Sections 1-6

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Future Effects of Long-Term Sulfur Deposition on Surface Water Chemistry in the Northeast and Southern Blue Ridge Province

(Results of the Direct/Delayed Response Project)

by

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A Contribution to the
National Acid Precipitation Assessment Program

U.S. Environmental Protection Agency
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NOTICE

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CONTENTS

CONTENTS (continued)

Page

CONTENTS (continued) Page

CONTENTS (continued) Page

CONTENTS (continued)

Page

CONTENTS (continued) Page

CONTENTS (continued)

Page

CONTENTS (continued) Page

CONTENTS (continued)

TABLES

TABLE PAGE

TABLES (continued)

Page

TABLES (continued) Page

TABLES (continued) Page

FIGURES

FIGURES (continued) Page

FIGURES (continued) Page

PLATES

PLATES (continued) Page

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PREFACE TO THE EXECUTIVE SUMMARY

This Executive Summary contains both summary results of Project analyses and overview information on the Project background and approach. Those readers wishing a synopsis only of major Project results may turn directly to Section 1.4. Because of the complexity of design and approach of this Project, however, we encourage readers to review Sections 1.1 through 1.3 of this Executive Summary.

M. Robbins Church, Technical Director
Direct/Delayed Response Project

SECTION 1

EXECUTIVE SUMMARY

1.1 INTRODUCTION

1.1.1 Project Background

Much scientific interest and public debate surround the effects of acidic deposition on freshwater ecosystems (e.g., Schindler, 1988; Mohnen, 1988). A comprehensive chemical survey (the National Surface Water Survey - NSWS) of the lakes and streams of the United States considered to be most vulnerable to acidic deposition (i.e., those with the lowest acid neutralizing capacity or ANC) was recently completed by the U.S. Environmental Protection Agency (EPA) (Linthurst et al., 1986a; Kaufmann et al., 1988). Analysis of these and other lake and stream chemistry data, together with data on temporal and spatial patterns of atmospheric deposition, indicates that long-term deposition of sulfur-containing compounds originating from the combustion of fossil fuels has acidified (i.e., decreased the ANC of) some surface waters in eastern North America (Altshuller and Linthurst, 1984; NAS, 1986; Sullivan et al., 1988b; Neary and Dillon, 1988; Asbury et al., 1989). Transport of mobile anions (primarily sulfate) through watershed soils and closely associated cation leaching are the most widely accepted mechanisms of this acidification process (Seip, 1980; Galloway et al., 1983a; Driscoll and Newton, 1985; Church and Turner, 1986). In addition, acidic deposition apparently has shifted the nature of some very low ANC or naturally acidic surface waters in the Northeast from organic acid "dominance" to mineral acid "dominance" (Driscoll et al., 1988; Driscoll et al., 1989a). This process is, perhaps, best explained as the effective titration of naturally occurring humic substances by sulfuric acid deposition (Krug and Frink, 1983; Krug et al., 1985; Krug, 1989). In both cases, the net effect of atmospheric deposition of sulfuric acid on surface water chemistry is a shift toward aquatic systems more dominated by mineral acidity and more likely to contain inorganic forms of aluminum, which are toxic to aquatic organisms.

Given that acidification of some surface waters has occurred, critical scientific and policy questions focus on whether acidification is continuing in the regions of concern, whether it is just beginning in other regions, how extensive effects might become, and over what time scales effects might occur. EPA is examining these questions through the activities of the Direct/Delayed Response Project (DDRP) (Church and Turner, 1986; Church, in press). The Project was begun in 1984 at the specific request of the EPA Administrator following a meeting of the Panel on Processes of Lake Acidification of the National Academy of Sciences. Principal among the conclusions of the Panel was that atmospheric deposition of sulfur-containing compounds is the major source of long-term surface water acidification in eastern North America (NAS, 1984). The Panel also debated at length the dynamic aspects of the acidification process. The DDRP was designed to focus on the topic of acidification dynamics and draws its name from consideration of whether acidification might be immediate (or immediately proportional to levels of deposition) (i.e., "direct") or whether it would lag in time (i.e., be "delayed") because of edaphic characteristics. A compilation and discussion of the processes of long-term surface water acidification and methods for its investigation were presented by Church and Turner (1986) at the beginning of the Project. A relatively brief and more current discussion of processes relevant to this Project is presented in Section 3 of this report.

Although recent research has indicated the potential importance of deposition of nitrogen-containing compounds to both the episodic (Galloway et al., 1987; Driscoll et al., 1987a) and long-term (Henriksen and Brakke, 1988) acidification of surface water, the DDRP does not address these effects. Such effects are the focus of developing or ongoing research within EPA's Aquatic Effects Research Program.

1.1.2 Primary Objectives

The DDRP has four technical objectives related to atmospheric/terrestrial/aquatic interactions:

(1) to describe the regional variability of soil and watershed characteristics,

(2) to determine which soil and watershed characteristics are most strongly related to surface water chemistry,

(3) to estimate the relative importance of key watershed processes in moderating regional effects of acidic deposition, and

(4) to classify a sample of watersheds with regard to their response characteristics to inputs of acidic deposition and to extrapolate the results from this sample of watersheds to the study regions.

The fourth objective is the critical "bottom line" of the Project.

It was never the intent of the DDRP to serve as a "research" project to investigate exact mechanisms and processes of surface water acidification. Rather, the principal mandate of the Project was to make regional projections of future effects of sulfur deposition on long-term surface water chemistry based on the best available data and most widely accepted hypotheses of the acidification process. In-depth investigations into processes of soil and surface water acidification are being conducted as part of other projects within the National Acid Precipitation Assessment Program.

1.1.3 Study Regions

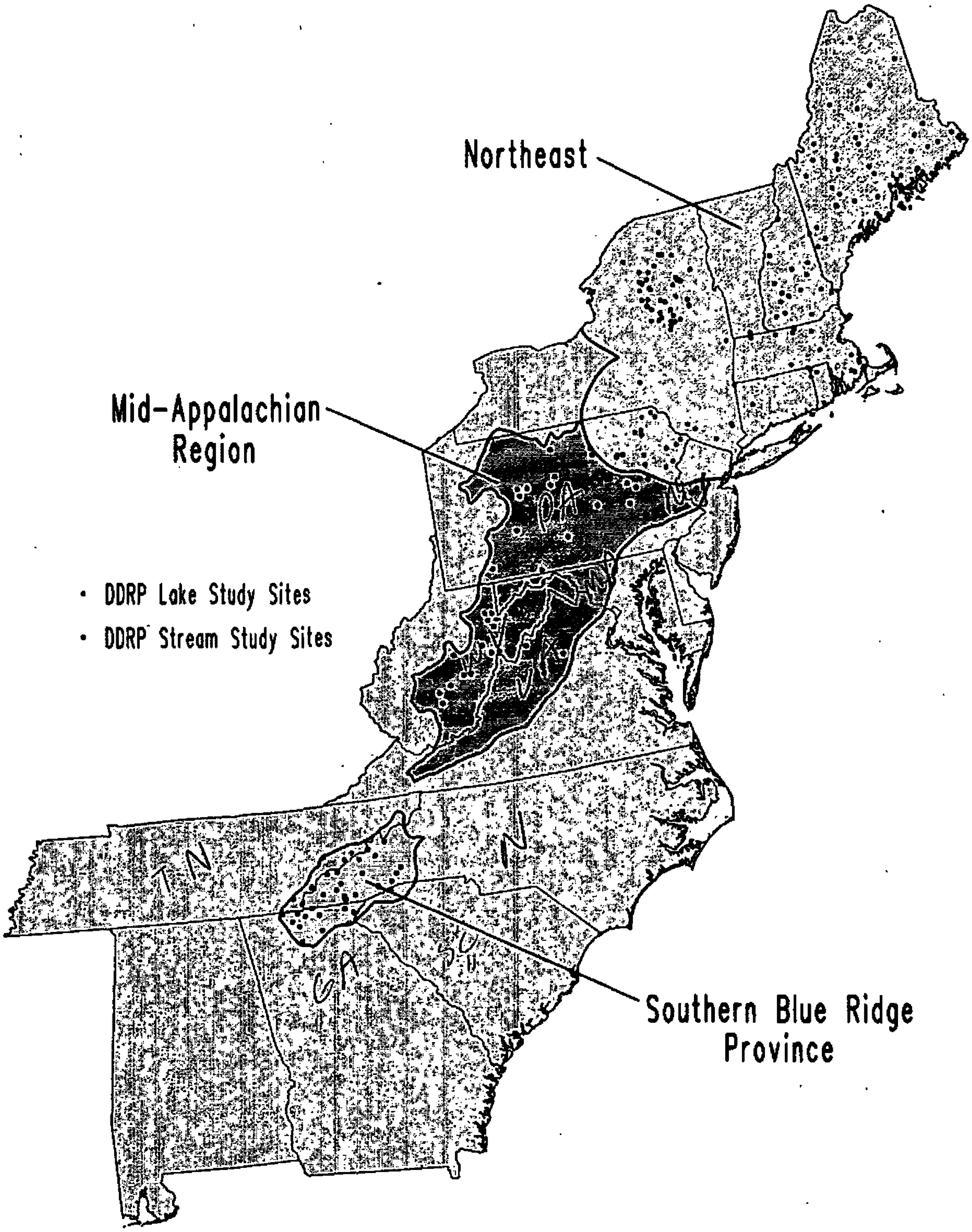
The Project focuses on three regions of the eastern United States where low ANC surface waters are located and where levels of atmospheric deposition (relative to other U.S. regions) are greatest: (1) the Northeast (NE), (2) upland areas of the Mid-Atlantic (referred to here as the Mid-Appalachian Region), and (3) the mountainous section of the Southeast called the Southern Blue Ridge Province (SBRP) (Plate 1-1). Initiation of the Project depended on the availability of the regional surface water chemistry data of the NSWS. Thus, the Project focused its initial work on the lake resources of the NE (Linthurst et al., 1986a) and the stream resources of the SBRP (Messer et al., 1986a). The results for these two regions are presented in this report. Complete results of subsequent work in the Mid-Appalachian Region will be reported at a later date.

1.1.4 Time Frames of Concern

The DDRP focuses on the potential effects of acidic deposition on surface water ANC at key annual "index" periods. These index periods were defined by NSWS sampling periods (i.e., fall period of complete mixing for lakes and spring baseflow for streams - see Section 5.3). The primary time horizon for DDRP analyses is 50 years. This horizon was selected on the basis of the projected lifetimes of existing power plants and the potential implementation of additional emissions controls relative to those lifetimes. Where possible and reasonable, some time-dependent analyses are extended beyond this 50-year horizon to better evaluate process rates and changes and potential future effects.

Plate 1-1. Direct/Delayed Response Project study regions and sites.

DDRP STUDY REGIONS



1.2 PROCESSES OF ACIDIFICATION

As discussed in Section 1.1, the NAS Panel identified (1) the retention of deposited sulfur within watersheds and (2) the supply of base cations from watersheds to surface waters as the most important watershed processes affecting or mediating long-term surface water acidification (NAS, 1984). These processes, thus, have become the focus of the DDRP. Factors other than sulfur retention and base cation supply affect surface water acidification, but were either deemed by the Panel to be relatively less important in long-term acidification or could not be addressed completely within the scope of the DDRP due to time, budgetary, or logistical constraints. Several of these alternative factors are discussed briefly in Section 3.1 of this report.

