Seitzinger SP; Styles RV; Boyer EW; Alexander R; Billen G; Howarth RW; Mayer B; Van Breemen N. (2002). Nitrogen retention in rivers: model development and application to watersheds in the northeastern USA. Biogeochemistry, 57/58, 199-237.

Seitzinger S; Harrison JA; Bohlke JK; Bouwman AF; Lowrance R; Peterson B; Tobias C; Van Drecht G. (2006). Denitrification across landscapes and waterscapes: A synthesis. Ecol Appl, 16, 2064-2090.

Shan JP; Morris LA; Hendrick RL. 2001. The effects of management on soil and plant carbon sequestration in slash pine plantations. J Appl Ecol, 38, 932-941.

Shanley JB; Chalmers A. (1999). The effect of frozen soil on snowmelt runoff at Sleepers River, Vermont. Hydrological Processes, 13, 1843-1857.

Shanley J; Mayer B; Mitchell M; Michel R; Bailey S; Kendall C. (2005). Tracing Sources of Streamwater Sulfate During Snowmelt Using S and O Isotope Ratios of Sulfate and 35S Activity. Biogeochemistry, 76, 161-185.

Sharpe WE; Kimmel WG; Young ES Jr; DeWalle DR. (1983). In-situ bioassays of fish mortality in two Pennsylvania streams acidified by atmospheric deposition. Northeast Environ Sci, 2, 171-178.

Shashoua Y. (2006). Inhibiting the inevitable; current approaches to slowing the deterioration of plastics. Macromol Symp, 238, 67-77.

Shaver GR; Billings WD. (1975). Root production and root turnover in a wet tundra ecosystem, Barrow, Alaska. Ecology, 56, 401-409.

Shaver GR; Chapin FS. (1980). Response to fertilization by various plant growth forms in an Alaskan tundra: nutrient accumulation and growth. Ecology, 61, 662-675.

Shaver GR; Melillo JM. (1984). Nutrient budgets of marsh plants: Efficiency concepts and relation to availability. Ecology, 65, 1491-1510

Shaver GR; Johnson LC; Cades DH; Murray G; Laundre JA; Rastetter EB; Nadelhoffer KJ; Giblin AE. (1998). Biomass and CO_2 flux in wet sedge tundras: Responses to nutrients, temperature, and light. Ecol Monogr, 68, 75-97.

Shaver GR; Bret-Harte SM; Jones MH; Johnstone J; Gough L; Laundre J; Chapin FS. (2001). Species composition interacts with fertilizer to control long-term change in tundra productivity. Ecology, 82, 3163-3181.

Shaw MR; Zavaleta ES; Chiariello NR; Cleland EE; Mooney HA; Field CB. (2002). Grassland responses to global environmental changes suppressed by elevated CO_2. Science, 298, 1987-1990.

Shaw WD. (1989). Valuing the effect of acidification damages on the Adirondack fishery: Comment. Am J Agric Econ, 71, 217-221.

Shepard JP; Mitchell MJ; Scott, TJ; Zhang YM; Raynal DJ. (1989). Measurements of wet and dry deposition in a northern hardwood forest. Water Air Soil Pollut, 48, 225.238.

Shepson PB; Bottenheim JW; Hastie DR; Venkatram A. (1992). Determination of the relative ozone and PAN deposition velocities at night. Geophys Res Lett, 19, 1121-1124.

Shepson PB; Mackay E; Muthuramu K. (1996). Henry's Law constants and removal processes for several atmospheric beta-hydroxy alkyl nitrates. Environ Sci Technol, 30, 3618-3623.

Sherrod SK; Seastedt TR. (2001). Effects of the northern pocket gopher (*Thomomys talpoides*).on alpine soil characteristics, Niwot Ridge, CO. Biogeochemistry, 55, 195-218.

Shindell DT; Faluvegi G; Stevenson DS; Krol MC; Emmons LK; Lamarque J-F; Pétron G; Dentener FJ; Ellingsen K; Schultz MG; Wild O; Amann M; Atherton CS; Bergmann DJ; Bey I; Butler T; Cofala J; Collins WJ; Derwent RG; Doherty RM; Drevet J; Eskes HJ; Fiore AM; Gauss M; Hauglustaine DA; Horowitz LW; Isaksen ISA; Lawrence MG; Montanaro V; Müller J-F; Pitari G; Prather MJ; Pyle JA; Rast S; Rodriguez JM; Sanderson MG; Savage NH; Strahan SE; Sudo K; Szopa S; Unger N; Van Noije TPC; Zeng G. (2006). Multimodel simulations of carbon monoxide: Comparison with observations and projected near-future changes. J Geophys Res, 111, doi: 10.1029/2006JD007100.

Shinn JH. (1978). A critical survey of measurements of foliar deposition of airborne sulfates and nitrates. Paper presented at the 71st annual meeting of the Air Pollution Control Association; June; Houston, TX, Pittsburgh, PA.

Shogren JF; Shin SY; Hayes DJ; Kliebenstein JB. (1994). Resolving differences in willingness to pay and willingness to accept. Am Econ Rev, 84, 255-270.

Shorter JH; Herndon S; Zahniser MS; Nelson DD; Wormhoudt J; Demerjian KL; Kolb CE. (2005). Real-time measurements of nitrogen oxide emissions from in-use New York City transit buses using a chase vehicle. Environ Sci Technol, 39 (20), 7991-8000.

Shortle WC; Smith KT. (1988). Aluminum-induced calcium deficiency syndrome in declining red spruce. Science, 240, 1017-1018.

Shortle WC; Smith KT; Minocha R; Lawrence GB; David MB. (1997). Acidic deposition, cation mobilization, and biochemical indicators of stress in healthy red spruce. J Environ Qual, 26, 871-876.

Shriner DS; Henderson GS. (1978). Sulfur distribution and cycling in a deciduous forest watershed. J Environ Qual, 7, 392-397.

Shugart HH; McLaughlin SB. (1985). Modeling SO_2 effects on forest growth and community dynamics. In: Winner WE; Mooney HA; Goldstein RA (Ed.), Sulfur dioxide and vegetation: Physiology, ecology, and policy issues. (pp 478-491). Stanford, CA: Stanford University Press.

Shy CM; Love GJ. (1980) Recent evidence on the human health effects of nitrogen dioxide. In: Lee SD (Ed.), Nitrogen oxides and their effects on health: [papers from the symposium "Biological studies of environmental pollutants, part II. Health effects of nitrogen oxides"]; April 1979; Honolulu, HI. Ann Arbor, MI: Ann Arbor Science Publishers, Inc; 291-305.

Sickles JE; Hodson LL; McClenny WA; Paur RJ; Ellestad TG; Mulik JD; Anlauf KG; Wiebe HA; Mackay GI; Schiff HI; Bubacz DK. (1990). Field comparison of methods for the measurement of gaseous and particulate contributors to acidic dry deposition, Atmos Environ 24, 155–165.

Siciliano SD; O'Driscoll NJ; Tordon R; Hill J; Beauchamp S; Lean DRS. (2005). Abiotic production of methylmercury by solar radiation. Environ Sci Technol, 39, 1071-1077.

Sickman JO; Melack JM; Stoddard JL. (2002). Regional analysis of inorganic nitrogen yield and retention in high-elevation ecosystems of the Sierra Nevada and Rocky Mountains. Biogeochem, 57/58, 341-374.

Sickman JO; Melack JM; Clow DW. (2003a). Evidence for nutrient enrichment of high-elevation lakes in the Sierra Nevada, California. Limnol Oceanogr, 48, 1885-1892.

Sickman JO; Leydecker A; Chang CCY; Kendall C; Melack JM; Lucero DM; Schimel J. (2003b). Mechanisms underlying export of N from high-elevation catchments during seasonal transitions. Biogeochem, 64, 1-24.

Siegfried CA; Bloomfield JA; Sutherland JW. (1989). Planktonic rotifer community structure in Adirondack lakes: Effects of acidity, trophic status, and related water quality characteristics. In: Sutherland JW (Ed.), Field studies of the biota and selected water chemistry parameters in 50 Adirondack mountain lakes. Albany, NY: New York State Department of Environmental Conservtion.

Siegwolf RTW; Matyssek R; Sauer M; Maurer S; Günthardt-Goerg MS; Schmutz P; Bucher JB. (2001). Stable isotope analysis reveals differential effects of soil nitrogen and nitrogen dioxide on the water use efficiency in hybrid poplar leaves. New Phytol, 149, 233-246.

Sievering H. (1999). Nitrogen deposition and carbon sequestration. Nature, 400, 629-630.

Sievering H; Fernandez I; Lee J; Hom J; Rustad L. (2000). Forest canopy uptake of atmospheric nitrogen deposition at eastern U.S. conifer sites: carbon storage implications? Glob Biogeochem Cycles, 14, 1153-1159.

Sievering H; Rusch D; Marquez L. (1996). Nitric acid, particulate nitrate and ammonium in the continental free troposphere: Nitrogen deposition to an alpine tundra ecosystem. Atmos Environ, 30, 2527-2537.

Sigal LL; Nash TH III. (1983). Lichen Communities on Conifers in Southern California Mountains: An Ecological Survey Relative to Oxidant Air Pollution. Ecology, 64, 1343-1354.

Sigüenza C. (2000). Nitrogen deposition and soil microorganisms of *Artemisia californica* and exotic grasses in southern California. (dissertation). Riverside, CA: University of California.

Sigüenza C; Corkidi L; Allen EB (2006). Feedbacks of soil inoculum of mycorrhizal fungi altered by N deposition on the growth of a native shrub and an invasive annual grass. Plant Soil, 286, 153-165.

Sikiotis D; Kirkitsos P. (1995). The adverse effects of nitrates on stone monuments. Sci Total Environ, 171, 173-182.

Sillman S; Logan J; Wofsy S. (1990). The sensitivity of ozone to nitrogen oxides and hydrocarbons in regional ozone episodes. J Geophys Res, 95, 1851.

Sillman S. (1995). The use of NO_Y, H_2O_2 and HNO_3 as indicators for ozone-NO_X-hydrocarbon sensitivity in urban locations. J Geophys Res, 100, 14175-14188.

Sillman S; Al-Wali KI; Marsik FJ; Nowacki P; Samson PJ; Rodgers MO; Garland LJ; Martinez JE; Stoneking C; Imhoff R; Lee J-H; Newman L; Weinstein-Lloyd J; Aneja VP. (1995). Photochemistry of ozone formation in Atlanta, GA: Models and measurements. Atmos Environ, 29, 3055-3066.

Sillman S; He D; Pippin MR; Daum PH; Imre DG; Kleinman LI; Lee JH; Weinstein-Lloyd J. (1998). Model correlations for ozone, reactive nitrogen, and peroxides for Nashville in comparison with measurements: Implications for O_3-NO_X-hydrocarbon chemistry. J Geophys Res, 103, 22629-22644.

Sillman S. (2000). Ozone production efficiency and loss of NO_X in power plant plumes: Photochemical model and interpretation of measurements in Tennessee. J Geophys Res, 105, 9189-9202.

Sillman S; He D-Y. (2002). Some theoretical results concerning O_3-NO_X-VOC chemistry and NO_X-VOC indicators. J Geophys Res, 107.

Silvola J; Saarnio S; Foot J; Sundh I; Greenup A; Heijmans M; Ekberg A; Mitchell E; van Breeman N. (2003). Effects of elevated CO_2 and N deposition on CH_4 emissions from European mires. Glob Biogeochem Cycles, 17, 1068-1079.

Siminon HA; Kretser WA; Bath DW; Olson M; Gallagher J. (1993). I*n situ* bioassays of brook trout (*Salvelinus fontinalis*) and blacknose dace (*Rhinichthys atratulus*) in Adirondack streams affected by episodic acidification. Can J For Res, 50, 902-912.

Simonsson M. (1998). Aluminium solubility related to secondary solid phases in upper B horizons with spodic characteristics. The European Journal of Soil Sci, 49, 317-326.

Simpson AJ; Lam B; Diamond ML; Donaldson DJ; Lefebvre BA; Moser AQ; Williams AJ; Larin N; Kvasha MP. (2006). Assessing the organic composition of urban surface films using nuclear magnetic resonance spectroscopy. Chemosphere, 63, 142-152.

Simpson KW; Bode, RW; Colquhoun JR. (1985). The macroinvertebrate fauna of an acid-stressed headwater stream system in the Adirondack Mountains, New York. Freshwater Biol, 15, 671-681.

Singh HB; Herlth D; Kolyer R; Salas L; Bradshaw JD; Sandholm ST; Davis DD; Crawford J; Kondo Y; Koike M; Talbot R; Gregory GL; Sachse GW; Browell E; Blake DR; Rowland FS; Newell R; Merrill J; Heikes B; Liu SC; Crutzen PJ; Kanakidou M. (1996). Reactive nitrogen and ozone over the western Pacific: distribution, partitioning, and sources. J Geophys Res, 101, 1793-1808.

Singh HB; Kasting JF. (1988). Chlorine-hydrocarbon photochemistry in the marine troposphere and lower stratosphere. J Atmos Chem , 7, 261-285.

Singh HB; Salas L; Herlth D; Kolyer R; Czech E; Avery M; Crawford JH; Pierce RB; Sachse GW; Blake DR; Cohen RC; Bertram TH; Perring A; Wooldridge PJ; Dibb J; Huey G; Hudman RC; Turquety S; Emmons LK; Flocke F; Tang Y; Carmichael GR; Horowitz LW. (2007). Reactive nitrogen distribution and partitioning in the North American troposphere and lowermost stratosphere. J Geophys Res, 112, doi: 10.1029/2006JD007664.

Sinsabaugh RL; Zak DR; Gallo M; Lauber C; Amonette R. (2004). Nitrogen deposition and dissolved organic carbon production in northern temperate forests. Soil Biol Biochem, 36, 1509-1515.

Sitaula BK; Bakken LR; Abrahamsen G. (1995). Nutrient balance in Scots pine (*Pinus sylvestris* L) forest. 3: Fluxes of N_2O from lysimeter as influenced by nitrogen input. Water Air Soil Pollut, 85, 1155-1159.

Skeffington RA; Wilson EJ. (1988). Excess nitrogen deposition: Issues for consideration. Environ Pollut, 54, 159-184.

Skiba U; Fowler D; Smith KA. (1997). Nitric oxide emissions from agricultural soils in temperate and tropical climates: sources, controls and mitigation options. Nutr Cycling Agroecosyst, 48, 139-153.

Skiba U; Sheppard LJ; Pitcairn CER; Van Dijk S; Rossall MJ. (1999). The effect of N deposition on nitrous oxide and nitric oxide emissions from temperate forest soils. Water Air Soil Pollut, 116, 89-98.

Skinner MW; Pavlik B. M. (Eds.) (1994). California Native Plant Society's inventory of rare and endangered vascular plants of California. Sacramento, CA: California Native Plant Society.

Skjelkvåle BL; Evans CD; Larssen T; Hindar A; Raddum GG. (2003). Recovery from acidification in European surface waters: A view to the future. Ambio, 30, 170-175.

Skjelkvåle BL; Stoddard JL; Andersen T. (2001). Trends in Surface Water Acidification in Europe and North America (1989–1998). Water Air Soil Pollut, 130, 787-792.

Skjelkvåle BL; Wright RF; Henriksen A. (1998). Norwegian lakes show widespread recovery from acidification; results from national surveys of lake-water chemistry. Hydrol and Earth Sci, 2, 555-562.

Skjelkvåle BL; Andersen T; Halvorsen GA; Raddum GG; Heegaard E; Stoddard J; Wright RF. (2000). The 12-year report: acidification of surface water in Europe and North America; trends, biological recovery and heavy metals. http://www.niva.no/symfoni/RappArkiv5.nsf/URL/C125730900463888C1256FB80053D51D/$FILE/4208_200dpi.pdf. (ICP Waters report 52/2000). Oslo, Norway: Norwegian Institute for Water Research.

Skogheim OK; Rosseland BO. (1986). Mortality of smolt of Atlantic salmon *Salmo-salar* L., at low levels of aluminum in acidic softwater. Bull Environ Contam Toxicol, 37, 258-265.

Skyllberg U. (1999). pH and solubility of aluminium in acidic forest soils: a consequence of reactions between organic acidity and aluminium alkalinity. European Journal of Soil Science, 50, 95-106.

Smidt S. (1994). Gefährdung von Wäldbaumen durch organische Luftschadstoffe [Endangering of forest trees by organic air pollutants]. Z Pflanzenkranks Pflanzenschutz, 101, 423-445.

Smith AM; Keene WC; Maben JR; Pszenny AAP; Fischer E; Stohl A. (2007). Ammonia sources, transport, transformation, and deposition in coastal New England during summer. J Geophys Res, 112, 10.1029/2006JD007574.

Smith GD; Clark RJH. (2002). The role of H_2S in pigment blackening. J Cult Heritage, 3, 101-105.

Smith GF; Nicholas NS. (1999). Post disturbance spruce-fir forest stand dynamics at seven disjunct sites. Castanea, 64, 175-186.

Smith LK; Voytek MA; Böhlke JK; Harvey JW. (2006a). Denitrification in nitrate-rich streams: Application of N_2:Ar and ^{15}N-tracer methods in intact cores. Ecol Appl, 16, 2191-2207.

Smith LV; deVries KL. (1993). Mechanical properties of polymeric fibres exposed to stress in a NO_X environment. Polymer, 34, 546-550.

Smith MD; Crowder LB. (2005). Valuing Ecosystem Services with Fishery Rents: A Lumped-Parameter Approach to Hypoxia in the Neuse River Estuary. (Fondazione Eni Enrico Mattei (FEEM).Nota di Lavoro (Natural Resources Management (NRM).Working Papers - FEEM no 2005.115). http://ideas.repec.org/p/fem/femwpa/2005.115.html. Milan, Italy; Fondazione Eni Enrico Mattei (FEEM).

Smith M-L; Ollinger SV; Martin ME; Aber JD; Hallett RA;Goodale CL. (2002). Direct estimation of aboveground forest productivity through hyperspectral remote sensing of canopy nitrogen. Ecol Appl, 12, 1286-1302.

Smith RA; Schwarz GE; Alexander RB. (1997). Regional interpretation of water-quality monitoring data. Water Resour Res, 33, 2781-2798.

Smith SM; Lee KD. (2006). Responses of periphyton to artificial nutrient enrichment in freshwater kettle ponds of Cape Cod National Seashore. Hydrobiologia, 571, 201-211.

Smith VH; Tilman GD; Nekola JC. (1999). Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. Environ Pollut, 100, 179-196.

Smith VH. (2006). Responses of estuarine and coastal marine phytoplankton to nitrogen and phosphorus enrichment. Limnol Oceanogr, 51, 377-384.

Smith VK; Desvousges WH. (1986). Measuring Water Quality Benefits. Boston, MA: Kluwer-Nijhoff.

Smith VK; Palmquist RB; Jakus P. (1991). Combining Farrell frontier and hedonic travel cost models for valuing estuarine quality. Rev Econ Stat, 73, 694-699.

Smith VK; Huang J.-C. (1995). Can markets value air quality? A meta-analysis of hedonic property value models. J Polit Econ, 103, 209-27.

Smith VK; Pattanayak SK. (2002). Is meta-analysis a Noah's Ark for non-market valuation? Environ Resour Econ, 22, 271-296.

Smith VK; Pattanayak S; Houtven GV. (2006b). Structural benefits transfer: An example using VSL estimates. Ecol Econ, 60, 361-371.

Smith VK. (2007). Reflections on the Literature. Rev Environ Econ Policy, 1, 152-165.

Smith WH. (1981). Air pollution and forests: Interactions between air contaminants and forest ecosystems: New York, NY: Springer-Verlag.

Smith WH. (1990). Forests as sinks for air contaminants: soil compartment. In: Smith WH (Ed.), Air pollution and forests: Interactions between air contaminants and forest ecosystems. 2nd edition. (Springer series on Environmental management; pp 113-146). New York, NY: Springer-Verlag.

Smith WH; Staskawicz BJ. (1977). Removal of atmospheric particles by leaves and twigs of urban trees: some preliminary observations and assessment of research needs. Environmental Management 1: 317-330.

Smock LA; Gazzera SB. (1996). Effects of experimental episodic acidification on a southeastern USA blackwater stream. Journal of Freshwater Ecology, 11, 81-90.

Smolders AJP; Roelofs JGM. (1996). The roles of internal iron hydroxide precipitation, sulphide toxicity and oxidizing ability in the survival of Stratiotes aloides roots at different iron concentrations in sediment pore water. New Phytol, 133, 253-260.

Smolders AJP; Lamers LPM; Moonen M; Zwaga K; Roelofs JGM. (2001). Controlling phosphate release from phosphate-enriched sediments by adding various iron compounds. Biogeochemistry, 54, 219-228.

Smolders AJP; Lamers LPM; den Hartog C; Roelofs JGM. (2003). Mechanisms involved in the decline of Stratiotes aloides L. The Netherlands: sulphate as a key variable Hydrobiologia, 506, 603-610.

Smolders AJP; Lamers LPM; Lucassen E; Van Der Velde G; Roelofs JGM. (2006). Internal eutrophication: How it works and what to do about it: A review. Chemistry and Ecology, 22, 93-111.

Sobczak WV; Findlay S; Dye S. (2003). Relationship between DOC variability and nitrate removal in and upland stream: An experimental approach. Biogeochemistry, 62, 309-327.

Söderström H; Hajslova J; Kocourek V; Siegmund B; Kocan A; Obiedzinski MW; Tysklind M; Bergqvist PA. (2005). PAHs and nitrated PAHs in air of five European countries determined using SPMDs as passive samplers. Atmos Environ, 39, 1627-1640.

Sollins P; Grier CC; McCorison FM; Cromack K Jr; Fogel R; Fredriksen RL. (1980). The internal element cycles of an old-growth Douglas-fir ecosystem in western Oregon. Ecol Monogr, 50, 261-285.

Solomon PA; Larson SM; Fall T; Cass G. (1988). Basinwide nitric acid and related species concentrations observed during the Claremont Nitrogen Species Comparison Study. Atmos Environ, 22, 1587-1594.

Solomon PA; Salmon LG; Fall T; Cass GR. (1992). Spatial and temporal distribution of atmospheric nitric acid and particulate nitrate concentrations in the Los Angeles area. Environ Sci Technol, 26, 1596-1601.

Solomon P; Cowling E; Hidy G; Furiness C. (2000). Comparison of scientific findings from major ozone field studies in North America and Europe. Atmos Environ, 34, 1885-1920.

Solomon PA; Hopke PK. (2008). A Special Issue of JA&WMA Supporting Key Scientific and Policy-and Health-Relevant Findings from EPA's Particulate Matter Supersites Program and Related Studies: An Integration and Synthesis of Results. J Air Waste Manage Assoc, 58, 137.

Solomon S. (1999). Stratospheric ozone depletion: A review of concepts and history. Rev Geophys, 37, 275–316.

Solomon S. (2007). Climate Change 2007: The Physical Science Basis: Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change: Cambridge University Press.

Soltic P; Weilenmann M. (2003). NO_2/NO emissions of gasoline passenger cars and light-duty trucks with Euro-2 emission standard. Atmos Environ, 37, 5207-5216.

Soulsby C; Turnbull D; Langan SJ; Owen R; Hirst D. (1995). Long-term trends in stream chemistry and biology in northeast Scotland: evidence for recovery. Water Air Soil Pollut, 85, 689-694.

Soussana JF; Allard V; Pilegaard K; Ambus P; Amman C; Campbell C; Ceschia E; Clifton-Brown J; Czobel S; Domingues R; Flechard C; Fuhrer J; Hensen A; Horvath L; Jones M; Kasper G; Martin C; Nagy Z; Neftel A; Raschi A; Baronti S; Rees RM; Skiba U; Stefani P; Manca G; Sutton M; Tubaf Z; Valentini R. (2007). Full accounting of the greenhouse gas (CO_2, N_2O, CH_4) budget of nine European grassland sites. Agric Ecosyst Environ, 121, 121-134.

Spalding MG; Forrester DJ. (1991). Effects of parasitism and disease on the nesting success of colonial wading birds (*Ciconiiformes*) in southern Florida. (Project NG88-008). Tallahassee, FL: Prepared by Department of Infectious Diseases; College of Veterinary Medicine; University of Florida: for Nongame Wildlife Program ; Florida Game and Fresh Water Fish Commission.

Sparks JP; Roberts JM; Monson RK. (2003). The uptake of gaseous organic nitrogen by leaves: a significant global nitrogen transfer process. Geophys Res Lett, 30, doi: 10.1029/2003GL018578.

Spash CL. (1997). Assessing the economic benefits to agriculture from air pollution control. J Econ Surv, 11, 47-70.

Spiecker H; Meielikainen K; Kohl M; Skovsgaard J. (1996). Growth trends in European forests: Studies from 12 countries. Report 5. Springer-Verlag, Berlin and New York: European Forest Research Institute.

Spoelstra J; Schiff SL; Elgood RJ; Semkin RG; Jeffries DS. (2001). Tracing the sources of exported nitrate in the Turkey Lakes watershed using $^{15}N/^{14}N$ and $^{18}O/^{16}O$ isotopic ratios. Ecosystems, 4, 536-544.

Spurny KR. (1989). On the release of asbestos fibers from weathered and corroded asbestos cement products. Environ Res, 48, 100-116.

Spurny KR. (1999). Trends in the chemical analysis of aerosols. In: Spurny KR (Ed.), Analytical chemistry of aerosols. Boca Raton, FL: Lewis Publishers.

St. Clair SB; Carlson JE; Lynch JP. (2005). Evidence for oxidative stress in sugar maple stands growing on acidic, nutrient imbalanced forest soils. Oecologia, 145, 258-269.

St. Louis VL; Breebaart L; Barlow JC. (1990). Foraging behaviour of tree swallows over acidified and nonacidic lakes. Can J Zool, 68, 2385-2392.

St. Louis VL; Rudd JWM; Kelly CA; Beaty KG; Bloom NS; Flett RJ. (1994). Importance of wetlands as sources of methyl mercury to boreal forest ecosystems. Can J Fish Aquat Sci, 51, 1065-1076.

St. Louis VL; Rudd JWM; Kelly CA; Beaty KG; Flett RJ; Roulet NT. (1996). Production and loss of methylmercury and loss of total mercury from boreal forest catchments containing different types of wetlands. Environ Sci Technol, 30, 2719 -2729.

Stacey PR; Wright MD. (2001). A proficiency testing scheme for aromatic hydrocarbons in air by the manual thermal desorption-GC method: A comparison of laboratory performance with the uncertainty requirements of the European Union Ambient Air Directive. Journal of Environmental Monitoring, 3, 425-431.

Stacey PE; Greening JS; Kremer JN; Peterson D; Tomasko DA. (2001). Contribution of atmospheric nitrogen deposition to U.S. estuaries: Summary and conclusions. In: Valigura RW; Alexander RB; Castro MS; Meyers TP; Paerl HW; Stacey PE; Turner RE., (Eds), Nitrogen loading in coastal water bodies: An atmospheric perspective. Washington, DC: American Geophysical Union; 187-226.

Staffelbach T; Neftel A; Blatter A; Gut A; Fahrni M; Stähelin J; Prévôt A; Hering A; Lehning M; Neininger B; Bäumle M; Kok GL; Dommen J; Hutterli M; Anklin M. (1997). Photochemical oxidant formation over southern Switzerland 1. results from summer 1994. J Geophys Res, 102, 23345-23362.

Stanford G; Dzienia S; Vander Pol RA. (1975). Effect of temperature on denitrification rate in soils. Soil Science Society Amer Proc, 39, 867-870.

Stange F; Butterbach-Bahl K; Papen H; Zechmeister-Boltenstern S; Li C; Aber J. (2000). Composition and Chemistry-A process-oriented model of N_2O and NO emissions from forest soils, 2, Sensitivity analysis and validation (Paper 1999JD900948). J Geophys Res-Part D-Atmospheres, 105, 4385-4398.

Stanley EH; Short RA; Harrison JW; Hall RI; Wiedenfeld RC. (1990). Variation in nutrient limitation of lotic and lentic algal communities in a Texas (USA) river. Hydrobiologia, 206, 61-71.

Staudt AC; Jacob DJ; Ravetta F; Logan JA; Bachiochi D; Krishnamurti TN; Sandholm ST; Ridley BA; Singh HB; Talbot B. (2003). Sources and chemistry of nitrogen oxides over the tropical Pacific. J Geophys Res, 1088239.

Stauffer RE. (1990). Granite weathering and the sensitivity of alpine lakes to acid deposition. Limnol Oceanogr, 35(5), 1112-1134.

Stauffer RE; Wittchen BD. (1991). Effects of silicate weathering on water chemistry in forested, upland, felsic terrain of the USA. Geochim Cosmochim Acta, 55, 3253-3271.

Stedman DH; Bishop G; Peterson JE; Guenther PL. (1991). On-road CO remote sensing in the Los Angeles Basin. (Final report). Sacramento, CA; California Air Resources Board (ARB).

Stehr JW; Dickerson RR; Hallock-Waters KA; Doddridge BG; Kirk D. (2000). Observations of NO_Y , CO, and SO2 and the origin of reactive nitrogen in the eastern United States. J Geophys Res, 105, 3553-3563.

Stein AF; Lamb D. (2003). Empirical evidence for the low- and high-NO_X photochemical regimes of sulfate and nitrate formation. Atmos Environ, 37, 3615-3625.

Stein AF; Lamb D; Draxler RR. (2000). Incorporation of detailed chemistry into a three-dimensional Lagrangian-Eulerian hybrid model: application to regional tropospheric ozone. Atmos Environ, 34, 4361-4372.

Steinbacher M; Zellweger C; Schwarzenbach B; Bugmann S; Buchmann B; Ordóñez C; Prevot ASH; Hueglin C. (2007). Nitrogen oxide measurements at rural sites in Switzerland: Bias of conventional measurement techniques. J Geophys Res, 112, 1-13.

Steltzer H; Bowman WD. (1998). Differential influence of plant species on soil N transformations within the alpine tundra. Ecosystems, 1, 464-474.

Stemmler K; Ammann M; Donders C; Kleffmann J; George C. (2006). Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid. Nature, 440, 195-198.

Stenchikov G; Dickerson R; Pickering K; Ellis WJ; Doddridge B; Kondragunta S; Poulida O; Scala J; Tao W-K. (1996). Stratosphere-troposphere exchange in a midlatitude mesoscale convective complex. 2. Numerical simulation. J Geophys Res, 101, 6837-6851.

Sterner RW; Elser JJ. (2002). Ecological stoichiometry: the biology of elements from molecules to the biosphere. Princeton, NJ: Princeton University Press.

Steudler PA; Bowden RD; Mellilo JM; Aber JD. (1989). Influence of nitrogen fertilization on methane uptake in temperate forest soil. Nature, 341, 314-316.

Stevens CJ; Dise NB; Mountford OJ; Gowing DJ. (2004). Impact of nitrogen deposition on the species richness of grasslands. Science, 303, 1876-1878.

Stevens CJ; Laughlin RJ; Malone JP. (1997). Measuring the contributions of nitrification and denitrification to the flux of nitrous oxide from soil. Soil Biol Biogeochem, 29, 139-151.

Stevens RK; Mulik JD; O'Keefe AE; Krost KJ. (1971). Gas chromatography of reactive sulfur gases in air at the parts-per-billion level. Anal Chem, 43, 827-831.

Stevens RK; O'Keeffe AE; Ortman GC. (1969). Absolute calibration of a flame photometric detector to volatile sulfur compounds at sub-part-per-million levels. Environ Sci Technol, 3, 652-655.

Stevenson DS; Dentener FJ; Schultz MG; Ellingsen K; van Noije TPC; Wild O; Zeng G; Amann M; Atherton CS; Bell N; Bergmann DJ; Bey I; Butler T; Cofala J; Collins WJ; Derwent RG; Doherty RM; Drevet J; Eskes HJ; Fiore AM; Gauss M; Hauglustaine DA; Horowitz LW; Isaksen ISA; Krol MC; Lamarque JF; Lawrence MG; Montanaro V; Mueller JF; Pitari G; Prather MJ; Pyle JA; Rast S; Rodriguez JM; Savage NH; Shindell DT; Strahan SE; Sudo K; Szopa S. (2006). Multimodel ensemble simulations of present-day and near-future tropospheric ozone. J Geophys Res, 111, doi: 10.1029/2005JD006338.

Stevenson FJ (Ed.). (1982). Origin and distribution of nitrogen in soil. Madison, WI: American Society of Agronomy.

Steyn DJ; Bottenheim JW; Thomson RB. (1997). Overview of tropospheric ozone in the Lower Fraser Valley, and the Pacific '93 field study. Atmos Environ, 31, 2025-2036.

Stienen H; Bauch J. (1988). Element content in tissues of spruce seedlings from hydroponic cultures simulating acidification and deacidification. Plant Soil, 106, 231-238.

Stith J; Dye J; Ridley B; Defer P; Defer E; Baumann K; Hubler G; Zerr R; Venticinque M. (1999). NO signatures from lightning flashes. J Geophys Res, 101, 16081-16089.

Stitt M; Krapp A. (1999). The interaction between elevated carbon dioxide and nitrogen nutrition: the physiological and molecular background. Plant Cell Environ, 22, 583-621.

Stockwell W; Middleton P; Chang J; Tang X. (1990). The second generation Regional Acid Deposition Model chemical mechanism for regional air quality modeling. J Geophys Res, 95, 16343-16367.

Stoddard JL. (1990). Plan for converting the NAPAP aquatic effects long-term monitoring (LTM) project to the temporally integrated monitoring of ecosystems (TIME) project. (International Report). Corvallis, OR; U.S. Environmental Protection Agency.

Stoddard JL. (1991). Trends in Catskill stream water quality: evidence from historical data. Water Resour Res, 27, 2855-2864.

Stoddard JL; Murdoch PS. (1991). Catskill Mountains: An overview of the impact of acidifying pollutants on aquatic resources. In: Charles DF (Ed.), Acidic deposition and aquatic ecosystems: Regional case studies. (pp 237-271). New York: Springer-Verlag, Inc.

Stoddard JL; Kellogg JH. (1993). Trends and patterns in lake acidification in the state of Vermont: Evidence from the Long-Term Monitoring project. Water Air Soil Pollut, 67, 301-317.

Stoddard JL. (1994). Long-term changes in watershed retention of nitrogen: its causes and aquatic consequences. In Baker LA (Ed.), Environmental chemistry of lakes and reservoirs. (pp. 223-284). Washington, D.C.: American Chemical Society.

Stoddard JL. (1995). Episodic acidification during snowmelt of high elevation lakes in the Sierra Nevada mountains of California. Water Air Soil Pollut, 85, 353-358.

Stoddard JL; Urquhart NS; Newell AD; Kugler D. (1996). The Temporally Interated Monitoring of Ecosystems (TIME) project design 2. Detection of regional acidification trends. Water Resour Res, 32, 2529-2538.

Stoddard JL; Driscoll CT; Kahl S; Kellogg J. (1998a). A regional analysis of lake acidification trends in the Northeastern U.S., 1982-1994. Environ Monit Assess, 51, 399-413.

Stoddard JL; Driscoll CT; Kahl S; Kellogg J. (1998b). Can site-specific trends be extrapolated to the regional level? A lake acidification example for the northeastern U.S. Ecol Appl, 8, 288-299.

Stoddard JL; Jeffries DS; Lükewille A; Clair TA; Dillon PJ; Driscoll CT; Forsius M; Johannessen M; Kahl JS; Kellogg JH; Kemp A; Mannio J; Monteith DT; Murdoch PS; Patrick S; Rebsdorf A; Skjelkvale BL; Stainton MP; Traaen T; Van Dam H; Webster KE; Wieting J; Wilander A. (1999). Regional trends in aquatic recovery from acidification in North American and Europe. Nature, 401, 575-578.

Stoddard J; Kahl JS; Deviney FA; DeWalle DR; Driscoll CT; Herlihy AT; Kellogg JH; Murdoch PS; Webb JR; Webster KE. (2003). Response of surface water chemistry to the Clean Air Act Amendments of 1990 (No. EPA 620/R-03/001). Research Triangle Park, NC; National Health and Environmental Effects Research Laboratory; Office of Research and Development; U.S. Environmental Protection Agency.

Stoermer EF; Smol JP (Eds.). (1999). The diatoms: Applications for the environmental and earth sciences. New York, NY: Cambridge University Press.

Stohlgren TJ; Binkley D; Chong GW; Kalkhan MA; Schell LD; Bull KA; Otsuki Y; Newman G; Bashkin M; Son Y. (1999). Exotic plant species invade hot spots of native plant diversity. Ecol Monogr, 69, 25-46.

Stoklasa J. (1923). Die Beschädigungen der Vegetation durch Rauchgase und Fabriksexhalation [Damage to vegetation from flue-gas and factory emissions]. (pp 101-131). Berlin, Germany: Urban and Schwarzenberg.

Stolte W; McCollin T; Noordeloos A; Riegman R. (1994). Effects of nitrogen source on the size distribution within marine phytoplankton populations. J Exp Mar Bio Ecol, 184, 83-97.

Stolzenburg MR; Hering SV. (2000). Method for the automated measurement of fine particle nitrate in the atmosphere. Environ Sci Technol, 34, 907-914.