1.2.1 Sulfur Retention

During the past decade there has been an increased recognition that surface water acidification is controlled not only by rates of hydrogen ion deposition, but also by the mobility of associated anions through the ecosystem. Galloway et al. (1983a) and the 1984 NAS Panel identified controls on anion mobility, specifically on sulfate adsorption, as one of the two dominant variables affecting the rate and extent of surface water acidification by atmospheric deposition of mineral acids.

Almost three decades ago, Nye and Greenland (1960) recognized the importance of anions as "carriers" for cations in solution. The "mobile anion" paradigm they proposed [more recently applied to surface water acidification (Johnson and Cole, 1980; Seip, 1980)] suggests that a variety of processes act more or less independently to control the concentrations of individual anions in solution, whereas exchange and weathering processes control the relative quantities of cations. Controls on, and changes in, anion mobility can thus be viewed as the proximate controls on rates of cation leaching from soils and, coupled with rates of cation resupply processes, on surface water acidification.

Within the DDRP the primary issue with regard to anion mobility lies in forecasting temporal changes in dissolved sulfate. Sulfur retention processes are discussed further in Section 3.3.

1.2.2 Base Cation Supply

The NAS Panel identified rates of base cation supply from watersheds as the second dominant factor determining the rate and ultimate acidification of surface waters by acidic deposition. Supply of base cations occurs principally from mineral weathering (as the "original" source) and cation exchange in soils. The exchange of cations from the soil complex to the soil solution is a rapid process whereas the supply of base cations from mineral weathering to the exchange complex proceeds much more slowly. The balance between these rates and the rate of cation leaching by mobile anions is a critical factor in determining the rate of soil and surface water acidification. Mineral weathering and cation exchange are discussed further in Section 3.4. Projections of rates of cation leaching from the exchange complex are presented in Section 9.3 and are incorporated in watershed modelling studies presented in Section 10.

1.3 GENERAL APPROACH

As H.B.N. Hynes (1975) once noted, "We must not divorce the stream from its valley in our thoughts at any time. If we do we lose touch with reality." Although surface waters can be affected by acidic deposition originating from emissions many miles distant, the concept of the watershed as a unit is critical in understanding current and future aquatic effects. Indeed, for drainage lake and reservoir systems in the Northeast, Upper Midwest, and Southern Blue Ridge Province, most ANC production occurs as a result of biogeochemical processes within the surrounding watershed (Section 7.2; Shaffer et al., 1988; Shaffer and Church, 1989).

Because of the importance of watershed processes (especially those occurring in soils) in determining future aquatic effects, new data on these processes and on related soil pools and capacities were required. Initially, we considered using existing regional soils data for the DDRP analyses. Existing soils databases, however, were limited with respect to their application to address surface water acidification issues. First, such data are available primarily from lowland agricultural regions, whereas surface water acidification occurs principally in relatively undisturbed upland systems. Second, such databases generally do not include a number of key variables relevant to soil chemical interactions with acidic deposition. We subsequently decided that a new regional soils database was required for the

Project, thus necessitating a major soil survey (Sections 5.1 - 5.5; also see Lee et al., 1989a). We further concluded that this survey should allow the specific soils (and specific soil types) to be linked with the existing NSWS databases that describe the chemistry of low ANC lakes and streams. Accordingly, we adopted the approach outlined in this section and illustrated in Figure 1-1.

1.3.1 Soil Survey

DDRP watersheds were selected as a high interest subset of lake and stream systems surveyed in the NSWS [for details see Section 5.2 and Lee et al. (1989a)]. The watersheds were chosen as probability samples to ensure that results could be extrapolated to a specified target population (see Section 6).

Maps of soils, vegetation, land use, and depth to bedrock were prepared for each DDRP watershed by the USDA Soil Conservation Service (SCS) (see Section 5.4). Soil sample classes were defined for each DDRP region, and soils selected from these classes were sampled and analyzed for physical and chemical characteristics. Soils were aggregated within sampling classes to develop characterizations (e.g., class means and variances) that were used to "rebuild" or represent (e.g., by mass or area weighting) the characteristics of study watersheds. Details of the sample class selection, sampling, and soil analysis are provided in Section 5.5.

1.3.2 Other Regional Datasets

The regional nature of the Project required estimates of precipitation, atmospheric deposition (wet and dry), and surface water runoff (as runoff depth) developed in a standardized manner across the eastern United States. Study sites for the DDRP were selected statistically, and most sites had no direct information for deposition and runoff. The development of these datasets for the DDRP is described in Sections 5.6 and 5.7, respectively.

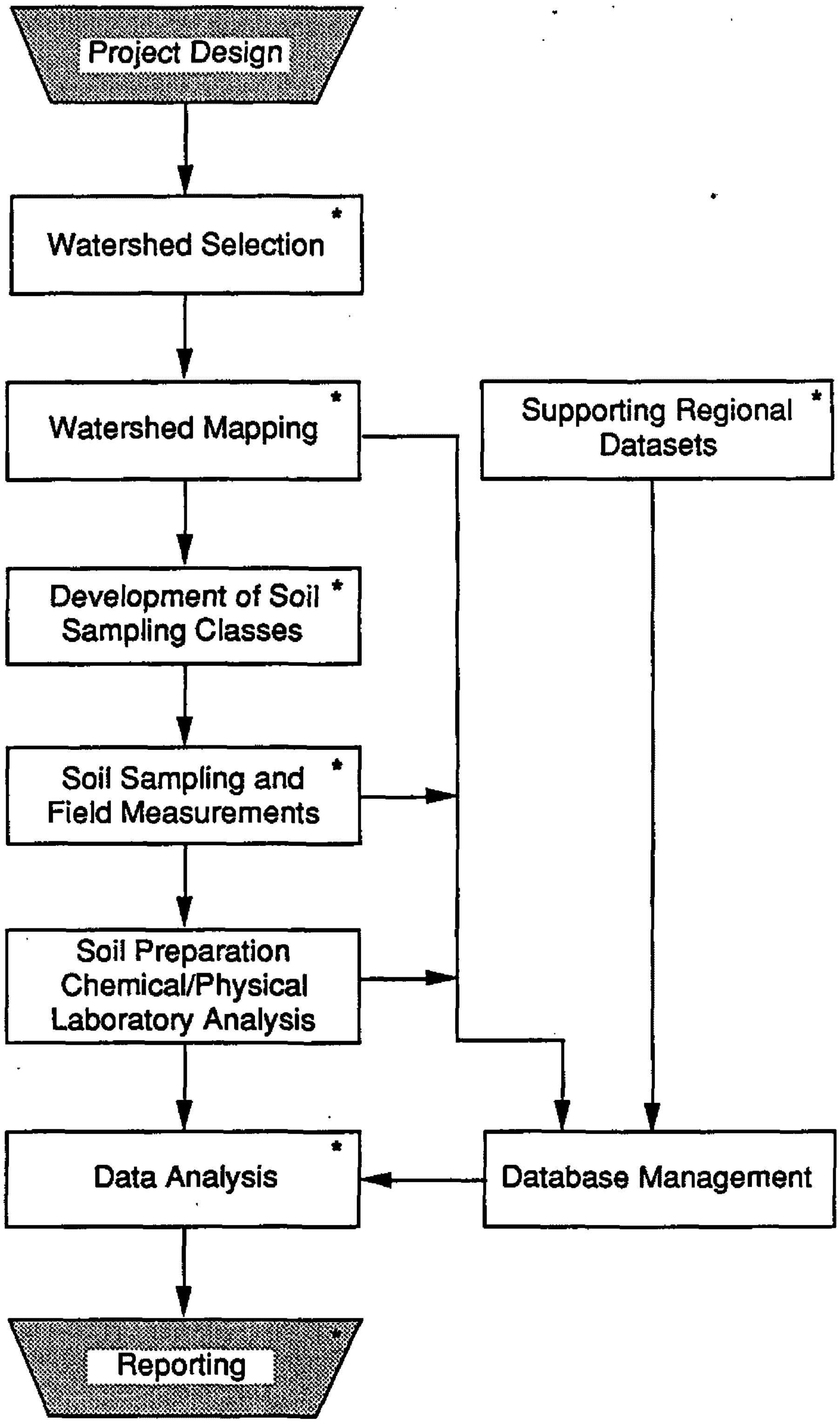


Figure 1-1. Steps of the Direct/Delayed Response Project (DDRP) approach. Asterisks denote steps that received significant support from Geographic Information Systems (GIS)-based activities (Campbell and Church, 1989; Campbell et al., in press).

1.3.3 Scenarios of Atmospheric Deposition

The major question driving the DDRP concerns the response of surface water chemistry to atmospheric deposition in the future. Within the DDRP we were requested by the Agency's Office of Air and Radiation to evaluate two sulfur deposition scenarios for each study region. The first deposition scenario for each region was that of constant deposition at current levels. For the Northeast, the second scenario was for sulfur deposition to remain constant at current levels for 10 years, then to ramp down for 15 years to a level 30 percent below current and to remain at that level. For the Southern Blue Ridge Province, the second scenario was for sulfur deposition to remain constant at current levels for 10 years, then to ramp up for 15 years to a level 20 percent above current and to remain at that level.

1.3.4 Data Analysis

A variety of complementary data analyses were performed within the project (see Section 4.4 for more details). The most basic of these analyses is the statistical evaluation of interrelationships among atmospheric deposition, mapped watershed characteristics, soil chemistry, and current surface water chemistry. The principal goal of these analyses is to verify that the processes and relationships incorporated in the subsequent modelling analyses reasonably represent the systems under study. The results of these statistical analyses are presented in Section 8.

Watershed retention of atmospherically deposited sulfur is an important consideration within the Project. Current regional retention is evaluated in Section 7, and the dynamics of retention via soil sulfate adsorption are considered in Section 9. Also considered in Section 9 are "single-factor" models (Bloom and Grigal, 1985; Reuss and Johnson 1985, 1986) of the influence of acidic deposition on the supply of base cations from soils to surface waters. The purpose of this modelling is to evaluate the potential relative importance of cation exchange as a process mediating surface water acidification.

Watershed models are used in the DDRP to project future integrated effects of atmospheric sulfur deposition on surface water chemistry. Three models specifically developed to investigate the effects of acidic deposition on watersheds and surface waters are being applied: (1) the Model of Acidification of Groundwater in Catchments (MAGIC) (Cosby et al., 1985a,b; 1986a,b), (2) the Enhanced Trickle Down

(ETD) Model (Lee, 1987; Nikolaidis et al., 1988; Schnoor et al., 1986b); and (3) the Integrated Lake-Watershed Acidification Study (ILWAS) Model (Chen et al., 1983; Gherini et al., 1985). The three models are being run using common datasets for forcing functions (e.g., rainfall, runoff, atmospheric deposition) and data aggregated from the DDRP soils database for state variables (e.g., soil physical and chemical variables). Projections of changes in annual average surface water chemistry are being made for each region for at least 50 years for the two scenarios of atmospheric sulfur deposition described in Section 1.3.3. Results of these modelling analyses are presented in Section 10.

1.4 RESULTS

This section presents an overview of the results of the DDRP analyses. DDRP statistical analyses (see Section 8) of the interrelationships among deposition, edaphic factors, and surface water chemistry generally supported the postulated relationships incorporated into both the single factor models (for sulfate adsorption and cation supply) and the integrated watershed models. For example, soil depth, soil chemical characteristics, and watershed hydrology factors will appear as important explanatory variables in the regressions that we performed. Additionally, wetlands in northeastern watersheds appear to have an important role in influencing sulfur dynamics (see Sections 7 and 8). Wetland effects are not explicitly represented in the integrated watershed models. Atmospheric deposition is an important explanatory variable for current surface water chemistry (especially sulfate concentrations) in northeastern lakes but not for chemistry of SBRP stream reaches. In both regions, watershed disturbances, especially agricultural activities, play important roles in affecting surface water chemistry and in masking interrelationships with acidic deposition.