Stottlemyer R; Troendle CA. (1992). Nutrient concentration pattern in streams draining alpine and subalpine catchments, Fraser Experimental Forest, Colorado. J Hydrol, 140, 179–208.

Stottlemyer R; Troendle CA; Markowitz D. (1997). Changes in snowpack, soil water, and stream water chemistry with elevation during 1990, Fraser Experimental Forest, Colorado. J Hydrol, 195, 114–136.

Strain BR; Bazzaz FA. (1983). Terrestrial plant communities. In: Lemon ER (Ed.), CO_2 and plants. (pp 177-222). Boulder, CO: Westview.

Strandberg H. (1998). Reactions of copper patina compounds—I. Influence of some air pollutants. Atmos Environ, 32, 3511-3520.

Streets DG; Bond TC; Carmichael GR; Fernandes SD; Fu Q; He D; Klimont Z; Nelson SM; Tsai NY; Wang MQ; Woo JH; Yarber KF. (2003). An inventory of gaseous and primary aerosol emissions in Asia in the year 2000. J Geophys Res-Atmos, 108.

Strengbom J; Nordin A; Näsholm T; Ericson L. (2001). Slow recovery of boreal forest ecosystem following decreased nitrogen input. Functional Ecology, 15, 451-457.

Strengbom J; Walheim M; Nasholm T; Ericson L. (2003). Regional differences in the occurrence of understorey species reflect nitrogen deposition in Swedish forests. Ambio, 32, 91-97.

Stribley DP; Read DJ. (1980). The biology of mycorrhiza in the Ericacae. VII. The relationship between mycorrhizal infection and the capacity to utilize simple and complex organic nitrogen sources. New Phytol, 86, 365-371.

Strickland TC; Holdren GRJ; Ringold PL; Bernard D; Smythe K; Fallon W. (1993). A national critical loads framework for atmospheric deposition effects assessment: I. method summary. Environ Manage, 17, 329-334.

Stoklasa J. (1923). Die Beschädigungen der Vegetation durch Rauchgase und Fabriksexhalation [Damage to vegetation from flue-gas and factory emissions]. (pp 101-131). Berlin, Germany: Urban and Schwarzenberg.

Stursova M; Crenshaw CL; Sinsabaugh RL. (2006). Microbial Responses to Long-Term N Deposition in a Semiarid Grassland. Microbial Ecology, 51, 90-98.

Stutz J; Hebestreit K; Alicke B; Platt U. (1999). Chemistry of halogen ozides in the troposphere: Comparison of model calculations with recent field data. J Atmos Chem , 34, 65-85.

Stutz J; Kim ES; Platt U; Bruno P; Perrino C; Febo A. (2000). UV-visible absorption cross sections of nitrous acid. J Geophys Res, 105, 14585-14592.

Stutz J; Ackermann R; Fast JD; Barrie L. (2002). Atmospheric reactive chlorine and bromine at the Great Salt Lake, Utah. Geophys Res Lett, 29, doi: 10.1029/2002GL014812.

Stutz J; Alicke B; Ackermann R; Geyer A; Wang S; White AB; Williams EJ; Spicer CW; Fast JD. (2004a). Relative humidity dependence of HONO chemistry in urban areas. J Geophys Res, 109, doi: 10.1029/2003JD004135.

Stutz, J; Alicke, B; Ackermann, R; Geyer, A; White, A; Williams, E. (2004).Vertical profiles of NO_3, N_2O_5, O_3, and NO_X in the nocturnal boundary layer: 1. Observations during the Texas Air Quality Study 2000. J Geophys Res, 109, doi: 10.1029/2003JD004209.

Sucoff EI; Thornton FC; Joslin JD. (1990). Sensitivity of tree seedlings to aluminum: I. Honeylocust. J Environ Qual, 19, 163-171.

Suding KN; Collins SL; Gough L; Clark C; Cleland EE; Gross KL; Milchunas DG; Pennings S. (2005). Functional- and abundance-based mechanisms explain diversity loss due to N fertlization. Proc Natl Acad Sci USA, 102, 4387-4392.

Suding KN; Miller AE; Bechtold H; Bowman WD. (2006). The consequence of species loss on ecosystem nitrogen cycling depends on community compensation. Ocecologia, 149, 141-149.

Suh HH; Spengler JD; Koutrakis P. (1992). Personal exposures to acid aerosols and ammonia. Environ Sci Technol, 26, 2507-2517.

Suh HH; Koutrakis P; Spengler JD. (1994). The relationship between airborne acidity and ammonia in indoor environments. Journal of Exposure Science and Environmental Epidemiology, 4, 1-23.

Sullivan TJ; Seip HM; Muniz IP. (1986). A comparison of frequently used methods for the determination of aqueous aluminum. Intern J Environ Anal Chem, 26, 61-75.

Sullivan TJ; Eilers JM; Church MR; Blick DJ; Eshleman KN; Landers DH; DeHaan MS. (1988). Atmospheric wet sulphate deposition and lakewater chemistry. Nature, 331, 607-609.

Sullivan TJ; Driscoll CT; Gherini SA; Munson RK; Cook RB; Charles DF; Yatsko CP. (1989). Influence of aqueous aluminium and organic acids on measurement of acid neutralizing capacity in surface waters. Nature, 338, 408-410.

Sullivan TJ. (1990). Historical changes in surface water acid-base chemistry in response to acidic deposition. (State of the Science Report no SOS/T 11). Washington, DC; National Acid Precipitation Assessment Program (NAPAP).

Sullivan TJ; Charles DF; Smol JP; Cumming BF; Selle AR; Thomas DR; Bernert JA; Dixit SS. (1990a). Quantification of changes in lakewater chemistry in response to acidic deposition. Nature, 345, 54-58.

Sullivan TJ; Kugler DL; Small MJ; Johnson CB; Landers DH; Rosenbaum BJ; Overton WS; Kretser WA; Gallagher J. (1990b). Variation in Adirondack, New York, lakewater chemistry as a function of surface area. Water Resour Bull, 26, 167–176.

Sullivan TJ; Turner RS; Charles DF; Cumming BF; Smol JP; Schofield CL; Driscoll CT; Cosby BJ; Birks HJ; Uutala AJ; Kingston JC; Dixit SS; Bernert JA; Ryan PF; Marmorek DR. (1992). Use of historical assessment for evaluation of process-based model projections of future environmental change: Lake acidification in the Adirondack mountains, New York, USA. Environ Pollut, 77, 253-262.

Sullivan TJ. (1993). Whole ecosystem nitrogen effects research in Europe. Environ Sci Technol, 27, 1482-1486.

Sullivan TJ; Charles DF. (1994). The feasibility and utility of a paleolimnology/paleoclimate data cooperative for North America. J Paleolimnol, 10, 265-273.

Sullivan TJ; Eilers JM. (1994). Assessment of deposition levels of sulfur and nitrogen required to protect aquatic resources in selected sensitive regions of North America (Final Report no PB-97-109441/XAB prepared by E&S Environmental Chemistry, Inc; prepared for Technical Resources, Inc. and U.S. Environmental Protection Agency). Corvallis, OR; Environmental Research Laboratory; U.S. Environmental Protection Agency.

Sullivan TJ; Cosby BJ; Driscoll CT; Charles DF; Hemond HF. (1996a). Influence of organic acids on model projections of lake acidification. Water Air Soil Pollut, 91, 271-282.

Sullivan TJ; McMartin B; Charles DF. (1996b). Re-examination of the role of landscape change in the acidification of lakes in the Adirondack Mountains, New York. Sci. Total Environ, 183, 231-248.

Sullivan TJ; Eilers JM; Cosby BJ; Vaché KB. (1997). Increasing role of nitrogen in the acidification of surface waters in the Adirondack Mountains, New York. Water Air Soil Pollut, 95, 313–336.

Sullivan TJ; Cosby BJ. (1998). Modeling the concentration of aluminium in surface waters. Water Air Soil Pollut, 105, 643-659.

Sullivan TJ; Cosby BJ; Bernert JA; Eilers JM. (1998). Model evaluation of dose/response relationships and critical loads for nitrogen and sulfur deposition to the watersheds of Lower Saddlebag and White Dome Lakes. Report No 97-10-01 to USDA Forest Service E&S Environmental Chemistry Inc, Corvallis, OR.

Sullivan TJ. (2000a). Aquatic effects of acidic deposition. Boca Raton, FL: Lewis Publishers.

Sullivan TJ. (2000b). Chemical dose-response relationships and critical loads. In: Sullivan, TJ, Aquatic Effects of Acidic Deposition. (Chapter 5). Boca Raton, FL: CRC Press.

Sullivan TJ; Peterson DL; Blanchard CL; Tannenbaum SJ. (2001). Assessment of air quality and air pollutant impacts in class I national parks of California. Report no NPS/CCSOUW/NRTR-00/xx). Denver, CO; Air Resources Division; National Park Service; U.S. Department of the Interior.

Sullivan TJ; Cosby BJ; Webb JR; Snyder KU; Herlihy AT; Bulger AJ; Gilbert EH; Moore D. (2002a). Assessment of the effects of acidic deposition on aquatic resources in the Southern Appalachian Mountains. (Report Prepared by E&S Environmental Chemistry, Inc. Corvallis, Oregon). http://www.esenvironmental.com/sami_download.htm. Asheville, NC; Southern Appalachian Mountains Initiative (SAMI).

Sullivan TJ; Johnson DW; Munson RK; Joslin JD. (2002b). Assessment of the effects of acidic deposition on forest resources in the Southern Appalachian Mountains. Asheville, NC; Southern Appalachian Mountains Initiative (SAMI).

Sullivan TJ; Cosby BJ; Laurence JA; Dennis RL; Savig K; Webb JR; Bulger AJ; Scruggs M; Gordon C; Ray J; Lee H; Hogsett WE; Wayne H; Miller D; Kern JS. (2003).Assessment of air quality and related values in Shenandoah National Park. (Technical report no NPS/NERCHAL/NRTR-03/090). Philadelphia, PA; Northeast Region; National Park Service; U.S. Department of the Interior.

Sullivan TJ; Cosby BJ; Herlihy AT; Webb JR; Bulger AJ; Snyder KU; Brewer P; Gilbert EH; Moore DL. (2004). Regional model projections of future effects of sulfur and nitrogen deposition on streams in the southern Appalachian Mountains. Water Resour Res, 40, W02101 doi:02110.01029/02003WR001998.

Sullivan TJ; Cosby BJ. (2005). Testing, improvement, and confirmation of a watershed model of acid-base chemistry. Water Air Soil Pollut, 85, 2607-2612.

Sullivan TJ; Cosby BJ; Tonnesen KA; Clow DW. (2005). Surface water acidification responses and critical loads of sulfur and nitrogen deposition in Loch Vale Watershed, Colorado. Water Resour Res, 41, doi:10.1029/2004WR003414.

Sullivan TJ; Fernandez IJ; Herlihy AT; Driscoll CT; McDonnell TC; Nowicki NA; Snyder KU; Sutherland JW. (2006a). Acid-base characteristics of soils in the Adirondack Mountains, New York. Soil Sci Soc Am J, 70, 141-152.

Sullivan TJ; Driscoll CT; Cosby BJ; Fernandez IJ; Herlihy AT; Zhai J; Stemberger R; Snyder KU; Sutherland JW; Nierzwicki-Bauer SA; Boylen CW; McDonnell TC; Nowicki NA. (2006b). Assessment of the extent to which intensively studied lakes are representative of the Adirondack Mountain region. (Final Report no 06-17).Corvallis, OR; prepared by Environmental Chemistry, Inc. for: Albany, NY; Environmental Monitoring Evaluation and Protection Program of the New York State Energy Research and Development Authority (NYSERDA).

Sullivan TJ; Cosby BJ; Herlihy AT; Driscoll CT; Fernandez IJ; McDonnell TC; Boylen CW; Nierzwicki-Bauer SA; Snyder KU. (2007a). Assessment of the extent to which intensively-studied lakes are representative of the Adirondack region and response to future changes in acidic deposition. Water Air Soil Pollut, 185, 279-291.

Sullivan TJ; Webb JR; Snyder KU; Herlihy AT; Cosby BJ. (2007b). Spatial distribution of acid-sensitive and acid-impacted streams in relation to watershed features in the southern Appalachian mountains. Water Air Soil Pollut, 182, 57-71.

Sullivan TJ; Cosby BJ; Webb JR; Dennis RL; Bulger AJ; Deviney JR., FA. (2007c). Streamwater acid-base chemistry and critical loads of atmospheric sulfur deposition in Shenandoah National Park, Virginia. Environ Monit Assess, doi: 10.1007/s10661-007-9731-1.

Sullivan TJ; Cosby BJ; Webb JR; Dennis RL; Bulger AJ; Deviney FA Jr. (2008). Streamwater acid-base chemistry and critical loads of atmospheric sulfur deposition in Shenandoah National Park, Virginia. Environ Monit Assess, 137, 85-99.

Sundberg B; Näsholm T; Palmqvist K. (2001). The effect of nitrogen on growth and key thallus components in the two tripartite lichens, *Nephroma arcticum* and *Peltigera aphthosa*. Plant, Cell and Environment, 24, 517-527.

Suns K; Hitchin G. (1990). Interrelationships between mercury levels in yearling yellow perch, fish condition and water quality. Water Air Soil Pollut, 50, 255-265.

Sutton MA; Erisman JW; Dentener F; Möller D. (2008a). Ammonia in the environment: From ancient times to the present. Environ Pollut. (Corrected proof; doi: 10:1016/j.envpol2008.03.013).

Sutton MA; Simpson D; Levy PE; Smith RI; Reis S; van Oijen M; de Vries W. (2008b). Uncertainties in the relationship between atmospheric nitrogen deposition and forest carbon sequestration. Glob Change Biol, 14, 2057-2063.

Sutton MA; Dragosits U; Tang YS; Fowler D. (2000). Ammonia emissions from non-agricultural sources in the UK. Atmos Environ, 34, 855-869.

Sutton RT; Hodson DLR. (2005). Atlantic Ocean forcing of North American and European summer climate. Science, 309, 115-118.

Svensson J-E; Johansson L-G. (1993a). A laboratory study of the effect of ozone, nitrogen dioxide, and sulfur dioxide on the atmospheric corrosion of zinc. J Electrochem Soc, 140, 2210-2216.

Svensson J-E; Johansson L-G. (1993b). A laboratory study of the initial stages of the atmospheric corrosion of zinc in the presence of NaCl; influence of SO_2 and NO_2. Corros Sci, 34, 721-740.

Svensson JE; Johansson LG. (1996). The temperature-dependence of the SO_2-induced atmospheric corrosion of zinc; a laboratory study. Corros Sci, 38, 2225-2233.

Svensson R; Ljungstroem E; Lindqvist O. (1987). Kinetics of the reaction between nitrogen dioxide and water vapour. Atmos Environ, 21, 1529-1539.

Sverdrup H; Warfvinge P. (1988). Weathering of primary silicate minerals in the natural soil environment in relation to a chemical weathering model. Water Air Soil Pollut, 38, 387-408.

Sverdrup H; de Vries W; Henriksen A. (1990). Mapping critical loads: a guidance to the criteria, calculations, data collection and mapping of critical loads. (Environmental report 1990:14; NORD 1990:98). Copenhagen, Denmark: Nordic Council of Ministers.

Sverdrup H; Warfvinge P; Rabenhorst M; Janicki A; Morgan R; Bowman M. (1992). Critical loads and steady-state chemistry for streams in the state of Maryland. Environ Pollut, 77, 195-203.

Sverdrup H; Warfvinge P. (1993). The effect of soil acidification on the growth of trees, grass and herbs as expressed by the (Ca^{+} Mg^{+} K)/Al ratio. Rep in Ecol & Eng, 2, 1993.

Sverdrup H; de Vries W. (1994). Calculating critical loads for acidity with the simple mass balance method. Water Air Soil Pollut, 72, 143-162.

Swackhamer DL; Paerl HW; Eisenreich SJ; Hurley J; Hornbuckle KC; McLachlan M; Mount D; Muir D; Schindler D. (2004). Impacts of atmospheric pollutants on aquatic ecosystems. Issues in Ecology, 12, 1-24.

Swain RE. (1949). Smoke fume investigations: A historical review. Ind Eng Chem, 41, 2384-2388.

Swank WT. (1988). Stream chemistry responses to disturbance. In: Swank WT; Crossley DS (Eds.), Forest hydrology and ecology at Coweeta. (pp 339-358). New York, NY: Springer-Verlag, Inc.

Swank WT; Vose JM. (1997). Long-term nitrogen dynamics of Coweeta forested watersheds in the southeastern United States of America. Glob Biogeochem Cycles, 11, 657-671.

Sweets PR. (1992). Diatom paleolimnological evidence for lake acidification in the Trail Ridge region of Florida. Water Air Soil Pollut, 65, 43-57.

Sweets PR; Bienert RW; Crisman TL; Binford MW. (1990). Paleoecological investigations of recent lake acidification in northern Florida. J Paleolimnol, 4, 103-137.

Swenson WA; McCormick JH; Simonson TD; Jensen KM; Eaton JG. (1989). Experimental acidification of Little Rock Lake (Wisconsin): Fish research approach and early responses. Arch. Environ Contam Toxicol, 18, 167-174.

Swietlik D; Faust M. (1984). Foliar nutrition of fruit crops. Horticulture Review 6: 287-355.

Takemoto BK; Bytnerowicz A; Fenn ME. (2001). Current and future effects of ozone and atmospheric nitrogen deposition on California's mixed conifer forests. For Ecol Manage, 144, 159-173.

Talbot RW; Vijgen AS; Harriss RC. (1990). Measuring tropospheric HNO_3: Problems and prospects for nylon filter and mist chamber techniques. J Geophys Res, 95, 7553-7561.

Tamm CO; Aronsson A; Popovic B. (1995). Nitrogen saturation in a long-term forest experiment with annual additions of nitrogen. In: Grennfelt P; Rodhe H; Thörnelöf, E; Wisniewski J. (Eds.), Acid Reign '95? Proceedings from the 5th International Conference on Acidic Deposition: Science & Policy, held in Göteborg, Sweden, June 26-30, 1995. Water Air Soil Pollut, 85, 1683-1688.

Tamm CO; Aronsson A; Popovic B; Flower-Ellis J. (1999). Optimum nutrition and nitrogen saturation in Scots pine stands. (Book Series: Studia forestalia Suecica - Technical report no 206). Uppsala, Sweden; Department for Production Ecology; Faculty of Forest Services; Swedish University of Agricultural Sciences.