1.4.1 Retention of Atmospherically Deposited Sulfur

1.4.1.1 Current Retention

At present (for watersheds not having apparent significant internal sources of sulfur; see Section 7), net retention of atmospherically deposited sulfur appears to be approximately at steady state (i.e., inputs equal outputs) in the NE. Median net retention is about 75 percent in the SBRP. These observations are qualitatively consistent with theory (Galloway et al., 1983a).

The Mid-Appalachian Region is a zone of transition between the NE and SBRP in terms of observed current sulfur retention. Because of the similarities between soils in this region and the SBRP, it is possible that this region at one time retained as much of the elevated sulfur deposition as is now evident in the SBRP (i.e., 70 - 80 percent). It is also possible that sulfur deposition has decreased this retention [perhaps very dramatically in the westernmost area (Subregion 2Cn of the National Stream Survey), which now has median percent sulfur retention of only 3 percent (Plate 1-2)] and has led to the low ANC and acidic stream reaches (excluding stream reaches affected by acid mine drainage) identified there by the National Stream Survey (Kaufmann et al., 1988). To further address this issue, in-depth soil sampling and analyses are being conducted in the Mid-Appalachian Region as part of the DDRP.

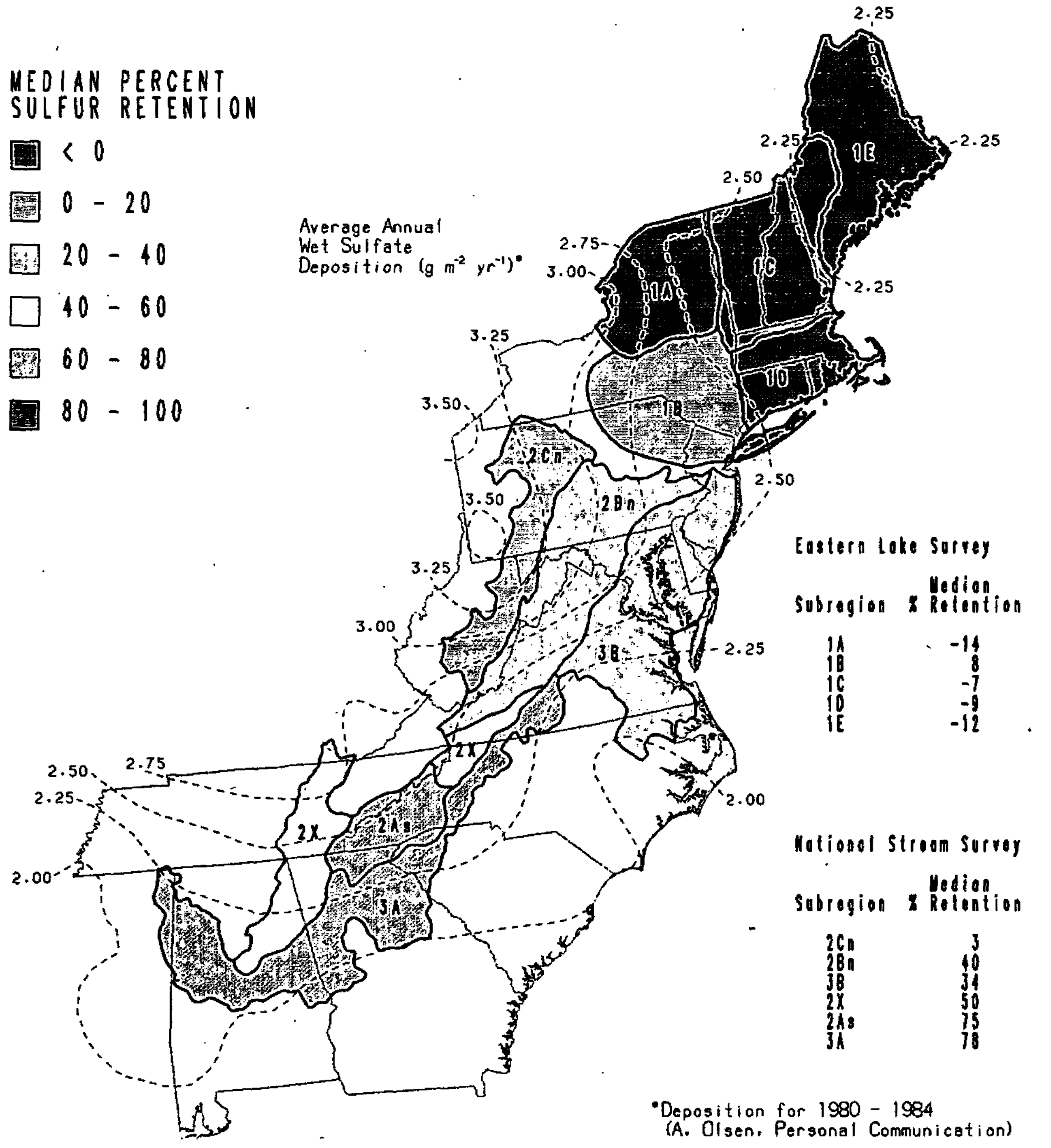
1.4.1.2 Projected Retention

Projections of sulfur retention were performed for the deposition scenarios described previously. Results discussed here are from MAGIC (as are discussions in Section 1.4.3 on projected changes in surface water ANC). Northeastern watersheds are projected to respond relatively rapidly (i.e., with a lag of 10 - 20 years) to changes in sulfur deposition. For the scenario of constant deposition, the median sulfate concentration in northeastern lakes is projected to decrease approximately 10 $\mu eq\ L^{-1}$ over the next 50 years. Under the scenario of decreased sulfur deposition, the projected decrease in median sulfate concentration is roughly 40 $\mu eq\ L^{-1}$ over the next 50 years.

Responses are projected to be slower but much more dramatic in the SBRP. Under the constant deposition scenario, the percent sulfur retention is projected by MAGIC to decrease to less than 50 percent in 20 years and to less than 30 percent in 50 years (Plate 1-3). The response is very similar under the increased deposition scenario, in terms of percent sulfur retention. These results correspond to an increase in median sulfate concentration of roughly 38 $\mu eq\ L^{-1}$ at 50 years for the constant deposition scenario and 55 $\mu eq\ L^{-1}$ at 50 years for the increased deposition scenario. Such changes will be accompanied by decreases in surface water ANC to an extent dependent upon the relative leaching of acids and base cations from watershed soils.

Plate 1-2. Sulfur retention and wet sulfate deposition for National Surface Water Survey and National Stream Survey regions in the eastern United States.

NSWS SUBREGIONS MEDIAN % SULFUR RETENTION AND WET SULFATE DEPOSITION



Eastern Lake Survey

Subregion	Median % Retention
1A	-14
1B	8
1C	-7
1D	-9
1E	-12

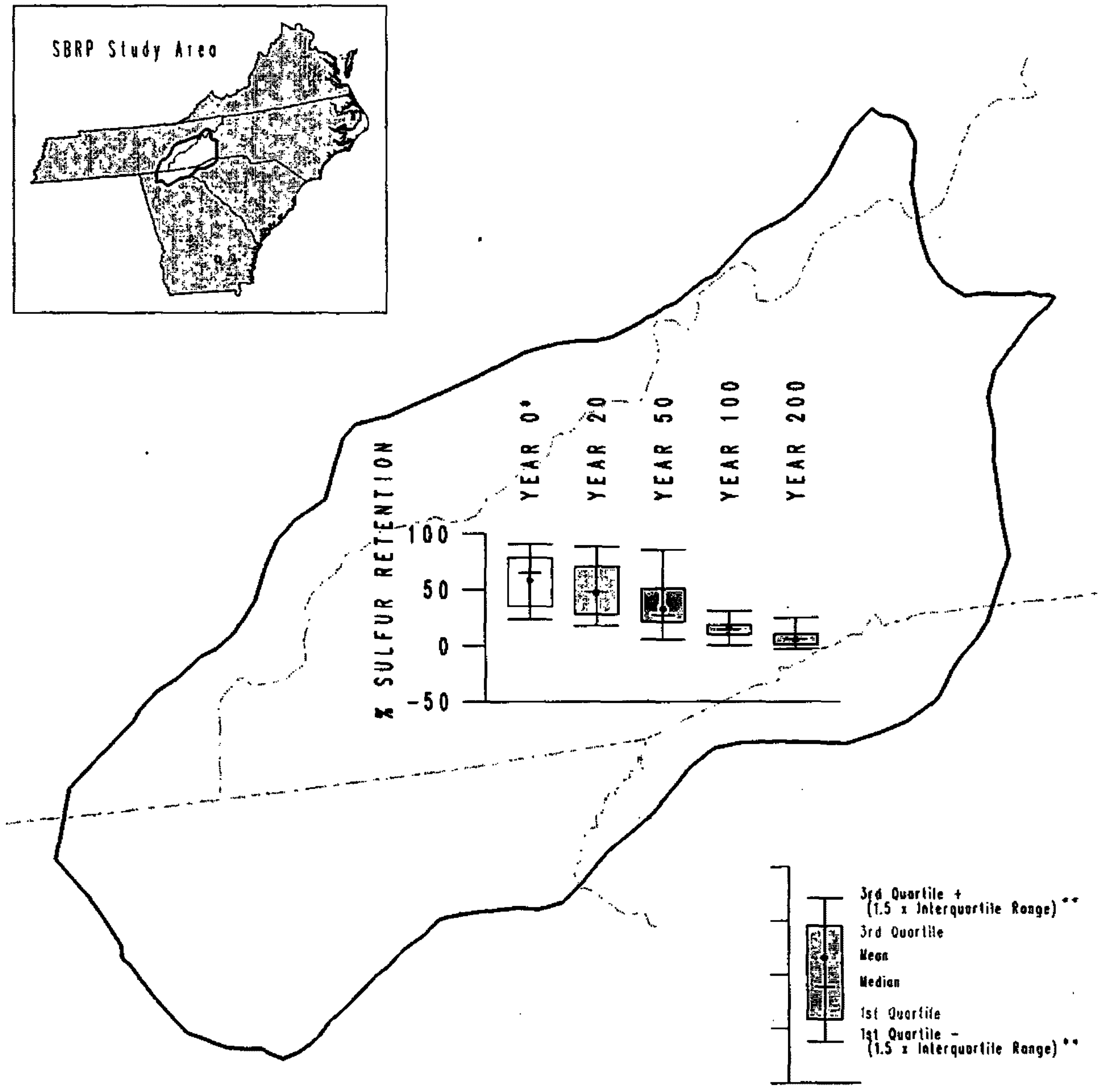
National Stream Survey

Subregion	Median % Retention
2Cn	3
2Bn	40
3B	34
2X	50
2As	75
3A	78

*Deposition for 1980 - 1984
(A. Olsen, Personal Communication)

Plate 1-3. Changes in sulfur retention in the Southern Blue Ridge Province as projected by MAGIC for constant sulfur deposition (see Section 1.3.4 for definition of deposition scenarios used).

% SULFUR RETENTION
Model = MAGIC
Deposition = Constant



*YEAR 0 = NSS Sample

** Not to exceed extreme value.

1.4.2 Base Cation Supply

1.4.2.1 Current Control

Base cations are supplied from watersheds to surface waters by two processes acting in concert. The initial source is mineral weathering, which is a "slow" process that supplies base cations to the soil exchange complex. Equilibrium between the exchange complex and soil water (and thus waters delivered to lakes and streams) is reached quickly. Inasmuch as current rates of acidic deposition in the eastern United States are unlikely to lead to significant decreases in soil pH, weathering rates are likely to increase only negligibly due to this effect. If weathering supplies base cations to surface waters at rates equal to or greater than rates of acid anion deposition, then systems are relatively "protected". If weathering rates are low and exchange dominates base cation supply rates, then the rate of depletion of the exchange complex becomes very important in determining rates of surface water acidification. Our analyses indicate that surface waters with ANC >100 $\mu eq\ L^{-1}$ are not explained by the cation exchange model of Reuss and Johnson (1986); thus, ANC generation appears to be dominated by weathering in these systems and they presumably are relatively protected against loss of ANC (Section 9). Surface waters with ANC <100 $\mu eq\ L^{-1}$ are likely controlled by a mix of weathering and cation exchange but the exact proportion of the mix is very difficult to determine.

1.4.2.2 Future Effects

In general, applying the model of Reuss and Johnson (1986), we performed a "worst-case" analysis by assuming that the supply of base cations was totally controlled by cation exchange. This analysis indicated that depletion of base cations from the exchange complex would occur under the sulfur deposition scenarios simulated. The effect on surface water ANC was initially slight but was not negligible. The magnitude of soil base cation depletion was projected to accelerate in the future. At current levels of deposition, about 15 percent of the lakes in the ELS target population are potentially susceptible to significant depletion of exchangeable cations and, thus, depletion of associated surface water ANC. The greatest portion of such changes are projected to occur on a time scale of about 50 years. In the SBRP, a greater percentage of systems are projected to be susceptible to adverse effects, but at longer time scales (i.e., about 100 years) than in the NE.

In general, effects of base cation depletion would be superimposed upon effects resulting from changes in sulfate mobility in soils. The combined effects were simulated using the integrated watershed models and are presented in the next section.

1.4.3 Integrated Effects on Surface Water ANC

The three watershed models were used to project the integrated watershed and surface water responses to the sulfur deposition scenarios. Results from MAGIC are presented here because this model was successfully calibrated to the largest number of watershed systems in the two regions (i.e., 123 of the 145 DDRP sample watersheds, representing a target population of 3,227 systems in the NE; and 30 of the 35 DDRP sample watersheds, representing a target population of 1,323 stream reaches in the SBRP). Results among the models were generally very comparable (see Sections 10 and 11). For example, for northeastern lakes with ANC < 25 μeq L^{-1}, the three models projected changes in median ANC (under the decreased deposition scenario) within 3 μeq L^{-1}.

As discussed in Section 10, the watershed modelling analyses make use of watershed soil representations as aggregated from the DDRP Soil Survey. Because the focus of the DDRP is on regional characteristics and responses, soils data were gathered and aggregated so as to capture the most important central tendencies of the study systems. As a result, extremes of individual watershed responses probably are not fully captured in the analyses presented here (see Section 8 for further discussion). Those systems that are projected to respond to the greatest extent or most quickly to current or altered levels of sulfur deposition might, in fact, respond even more extensively or more quickly than indicated here. This possibility should be kept in mind when reviewing the simulation results presented in this section.

1.4.3.1 Northeast Lakes

Results of the projections for both deposition scenarios are given in Plate 1-4 and Table 1-1. Plate 1-4 illustrates the projected change in the median ANC at 50 years for lakes classified into four ANC groups (i.e., <0 μeq L^{-1}, 0-25 μeq L^{-1}, 25-100 μeq L^{-1}, and 100-400 μeq L^{-1}). These projections indicate a generally very slight decline in ANC over the 50-year period under the current deposition scenario and an increase of roughly 5-15 $\mu eq\ L^{-1}$ in ANC for all groups under the decreased sulfur deposition scenario. Plate 1-4 shows the changes projected by MAGIC. Changes projected by the ETD and ILWAS models are quite comparable.

Table 1-1 presents the population estimates (with 95 percent confidence intervals) of northeastern lakes having values of ANC <0 $\mu eq\ L^{-1}$ and <50 $\mu eq\ L^{-1}$ at 20 and 50 years as projected by MAGIC for the two deposition scenarios. The ANC = 0 $\mu eq\ L^{-1}$ value is used to define acidic systems, and the ANC value of 50 $\mu eq\ L^{-1}$ (for index values as sampled in the NSWS, see Section 5.3) has recently been suggested as useful in approximating the level at or below which systems are susceptible to severe episodic acidification (i.e., brief periods of ANC down to very low or negative values) (Eshleman, 1988) with consequent adverse effects on biota. It is extremely important to keep in mind that these values only serve as indices in an otherwise smooth continuum of surface water chemistry conditions and responses to acidic deposition. It is also important to remember that adverse biological effects occur at higher ANCs (i.e., greater than 50 $\mu eq\ L^{-1}$) in systems that previously (i.e., prior to the advent of acidic deposition) were adapted to more circumneutral conditions (Schindler, 1988).

Model projections indicate a mixed response of northeastern lake systems at current levels of sulfur deposition. Although slight decreases in median ANC for all ANC groups are projected, as is a slight increase in the number of systems with ANC <0 $\mu eq\ L^{-1}$, the total number of systems having ANC < 50 $\mu eq\ L^{-1}$ (and thus potentially susceptible to episodic acidification) is projected to decrease (Table 1-1). Projected responses to decreased sulfur deposition show a clearer pattern; MAGIC projects surface water ANCs to increase and the number of lakes with ANC <0 $\mu eq\ L^{-1}$ and ANC <50 $\mu eq\ L^{-1}$ to decrease. Such a response would be consistent qualitatively with reported changes in the chemistry of lakes near Sudbury, Ontario, following reductions of sulfur dioxide emissions from the Sudbury smelter (Dillon et al., 1986; Hutchinson and Havas, 1986; Keller and Pitbaldo, 1986).

Plate 1-4. Changes in median ANC of northeastern lakes at 50 years as projected by MAGIC (see Section 1.3.4 for definition of the deposition scenarios used).

CHANGE IN MEDIAN ANC
Year 10 to Year 50
Model = MAGIC

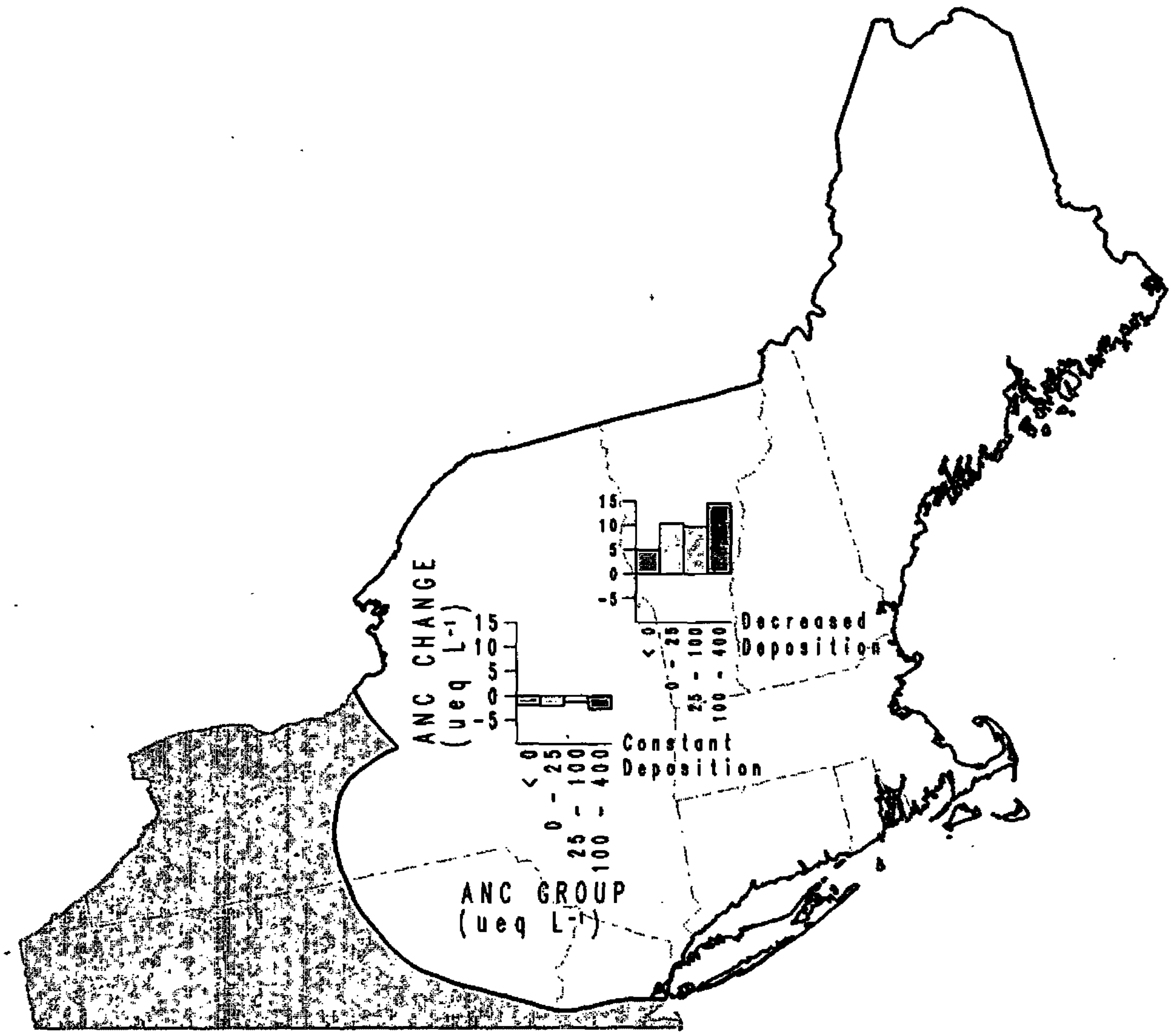


Table 1-1. Lakes in the NE Projected to Have ANC Values <0 and <50 $\mu eq\ L^{-1}$ for Constant and Decreased Sulfur Deposition[a,b]

Time from Present (yr)		Constant Deposition		Decreased Deposition	
		ANC <0	ANC <50	ANC <0	ANC <50
0	#[c]	162[d]	880[d]	162[d]	880[d]
	%	5	27	5	27
20	#	161 (134)	648 (246)	136 (124)	621 (242)
	%	5 (4)	20 (8)	4 (4)	19 (18)
50	#	186 (143)	648 (246)	87 (100)	586 (237)
	%	5 (4)	20 (8)	3 (3)	18 (7)

[a] Projections are based on 123 lake/watersheds successfully calibrated by MAGIC.

[b] See Section 1.3.4 for definition of the deposition scenarios used.

[c] # is the number of lakes; % is percent of the target population of 3,227 lakes; ( ) indicate 95 percent confidence estimates.

[d] Indicates estimate from NSWS Phase I sample for the same 123 lakes; target population = 3,227 lakes

Because of the organic nature of some soils in the NE, the exact nature of chemical "recovery" of northeastern lakes is uncertain. Under decreased sulfur deposition scenarios, organic acidity leached from soils could replace mineral acidity associated with sulfur deposition (Krug and Frink, 1983; Krug et al., 1985; Krug, 1989). Available evidence from catchment manipulations indicates that this process partially occurs under extreme conditions but the effect probably is not regionally important in regions such as the NE (Wright et al., 1988). Even if there was an appreciable increase in organic acid leaching as a response to reduced deposition acidity, the net effect would be beneficial to aquatic biota inasmuch as it would most likely be accompanied by reductions in surface water concentrations of inorganic monomeric aluminum, which is highly toxic to fish.