Tanaka PL; Riemer DD; Chang S; Yarwood G; McDonald-Buller EC; Apel EC; Orlando JJ; Silva PJ; Jimenez JL; Canagaratna MR; Neece JD; Mullins CB; Allen DT. (2003). Direct evidence for chlorine-enhanced urban ozone formation in Houston, Texas. Atmos Environ, 37, 1393-1400.

Tang IN; Munkelwitz HR. (1993). Composition and temperature dependence of the deliquescence properties of hygroscopic aerosols. ATMOS ENVIRON PART A GER TOP, 27, 467-473.

Tang IN; Tridico AC; Fung KH. (1997). Thermodynamic and optical properties of sea salt aerosols. J Geophys Res, 102, 269–223.

Tank JL; Dodds WK. (2003). Nutrient limitation of epilithic and epixylic biofilms in ten North American streams. Freshw Biol, 48, 1031-1049.

Tanner RL; D'Ottavio T; Garber R; Newman L. (1980). Determination of ambient aerosol sulfur using a continuous flame photometric detection system. I. Sampling system for aerosol sulfate and sulfuric acid. Atmos Environ, 14, 121-127.

Tanner RL; Kelly TJ; Dezaro DA; Forrest J. (1989). A comparison of filter, denuder, and real-time chemiluminescence techniques for nitric acid determination in ambient air. Atmos Environ (1967), 23, 2213-2222.

Tao W-K; Simpson J. (1993). The Goddard Cumulus Ensemble Model. Part I: model description. Terr Atmos Oceanic Sci (TAO), 4, 35-71.

Tarnay L; Gertler AW; Blank RR; Taylor GE Jr. (2001). Preliminary measurements of summer nitric acid and ammonia concentrations in the Lake Tahoe Basin air-shed: implications for dry deposition of atmospheric nitrogen. Environ Pollut, 113, 145-153.

Taylor GE Jr; Hanson PJ; Baldocchi DD. (1988). Pollutant deposition to individual leaves and plant canopies: sites of regulation and relationship to injury. In: Heck WW; Taylor OC; Tingey DT (Eds.), Assessment of crop loss from air pollutants. (pp 227-257). New York, NY: Elsevier Applied Science.

Taylor GE Jr; Hanson PJ. (1992). Forest trees and tropospheric ozone: role of canopy deposition and leaf uptake in developing exposure-response relationships. Agric Ecosyst Environ, 42, 255-273.

Taylor GE Jr; Pitelka LF. (1992). Genetic diversity of plant populations and the role of air pollution. In: Barker JR; Tingey DT (Eds.), Air pollution effects on biodiversity. (pp 111-130). New York, NY: Van Nostrand Reinhold.

Taylor OC; MacLean DC. (1970). Nitrogen oxides and the peroxyacyl nitrates. In: Jacobson JS; Hill AC (Eds.), Recognition of air pollution injury to vegetation: A pictorial atlas. (pp E1-E14). Pittsburgh, PA: Air Pollution Control Association.

Teklemariam TA; Sparks JP. (2004). Gaseous fluxes of peroxyacetyl nitrate (PAN).into plant leaves. Plant Cell and Environment, 27, 1149-1158.

Teklemariam TA; Sparks JP. (2006). Leaf fluxes of NO and NO_2 in four herbaceous plant species: the role of ascorbic acid. Atmos Environ, 40, 2235-2244.

Temple PJ; Riechers GH; Miller PR; LenNO$_X$ RW. (1992). Growth responses of ponderosa pine to long-term exposure to ozone, wet and dry acidic deposition, and drought. Can J For Res, 23, 59-66.

Temple PJ; Taylor OC. (1983). World-wide ambient measurements of peroxyacetyl nitrate (PAN).and implications for plant injury. Atmos Environ, 17, 1583-1587.

Temple PJ; Riechers GH; Miller PR. (1992). Foliar injury responses of ponderosa pine seedlings to ozone, wet and dry acidic deposition, and drought. Environ Exp Bot, 32, 101-113.

Templer PH; Lovett GM; Weathers KC; Findlay SE; Dawson TE. (2005). Influence of tree species on forest nitrogen retention in the Catskill Mountains, New York, USA. Ecosystems, 8, 1-16.

ter Braak CJF; Wiertz J. (1994). On the statistical analysis of vegetation change: a wetland affected by water extraction and soil acidification. Journal of Vegetation Science, 5, 361-372.

Tester PA; Varnam SM; Culver ME; Eslinger DL; Stumpf RP; Swift RN; Yungel JK; Black MD; Litaker RW. (2003). Airborne detection of ecosystem responses to an extreme event: Phytoplankton displacement and abundance after hurricane induced flooding in the Albemarle-Pamlico Sound System, North Carolina. Estuaries, 26, 1353-1364.

Theodose TA; Bowman WD. (1997). Nutrient availability, plant abundance, and species diversity in two alpine tundra communities. Ecology, 78, 1861-1872.

Thielman A; Prévôt ASH; Grüebler FC; Staelhelin J. (2001). Empirical ozone isopleths as a tool to identify ozone production regimes. Geophys Res Lett, 28, 2369-2372.

Thoene B; Schroder P; Papen H; Egger A; Rennenberg H. (1991). Absorption of Atmospheric NO_2 by Spruce (*Picea abies* L. Karst.) Trees: 1. NO_2 Influx and Its Correlation with Nitrate Reduction. New Phytol, 117, 575-585.

Thomas MD; Hendricks HR; Hill GR. (1944). Some chemical reactions of sulfur dioxide after absorption by alfalfa and sugarbeets. Plant Physiol, 19, 212-226.

Thomas MD. (1951). Gas damage to plants. Annu Rev Plant Physiol, 2, 293-322.

Thompson AM; Pickering KE; Dickerson RR; Ellis WG Jr; Jacob DJ; Scala JR; Tao W-K; McNamara DP; Simpson J. (1994). Convective-transport over the central United States and its role in regional CO and O_3 budgets. J Geophys Res, 99, 18703-18711.

Thompson AM; Singh HB; Schlager H. (2000). Subsonic assessment ozone and nitrogen oxide experiment (SONEX) and pollution from aircraft emissions in the North Atlantic Flight Corridor (POLINAT 2). J Geophys Res, 105, 3595-3603.

Thompson CR; Hensel EG; Kats G; Taylor OC. (1970). Effects of continuous exposure of naval oranges to nitrogen dioxide. Atmos Environ, 4, 349-355.

Thorne RSJ; Williams WP; Gordon C. (2000). The macroinvertebrates of a polluted stream in Ghana. Journal of Freshwater Ecology, 15, 209-217.

Thornton DC; Bandy AR. (1993). Sulfur dioxide and dimethyl sulfide in the central Pacific troposphere. J Atmos Chem , 17, 1-13.

Thornton DC; Bandy AR; Blomquist BW; Anderson BE. (1996). Impact of anthropogenic and biogenic sources and sinks on carbonyl sulfide in the North Pacific troposphere. J Geophys Res, 101, 1873-1881.

Thornton DC; Brandy AR; Blomquist BW; Driedger AR; Wade TP. (1999). Sulfur dioxide distribution over the Pacific Ocean 1991-1996. J Geophys Res, 104, 5845-5854.

Thornton DC; Bandy AR; Tu FH; Blomquist BW; Mitchell GM; Nadler W; Lenschow DH. (2002). Fast airborne sulfur dioxide measurements by atmospheric pressure ionization mass spectrometry (APIMS). J Geophys Res, 107, doi: 10.1029/2002JD02289.

Thornton FC; Schaedle M; Raynal DJ. (1986a). Effect of aluminum on the growth of sugar maple in solution culture. Can J For Res, 16, 892-896.

Thornton FC; Schaedle M; Raynal DJ. (1986b). Effects of aluminum on the growth, development, and nutrient composition of honeylocust (*Gleditia triacanthos* L.) seedling. Tree Physiol, 2, 307-316.

Thornton FC; Schaedle M; Raynal DJ; Zipperer C. (1986c). Effects of aluminum on honeylocust (*Gleditsia triacanthos* L.) seedlings in solution culture. J Exp Bot, 37, 775-785.

Thornton FC; Schaedle M; Raynal DJ. (1987). Effects of aluminum on red spruce seedlings in solution culture. Environ Exp Bot, 27, 489-498.

Thornton JA; Braban CF; Abbatt JPD. (2003). N_2O_5 hydrolysis on sub-micron organic aerosol: The effect of relative humidity, particle phase, and particle size. Phys Chem Chem Phys, 5, 4593-4603.

Throop HL. (2005). Nitrogen deposition and herbivory affect biomass production and allocation in an annual plant. Oikos, 111, 91-100.

Throop HL; Lerdau MT. (2004). Effects of nitrogen deposition on insect herbivory: Implications for community and ecosystem processes. Ecosystems, 7, 109-133

Tie XX; Emmons L; Horowitz L; Brasseur G; Ridley, B; Atlas E; Stround C; Hess P; Klonecki A; Madronich S; Talbot R; Dibb J. (2003). Effect of sulfate aerosol on tropospheric NO_X and ozone budgets: Model simulations and TOPSE evidence. J Geophys Res, 108, 10.1029/2001JD001508.

Tietema A; Beier C. (1995). A correlative evaluation of nitrogen cycling in the forest ecosystems of the EC projects NITREX and EXMAN. For Ecol Manage, 71, 143-151.

Tietema A; Emmett BA; Gundersen P; Kjønaas OJ; Koopmans CJ. (1998). The fate of ^{15}N-labelled nitrogen deposition in coniferous forest ecosystems. For Ecol Manage, 101, 19-27.

Tietge JE; Johnson RD; Bergman HL. (1988). Morphometric changes in gill secondary lamellae of brook trout (*Salvelinus fontinalis*).after long-term exposure to acid and aluminum. Can J Fish Aquat Sci, 45, 1643-1648.

Tilman, D. (1981). Tests of resource competition theory using four species of Lake Michigan algae. Ecology, 62, 802-815.

Tilman D. (1987). Secondary succession and the pattern of plant dominance along experimental nitrogen gradients. Ecol Monogr, 57, 189-214.

Tilman D; Wedin D. (1991). Dynamics of nitrogen competition between successional grasses. Ecology, 72, 1038-1049.

Tilman D; Downing JA. (1994). Biodiversity and stability in grasslands. Nature, 367, 363-365.

Tilman D. (1996). Biodiversity: Population versus ecosystem stability. Ecology, 77, 350-363.

Tilman D. (2000). Causes, consequences, and ethics of biodiversity. Nature, 405, 208-211.

Tingey DT; Hodsett WE; Henderson S. (1990). Definition of adverse effects for the purpose of establishing secondary national ambient air quality standards. J Environ Qual, 19, 635-639.

Tingey DT; Johnson MG; Phillips DL; Storm MJ. (1995). Effects of elevated CO_2 and nitrogen on ponderosa pine fine roots and associated fungal components. J Biogeogr, 22, 281-287.

Tipping E; Berggren D; Mulder J; Woof C. (1995). Modelling the solid-solution distributions of protons, aluminium, base cations and humic substances in acid soils. European Journal of Soil Science, 46, 77-94.

Tipping E; Bass JAB; Hardie D; Haworth EY; Hurley MA; Wills G. (2002). Biological responses to the reversal of acidification in surface waters of the English Lake District. Environ Pollut, 116, 137-146.

Tokiwa H; Ohnishi Y. (1986). Mutagenicity and carcinogenicity of nitroarenes and their sources in the environment. Critical Reviews in Toxicology, 17, 23-60.

Tokiwa H; Nakanishi Y; Sera N; Hara N; Inuzuka S. (1998). Analysis of environmental carcinogens associated with the incidence of lung cancer. Toxicology letters, 99, 33-41.

Toman MA. (1998). Introduction to special Section: Forum on valuation of ecosystem services - Why not to calculate the value of the world's ecosystem services and natural capital. Ecol Econ, 25, 57-60.

Tomassen HBM; Smolders AJP; Lamers LPM; Roelofs JGM. (2003). Stimulated growth of *Betula pubescens* and *Molinia caerulea* on ombrotrophic bogs: Role of high levels of atmospheric nitrogen deposition. J Ecol, 91, 357-370.

Tomassen HBM; Smolders AJP; Limpens J; Lamers LPM; Roelofs JGM. (2004). Expansion of invasive species on ombrotrophic bogs: dessication or high N deposition? J Appl Ecol, 41, 139-150.

Tonnesen GS; Dennis RL. (2000). Analysis of radical propagation efficiency to assess ozone sensitivity to hydrocarbons and NO_X: 2. Long-lived species as indicators of ozone concentration sensitivity. J Geophys Res, 105, 9227-9241.

Tonnessen KA. (1991). The Emerald Lake Watershed Study: Introduction and site description. Water Resour Res, 27(7), 1537-1539.

Torfs K; Van Grieken R. (1996). Effect of stone thickness on run-off water composition and derived damage functions in ambient exposure experiments. Atmos Environ, 30, 1-8.

Toumi R. (1994). BrO as a sink for dimethylsulfide in the marine atmosphere. Geophys Res Lett, 21, 117-120.

Townsend AR; Braswell BH; Holland EA; Penner JE. (1996). Spatial and temporal patterns in terrestrial carbon storage due to deposition of fossil fuel nitrogen. Ecol Appl, 6, 806-814.

Townsend AR; Howarth RW; Bazzaz FA; Booth MS; Cleveland CC; Collinge SK; Dobson AP; Epstein PR; Keeney DR; Mallin MA; Rogers CA; Wayne P; Wolfe AH. (2003). Human health effects of a changing global nitrogen cycle. Front Ecol Environ, 1, 240-246.

Townsend CR; Hildrew AG; Francis J. (1983). Community structure in some southern English streams: the influence of physiochemical factors. Freshw. Biol, 13, 521-544.

Trabaud L. (1994). The effect of fire on nutrient losses and cycling in a *Quercus coccifera* garrigue (southern France). Oecologia, 99, 379-386.

Trainer M; Parrish DD; Buhr MP; Norton RB; Fehsenfeld FC; Anlauf KG; Bottenheim JW; Tang YZ; Wiebe HA; Roberts JM; Tanner RL; Newman L; BowerSO$_X$ VC; Meagher JF; Olszyna KJ; Rodgers MO; Wang T; Berresheim H; Demerjian KL; Roychowdhury UK. (1993). Correlation of ozone with NO_Y in photochemically aged air. J Geophys Res, 98, 2917-2925.

Trainer M; Parrish DD; Golday PD; Roberts J; Fehsenfeld FC. (2000). Review of observation-based analysis of the regional factors influencing ozone concentrations. Atmos Environ, 34, 2045-2061.

Treiman T. (2006). Are residents willing to pay for their community forests? Results of a contingent valuation survey in Missouri, USA. Urban Studies, 43, 1537-1548.

Treseder KK; Allen MF. (2000). Mycorrhizal fungi have a potential role in soil carbon storage under elevated CO_2 and nitrogen deposition. New Phytol, 147, 189-200.

Treseder KK. (2004). The meta-analysis of mycorrhizal response to nitrogen, phosphorus, and atmospheric CO_2 in field studies. New Phytol, 164, 347-355.

Treshow M. (1980). Pollution effects on plant distribution. Environ Conserv, 7, 279-286.

Trettin CC; Johnson DW; Todd DE Jr. (1999). Forest Nutrient and Carbon Pools at Walker Branch Watershed: Changes during a 21-Year Period. Soil Sci Soc Am J, 63, 1436-1448.

Treves K; Shragina L; Rudich Y. (2000). Henry's Law constants of some beta-, gamma-, and delta-hydroxy alkyl nitrates of atmospheric interest. Environ Sci Technol, 34, 1197-1203.

Tritton LM; Martin CW; Hornbeck JW; Pierce RS. (1987). Biomass and nutrient removals from commercial thinning and whole-tree clearcutting of central hardwoods. Environ Manage, 11, 659-666.

Trojnar JR. (1977). Egg and larval survival of white suckers (*Catostomus commersoni*) at low pH. J Fish Res Board Can, 34, 262-266.

Trombulak SC; Frissell CA. (2000). Review of ecological effects of roads on terrestrial and aquatic communities. Conserv Biol, 14, 18-30.

Truman RA; Humphreys FR; Ryan PJ. (1986). Effect of varying solution ratios of Al to Ca and Mg on the uptake of phosphorus by *Pinus radiata*. Plant Soil, 96, 109-123.

Tsai C-J; Huang H-Y. (1995). Atmospheric aerosol sampling by an annular denuder system and a high-volume PM_{10} sampler. Environ Int, 21, 283-291.

Turco RP; Toon OB; Whitten RC; Hamill P; Keesee RG. (1983). The 1980 eruptions of Mount St. Helens: Physical and chemical processes in the stratospheric clouds. J Geophys Res, 88, 5299-5319.

Turekian VC; Macko SA; Keene WC. (2001). Application of stable sulfur isotopes to differentiate sources of size-resolved particulate sulfate in polluted marine air at Bermuda during spring. Geophys Res Lett, 28, 1491-1494.

Turk JT; Spahr NE. (1991). Rocky Mountains. In :Charles DF; Christie S (Eds.), Acidic deposition and aquatic ecosystems: Regional case studies (pp. 471-501). New York: Springer-Verlag, Inc.

Turk JT; Campbell DH; Spahr NE. (1992). Initial findings of synoptic snowpack sampling in Colorado Rocky Mountains. (Open file report 92-645). Denver, CO; Geologic Survey;. U.S. Department of the Interior.

Turk JT; Campbell DH; Spahr NE. (1993). Use of chemistry and stable sulfur isotopes to determine sources of trends in sulfate of Colorado lakes. Water Air Soil Pollut, 67, 415-431.

Turner J; Lambert MJ; Gessel SP. (1977). Use of foliage sulphate concentrations to predict response to urea application by Douglas-fir. Can J For Res, 7, 476-480.

Turner J; Lambert MJ. (1980). Sulfur nutrition of forests. In: Shriner DS; Richmond CR; Lingberg SE., (Eds.), Atmospheric sulfur deposition: Environmental impact and health effects. (Proceedings of the 2nd life sciences symposium held in Gatlinburg, TN; October 1979; pp 321-333). Ann Arbor, MI: Ann Arbor Science Publishers, Inc.

Turner RE; Qureshi N; Rabalais NN; Dortch Q; Justic D; Shaw RF; Cope J. (1998). Fluctuating silicate: Nitrate ratios and coastal plankton food webs. Proc Natl Acad Sci USA 95:13048-13051.

Turner RE; Stanley D; Brock D; Pennock J; Rabalais NN. (2001). A comparison of independent N-loading estimates for U.S. estuaries. In: Valigura RA; Alexander RB; Castro MS; Meyers TP; Paerl HW; Stacey PE; Turner RE (Eds.), Nitrogen loading in coastal water bodies: An atmospheric perspective. (AGU Coastal Estuaries Studies; Series Volume 57). Washington, DC: American Geophysical Union.