Thus, although the exact chemical response of the DDRP NE systems is unknown, projections consistently indicate some improvement in surface water quality as a consequence of reduced sulfur deposition in the region.

1.4.3.2 Southern Blue Ridge Province

Plate 1-5 illustrates the projected changes (MAGIC) in median ANC at 50 years for stream reaches in the SBRP. In this analysis, MAGIC was successfully calibrated to 32 of the 35 DDRP SBRP stream reach watersheds. Two stream reaches had ANC values > 1,000 μeq L^{-1} and were dropped from this analysis. The remaining 30 stream reaches had ANC values > 25 μeq L^{-1} and < 400 μeq L^{-1} and represent a target population of 1,323 stream reaches in the SBRP. The projected changes in median ANC have been computed for the same ANC groups (25-100 μeq L^{-1} and 100-400 μeq L^{-1}) as for the NE (Plate 1-3).

Table 1-2 presents the population estimates (with 95 percent confidence intervals) of SBRP stream reaches having ANC < 0 μeq L^{-1} and <50 μeq L^{-1} at 20 and 50 years as projected by MAGIC for the two deposition scenarios. The 95 percent confidence intervals about these projections are broad but understandable given the low number of systems available for simulation (30) and the inherent uncertainties involved in such a complex simulation of environmental response.

Plate 1-5. Changes in median ANC of Southern Blue Ridge Province stream reaches at 50 years as projected by MAGIC (see Section 1.3.4 for definition of the deposition scenarios used).

CHANGE IN MEDIAN ANC
Year 10 to Year 50
Model = MAGIC

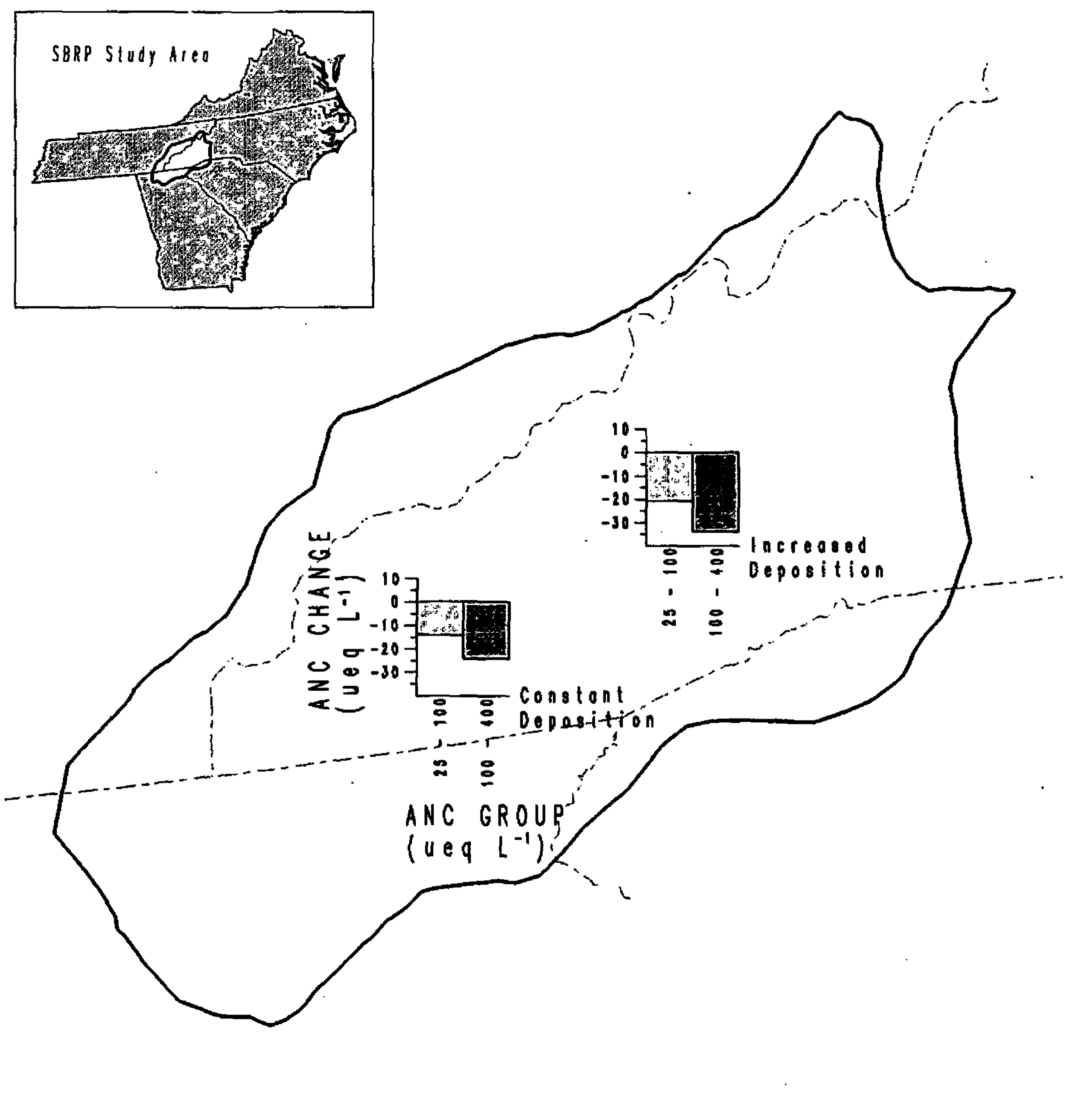


Table 1-2. SBRP Stream Reaches Projected to Have ANC Values <0 and <50 $\mu eq\ L^{-1}$ for Constant and Increased Sulfur Deposition[a,b]

Time from Present (yr)		Constant Deposition		Increased Deposition	
		ANC <0	ANC <50	ANC <0	ANC <50
0	#[c]	0[d]	3[d]	0[d]	3[d]
	%	0	0.2	0	0.2
20	#	0	187 (228)	0	187 (228)
	%	0	14 (17)	0	14 (17)
50	#	129 (195)	203 (236)	159 (213)	340 (286)
	%	10 (15)	15 (18)	12 (16)	26 (22)

[a] Projections are based on 30 stream/watersheds successfully calibrated by MAGIC.

[b] See Section 1.3.4 for definition of the deposition scenarios used.

[c] # is the number of lakes; % is percent of the target population of 1,323 stream reaches; ( ) indicate 95 percent confidence estimates.

[d] Indicates estimate from NSWS Pilot Stream Survey sample for the same 30 streams; target population = 1,323 stream reaches.

Model projections for the SBRP stream reaches indicate decreased surface water quality under scenarios of either current or increasing sulfur deposition. Due to the fact that soils in this region are much less organic in nature than those in the NE [e.g., wetlands in the SBRP are virtually non-existent; maximum stream DOC at lower stream reach nodes = 2.0 mg L^{-1}, mean = 0.8 mg L^{-1} (Kaufmann et al., 1988)], these model projections are uncomplicated by any potential effects of organic acid leaching. Model projections for the increased sulfur deposition scenario indicate the potential for about one-fourth of the target population of stream reaches in the SBRP to reach an ANC of < 50 $\mu eq\ L^{-1}$ in 50 years, and thus to have the potential to be acidified to an ANC of ~0 $\mu eq\ L^{-1}$ during storm event episodes (Eshleman, 1988). As noted in Section 1.4.1.2, responses to changes in sulfur deposition levels in the SBRP are projected to be slower than those in the NE; i.e., there is a considerable lag in the response of the systems due to the storage of sulfur in the soils. The result is that there is a delay not only in the acidification of surface waters in the region, but also in any potential chemical recovery if sulfur deposition were to be decreased.

Projections of stream water quality response for the DDRP SBRP target population clearly indicate future adverse effects of sulfur deposition at increased or current levels.

1.5 SUMMARY DISCUSSION

The NE is currently at sulfur steady state, and sulfate concentrations in surface waters would respond relatively rapidly to decreases in sulfur deposition. Associated with these changes would be small increases in surface water ANC. Continued sulfur deposition at current levels is gradually depleting the cation exchange pool in northeastern soils with consequent decreases in surface water ANC. Such changes are relatively slow and minor, however, relative to direct effects on surface water chemistry of increased sulfate mobility in watersheds.

Watersheds in the SBRP are currently retaining nearly three-quarters of the atmospherically deposited sulfur on the average, but soils are projected to become more saturated with regard to sulfur. Sulfate concentrations are projected to increase in the surface waters of the region. This response is projected to be marked over the next 50 years at either current or increased levels of sulfur deposition, as are decreases in stream water ANC. Superimposed upon this effect is a relatively minor acidification effect of base cation depletion.

Results from all levels of DDRP analyses are (1) consistent internally, (2) consistent with theory (Galloway et al., 1983a), and (3) consistent with observations of lakes monitored during changing sulfur deposition regimes (Dillon et al., 1986; Hutchinson and Havas, 1986; Keller and Pitbaldo, 1986).

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SECTION 2

INTRODUCTION TO THE DIRECT/DELAYED RESPONSE PROJECT

2.1 PROJECT BACKGROUND

Much scientific interest and public debate surround the effects of acidic deposition on freshwater ecosystems (e.g., Schindler, 1988; Mohnen, 1988). A comprehensive chemical survey (the National Surface Water Survey - NSWS) of the lakes and streams of the United States considered to be most vulnerable to acidic deposition (i.e., those with the lowest acid neutralizing capacity or ANC) was recently completed by the U.S. Environmental Protection Agency (EPA) (Linthurst et al., 1986a; Kaufmann et al., 1988). Analysis of these and other lake and stream chemistry data, together with data on temporal and spatial patterns of atmospheric deposition, indicates that long-term deposition of sulfur-containing compounds originating from the combustion of fossil fuels has acidified (i.e., decreased the ANC of) some surface waters in eastern North America (Altshuller and Linthurst, 1984; NAS, 1986; Sullivan et al., 1988b; Neary and Dillon, 1988; Asbury et al., 1989). Transport of mobile anions (primarily sulfate) through watershed soils and closely associated cation leaching are the most widely accepted mechanisms of this acidification process (Seip, 1980; Galloway et al., 1983a; Driscoll and Newton, 1985; Church and Turner, 1986). In addition, acidic deposition apparently has shifted the nature of some very low ANC or naturally acidic surface waters in the Northeast from organic acid "dominance" to mineral acid "dominance" (Driscoll et al., 1988; Driscoll et al., 1989a). This process is, perhaps, best explained as the effective titration of naturally occurring humic substances by sulfuric acid deposition (Krug and Frink, 1983; Krug et al., 1985; Krug, 1989). In both cases, the net effect of atmospheric deposition of sulfuric acid on surface water chemistry is a shift toward aquatic systems more dominated by mineral acidity and more likely to contain inorganic forms of aluminum, which are toxic to aquatic organisms.

Given that acidification of some surface waters has occurred, critical scientific and policy questions focus on whether acidification is continuing in the regions noted, whether it is just beginning in other regions, how extensive effects might become, and over what time scales effects might occur. EPA is examining these questions through the activities of the Direct/Delayed Response Project (DDRP) (Church and Turner, 1986; Church, in press). The Project was begun in 1984 at the specific request of the EPA Administrator following a meeting of the Panel on Processes of Lake Acidification of the National Academy of Sciences (NAS). Principal among the conclusions of the Panel was that atmospheric deposition of sulfur-containing compounds is the major source of long-term surface water acidification in eastern North America (NAS, 1984). The Panel also debated at length the dynamic aspects of the acidification process. The DDRP was designed to focus on this question and, thus, draws its name from consideration of whether acidification might be immediate (or immediately proportional to levels of deposition) (i.e., "direct") or whether it would lag in time (i.e., be "delayed") because of edaphic characteristics. A compilation and discussion of the processes of long-term surface water acidification and methods for its investigation were presented by Church and Turner (1986) at the beginning of the Project. A relatively brief and more current discussion of processes relevant to this Project is presented in Section 3 of this report.

Although more recent research has indicated the potential importance of deposition of nitrogen-containing compounds to both the episodic (Galloway et al., 1987; Driscoll et al., 1987a) and long-term (Henriksen and Brakke, 1988) acidification of surface water, the DDRP does not address these effects. Such effects are the focus of developing or ongoing research within EPA's Aquatic Effects Research Program.

2.2 PRIMARY OBJECTIVES

The DDRP has four technical objectives related to atmospheric/terrestrial/aquatic interactions:

(1) to describe the regional variability of soil and watershed characteristics,

(2) to determine which soil and watershed characteristics are most strongly related to surface water chemistry,

(3) to estimate the relative importance of key watershed processes in moderating regional effects of acidic deposition, and

(4) to classify a sample of watersheds with regard to their response characteristics to inputs of acidic deposition and to extrapolate the results from this sample of watersheds to the study regions.

The fourth objective is the critical "bottom line" of the Project.

The relationship of the DDRP to other projects within the Aquatic Effects Research Program (AERP) of the National Acid Precipitation Assessment Program (NAPAP) is shown in Figure 2-1. It was never the intent of the DDRP to serve as a "research" project to investigate exact mechanisms and processes of surface water acidification. Rather, the principal mandate of the Project was to make regional projections of future effects of sulfur deposition on long-term surface water chemistry (principally ANC) based upon the best available data and most widely accepted hypotheses of the acidification process. Further watershed modelling activities within the NAPAP Integrated Assessment (see Figure 1-2) will investigate a variety of sulfur deposition scenarios and potential future effects on biologically relevant surface water chemistry (e.g., pH, and concentrations of calcium and inorganic monomeric aluminum).

2.3 STUDY REGIONS

The Project focuses on three regions of the eastern United States where low ANC surface waters are located and where levels of atmospheric deposition (relative to other U.S. regions) are greatest: (1) the Northeast (NE), (2) upland areas of the Mid-Atlantic (referred to here as the Mid-Appalachian Region), and (3) the mountainous section of the Southeast called the Southern Blue Ridge Province (SBRP) (Plate 2-1). Initiation of the Project depended on the availability of the regional surface water chemistry data of the NSWS. Thus, the Project focused its work initially on the lake resources of the NE (Linthurst et al., 1986a) and the stream resources of the SBRP (Messer et al., 1986a). The results for these two regions are presented in this report. Complete results of subsequent work in the Mid-Appalachian Region will be reported at a later date.

2.4 TIME FRAMES OF CONCERN

The DDRP focuses on potential effects of acidic deposition on surface water ANC as evaluated at key annual "index" periods. These index periods follow the sampling schemes of the NSWS (i.e., fall period of complete mixing for lakes and spring baseflow for streams - see Section 5.3). "Episodic" acidification (e.g., due to snowmelt or intense rainstorms) is not considered within the DDRP but is the primary consideration of a companion project within the AERP, the Episodic Research Project (Figure 2-1).

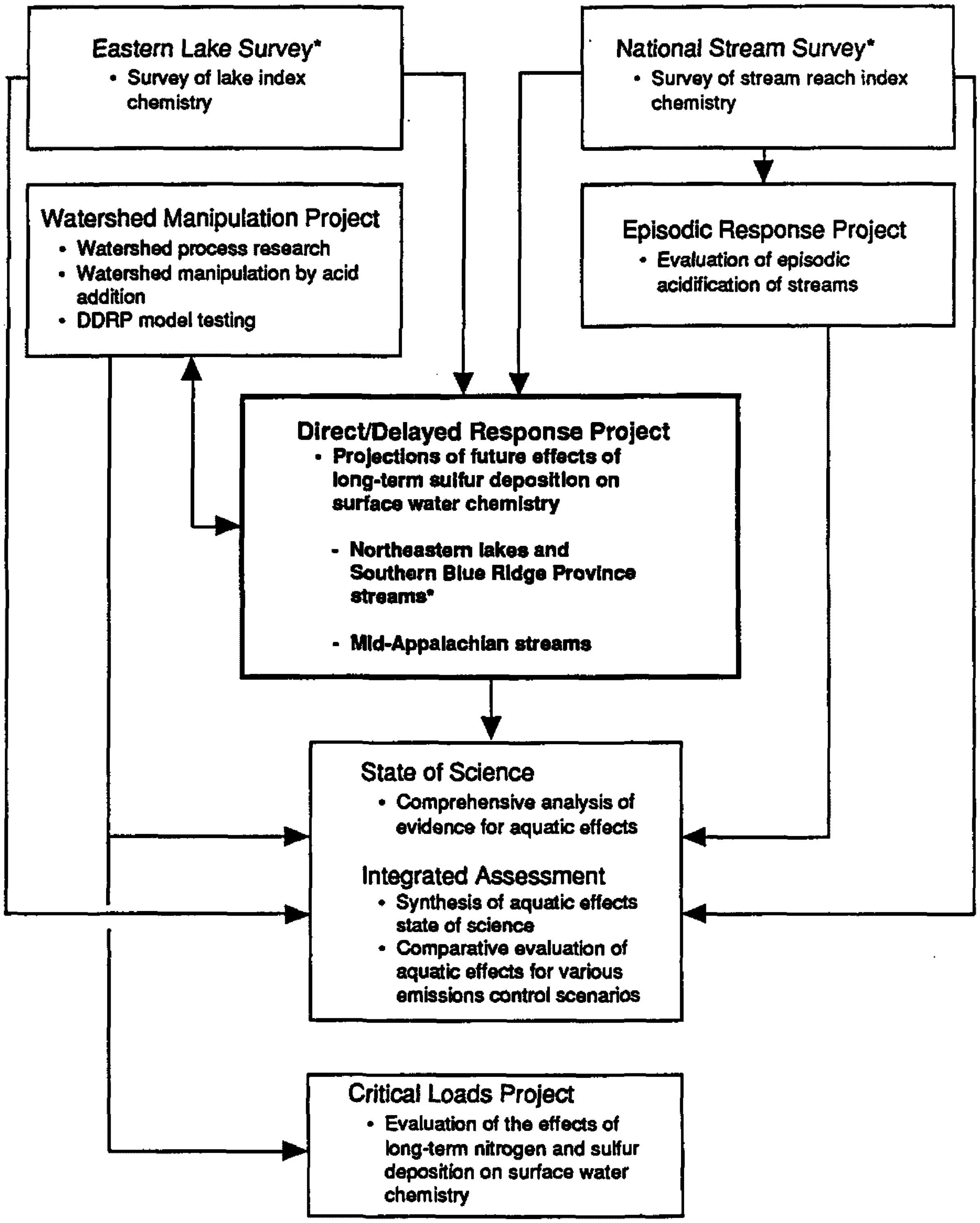
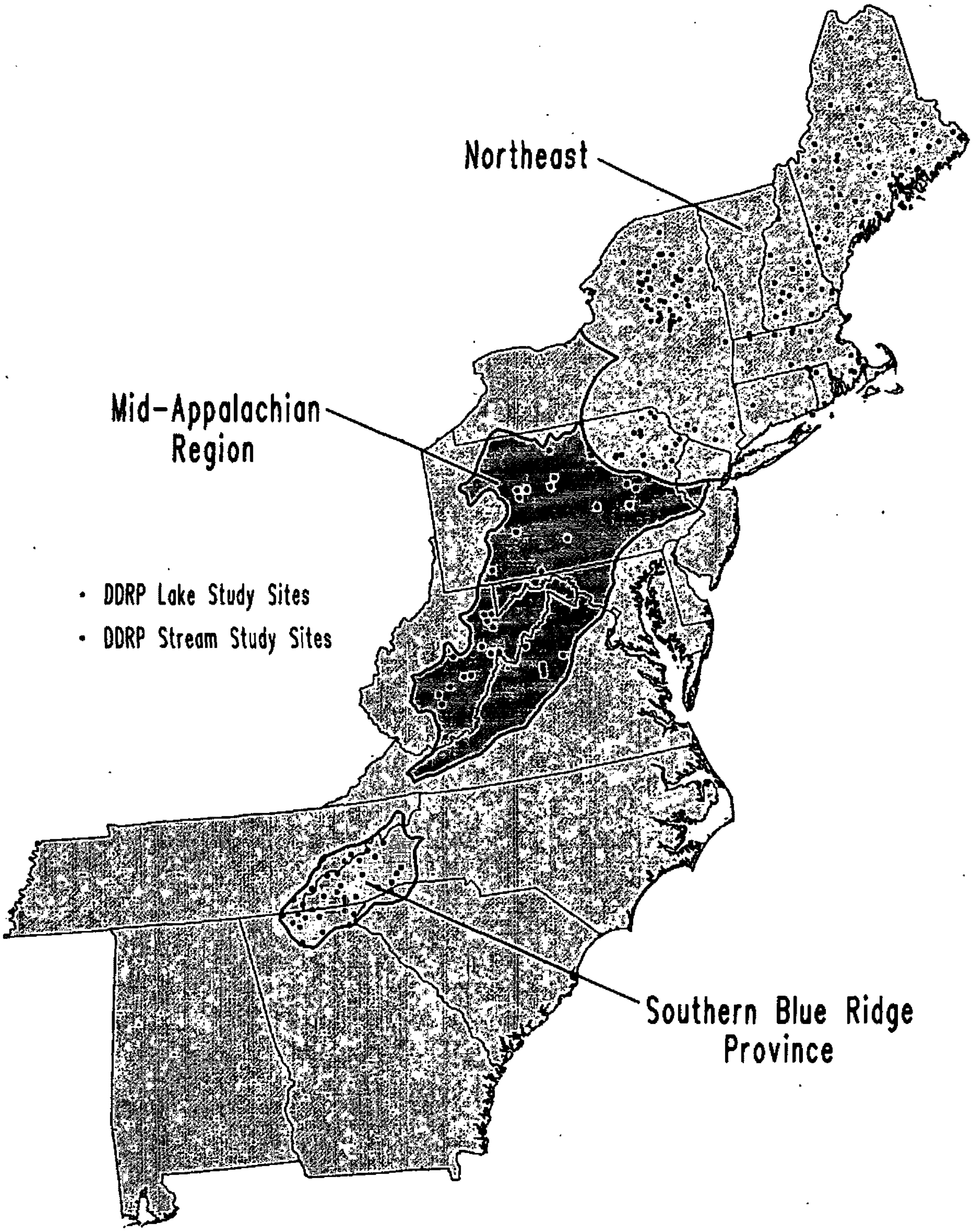


Figure 2-1. Activities of the Aquatic Effects Research Program within the National Acid Precipitation Assessment Program. Completed projects are designated by asterisks.

Plate 2-1. Direct/Delayed Response Project study regions and sites.