Turner RE; Stanley D; Brock D; Pennock J; Rabalais NN. (2001). A Comparison of Independent N-loading Estimates for U.S. Estuaries. COASTAL AND ESTUARINE STUDIES, 107-118.

Turner RE. (2002). Element ratios and aquatic food webs. Estuaries, 25, 694-703.

Turner RS; Cook RB; Van Miegroet H; Johnson DW; Elwood JW; Bricker OP; Lindberg SE; Hornberger GM. (1991). Watershed and lake processes affecting surface water acid-base chemistry. In: Irving PM (Ed.), Acidic deposition: state of science and technology report no 10; volume II: Aquatic processes and effects. Washington, DC: The U.S. National Acid Precipitation Assessment Program (NAPAP).

Turner RS; Ryan PF; Marmorek DR; Thornton KW; Sullivan TJ; Baker JP; Christensen SW; Sale MJ. (1992). Sensitivity to change for low-ANC eastern U.S. lakes and streams and brook trout populations under alternative sulfate deposition scenarios. Environ Pollut, 77, 269-277.

Turnipseed AA; Huey LG; Nemitz E; Stickel R; Higgs J; Tanner DJ; Slusher DL; Sparks JP; Flocke F; Guenther A. (2006). Eddy covariance fluxes of peroxyacetyl nitrates (PANs) and NO_Y to a coniferous forest. J Geophys Res, 111, 10.1029/2005JD006631.

Turnpenny AWH; Sadler K; Aston RJ; Milner AGP; Lynam S. (1987). The fish populations of some streams in Wales and northern England in relation to acidity and associated factors. Journal of Fish Biology, 31, 415-434.

Turunen J; Roulet NT; Moore TR; Richard PJH. (2004). Nitrogen deposition and increased carbon accumulation in ombrotrophic peatlands in eastern Canada. Glob Biogeochem Cycles, 18, GB3002, doi:10.1029/2003GB002154.

Twilley RR; Kemp WM; Staver KW; Stevenson JC; Boynton WR. (1985). Nutrient enrichment of estuarine submersed vascular plant communities. 1. Algal growth and effects on production of plants and associated communities. Marine Ecology Progress Series, 23, 179-191.

Twomey LJ; Piehler MF; Paerl HW. (2005). Phytoplankton uptake of ammonium, nitrate and urea in the Neuse River Estuarry, NC, USA. Hydrobiologia, 533, 123-134.

Tyler AC; Lambrinos JG; Grosholz ED. (2007). Nitrogen inputs promote the spread of an invasive marsh grass. Ecol Appl, 17, 1886-1898.

Tyler SJ; Ormerod SJ. (1992). A Review of the Likely Causal Pathways Relating the Reduced Density of Breeding Dippers Cinclus cinclus to the Acidification of Upland Streams. Environ Pollut, 78, 49-55.

U.K. AQEC. (2004). Nitrogen dioxide in the United Kingdom. London, UK; Department for Environment, Food and Rural Affairs. U.K. Air Quality Expert Group (AQEC) http://www.defra.gov.uk/environment/airquality/publications/nitrogen-dioxide/index.htm.

Ulrich B; Mayer R; Khanna PK. (1980). Chemical changes due to acid precipitation in loess-derived soil in central Europe. Soil Sci, 130, 193-199.

Ulrich B. (1983). Soil acidity and its relations to acid deposition. In: Ulrich, B; Pankrath, J (Eds.), Effects of accumulation of air pollutants in forest ecosystems. (Proceedings of a workshop held in Göttingen, Federal Republic of Germany; May 1982 pp. 127-146). Dordrecht, The Netherlands: D. Reidel Publishing Company.

UNECE. (2004). Manual on methodologies and criteria for modeling and mapping critical loads and levels and air pollution effects, risks, and trends. http://www.icpmapping.org. Geneva, Switzerland; Convention on Long-Range Transboundary Air Pollution; United Nations Economic Commission for Europe (UNECE)

UNEP (1999). Levine JS; Bobbe T; Ray N; Singh A; and Witt RG. Wildland Fires and the Environment: A Global Synthesis. (UNEP/DEIAEW/TR.99-1). Nairobi, Kenya; Division of Environmental Information; Assessment and Early Warning (DEIA&EW); United Nations Environment Programme (UNEP).

UNEP 2007

Unsworth MH; Wilshaw JC. (1989). Wet, occult and dry deposition of pollutants on forests. Agricultural and Forest Meteorology 47: 221-238.

Urban NR; Bayley SE. (1986). The acid-base balance of peatlands: a short-term perspective. Water Air Soil Pollut, 30, 791-800.

Urban NR; Eisenreich SJ. (1988). Nitrogen cycling in a forested Minnesota bog. Canadian Journal of Botany, 66, 435-449.

Urquhart NS; Paulsen SG; Larsen DP. (1998). Monitoring for regional and policy-relevant trends over time. Ecol Appl, 8, 246-257.

USDA. (1996). Southern Appalachian Man and the Biosphere (SAMAB), Southern Appalachian Assessment Aquatics Technical (Report 2 of 5). Atlanta, GA: Southern Region; U.S. Forest Service, U.S. Department of Agriculture (USDA).

U.S.CFR. (2006). Lower detectable limit—(1).technical definition. CFR 40: §53.23c. Washington DC; U.S. Code of Federal Regulations.

U.S. Code. (1970a). Clean Air Act, §108, Air quality criteria and control techniques. Amended in 1977, 1990. (Title 42§7408-108).

U.S. Code. (1970b). Clean Air Act, §109, National Ambient Air Quality Standards. Amended in 1977, 1990. (Title 42§7408-109).

U.S. Congress (1990). Clean Air Act amendments of 1990 (PL 101-549). Washington DC.

U.S. Department of Health Education, and Welfare. (1970). Air quality criteria for sulfur oxides (No. AP-50A). Washington, DC; National Air Pollution Control Administration; Public Health Service. .

U.S. EPA. (1971). Air quality criteria for nitrogen oxides. (Report no. AP-84). Washington, DC; Air Pollution Control Office; U.S. Environmental Protection Agency.

U.S. EPA. (1973). Effects of sulfur oxide in the atmosphere on vegetation: Revised chapter 5 of air quality criteria for sulfur oxides. (Report no. EPA-R3-73-030). Research Triangle Park, NC; National Environmental Research Center, Office of Research and Development; U.S. Environmental Protection Agency.

U.S. EPA. (1974). A preliminary report on asbestos in the Duluth, Minnesota area. Washington, DC; Office of Technical Analysis; U.S. Environmental Protection Agency.

U.S. EPA. (1982a). Air quality criteria for oxides of nitrogen (No. EPA-600/8-82-026). Research Triangle Park, NC; Office of Health and Environmental Assessment; Environmental Criteria and Assessment Office; Available from: NTIS, Springfield, VA; PB83-131011.

U.S. EPA. (1982b). Air quality criteria for particulate matter and sulfur oxides (Report no. EPA/600/8-82/029aF-cF; 3 Volumes). Research Triangle Park, NC: Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office; U.S. Environmental Protection Agency.

U.S. EPA. (1982c). Review of the national ambient air quality standards for sulfur oxides: Assessment of scientific and technical information; OAQPS staff paper. (Report no. EPA-450/5-82-007). Research Triangle Park, NC; Office of Air Quality Planning and Standards; U.S. Environmental Protection Agency.

U.S. EPA. (1984a). The acidic deposition phenomenon and its effects: Critical assessment review papers. Volume I: Atmospheric sciences (No. EPA-600/8-83-016-AF). Washington, DC; Office of Acid Deposition; Environmental Monitoring, and Quality Assurance; National Exposure Research Laboratory; Office of Research and Development; U.S. Environmental Protection Agency.

U.S. EPA. (1984b).The acidic deposition phenomenon and its effects: Critical assessment review papers. Volume II: Effects sciences. (Report no. EPA-600/8-83-016-BF). Washington, DC; Office of Acid Deposition, Environmental Monitoring and Quality Assurance; National Exposure Research Laboratory; Office of Research and Development; U.S. Environmental Protection Agency.

U.S. EPA. (1985). The acidic deposition phenomenon and its effects: Critical assessment review papers. Critical assessment document (No. EPA/600/8-85/001). Washington, DC; Office of Acid Deposition; Environmental Monitoring, and Quality Assurance; National Exposure Research Laboratory; Office of Research and Development; U.S. Environmental Protection Agency.

U.S. EPA. (1991). Guideline for regulatory application of the urban airshed model. (Report no. EPA-450/4-91-013). Research Triangle Park, NC; Office of Air Quality Planning and Standards; U.S. Environmental Protection Agency.

U.S. EPA. (1993a). Air Quality Criteria for Oxides of Nitrogen (Report no. EPA/600/8-91/049aF-cF; 3 Volumes). Research Triangle Park, NC; Environmental Criteria and Assessment Office; Office of Health and Environmental Assessment; U.S. Environmental Protection Agency.

U.S. EPA. (1993b).Ambient air quality surveillance. (40CFR-Part 58: Federal Register 58FR8452 [pp 8452-8475]). Washington, DC; U.S. Environmental Protection Agency.

U.S. EPA. (1995a). Acid deposition standard feasibility study. Report to Congress. (Report no EPA 430-R-95-001a). Washington, DC; Office of Air and Radiation; Environmental Protection Agency:.

U.S. EPA. (1995b). Review of the national ambient air quality standards for nitrogen dioxide: Assessment of scientific and technical information, OAQPS staff paper.(Report no EPA-452/R-95-005). Research Triangle Park, NC; Office of Air Quality Planning and Standards; U.S. Environmental Protection Agency.

U.S. EPA. (1996a). Air quality criteria for particulate matter (No. EPA/600/P-95/001aF-cF). Research Triangle Park, NC; National Center for Environmental Assessment-RTP; Office of Research and Development; U.S. Environmental Protection Agency.

U.S. EPA. (1996b). Mercury study report to Congress. Volume. III: An assessment of exposure from anthropogenic mercury emissions in the United States (Report no. EPA-452/R-96-001c). Research Triangle Park, NC; Office of Air Quality Planning and Standards and Office of Research and Development; U.S. Environmental Protection Agency.

U.S. EPA. (1996c). Air quality criteria for ozone and related photochemical oxidants. (Report no EPA/600/AP-93/004aF-cF; 3 Volumes). Research Triangle Park, NC; National Center for Environmental Assessment-RTP; Office of Research and Development; U.S. Environmental Protection Agency.

U.S. EPA. (1997a). Mercury study report to Congress. Volume VI: An ecological assessment for anthropogenic mercury emissions in the United States. (Report no. EPA- 452/R-97-008). Research Triangle Park, NC; Office of Air Quality Planning and Standards and Office of Research and Development; U.S. Environmental Protection Agency.

U.S. EPA. (1997b). National air pollutant emission trends 1990-1996. (Report no. EPA/454/R-97/011). Research Triangle Park, NC; Office of Air Quality Planning and Standards; U.S. Environmental Protection Agency.

U.S. EPA. (1998). U.S. Environmental Protection Agency. (1998).SLAMS/NAMS/PAMS network review guidance. (Report no EPA-454/R-98-003). Research Triangle Park, NC; Office of Air Quality Planning and Standards; U.S. Environmental Protection Agency.

U.S. EPA. (1999a). Getting started: Emissions inventory methods for PM-2.5. Technical report (Emission factor and inventory group; EIIP document series; Volume IX). Research Triangle Park, NC; Office of Air Quality Planning and Standards; U.S. Environmental Protection Agency.

U.S. EPA. (1999b). The benefits and costs of the Clean Air Act, 1990-2010. EPA report to Congress. (No. EPA-410-R-99-001). Washington, DC; Office of Air and Radiation and Office of Policy; U.S. Environmental Protection Agency.

U.S. EPA. (2000a). Air quality criteria for carbon monoxide. (Report no. EPA/600/P-99/001F). Research Triangle Park, NC; National Center for Environmental Assessment; Office of Research and Development; U.S. Environmental Protection Agency.

U.S. EPA. (2000b). Deposition of air pollutants to the great waters: Third report to Congress. (EPA-453/R-00-005) http://www.epa.gov/air/oaqps/gr8water/3rdrpt/index.html; Research Triangle Park, NC; Office of Air Quality Planning and Standards; U.S. Environmental Protection Agency.

U.S. EPA. (2000c). Nutrient Criteria Technical Guidance Manual: Rivers and Streams. (Report no EPA-822-B00-022). Washington, DC; U.S. Environmental Protection Agency.

U.S. EPA. (2000d). Nutrient Criteria Technical Guidance Manual: Lakes and Reservoirs. (EPA-822-B00-001). Washington, DC; U.S. Environmental Protection Agency.

U.S. EPA. (2000e). National air pollutant emission trends 1990-1998. (Report no. EPA/454/R-00/002). Research Triangle Park, NC; Office of Air Quality Planning and Standards; U.S. Environmental Protection Agency.

U.S. EPA. (2001). National coastal condition report. (EPA-620/R-01/005). Washington, DC; Office of Water ; Office of Research and Development, U.S. Environmental Protection Agency.

U.S. EPA. (2002a). A framework for the economic assessment of ecological benefits. Washington, DC; Ecological Benefit Assessment Workgroup; Social Sciences Discussion Group; Science Policy Council; U.S. Environmental Protection Agency.

U.S. EPA. (2002b). Inventory of U.S. greenhouse gas emissions and sinks: 1990-2000. (Report no EPA 430-R-02-003). Washington, DC; Office of Atmospheric Programs; U.S. Environmental Protection Agency.

U.S. EPA. (2003). Economic analyses of nutrient and sediment reduction actions to restore Chesapeake Bay water quality. Annapolis, MD; Chesapeake Bay Program Office; Region III; U.S. Environmental Protection Agency.

U.S. EPA. (2004). Air quality criteria for particulate matter. Volumes I and II (Report no. EPA/600/P-99/002aF; 2 Volumes). Research Triangle Park, NC; National Center for Environmental Assessment-RTP; Office of Research and Development; U.S. Environmental Protection Agency.

U.S. EPA. (2005a). Review of the national ambient air quality standards for particulate matter: policy assessment of scientific and technical information. OAQPS staff paper. (Report no. EPA/452/R-05-005a). Research Triangle Park, NC; Office of Air Quality Planning and Standards; U.S. Environmental Protection Agency.

U.S. EPA. (2005b). Technical assistance document (TAD) for precursor gas measurements in the NCore multi-pollutant monitoring network. Version 4. (report no. EPA-454/R-05-003). Research Triangle Park, NC; Office of Air Quality Planning and Standards; U.S. Environmental Protection Agency.

U.S. EPA. (2006a). 2002 National Emissions Inventory: Data and Documentation for the final 2002 point source national emissions inventory. http://www.epa.gov/ttn/chief/net/2002inventory.html. Research Triangle Park, NC; Emission Inventory and Analysis Group; Air Quality and Analysis Division; U.S. Environmental Protection Agency.

U.S. EPA. (2006b). Air quality criteria for ozone and related photochemical oxidants (Report no. EPA/600/R-05/004aF – cF; 3 Volumes). Research Triangle Park, NC; National Center for Environmental Assessment-RTP; Office of Research and Development; U.S. Environmental Protection Agency.

U.S. EPA. (2006c). Multi-agency critical loads workshop: Sulfur and nitrogen deposition effects on freshwater and terrestrial ecosystems. Paper presented at the Multi-agency critical loads workshop held at Charlottesville, VA; University of Virginia-Charlottesville. (Final Report no EPA/68-W-03-02). Washington, DC; Clean Air Markets Division; U.S. Environmental Protection Agency.

U.S. EPA. (2006d). Wadeable streams assessment: A collaborative survey of the nation's streams. (Report no EPA-841-B-06-002). Washington, DC; Office of Water; Office of Research and Development; U.S. Environmental Protection Agency.

U.S. EPA. (2006e).Acid rain program (ARP) 2005 progress report. Washington, DC; Office of Air and Radiation; Clean Air Markets Division; EPA-430-R-06-015. Available: http://www.epa.gov/airmarkets/progress/docs/2005report.pdf [12 March, 2007].

U.S. EPA. (2007a). Integrated review plan for the secondary national ambient air quality standards for nitrogen dioxide and sulfur dioxide. (Report no. EPA-452/R-08-006). Research Triangle Park, NC; U.S. Environmental Protection Agency.

U.S. EPA. (2007b). Inventory of U.S. greenhouse gas emissions and sinks: 1990-2005. (Report no. EPA 430-R-07-002). Washington, DC; Office of Atmospheric Programs; U.S. Environmental Protection Agency.

U.S. EPA. (2008a). Integrated science assessment for oxides of nitrogen: Health criteria. (Report no. EPA/600/R-08/071). Research Triangle Park, NC; National Center for Environmental Assessment; Office of Research and Development; U.S. Environmental Protection Agency.

U.S. EPA. (2008b). Integrated science assessment for sulfur oxides: Health criteria. (Report no. EPA/600/R-08/047F). Research Triangle Park, NC; National Center for Environmental Assessment; Office of Research and Development; U.S. Environmental Protection Agency.

U.S. EPA. (2008c). Risk and exposure assessment for the review of the secondary national ambient air quality standards foroxides of nitrogen and oxides of sulfur (Draft). Research Triangle Park, NC; Office of Air Quality Planning and Standards; U.S. Environmental Protection Agency.

U.S. FWS. (2005). Dahl TE (Ed.). Status and Trends of Wetlands in the Conterminous United States 1998 to 2004. http://wetlandsfws.er.usgs.gov/status_trends/national_reports/trends_2005_report.pdf. Washington, DC; Fisheries and Habitat Conservation; U.S., Fish and Wildlife Service (FWS); Department of the Interior.

U.S. GAO. (2000). Acid Rain. Emissions trends and effects in the eastern United States (Report to Congressional Requesters: GAO/RCED-00-47). Washington, DC; U.S. General Accounting Office (GAO).

Valiela I; Costa JE. (1988). Eutrophication of Buttermilk Bay, a Cape Cod coastal embayment: concentrations of nutrients and watershed nutrient budgets. Environ Manage, 12, 539-553.

Valiela I; Costa JE; Foreman K. (1990). Transport of groundwater-borne nutrients from watersheds and their effects on coastal waters. Biogeochemistry, 10, 177-197.

Valiela I; Foreman K; LaMontagne M; Hersh D; Costa J; Peckol P; DeMeo-Andreson B; D'Avanzo C; Babione M; Sham C; Brawley J; Lajtha K. (1992). Couplings of watersheds and coastal waters: sources and consequences of nutrient enrichment in Waquoit Bay, Massachusetts. Estuaries, 15, 443-457.