DDRP STUDY REGIONS



The primary time horizon for DDRP analyses is 50 years. This horizon relates to the projected lifetimes of existing power plants and the potential implementation of additional emissions controls relative to those lifetimes. Where possible and reasonable, some time-dependent analyses are extended beyond this 50-year horizon to better evaluate process rates and changes and potential future effects.

2.5 PROJECT PARTICIPANTS

The DDRP was designed and implemented at EPA's Environmental Research Laboratory - Corvallis (ERL-C) and is a very large effort involving many participants. The Project involves two other EPA laboratories, the Atmospheric Research and Exposure Assessment Laboratory - Research Triangle Park (AREAL-RTP) and the Environmental Monitoring and Systems Laboratory - Las Vegas (EMSL-LV). The DDRP is assisted by three other federal agencies, the U.S. Department of Agriculture (including the Forest Service and the National Office, two National Technical Centers, and 12 state offices of the Soil Conservation Service), the U.S. Geological Survey, and National Oceanographic and Atmospheric Administration. Two national laboratories [Oak Ridge National Laboratory (ORNL) and Battelle - Pacific Northwest Laboratories (PNL)], five state and private universities, and four consulting firms also have participated in this Project. In all, over 200 field, laboratory, database management, scientific, and management personnel have contributed to this effort.

2.6 REPORTING

This report documents and discusses the data analyses performed for the NE and SBRP Regions. It does not contain a complete list of all data used or all results produced in the analyses. The complete list and documentation will be available at a later date. Section 5 of this report, however, does contain appropriate summary and example data.

During the course of the Project many of its activities have been documented, externally peer reviewed and approved, and published as EPA reports. Any reference used in this report that has an EPA publication number is the final, externally peer-reviewed product of this (or another) EPA project. Usually, such documents contain more complete descriptions and details of the work undertaken than can be presented within this report. Copies of these cited EPA published reports are available upon request from the Project Technical Director, M. Robbins Church, at ERL-C.

Project participants have published descriptions of activities and results of the DDRP in the peer-reviewed literature. Published papers and manuscripts in review are cited throughout the report and, like the published EPA reports, can be obtained by request from the Technical Director. As of this writing, many additional peer-reviewed publications that document the activities and results of the DDRP are in preparation or are planned. Other preliminary results and discussions of the Project have been presented at meetings and workshops of the American Geophysical Union (fall, 1987); Association of American Geographers (November 1987); Biometric Society (July 1986); International Society of Ecological Modelling (August 1987); North American Lake Management Society (November 1986); and the Soil Science Society of America (December 1987 and 1988).

SECTION 3

PROCESSES OF ACIDIFICATION

3.1 INTRODUCTION

As discussed in Section 2.1, the Direct/Delayed Response Project was developed as a result of the conclusions of the NAS Panel on Processes of Lake Acidification (NAS, 1984) concerning the most important watershed processes affecting or mediating long-term surface water acidification. The Panel identified these processes as (1) the retention of deposited sulfur within watersheds and (2) the supply of base cations from watersheds to surface waters. These processes have therefore become the focus of the DDRP. The purpose of this section is to review these processes briefly in the context of the DDRP watershed and soil survey (Section 5) and the analyses that follow (Sections 6-10).

Factors other than sulfur retention and base cation supply affect surface water acidification, but were either deemed by the Panel to be relatively less important in long-term acidification or could not be addressed completely within the scope of the DDRP due to time, budgetary, or logistical constraints. Several of these alternative factors (nitrate deposition, land use, leaching of organic acids from soils, and hydrologic flowpaths) are discussed briefly below in the context of the design and objectives of the DDRP, but they are not addressed in detail in this report.

Leaching of nitrate from soils has been identified as a potential source of acid transport to surface waters during spring snowmelt events (Galloway et al., 1987; Driscoll et al., 1987a). Inasmuch as the DDRP focuses on long-term acidification, this effect is not considered here. Although nitrogen appears to be retained almost entirely in most forested watersheds by biological uptake and accretion in biomass (Abrahamsen, 1980), recent studies suggest that nitrogen throughput (with leaching as nitrate) is a significant contributor to long-term acidification at some selected sites with mature forests (C. Driscoll, personal communication). Evidence for such chronic effects was not available when the DDRP began and is not considered within the analyses presented here. It will likely be the focus of future studies by the EPA.

Land use and changing land use [e.g., forest growth; Krug and Frink (1983)] can affect both the chemistry of surface waters and the interaction of acidic deposition with soils, which, in turn, can affect surface water acidification. Apparent influences of land use are discussed in Section 8. Projection of changes in land use and projection of changes in surface water chemistry associated with such alterations (either on the DDRP study watersheds or in the DDRP study regions) are outside of the scope of the DDRP analyses.

Krug and Frink (1983) discussed the importance of natural soil acidification processes and hypothesized that acidic deposition could lower the pH of soils proximate to surface waters, thereby decreasing the dissociation of humic acids and decreasing the mobility of organic "carrier anions." Reverse conditions could occur under a scenario of decreased deposition acidity. Although LaZerte and Dillon (1984) have presented evidence that the Krug and Frink hypothesis is not supported in studies of acidified lakes in Ontario, Canada, such changes could affect both the pH and buffering capacity of surface waters. Potential dynamic effects on watershed soils and surface water chemistry (as presented by Krug and Frink, 1983) are not discussed here in detail, nor are they considered explicitly within the DDRP except when such interactions are incorporated in the Integrated Lake/Watershed Acidification Study (ILWAS) Model (see Section 10).

The route that water follows within watersheds plays a very important role in the determination of surface water chemistry and in the response of soils and surface waters to acidic deposition (e.g., see Chen et al., 1984; Peters and Driscoll, 1987). Such interactions and effects were reviewed by Church and Turner (1986) at the outset of the DDRP, and these discussions are not repeated here. The in-depth determination of flowpaths within individual DDRP study watersheds was not within the time, budgetary, or logistical scope of the Project. The apparent associations between watershed hydrologic parameters or indicators is presented in Section 8. Assumptions concerning flowpaths and their effects on analyses are presented in Section 9, and descriptions of the hydrologic modules of integrated watershed models are presented in Section 10.

3.2 FOCUS OF THE DIRECT/DELAYED RESPONSE PROJECT

During the past decade there has been an increased recognition that surface water acidification is controlled not only by rates of hydrogen deposition, but also by the mobility of associated anions through the ecosystem. A conceptual model of surface water acidification (Galloway et al., 1983a) and the 1984 NAS Panel identified two dominant variables affecting the rate and extent of watershed acidification: (1) control on anion mobility, specifically on sulfate adsorption and (2) rates of base cation supply from watersheds.

Almost three decades ago, Nye and Greenland (1960) recognized the importance of anions as "carriers" for cations in solution. The "mobile anion" paradigm they proposed, more recently applied to surface water acidification (Johnson and Cole, 1980; Seip, 1980), suggests that a variety of processes (e.g., adsorption of sulfate and phosphate, biological uptake of nitrate, pH- and pCO_2-dependent dissociation of carbonic acid) act more or less independently to control the concentrations of individual anions in solution, whereas cation exchange and weathering processes control the relative quantities of cations. Controls on, and changes in, anion mobility can thus be viewed as the proximate controls on rates of cation leaching from soils and, coupled with rates of cation resupply processes, on surface water acidification. Within the DDRP the primary issue with regard to anion mobility lies in forecasting temporal changes in dissolved sulfate. Sulfur retention processes are further discussed in the following section.

Rates of base cation supply from watersheds were identified as the second dominant factor determining the rate and ultimate acidification of surface waters by acidic deposition. Supply of base cations occurs principally from mineral weathering (as the "original" source) and cation exchange in soils. These processes are discussed further in Section 3.4.

3.3 SULFUR RETENTION PROCESSES

3.3.1 <u>Introduction</u>

Watershed sulfur budgets and regional summaries of sulfur input/output budgets indicate substantial regional differences in sulfate mobility between the Northeast (NE) and the Southern Blue Ridge Province

(SBRP) (Rochelle et al., 1987; Rochelle and Church, 1987). Understanding and characterizing these differences are important objectives of the DDRP, and efforts toward fulfilling these objectives are discussed in Sections 7.3 and 9.2. This section provides a background for those efforts, summarizes the current understanding of controls on sulfate mobility in soils and watersheds, and assesses the relative importance of the control processes. Discussion is focused on sulfate adsorption, which is regarded as a major process in sulfur retention by forest soils (Johnson and Todd, 1983; NAS, 1984; Fuller et al., 1985).

3.3.2 Inputs

The upper limit on sulfate concentration in surface waters is controlled by sulfur inputs to the system, i.e., the deposition flux to the watershed and the generation of additional sulfate within that system. The principal concern with regard to acidification, and often the only sulfur source considered, is deposition of atmospheric sulfur derived from anthropogenic sources. Sea salt can supply a significant amount of sulfate to watersheds and surface waters in near-coastal areas. Concentrations and deposition fluxes of sulfate from natural sources other than sea salt (e.g., biogenic emissions, volcanoes) in "clean" areas, however, are roughly an order of magnitude lower than the anthropogenically enhanced fluxes in parts of eastern North America, which are heavily influenced by acidic deposition (Olsen and Watson, 1984).

A second potential contributor of sulfate to watersheds is oxidation of sulfides in soils or bedrock. Net mineralization of organic matter, if it occurs, provides a significant source of sulfate, although it represents release of sulfur sequestered by biomass at some previous time rather than "new" sulfur. *Oxidation of minerals such as pyrite is more common and the most important internal sulfur source.* Sulfide oxidation typically is not quantified in watershed studies, except inferentially from detailed sulfur input/output budgets. In the absence of specific sulfide oxidation data or of other strong evidence for internal sulfur sources (e.g., net sulfur efflux, geologic data), watershed sulfur sources are typically ignored altogether (e.g., Christophersen and Wright, 1981; Helvey and Kunkle, 1986; Jeffries et al., 1986) or are assumed to be unimportant contributors to sulfur budgets (e.g., Dillon et al., 1982; Schafran and

Driscoll, 1987). Cyclic reoxidation of reduced sulfur from wetlands and/or flooded soils during dry periods can generate substantial transient sulfate effluxes (deGrosbois et al., 1986; Bayley et al., 1986), but should be recognized as a recycling of previously retained sulfate rather than as a true source of "new" sulfur to a watershed.

Dissolution of sulfate minerals (e.g., gypsum) is another potential watershed source of sulfate. Mineral sulfates occur in soils in arid to semi-arid climates in association with other evaporites, including carbonates. In bedrock, sulfates are also associated with carbonates (coprecipitated with) (Doner and Lynn, 1977; Hurlbut and Klein, 1977). Because of the co-occurrence of mineral sulfates with carbonates, and because even small amounts of carbonate provide substantial ANC to receiving waters, watersheds with significant inputs of sulfate from sulfate mineral dissolution likely will have high ANC and thus will not be sensitive to acidification.

In the DDRP, there has been an extensive effort to quantify atmospheric deposition to the study watersheds (Section 5.6). Both direct and indirect efforts have been made to assess internal sulfur sources to watersheds based on mapped lithology and on analysis of uncertainties in watershed sulfur input/output budgets (Section 7).