Valigura RA; Alexander RB; Brock DA; Castro MS; Meyers TP; Paerl HW; Stacey PE; Stanley D. (2000). An assessment of nitrogen inputs to coastal areas with an atmospheric perspective. In: Valigura RA; Alexander RB; Castro MS; Meyers TP; Paerl HW; Stacey PE; Turner RE (Eds.), Nitrogen loading in coastal water bodies: An atmospheric perspective. (AGU Coastal Estuaries Studies; Series Volume 57). Washington, DC: American Geophysical Union.

Vallano DM; Sparks JD. (2008). Quantifying foliar uptake of gaseous nitrogen dioxide using enriched foliar N values. New Phytol, 177, 946-955.

Van Aalst RM. (1982). Dry deposition of NOx. In Schneider T, Grant L (Eds.), Air pollution by nitrogen oxides (pp. 263-270). Amsterdam, The Netherlands: Elsevier Scientific Publishing Company.

Van Aardenne JA; Dentener FJ; Olivier JGJ; Klein Goldewijk CGM; Lelieveld J. (2001). A 1degree x 1degree resolution data set of historical anthropogenic trace gas emissions for the period 1980-1990. Glob Biogeochem Cycles, 15, 909-928.

van Breemen N; Boyer EW; Goodale CL; Jaworski NA; Paustian K; Seitzinger SP; Lajtha K; Mayer B; Van Dam D; Howarth RW; Nadelhoffer KJ. (2002). Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern USA Biogeochemistry, 57/58, 267-293.

van Breemen N; Finlay R; Lundström U; Jongmans AG; Giesler R; Olsson M. (2000). Mycorrhizal weathering: A true case of mineral plant nutrition? Biogeochemistry, 49, 53-67.

van Breemen N; Mulder J; Driscoll C. (1983). Acidification and alkalinization of soils. Plant Soil, 75, 283-308.

van Breemen N; Van Dijk HFG. (1988). Ecosystem effects of atmospheric deposition of nitrogen in The Netherlands. Environ Pollut, 54, 249-274

van de Graaf A; Mulder A; de Brujin P; Jetten MSM; Robertson LA; Kuenen JG. (1995). Anaerobic oxidation of ammonium is a biologically mediated process. Appl Environ Microbiol, 61, 1246-1251.

van der Nat FWA; deBrouwer JFC; Middelburg JJ; Laanbroek HJ. (1997). Spatial distribution and inhibition by ammonium of methane oxidation in intertidal freshwater marshes. Appl Environ Microbiol, 63, 4734-4740.

Van Der Welle MEW; Smolders AJP; Op Den Camp HJM; Roelofs J; Lamers LPM. (2007). Biogeochemical interactions between iron and sulphate in freshwater wetlands and their implications for interspecific competition between aquatic macrophytes. Freshw Biol, 52, 434-447.

Van der Werf GR; Randerson JT; Collatz J; Giglio L. (2003). Carbon emissions from fires in tropical and subtropical ecosystems. Glob Change Biol, 9, 547-562.

van Diepen L; Lilleskov E; Pregitzer K; Miller R. (2007). Decline of mycorrhizal fungi in northern hardwood forests exposed to chronic nitrogen inputs. New Phytol, 176, 175–183.

Van Dijk HFG; Roelofs JGM. (1988). Effects of excessive ammonium deposition on the nutritional status and condition of pine needles. Physiol Plant, 73, 494-501.

Van Dobben HF; de Bakker AJ. (1996). Re-mapping of lichen biodiversity in The Netherlands: Effects of decreasing SO_2 and increasing NH_3. Acta Bot Neerl, 45, 55-71.

van Dobben HF; Wolterbeek HT; Wamelink GW; Ter Braak CJ. (2001). Relationship between epiphytic lichens, trace elements and gaseous atmospheric pollutants. Environ Pollut, 112, 163-169.

Van Drecht G; Bouwman AF; Knoop JM; Beusen AHW; Meinardi CR. (2003). Global modeling of the fate of nitrogen from point and nonpoint sources in soils, groundwater, and surface water. Glob Biogeochem Cycles, 17, 1115.

Van Egmond K; Bresser T; Bouwman L. (2002). The European nitrogen case. Ambio, 31, 72-78.

van Griensven A; Bauwens W. (2001). Integral water quality modelling of catchments. Water Sci Technol, 43, 321-328.

Van Groenigen K-J; Six J; Hungate BA; De Graaff M-A; Van Breemen N; Van Kessel C. (2006). Element interactions limit soil carbon storage. Proc Natl Acad Sci USA, 103, 6571-6574.

van Haluwyn C; van Herk CM. (2002). Bioindication: The community approach. In: Nimis PL; Scheidegger C; Wolseley PA (Eds.), Monitoring with lichens-monitoring lichens (Vol. IV. Earth and environmental sciences, pp. 39-64). Dordrecht, The Netherlands: Kluwer Academic Publishers.

van Herk CM. (1999). Mapping of ammonia pollution with epiphytic lichens in The Netherlands. Lichenologist, 31, 9-20.

van Herk CM. (2001). Bark pH and susceptibility to toxic air pollutants as independent causes of changes in epiphytic lichen composition in space and time. Lichenologist, 33, 419-441.

Van Houtven G; Powers J; Pattanayak S. (2007). Valuing water quality improvements using meta-analysis: Is the glass half-full or half-empty for national policy analysis? Resource and Energy Economics, 29, 206-228.

Van Miegroet H; Cole DW; Foster NW. (1992a).Nitrogen distribution and cycling. In: Johnson DW; Lindberg SE (Eds.), Atmospheric deposition and forest nutrient cycling: A synthesis of the integrated forest study. (Series: Billings WD; Golley F; Lange OL; Olson JS; Remmert H (Eds.), Ecological studies: Analysis and synthesis; Volume 91, pp 178-196). New York, NY: Springer-Verlag.

Van Miegroet H; Cole DW; Foster NW. (1992b). Analysis of N cycles in polluted vs. unpolluted environment. In: Johnson DW; Lindberg SE (Eds.), Atmospheric deposition and forest nutrient cycling: A synthesis of the integrated forest study. (Series: Billings WD; Golley F; Lange OL; Olson JS; Remmert H (Eds.), Ecological studies: Analysis and synthesis; Volume 91, pp 199-202). New York, NY: Springer-Verlag.

Van Miegroet H; Johnson DW. (1993). Nitrate dynamics in forest soils. In: Burt TP; Heathwaite AL; Trudgill ST (Eds.), Nitrate: Processes, Patterns and Management. (pp 75-97). New York, NY: John Wiley & Sons Ltd.

Van Miegroet H; Moore PT; Tewksbury CE; Nicholas NS. (2007). Carbon sources and sinks in high-elevation spruce–fir forests of the Southeastern U.S. For Ecol Manage, 238, 249-260.

van Noije TPC; Eskes HJ; Dentener FJ; Stevenson DS; Ellingsen K; Schultz MG; Wild O; Amann M; Atherton CS; Bergmann DJ; Bey I; Boersma KF; Butler T; Cofala J; Drevet J; Fiore AM; Gauss M; Hauglustaine DA; Horowitz LW; Isaksen ISA; Krol MC; Lamarque J-F; Lawrence MG; Martin RV; Montanaro V; Müller JF; Pitari G; Prather MJ; Pyle JA; Richter A; Rodriguez JM; Savage NH; Strahan SE; Sudo K; Szopa S; van Roozendael M. (2006). Multi-model ensemble simulations of tropospheric NO_2 compared with GOME retrievals for the year 2000. Atmos Chem Phys, 6, 2943-2979.

Van Sickle J; Baker JP; Simonin HA; Baldigo BP; Kretser WA; Sharpe WE. (1996). Episodic acidification of small streams in the northeastern United States: Fish mortality in field bioassays. Ecol Appl, 6, 408-421.

Van Sickle J; Church MR. (1995). Nitrogen Bounding Study Methods for Estimating the Relative Effects of Sulfur and Nitrogen Deposition on Surface Water Chemistry. Corvallis, OR; Environmental Research Laboratory; National Health and Environmental Effects Research Laboratory, Office of Research and Development; U.S. Environmental Protection Agency.

Van Tienhoven AM; Olbrick KA; Skoroszewski R; Taljaard J; Zunckel M. (1995). Application of the critical loads approach in South Africa. Water Air Soil Pollut, 85, 2577-2582.

Vautard R; Martin D; Beekman M; Drobinski P; Friedrich R; Jaubertie A; Kley D; Lattuati M; Moral P; Neininger B; Theloke J. (2002). Paris emission inventory diagnostics from the ESQUIF airborne measurements and a chemistry transport model. J Geophys Res, 108, doi: 10.1029/2002JD002797.

Vaux HJ Jr; Gardner PD; Mills TJ. (1984). Methods for assessing the impact of fire on forest recreation. (No. General Technical Report PSW-79). Berkeley, CA: Pacific Southwest Forest and Range Experiment Station; U.S. Forest Service; U.S. Department of Agriculture (USDA).

Venterea RT; Groffman PM; Verchot LV; Magill AH; Aber JD. (2004). Gross nitrogen process rates in temperate forest soils exhibiting symptoms of nitrogen saturation. For Ecol Manage, 196.

Venterea RT; Groffman PM; Verchot LV; Magill AH; Aber JD; Steudler PA. (2003). Nitrogen oxide gas emissions from temperate forest soils receiving long-term nitrogen inputs. Glob Chang Biol, 9, 346-357.

Venterea RT; Groffman PM; Castro MS; Verchot LV; Fernandez IJ; Adams MB. (2004a). Soil emissions of nitric oxide in two forest watersheds subjected to elevated N inputs. For Ecol Manage, 196, 335-349.

Venterea RT; Groffman PM; Verchot LV; Magill AH; Aber JD. (2004b).Gross nitrogen process rates in temperate forest soils exhibiting symptoms of nitrogen saturation. For Ecol Manage, 196, 129-142.

Vertucci FA; Eilers JM. (1993). Issues in monitoring wilderness lake chemistry: a case study in the Sawtooth Mountains, Idaho. Environ Monit Assess, 28, 277-294.

Vilche JR; Varela FE; Acuna G; Codaro E. N; Rosales B. M; Fernandez A; Moriena G. (1995). A survey of Argentinean atmospheric corrosion: I. Aluminum and zinc samples. Corros Sci, 37, 941-961.

Vitek L; Schwertner HA. (2007). The heme catabolic pathway and its protective effects on oxidative stress-mediated diseases. In: Advances in Clinical Chemistry, Vol 43 (Vol. 43, pp. 1-57). San Diego: Elsevier Academic Press Inc.

Vitousek PM; Aber JD; Howarth RW; Likens GE; Matson PA; Schindler DW; Schlesinger WH; Tilman DG. (1997). Human alteration of the global nitrogen cycle: sources and consequences. Ecol Appl, 7, 737-750.

Vitousek PM; Howarth RW. (1991). Nitrogen limitation on land and in the sea: how can it occur? Biogeochemistry, 13, 87-115.

Vitousek PM; Aber JD; Howarth RW; Likens GE; Matson PA; Schindler DW; Schlesinger WH; Tilman DG. (1997a). Human alteration of the global nitrogen cycle: Sources and consequences. Ecol Appl, 7, 737-750.

Vitousek PM; Mooney HA; Lubchenco J; Melillo JM. (1997b). Human domination of Earth's ecosystems. Science, 277, 494-499.

Vitousek PM; Hedin, L; Matson, P; Fownes, J; Neff, J. C. (1998).Within-system element cycles, input-output budgets, and nutrient limitations. In: Pace M; Groffman P (Eds.), Successes, limitations and frontiers in ecosystem science. (pp 432-451). New York, NY: Springer-Verlag.

Vitt DH; Wieder K; Halsey LA; Turetsky M. (2003). Response of *Sphagnum fuscum* to nitrogen deposition: A case study of ombrogenous peatlands in Alberta, Canada. Bryologist, 106, 235-245.

Vogt KA; Grier CC; Meier CE; Edmonds RL. (1982). Mycorrhizal role in net primary production and nutrient cycling in *Abies amabilis* ecosystems in western Washington. Ecology, 63, 370-380.

Vogt KA; Dahlgren R; Ugolini F; Zabowski D; Moore EE; Zasoski R. (1987a). Aluminum, Fe, Ca, Mg, K, Mn, Cu, Zn and P in above- and belowground biomass. I. *Abies amabilis* and *Tsuga mertensiana*. Biogeochem, 4, 277-294.

Vogt KA; Dahlgren R; Ugolini F; Zabowski D; Moore EE; Zasoski R. (1987b). Aluminum, Fe, Ca, Mg, K, Mn, Cu, Zn and P in above- and belowground biomass. II. Pools, and circulation in a subalpine *Abies amabilis* stand. Biogeochem, 4, 295-311.

Vogt R; Crutzen PJ; Sander R. (1996). A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer. Nature, 383, 327-330.

Vogt R; Sander R; Von Glasow R; Crutzen PJ. (1999). Iodine chemistry and its role in halogen activation and ozone loss in the marine boundary layer: A model study. J Atmos Chem , 32, 375-395.

Vollenweider RA. (1968). Water management research: Scientific fundamentals of the eutrophication of lakes and flowing waters, with particular reference to nitrogen and phosphorus as factors in eutrophication. (Report no DAS/CSI/68.27). Paris, France: Organisation for Economic Co-operation and Development (OECD).

Von Ballmoos P; Nussbaum S; Brunold C. (1993). The Relationship of Nitrate Reductase Activity to Uptake and Assimilation of Atmospheric $^{15}NO_2^-$Nitrogen in Needles of Norway Spruce (*Picea abies* [L.] Karst.). Isotopes in Environmental and Health Studies, 29, 59-70.

Von Glasow R; Sander R; Bott A; Crutzen PJ. (2002a). Modeling halogen chemistry in the marine boundary layer. 1. Cloud-free MBL. J Geophys Res, 107, doi: 10.1029/2001JD000942.

Von Glasow R; Sander R; Bott A; Crutzen PJ. (2002b). Modeling halogen chemistry in the marine boundary layer. 2. Interactions with sulfur and cloud-covered MBL. J Geophys Res, 107, doi: 10.1029/2001JD000943.

Von Glasow R; Von Kuhlmann R; Lawrence MG; Platt U; Crutzen PJ. (2004). Impact of reactive bromine chemistry in the troposphere. Atmos Chem Phys, 4, 2481-2497.

Vose JM; Elliott KJ; Johnson DW; Walker RF; Johnson MG; Tingey DT. (1995). Effects of elevated CO_2 and N fertilization on soil respiration from Ponderosa pine (*Pinus Ponderosa*) in open-top chambers. Can J For Res, 25, 1243-1251.

Vose JM; Swank WT. (1990). Preliminary estimates of foliar absorption of 15 N-labeled nitric acid vapor (HNO 3) by mature eastern white pine (Pinus strobus). Can J For Res, 20, 857-860.

Vutukuru S; Dabdub D. (2008). Modeling the effects of ship emissions on coastal air quality: A case study of Southern California. Atmos Environ, 42, 3651-3764.

Waddell, E; Greenwood, R. (2006). Pacific Northwest nitrogen and sulfur deposition critical loads workshop; held at North Cascades Environmental Learning Center in September; 2006. (Workshop summary report). Co-sponsored by: Northwest Clean Air Agency; National Park Service; U.S. Forest Service; U.S. Geological Survey; U.S. Department of Agriculture (USDA). http://nadp.sws.uiuc.edu/clad/PNWCL2006WS.pdf.

Wade AJ; Neal C; Whitehead PG; Flynn NJ. (2005). Modelling nitrogen fluxes from the land to the coastal zone in European systems: Q perspective from the INCA project. J Hydrol, 304, 413-429.

Wagner T; Leue C; Wenig M; Pfeilsticker K; Platt U. (2001). Spatial and temporal distribution of enhanced boundary layer BrO concentrations measured by the GOME instrument aboard ERS-2. J Geophys Res, 106, 24225-24235.

Waiwood BA; Haya K. (1983). Levels of chorionase activity during embryonic development of *Salmo salar* under acid conditions. Bull Environ Contam Toxicol, 30, 511-515.

Wake DB. (1991). Declining amphibian populations. Science, 253, 860.

Walcek CJ; Stockwell WR; Chang JS. (1990). Theoretical estimates of the dynamic, radiative and chemical effects of clouds on tropospheric trace gases. Atmospheric Research, 25, 53-69.

Walcek CJ; Taylor GR. (1986). A theoretical method for computing vertical distributions of acidity and sulfate production within cumulus clouds. Journal of the Atmospheric Sciences, 43, 339-355.

Walega JG; Stedman DH; Shetter RE; Mackay GI; Iguchi T; Schiff HI. (1984). Comparison of a chemiluminescent and a tunable diode laser absorption technique for the measurement of nitrogen oxide, nitrogen dioxide, and nitric acid. Environ Sci Technol, 18, 823-826.

Wales DL; Liimatainen VA. (1987). Preliminary assessment of the current impact and potential risk of acidic deposition on walleye populations in Ontario. (Fisheries acidification series report no. 87-11). Toronto, ON, Canada; Ministry of Natural Resources.

Walker JT; Whitall DR; Robarge W; Paerl HW. (2004). Ambient ammonia and ammonium aerosol across a region of variable ammonia emission density. Atmos Environ, 38, 1235-1246.

Wall DH. (1999). Biodiversity and ecosystem functioning. BioScience, 49, 107-108.

Wall DH; Moore JC. (1999). Interaction underground: Soil biodiversity, mutualism, and ecosystem processes. Bioscience, 49, 109-117.

Wallace JB; Webster JR; Lowe RL. (1992). High-gradient streams of the Appalachians. In: Hackney CT; Adams SM; Martin WH (Eds.), Biodiversity of southern United States aquatic communities, (pp 133–191). New York, NY: John Wiley & Sons.

Walse C; Berg B; Sverdrup H. (1998). Review and synthesis on experimental data on organic matter decomposition with respect to the effect of temperature, moisture and acidity. Environmental Review, 6, 25-40.

Walsh RG; Bjonback RD; Aiken RA; Rosenthal DH. (1990). Estimating the public benefits of protecting forest quality. J Environ Manage, 30, 175-189.

Walsh RG; Ward FA; Olienyk JP. (1989). Recreational demand for trees in national forests. J Environ Manage, 28, 255-268.

Wang C; Corbett JJ; Firestone J. (2007). Modeling Energy Use and Emissions from North American Shipping: Application of the Ship Traffic, Energy, and Environment Model. Environ Sci Technol, 41, 3226-3232.

Wang D; Lu WZ. (2006). Forecasting of ozone level in time series using MLP model with a novel hybrid training algorithm. Atmos Environ, 40, 913-924.

Wang LH; Milford JB; Carter WPL. (2000a). Reactivity estimates for aromatic compounds. Part 2. Uncertainty in incremental reactivities. Atmos Environ, 4349-4360.

Wang LH; Milford JB; Carter WPL. (2000b). Reactivity estimates for aromatic compounds. Part 1: Uncertainty in chamber-derived parameters. Atmos Environ, 34, 4337-4348.

Wang X-K; Lu W-Z. (2006). Seasonal variation of air pollution index: Hong Kong case study. Chemosphere, 63, 1261-1272.

Wang Y; Tao W-K; Pickering KE; Thompson AM; Kain JS; Adler RF; Simpson J; Keehn PR; Lai GS. (1996). Mesoscale model simulations of TRACE A and preliminary regional experiment for storm-scale operational and research meteorology convective systems and associated tracer transport. J Geophys Res, 101, 24013-24027.

Wang Y; DeSilva AW; Goldenbaum GC; Dickerson RR. (1998). Nitric oxide production by simulated lightning: dependence on current, energy, and pressure. J Geophys Res, 103, 19149-19159.

Warby RAF; Johnson CE; Driscoll CT. (2005). Chemical recovery of surface waters across the northeastern U.S. from reduced inputs of acidic deposition: 1984-2001. Environ Sci Technol, 39, 6548-6554.

Warby RAF; Johnson CE; Driscoll CT. (2008). Continuing Acidification of Organic Soils across the Northeastern USA: 1984–2001. Soil Sci. Soc. Am. J, 73, 274-284. doi:10.2136/sssaj2007.0016

Ward BB. (2003). Significance of anaerobic ammonium oxidation in the ocean. Trends in Microbiology, 11, 408-410.

Warfvinge P; Falkengren-Greup U; Sverdrup H; Andersen B. (1993). Modelling long-term cation supply in acidified forest stands. Environ Pollut, 80, 209-221.

Warfvinge P; Sverdrup H. (1992). Calculating critical loads of acid deposition with PROFILE - a steady-state soil chemistry model. Water Air Soil Pollut, 63, 119-143.

Wargo PM. (1988). Amino nitrogen and phenolic constituents of bark of American beech, *Fagus grandifolia*, and infestation by beech scale, *Cryptococcus fagisuga*. Eur J Forest Pathol, 18, 279-290.

Wargo PM; Tilley J; Lawrence G; David M; Vogt K; Vogt D; Holifield Q. (2003). Vitality and chemistry of roots of red spruce in forest floors of stands with a gradient of soil Al/Ca ratios in the northeastern United States. Can J Forest Res, 33, 635-652.

Warneck P. (1999a). Chemistry of the Natural Atmosphere (2nd edition). San Diego, CA: Academic Press.

Warneck P. (1999b). The relative importance of various pathways for the oxidation of sulfur dioxide and nitrogen dioxide in sunlit continental fair weather clouds. Phys Chem Chem Phys, 1, 5471-5483.

Watmough SA; Dillon PJ. (2003). Calcium losses from a forested catchment in south-central Ontario, Canada. Environ Sci Technol, 37, 3085-3089.

Watmough SA; Aherne J; Dillon PJ. (2005). Effect of declining lake base cation concentration on freshwater critical load calculations. Environ Sci Technol, 39, 3255-3260.

Watmough SA; Dillon PJ. (2003). Do critical load models adequately protect forests? A case study in south-central Ontario. Can J For Res, 33, 1544-1556.

Watmough SA; Eimers MC; Aherne J; Dillon PJ. (2004). Climate effects on nitrate export from forested catchments in south-central Ontario. Environ Sci Technol, 38, 2383-2388.

Watras CJ; Frost TM. (1989). Little Rock (Wisconsin): Perspectives on an experimental ecosystem approach to seepage lake acidification. Archives of environmental contamination and toxicology, 18, 157-165.

Watras CJ; Morrison KA. (2008). The response of two remote, temperate lakes to changes in atmospheric mercury deposition, sulfate, and the water cycle. Can J Fish Aquat Sci, 65.

Watras CJ; Morrison KA; Regnell O; Kratz TK. (2006). The methylmercury cycle in Little Rock Lake during experimental acidification and recovery. Limnol Oceanogr, 51, 257-270.

Watson JG; Chow JC; Lurmann FW; Musarra SP. (1994). Ammonium nitrate, nitric acid, and ammonia equilibrium in wintertime Phoenix, Arizona. J Air Waste Manage Assoc, 44, 405-412.

Watson JG; Fujita EM; Chow JC; Zielinska B; Richards LW; Neff W; Dietrich D. (1998). Northern front range air quality study. (Final report). http://www.nfraqs.colostate.edu/index2. Fort Collins, CO; Cooperative Institute for Research in the Atmosphere; Colorado State University.

Watts SH; Seitzinger SP. (2001). Denitrification rates in organic and mineral soils from riparian sites: a comparison of N_2 flux and acetylene inhibition methods. Soil Biol Biogeochem, 22, 331-335.

Wayland M; McNicol DK. (1990). Status report on the effects of acid precipitation on common loon reproduction in Ontario: the Ontario Lakes loon survey. Ottawa, ON, Canada: Canadian Wildlife Service.

Weathers KC; Lovett GM; Likens GE; Lathrop R. (2000). The Effect of Landscape Features on Deposition to Hunter Mountain, Catskill Mountains, New York. Ecol Appl, 10, 528-540.

Webb JR; Cosby BJ; Galloway JN; Hornberger GM. (1989). Acidification of native brook trout streams in Virginia. Water Resour Res, 25(6), 1367-1377.

Webb JR; Deviney FA; Galloway JN; Rinehart CA; Thompson PA; Wilson S. (1994). The acid-base status of native brook trout streams in the mountains of Virginia. Charlottesville, VA; Department of Environmental Sciences; University of Virginia.

Webb JR; Cosby BJ; Deviney FA Jr; Eshleman KN; Galloway JN. (1995). Change in the acid-base status of an Appalachian Mountain catchment following forest defoliation by the gypsy moth. Water Air Soil Pollut, 85, 535-540.

Webb JR. (1999). Synoptic stream water chemistry. In: Bulger AJ; Cosby BJ; Dolloff CA; Eshleman KN; Webb JR; Galloway JN (Eds.), Shenandoah National Park: Fish in sensitive habitats (SNP:FISH); final report vol. II, Ch. 3. Prepared for: National Park Service. Charlottesville, VA; University of Virginia; Department of Environmental Sciences.

Webb JR; Cosby BJ; Deviney FA; Galloway JN; Maben SW; Bulger AJ. (2004). Are brook trout streams in western Virginia and Shenandoah National Park recovering from acidification? Environ Sci Technol, 38, 4091-4096.

Weber JH. (1993). Review of possible paths for abiotic methylation of mercury(II) in the aquatic ecosystem. Chemosphere, 26, 2063-2077.

Weber P; Nussbaum S; Fuhrer J; Gfeller H; Schlunegger UP; Brunold C; Rennenberg H. (1995). Uptake of atmospheric [15]NO_2 and its incorporation into free amino-acids in wheat (*Triticum-aestivum*). *Physiologia Plantarum*, 94, 71-77.

Weber P; Thoene B; Rennenberg H. (1998). Absorption of atmospheric NO_2 by spruce (Picea abies).trees. III. Interaction with nitrate reductase activity in the needles and phloem transport. Plant Biology, 111, 377-382.

Webster KE; Newell AD; Baker LA; Brezonik PL. (1990). Climatically induced rapid acidification of a softwater seepage lake. Nature, 347, 374-376.

Webster KE; Brezonik PL; Holdhusen BJ. (1993). Temporal trends in low alkalinity lakes of the Upper Midwest (1983-1989). Water Air Soil Pollut, 67, 397-414.

Webster KL; Creed IF; Nicholas NS; Miegroet HV. (2004). Exploring interactions between pollutant emissions and climatic variability in growth of red spruce in the Great Smoky Mountains National Park. Water Air Soil Pollut, 159, 225-248.

Webster PJ; Holland GJ; Curry JA; Chang H-R. (2005). Changes in tropical cyclone number, duration, and intensity in a warming environment. Science, 309, 1844-1846.

Wedemeyer GA; Barton BA; MeLeay DJ. (1990). Stress and acclimation. In: Schreck CB, Moyle PB (Eds.), Methods for fish biology (pp. 178-196). Bethesda, MD: American Fisheries Society.

Wedin DA; Tilman D. (1996). Influence of Nitrogen Loading and Species Composition on the Carbon Balance of Grasslands. Science, 274, 1720-1723.

Weintraub MN; Schimel JP. (2005). Nitrogen cycling and the spread of shrubs control changes in the carbon balance of Arctic tundra ecosystems. BioScience, 55, 408-415.

Weis W; Rotter V; Göttlein A. (2006).Water and element fluxes during the regeneration of Norway spruce with European beech: Effects of shelterwood-cut and clear-cut. Water Air Soil Pollut, 224, 304-317.

Weiss SB. (1999). Cars, cows, and checkerspot butterflies: Nitrogen deposition and management of nutrient-poor grasslands for a threatened species. Conserv Biol, 13, 1476-1486.

Weiss SB. (2006). Impacts of nitrogen deposition on California ecosystems and biodiversity (No. CEC-500-2005-165). Santa Barbara, CA: Prepared for California Energy Commission Report by Bren School of Environmental Science, University of California.

Weissenrieder J; Kleber C; Schreiner M; Leygraf C. (2004). In Situ Studies of Sulfate Nest Formation on Iron. J Electrochem Soc, 151, B497.

Weitz AM; Keller M; Linder E; Crill PM. (1999). Spatial and temporal variability of nitrogen oxide and methane fluxes from a fertilized tree plantation in Costa Rica. J Geophys Res-Atmos, 104, 30097-30107.

Wellburn AR. (1990). Why are atmospheric oxides of nitrogen usually phytotoxic and not alternative fertilizers? Tansley Review 24. New Phytol, 115, 395-429.

Wendel GJ; Stedman DH; Cantrell CA; Damrauer L. (1983). Luminol-based nitrogen dioxide detector. Anal Chem, 55, 937-940.

Wesely ML; Hicks BB. (1977). Some factors that affect the deposition rates of sulfur dioxide and similar gases on vegetation. J Air Waste Manage Assoc, 27, 1110-1116.

Wesely ML. (1989). Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models. Atmos Environ, 23, 1293-1304.

Wesely ML; Lesht BM. (1989). Comparison of RADM dry deposition algorithms with a site-specific method for inferring dry deposition. Water Air Soil Pollut, 44, 3-4.

Wesely ML; Hicks BB. (2000). A review of the current status of knowledge on dry deposition. Atmos Environ, 34, 2261-2282.

Westenbarger DV; Frisvold GB. (1995). Air pollution and farm-level crop yields: An empirical analysis of corn and soybeans. Agric Resour Econ Rev, 24, 156-165.

Westerling AL; Hildalgo HG; Cayan DR; Swetnam TW. (2006). Warming and earlier spring increase western U.S. forest wildfire activity. Science, 313, 940-943.

Westman WE. (1977). How much are nature's services worth? Measuring the social benefits of ecosystem functioning is both controversial and illuminating. Science, 197, 960-964.

Westman WE; Preston KP; Weeks LB. (1985). SO_2 effects on the growth of native plants. In: Winter WE; Mooney HA; Goldstein RA (Eds.), Sulfur dioxide and vegetation: Physiology, ecology, and policy issues. (pp 264-279). Stanford, CA: Stanford University Press.

Wetmore CM. (1985). Lichens and air quality in Isle Royale National Park. Denver, CO; National Park Service ; U.S. Department of the Interior.

Wetzel RG. (2001). Limnology: lake and river ecosystems. San Diego, CA: Academic Press.

Wexler AS; Seinfeld JH. (1991). Second-generation inorganic aerosol model. Atmos Environ Part A General Topics, 25, 2731-2748.

Whitall D; Bricker S. (2006). Assessment of eutrophication in estuaries: pressure-state-response and source apportionment. (USDA Forest Service Proceedings RMRS-P-42CD) Silver Spring, MD: National Oceanic and Atmospheric Administration National Centers for Coastal Ocean Science Center for Coastal Monitoring and Assessment. U.S. Forest Service; U.S. Department of Agriculture (USDA).

Whitall D; Castro M; Driscoll C. (2004). Evaluation of management strategies for reducing nitrogen loadings to four U.S. estuaries. Sci Total Environ, 333, 25-36.

Whitall DR; Paerl HW. (2001). Spatiotemporal variability of wet atmospheric nitrogen deposition to the Neuse River estuary, North Carolina. J Environ Qual, 30, 1508-1515.

White GN; Zelazny LW. (1986). Charge properties of soil colloids. In: Sparks DL (Ed.), Soil Physical Chemistry (pp. 39–81). Boca Raton, FL: CRC Press.

White PS; Cogbill CV. (1992). Spruce-fir forests of eastern North America. In: Eagar C; Adams MB (Eds.) Ecology and decline of red spruce in the eastern United States. (pp 3-39). New York, NY: Springer-Verlag.

Whitehead JC; Groothuis PA. (1992). Economic benefits of improved water quality: A case of North Carolina's Tar-Pamlico River. Rivers, 3, 170-178.

Whitehead JC; Haab TC; Huang J-C. (2000). Measuring recreation benefits of quality improvements with revealed and stated behavior data. Resource and Energy Economics, 22, 339-354.

Whitehead PG; Barlow J; Haworth EY; Adamson JK. (1997). Acidification in three Lake District tarns: Historical long term trends and modelled future behaviour under changing sulphate and nitrate deposition. HydrolEarth System Sci, 1, 197-204.

Whitehead PG; Reynolds B; Hornberger GM; Neal C; Cosby BJ; Paricos P. (1988). Modeling long term stream acidification trends in upland Wales at Plynlimon. Hydrological Processes, 2, 357-368.

Whiting MC; Whitehead DR; Holmes RW; Norton SA. (1989). Paleolimnological reconstruction of recent acidity changes in four Sierra Nevada lakes. J Paleolimnol, 2, 285-304.

Whitmore ME; Mansfield TA. (1983). Effects of long-term exposure to SO2 and NO_2 on Poa pratensis and other grasses. Environ Pollut (Series A), 31, 217-235.

Whittier TR; Paulsen SB; Larsen DP; Peterson SA; Herlihy AT; Kaufmann PR. (2002). Indicators of ecological stress and their extent in the population of northeastern lakes: a regional-scale assessment. Bioscience, 52, 235-247.

Wiemeyer SN; Schmeling SK; Anderson A. (1987). Environmental pollutant and necropsy data for ospreys from the eastern United States, 1975-1982. J Wildl Dis, 23, 279-291.

Wiener JG; Krabbenhoft DP; Heinz GH; Scheuhammer AM. (2003). Ecotoxicology of mercury. In: Hoffman DJ; Rattner BA; Burton GA; Cairns J (Eds.), Handbook of Ecotoxicology. 2nd edition. (pp. 409-643). Boca Raton, FL: CRC Press.

Wiener JG; Knights BC; Sandheinrich MB; Jeremiason JD; Brigham ME; Engstrom DR; Woodruff LG; Cannon WF; Balogh SJ. (2006). Mercury in Soils, Lakes, and Fish in Voyageurs National Park, Minnesota: Importance of Atmospheric Deposition and Ecosystem Factors. Environ Sci Technol, 40, 6261.

Wigand C; McKinney RA; Charpentier MA; Chintala MM; Thursby GB. (2003). Relationships of nitrogen loadings, residential development, and physical characteristics with plant structure in New England salt marshes. Estuaries and Coasts, 26, 1494-1504.

Wigington PJ. (1990). Episodic Acidification of Surface Waters Due to Acidic Deposition. (NAPAP State of the Science (SOS).Technical Report #12: Summary Compendium). Washington, DC; National Acid Precipitation Assessment Program (NAPAP).

Wigington PJ Jr; Davis TD; Tranter M; Eshleman KN. (1991). Episodic acidification of surface waters due to acidic deposition. In: Irving PM (Ed.), Acidic deposition. (NAPAP State of science and technology report no 12, Volume II: Aquatic processes and effects). Washington, DC; National Acid Precipitation Assessment Program (NAPAP).

Wigington PJ Jr; Baker JP; DeWalle DR; Kretser WA; Murdoch PS; Simonin HA; Van Sickle J; McDowell MK; Peck DV; Barchet WR. (1993). Episodic acidification of streams in the northeastern United States: Chemical and biological results of the episodic response project (Report no EPA/600/R-93/190). Corvallis, OR; Environmental Research Lab; National Health and Enviornmental Effects Research Laboratory; Office of Research and Development; U.S. Environmental Protection Agency.

Wigington PJ; Baker JP; DeWalle DR; Kretser WA; Murdoch PS; Simonin HA; Van Sickle J; McDowell MK; Peck DV; Barchet WR. (1996a). Episodic acidification of small streams in the northeastern United States: Episodic response project. Ecol Appl, 6, 374-388.

Wigington PJ Jr; DeWalle DR; Murdoch PS; Kretser WA; Simonin HA; Van Sickle J; Baker JP. (1996b). Episodic acidification of small streams in the northeastern United States: Ionic controls of episodes. Ecol Appl, 6, 389-407.

Wigington PJ. (1999). Episodic acidification: Causes, occurrence and significance to aquatic resources. In: Sharpe WE, Drohan JR (Eds.), Proceedings of the 1998 Pennsylvania acidic deposition conference. Vol. 2: The effects of acidic deposition on aquatic ecosystems in Pennsylvania. September 14-16; 1998. University Park, PA. (pp 1-5). University Park, PA; Environmental Resources Research Institute; The Pennsylvania State University.

Wilcox G; Decosta J. (1982). The effect of phosphorus and nitrogen addition on the algal biomass and species composition of an acidic lake. Archiv fur Hydrobiologie, 94, 393-424.

Williams EJ; Parrish DD; Fehsenfeld FC. (1987). Determination of nitrogen oxide emissions from soils: results from a grassland site in Colorado, United States. JGR J Geophys Res Part D, Atmospheres, 92, 2173-2179.

Williams EJ; Guenther A; Fehsenfeld FC. (1992). An inventory of nitric oxide emissions from soils in the United States. J Geophys Res, 97, 7511-7519.

Williams MR; Melack JM. (1997). Effects of prescribed burning and drought on the solute chemistry of mixed-conifer forest streams of the Sierra Nevada, California. Biogeochem, 39, 225-253.

Williams MW; Melack JM. (1991). Precipitation chemistry in and ionic loading to an alpine basin. Sierra Nevada Water Resour Res, 27, 1563-1574.

Williams MW; Bales RC; Brown AD; Melack JM. (1995). Fluxes and transformations of nitrogen in a high-elevation catchment, Sierra Nevada. Biogeochemistry, 28, 1-31.

Williams MW; Platts-Mills T; Caine N. (1996a). Landscape controls on surface water nitrate concentrations at catchment and regional scales in the Colorado Rocky Mountains. Paper presented at the Chapman Conference: Nitrogen cycling in forested catchments, held in Sun River, OR; September 16-20, 1996.

Williams MW; Baron JS; Caine N; Sommerfeld R; Sanford JR. (1996b). Nitrogen saturation in the Rocky Mountains. Environ Sci Technol, 30, 640-646.

Williams MW; Bardsley T; Rikkers M. (1998). Overestimation of snow depth and inorganic nitrogen wetfall using NADP data, Niwot Ridge, Colorado. Atmos Environ, 32, 3827–33

Williams MW; Tonnessen KA. (2000). Critical loads for inorganic nitrogen deposition in the Colorado Front Range, USA. Ecol Appl, 10, 1648-1665.

Willig RD. (1976). Consumer's Surplus Without Apology. Am Econ Rev, 66, 589-597.

Wilmot TR; Ellsworth DS; Tyree MT. (1995). Relationships among crown condition, growth, and stand nutrition in seven northern Vermont sugarbushes. Can J For Res, 25, 386-397.

Wilson MA; Carpenter SR. (1999). Economic valuation of freshwater ecosystem services in the United States: 1971-1997. Ecol Appl, 9, 772-783.

Wilson PR; Karl BJ; Toft RJ; Beggs JR; Taylor RH. (1998). The role of introduced predators and competitors in the decline of kaka (Nestor meridionalis).populations in New Zealand. Biological Conservation, 83, 175-185.

Wilson SD; Tillman D. (1991). Components of plant competition along an experimental gradient of nitrogen availability. Ecology, 72, 1050-1065.

Winberry WT Jr; Ellestad T; Stevens B. (1999). Compendium method IO-4.2: determination of reactive acidic and basic gases and strong acidity of atmospheric fine particles (< 2.5 µm). In: Compendium of methods for the determination of inorganic compounds in ambient air. (Report no. EPA/625/R-96/010a). Cincinnati, OH; Center for Environmental Research Information; U.S. Environmental Protection Agency.

Winfrey MR; Rudd JWM. (1990). Environmental factors affecting the formation of methylmercury in low pH lakes. Environ Toxicol Chem, 9, 853-869.

Winner WE; Atkinson CJ. (1986). Absorption of air pollution by plants, and consequences for growth. Trends Ecol Evol, 1, 15-18.

Winterbourn MJ; Collier KJ. (1987). Distribution of benthic invertebrates in acid, brown water streams in the South Island of New Zealand. Hydrobiologia, 153, 255-286.

Wislicenus H. (1914). Sammlung von Abhandlungen uber Abgase und Rauschaden. Berlin, Germany; P Parey.

Wittig AE; Solomon PA. (2006). Preface: Special issue of Atmos Environ for particulate matter supersites program and related studies. Atmos Environ, 40, 179-181.

Witting PK; Zeng B; Wong M; McMahon AC; Rayner BS; Sapir AJ; Lowe HC; Freedman SB; Brieger DB. (In Press). Polymorphonuclear leukocyte phagocytic function increases in plasminogen knockout mice. Thrombosis research, In Press, Corrected Proof.

Witz S; Eden RW; Wadley MW; Dunwoody C; Papa R; Torre KJ. (1990). Rapid loss of particulate nitrate, chloride and ammonium on quartz fiber filters during storage. J Air Waste Manage Assoc, 40, 53-61.

Wodzinski RS; Labeda DP; Alexander M. (1977). Toxicity of SO_2 and NO_X: Selective inhibition of blue-green algae by bisulfite and nitrite. J Air Pollut Control Assoc, 27, 891-893.

Wold AP; Hershey AE. (1999). Spatial and temporal variability of nutrient limitation in 6 North Shore tributaries to Lake Superior. J North Am Benthol Soc, 18, 2-14.

Wolf I; Russow R. (2000). Different pathways of formation of N_2O, N_2 and NO in black earth soil. Soil Biol Biochem, 32, 229-239.

Wolfe AP; Baron JS; Cornett RJ. (2001). Anthropogenic nitrogen deposition induces rapid ecological changes in alpine lakes of the Colorado Front Range (USA). J Paleolimnol, 25, 1-7.

Wolfe AP; Van Gorpe AC; Baron JS. (2003). Recent ecological and biogeochemical changes in alpine lakes of Rocky Mountain National Park (Colorado, USA): A response to anthropogenic nitrogen deposition. Geobiology, 1, 153-168.

Wolfe AP; Cooke CA; Hobbs WO. (2006). Are current rates of atmospheric nitrogen deposition influencing lakes in the eastern Canadian Arctic? Arct Antarct Alp Res, 38, 465-476.

Wolfe MF; Schwarzbach S; Sulaiman RA. (1998). Effects of mercury on wildlife: A comprehensive review. Environ Toxicol Chem, 17, 146-160.

Wolfe MH; Joslin JD. (1989). Honeylocust (*Gleditsia triacanthos* L.) root response to aluminum and calcium. Plant Soil, 119, 181-185.

Wolff GT. (1993). On a NO_X-focused control strategy to reduce O_3. J Air Waste Manage Assoc, 43, 1593-1596.

Wollmer H; Kottke I. (1990). Fine root studies in situ and in the laboratory. Environ Pollut, 68, 383-407.

Wood CM; McDonald DG. (1982). Physiological mechanisms of acid toxicity to fish. In: Johnson RE (Ed.), Acid rain/fisheries (pp. 197-226). Bethesda, MD: American Fisheries Society.

Wood CM; McDonald DG. (1987). The physiology of acid/aluminum stress in trout. Ann Soc R Zool Belg, 177, 399-410.

Wood CM. (1989). The physiological problems of fish in acid waters. Acid Toxicity and Aquatic Animals, 125–152.

Wood CM; McDonald DG; Ingersoll CG; Mount DR; Johannsson OE; Landsberger S; Bergman HL. (1990). Effects of water acidity, calcium, and aluminum on whole body ions of brook trout (Salvelinus fontinalis) continuously exposed from fertilization to swim-up: A study by instrumental neutron activation analysis. Can J Fish Aquat Sci, 47, 1593-1603.

Wood YA; Meixner T; Shouse, PJ; Allen, EB. (2006). Altered ecohydrologic response drives native Shrub loss under conditions of elevated nitrogen deposition. J Environ Qual, 35, 76-92.

Woodmansee RG. (1978). Additions and losses of nitrogen in grassland ecosystems. Bioscience, 28, 448-453.

Woodward DF; Farag AM; Mueller ME; Little EE; Vertucci FA. (1989). Sensitivity of endemic Snake River cutthroat trout to acidity and elevated aluminum. Trans Am Fish Soc, 118, 630-641.

Woodward DF. (1991). Sensitivity of greenback cutthroat trout to acidic pH and elevated aluminum. Trans Am Fish Soc, 120, 34-42.

Woodward RT; Wui Y-S. (2001). The economic value of wetland services: A meta-analysis. Ecol Econ 37, 257-270.

Woodwell GM. (1970). Effects of pollution on the structure and physiology of ecosystems: Changes in natural ecosystems caused by many different types of disturbances are similar and predictable. Science, 168, 429-433.

World Resources Institute (2000). World resources 2000-2001: People and ecosystems: The fraying web of life. Washington, DC; United Nations; United Nations Environment Programme (UNEP); Development Programme (UNDP); World Bank; World Resources Institute (WRI).

Wright RF; Snekvik E. (1978). Acid precipitation: chemistry and fish populations in 700 lakes in southernmost Norway. Verh Int Ver Theor Angew Limnol, 20, 765-775.

Wright RF; Lotse E; Semb A. (1988a). Reversibility of acidification shown by whole-catchment experiments. Nature, 334, 670-675.

Wright RF; Norton SA; Brakke DF; Frogner T. (1988b). Experimental verification of episodic acidification of freshwaters by sea salts. Nature, 334, 422-424.

Wright RF; Cosby BJ; Flaten MB; Reuss JO. (1990). Evaluation of an acidification model with data from manipulated catchments in Norway. Nature, 343, 53-55.

Wright RF; Lotse E; Semb A. (1993). RAIN project: Results after 8 years of experimentally reduced acid deposition to a whole catchment. Can J Fish Aquat Sci, 50, 258-268.

Wright RF; Cosby BJ; Ferrier RC; Jenkins A; Bulger AJ; Harriman R. (1994). Changes in the acidification of lochs in Galloway, southwestern Scotland, 1979-1988: The MAGIC model used to evaluate the role of afforestation, calculate critical loads, and predict fish status. J Hydrol, 161, 257-285.

Wright RF; Emmett BA; Jenkins A. (1998). Acid deposition, land-use change and global change: MAGIC7 model applied to Risdalsheia, Norway (RAIN and CLIMEX projects) and Aber, UK (NITREX project). Hydrol Earth System Sci, 2, 385-397.

Wright RF; Larssen T; Camarero L; Cosby BJ; Ferrier RC; Helliwell R; Forsius M; Jenkins A; Kopacek J; Majer V; Moldan F; Posch M; Rogora M; Schopp W. (2005). Recovery of acidified European surface waters. Environ Sci Technol, 39, 64A-72A.

Wulff A; Karenlampi L. (1996). Effects of long-term open-air exposure to fluoride, nitrogen compounds and SO2 on visible symptoms, pollutant accumulation and ultrastructure of Scots pine and Norway spruce seedlings. Trees-Struct Funct, 10, 157-171.

Wyers GP; Otjes RP; Slanina J. (1993). A continuous-flow denuder for the measurement of ambient concentrations and surface-exchange fluxes of ammonia. Atmos Environ, 27, 2085-2090.

Xie SD; Hao JM; Zhou ZP; Qi L; Yin H. (1995). Assessment of critical loads in Liuzhou, China using static and dynamic models. Water Air Soil Pollut, 85, 2401-2406.

Xu J; DuBois D; Pitchford M; Green M; Etyemezian V. (2006). Attribution of sulfate aerosols in Federal Class I areas of the western United States based on trajectory regression analysis. Atmospheric Environment: 40, 3433-3447.

Xun L; Campbell NER; Rudd JWM. (1987). Measurements of specific rates of net methyl mercury production in the water column and surface sediments of acidified and circumneutral lakes. Can. J Fish Aquat Sci, 44, 750-757.

Yan ND; Keller W; Somers KM; Pawson TW; Girard RE. (1996a). Recovery of crustacean zooplankton communities from acid and metal contamination: comparing manipulated and reference lakes. Can J Fish Aquat Sci, 53, 1301-1327.

Yan ND; Welsh PG; Lin H; Taylor DJ; Filion J-M. (1996b). Demographic and genetic evidence of the long-term recovery of *Daphnia galeata* mendotae (Crustacea: Daphniidae) in Sudbury lakes following additions of base: the role of metal toxicity. Can J Fish Aquat Sci, 53, 1328-1344.

Yan XY; Akimoto H; Ohara T. (2003). Estimation of nitrous oxide, nitric oxide and ammonia emissions from croplands in East, Southeast and South Asia. Glob Chang Biol, 9, 1080-1096.

Yanai RD; Phillips RP; Arthur MA; Siccama TG; Hane EN. (2005). Spatial and Temporal Variation in Calcium and Aluminum in Northern Hardwood Forest Floors. Water Air Soil Pollut, 160, 109-118.

Yanai RD; Siccama TG; Arthur MA; Federer CA; Friedland AJ. (1999). Accumulation and depletion of base cations in forest floors in the northeastern United States. Ecology, 80, 2774-2787.

Ye XM; Hao JM; Duan L; Zhou ZP. (2002). Acidification sensitivity and critical loads of acid deposition for surface waters in China. Sci Total Environ, 289, 189-203.

Yeakley JA; Coleman DC; Haines BL; Kloeppel BD; Meyer JL; Swank WT; Argo BW; Deal JM; Taylor SF. (2003) Hillslope nutrient dynamics following upland riparian vegetation disturbance. Ecosystems, 6, 154-167.

Yerrapragada SS; Chirra SR; Jaynes JH; Li S; Bandyopadhyay JK; Gauri KL. (1996). Weathering Rates of Marble in Laboratory and Outdoor Conditions. Journal of Environmental Engineering, 122, 856-863.

Yienger JJ; Levy H II. (1995). Empirical model of global soil-biogenic NO_X emissions. J Geophys Res, 100, 11447-11464.

Ying Q; Kleeman MJ. (2006). Source contributions to the regional distribution of secondary particulate matter in California. Atmos Environ, 40, 736-752.

Ylimartimo A. (1991). Effects of foliar nitrogen, potassium and magnesium concentrations on the resistance of Scots pine seedlings, to Scleroderris canker infection. Eur J Forest Pathol, 21, 414-423.

Yoshida LC; Allen EB. (2001). Response to ammonium and nitrate by a mycorrhizal annual invasive grass and a native shrub in southern California. American Journal of Botany, 88, 1430-1436.

Young TF; Sanzone S. (Eds.) (2002). A framework for assessing and reporting on ecological condition: An SAB report. (Report no. EPA-SAB-EPEC-02-009). http://www.epa.gov/sab/pdf/epec02009.pdf. Washington, DC; Science Advisory Board; U.S. Environmental Protection Agency.

Young VL; Kieser BN; Chen SP; Niki H. (1997). Seasonal trends and local influences on nonmethane hydrocarbon concentrations in the Canadian boreal forest. J Geophys Res, 102, 5913-5918.

Zafiriou OC; True MB. (1979). Nitrate photolysis in seawater by sunlight. Mar Chem, 8, 33-42.

Zak DR; Pregitzer, KS; Curtis PS; Vogel CS; Holmes WE; Lussenhop J. (2000a). Atmospheric CO_2, soil-N availability, and allocation of biomass and nitrogen by *Populus tremuloides*. Ecol Appl, 10, 34-46.

Zak DR; Pregitzer KS; King JS; Holmes WE. (2000b). Elevated atmospheric CO_2, fine roots and the response of soil microorganisms: A review and hypothesis. New Phytol, 147, 201-222.

Zak DR; Pregitzer KS; Curtis PS; Holmes WE. (2000c). Atmospheric CO_2 and the composition and function of soil microbial communities. Ecol Appl, 10, 47-59.

Zak DR; Holmes WE; Finzi AC; Norby RJ; Schlesinger WH. (2003). Soil nitrogen cycling under elevated CO_2: A synthesis of forest face experiments. Ecol Appl, 13, 1508-1514.

Zanis P; Trickl T; Stohl A; Wernli H; Cooper O; Zerefos C; Gaeggeler H; Schnabel C; Tobler L; Kubik PW; Priller A; Scheel HE; Kanter HJ; Cristofanelli P; Forster C; James P; Gerasopoulos E; Delcloo A; Papayannis A; Claude H. (2003). Forecast, observation and modelling of a deep stratospheric intrusion event over Europe. Atmos Chem Phys, 3, 763-777.

Zappia G; Sabbioni C; Riontino C; Gobbi G; Favoni O. (1998). Exposure tests of building materials in urban atmosphere. Science of the Total Environment, The, 224, 235-244.

Zavaleta ES; Shaw MR; Chiariello NR; Thomas BD; Cleland EE; Field CB; Mooney HA. (2003). Grassland responses to three years of elevated temperature, CO_2, precipitation, and N deposition. Ecol Monogr, 73, 585-604.

Zeigler I. (1975). The effects of SO_2 pollution on plant metabolism. Residue Rev, 56, 79.

Zhai J; Driscoll CT; Sullivan TJ; Cosby BJ. (2008). Regional application of the PnET-BGC model to assess historical acidification of Adirondack Lakes. Water Resour Res, 44, doi:10.1029/2006WR005532 .

Zhang GJ; McFarlane NA. (1995). Sensitivity of climate simulations to the parameterization of cumulus convection in the Canadian Climate Centre general circulation model. Atmos Ocean, 33, 407-446.

Zhang JZ; Millero FJ. (1991). The rate of sulfite oxidation in seawater. Geochim Cosmochim Acta, 55, 677-685.

Zhang LH; Song CC; Zheng XH; Wang DX; Wang YY. (2007). Effects of nitrogen on the ecosystem respiration, CH_4 and N_2O emissions to the atmosphere from the freshwater marshes in northeast China. Environmental Geology, 52, 529-539.

Zhang XQ; McMurry PH. (1987). Theoretical analysis of evaporative losses from impactor and filter deposits. Atmos Environ, 21, 1779-1789.

Zhang Y; Liu P; Pun B; Seigneur C. (2006). A comprehensive performance evaluation of MM5-CMAQ for the Summer 1999 Southern Oxidants Study episode - Part I: Evaluation protocols, databases, and meteorological predictions. Atmos Environ, 40, 4825-4838.

Zhao DW; Seip HM. (1991). Assessing effects of acid deposition in southwestern China using the MAGIC model. Water Air Soil Pollut, 60, 83-97.

Zhou X; Beine HJ; Honrath RE; Fuentes JD; Simpson W; Shepson PB; Bottenheim J. (2001). Snowpack photochemical production of HONO: A major source of OH in the Arctic boundary layer in springtime. Geophys Res Lett, 28, 4087–4090.

Zhou X; Civerolo K; Dai H. (2002a). Summertime nitrous acid chemistry in the atmospheric boundary layer at a rural site in New York state. J Geophys Res, 107, doi: 10.1029/2001JD001539.

Zhou XL; He Y; Huang G; Thornberry TD; Carroll MA; Bertman SB. (2002b). Photochemical production of nitrous acid on glass sample manifold surface. Geophys Res Lett, 29, doi 10.1029/2002GL015080.

Zhou X; Gao H; He Y; Huang G. (2003). Nitric acid photolysis on surfaces in low-NO_X environments: significant atmospheric implications. Geophys Res Lett, 30, doi:10.1029/2003GL018620.

Zielinska B; Arey J; Atkinson R; McElroy PA. (1989). Formation of methylnitronaphthalenes from the gas-phase reactions of 1- and 2-methylnaphthalene with OH radicals and N_2O_5 and their occurrence in ambient air. Environ Sci Technol, 23, 723-729.

Zillioux EJ; Porcella DB; Benoit JM. (1993). Mercury cycling and effects in freshwater wetland ecosystems. Environ Toxicol Chem, 12, 2245-2264.

Zimmermann J; Poppe D. (1993). Nonlinear chemical couplings in the tropospheric NO_X--HO_X gas phase chemistry. J Atmos Chem , 17, 141-155.

Zingler J; Platt U. (2005). Iodine oxide in the Dead Sea Valley: evidence for inorganic sources of boundary layer IO. J Geophys Res, doi: 10.1029/2004JD004993.

Zulla Y; Billett MF. (1994). Long-term changes in chemical weathering rates between 1949-50 and 1987 in forest soils from north-east Scotland. Eur J Soil Sci, 45, 327-335.