3.3.3 Controls on Sulfate Mobility within Forest/Soil Systems

The sulfur cycle in forest ecosystems is strongly influenced by both inorganic and biologically mediated processes (Figure 3-1). The forest canopy acts as a collection surface for dry deposited sulfur, both for particulate sulfate aerosols and for gaseous sulfur dioxide. Precipitation subsequently washes a large portion of dry deposited sulfur along with, in some cases, sulfate leached from leaf surfaces in the canopy (Lindberg et al., 1986; Lindberg and Garten, 1988). The increase in sulfur flux in throughfall compared to that of incident precipitation has been used as an estimator of the amount of dry deposition to a system (Khanna et al., 1987; Lindberg et al., 1986; Lindberg and Garten, 1988).

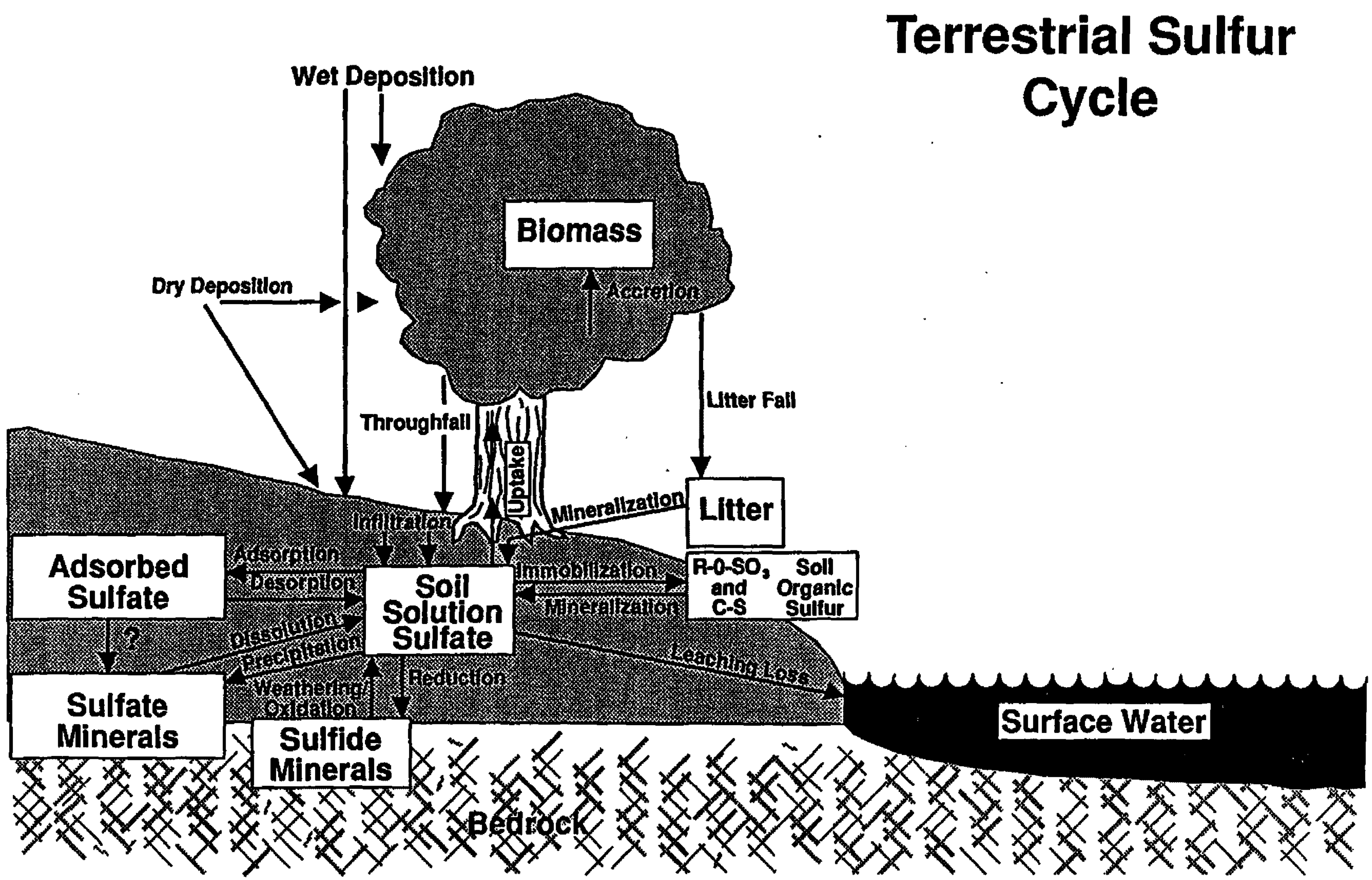


Figure 3-1. Diagram of sulfur cycle in forest ecosystems.

Within the soil, solution concentrations of sulfate are strongly regulated by sorption reactions, which may add (desorb) or remove (adsorb) sulfate from solution, depending on the sulfur status of soil and concentration of sulfate in incoming solution. A variety of other inorganic and biologically mediated processes also occur within forest ecosystems and are discussed briefly below.

3.3.3.1 Precipitation/Dissolution of Secondary Sulfate Minerals

Along with sorption reactions, secondary mineral phases of aluminum or iron can control sulfate concentrations in solution (Adams and Rawajfih, 1977; Nordstrom, 1982; Khanna et al., 1987). Evidence for occurrence and control of sulfate (and/or aluminum) concentrations by these phases is usually indirect (saturation indices) and thus is not unequivocal. These minerals are likely to occur only in soils with very low pH (ca. 4.0 or lower) and with high sulfate concentrations in which formation of jurbanite ($AlOHSO_4$), basaluminite ($Al_4(OH_{10})SO_4$), or alunite ($(K,Na)Al_3(OH)(SO_4)_2$) is likely. Although control of dissolved sulfate by jurbanite apparently occurs at two sites in Germany, both sites are characterized by very high sulfur fluxes apparently due to internal sources at Goettingen (Weaver et al., 1985) or to extremely high atmospheric deposition (up to 40 kg S ha^{-1} yr^{-1}) at Solling (Khanna et al., 1987). At more typical sites where acidification is a concern (soil pH >4.0, wet sulfate deposition $\leq$ 15 kg S ha^{-1} yr^{-1}), soil solutions are not likely to be saturated with respect to secondary $Al\text{-}OH\text{-}SO_4$ phases. Saturation index data should be interpreted with caution, however, because little is known about solution chemistry in most soils under dry or unsaturated conditions, and there is a possibility of cyclic formation/dissolution of $Al\text{-}OH\text{-}SO_4$ mineral phases during dry and wet periods (Nordstrom, 1982; Weaver et al., 1985). For the vast majority of watersheds in the eastern United States, including DDRP watersheds, control of solution sulfate by aluminum sulfate mineral phases cannot be ruled out, but is unlikely.

3.3.3.2 Sulfate Reduction in Soils and Sediments

In intermittently or permanently anaerobic soils, in wetlands, and in lake sediments, significant reduction of sulfate can occur. The principal reduction products in soils are metal sulfides, which are evident as gleying or mottling of the soil. Little is known about the overall magnitude of sulfur retention in such soils. Long-term retention of sulfur by reduction occurs only in soil environments that are permanently anaerobic. In seasonally reduced zones, sulfides are quickly reoxidized upon drying of the soil (Nyborg, 1978). Partially oxidized sulfur species (i.e., oxidation states between -2 and +6) also occur in soils, but usually represent a very small fraction of total soil sulfur (Freney, 1961; David et al., 1982), and are likely to occur mostly as labile redox intermediates in the oxidation of mineral or organic sulfides.

In wetlands and in anaerobic lake sediments, sulfate is used as an electron acceptor by bacteria, with reduced sulfur sequestered as metal or organic sulfides. Retention is first order with respect to sulfate concentration (Baker et al., 1986b; Kelly et al., 1987). Total retention within lakes increases with hydrologic retention time, so the relative importance of in-lake processes varies as a function of watershed-to-lake area ratio and other lake hydrologic characteristics. In seepage lakes and other systems with long hydrologic retention times, in-lake reduction is a critical factor in sulfur budgets. In lakes with short retention times (one year or less, see Baker et al., 1986b), including the great majority of lakes in the DDRP regions, in-lake retention has a very minor influence on sulfur budgets (Norton et al., 1988; Shaffer et al., 1988; Shaffer and Church, 1989; see also Section 7.2).

3.3.3.3 Plant Uptake

Sulfur is an essential plant nutrient and is extensively cycled through vegetation. Soils in certain areas of the world have serious sulfur deficiencies (Turner et al., 1980), but deposition in areas receiving acidic deposition typically provides sulfur far in excess of plant requirements (Johnson et al., 1982a). Recent studies of sulfur cycling at 10 U.S. and German sites, summarized by Johnson et al. (1982a), indicated annual sulfur biomass accretion of 0.5-1.6 kg S ha^{-1} yr^{-1} and standing sulfur biomass of 19-98 kg S ha^{-1}. Accretion at the 10 sites averaged less than 10 percent of wet deposition (including data for two sites in the western United States with low deposition), and biomass was equivalent to only one to four times annual deposition. In young forests with aggrading litter mass, significant sulfur accretion within the litter can also occur (Switzer and Nelson, 1972; D. Johnson, personal communication). Although such data suggest that biomass accretion is a relatively small net sink for sulfur, the significance of biological sulfur cycling in the soil cannot be overlooked. Fluxes of sulfur through vegetation and between soil pools are very dynamic and play important roles in storage and translocation of sulfur within the soil.

3.3.3.4 Retention as Soil Organic Sulfur

Probably the most controversial issue regarding sulfur retention in soils is the role of soil organic sulfur. Organic sulfur, largely contained in or derived from litter, represents by far the largest sulfur pool in forest soils (>90 percent of total sulfur in many northern soils, and well over half the total sulfur at Walker Branch, TN, the only southeastern system for which adequate data are available) (Bettany et al., 1973; David et al., 1982; Schindler et al., 1986a; Johnson et al., 1982b). Several recent studies have documented rapid uptake of sulfate by soil bacteria and conversion to ester sulfate (R-O-SO_3 linkages) and to reduced sulfur (C-S bonds), suggesting a major role for organic forms as net watershed sulfur sinks (e.g., Fitzgerald et al., 1982; Swank et al., 1984; David et al., 1984; Schindler et al., 1986a). Initial transformations of inorganic sulfur, primarily to ester sulfate, are rapid and extensive. Ester sulfate is then mineralized rapidly to form inorganic sulfate (Houghton and Rose, 1976; Fitzgerald and Johnson, 1982; Schindler et al., 1986a). Formation of carbon-bonded (reduced) sulfur from ester sulfates occurs more slowly, but turnover is also much slower. Carbon-bonded sulfur, along with the reduced sulfur generated by vegetation and stored in litter, represents a large pool of sulfur that turns over very slowly.

Because of the numerous pools, transformations, and kinetic variables in the soil organic sulfur cycle, the magnitude of net organic sulfur retention is unclear. Watersheds in Coweeta, NC, are characterized by high net sulfur retention (Swank and Waide, 1988). Field and laboratory studies have been used to assess contributions of adsorption and organic sulfur formation to watershed sulfur retention. Short-term uptake indicated high potential flux into organic pools in upper soil horizons (Swank et al., 1984); later studies have shown high adsorption by soils at Coweeta, with subsequent transformation of a portion of the adsorbed sulfate to organic forms (Strickland and Fitzgerald, 1984; Strickland et al., 1987). Strickland and Fitzgerald (1984), Strickland et al. (1987), and Fitzgerald and Watwood (1987) have concluded that both adsorption and organic accumulation are important contributors to net watershed sulfur retention. Studies at Coweeta have focused principally on transformations in the upper (O and A) soil horizons, however, so considerable uncertainty remains concerning net fluxes to adsorbed and organic pools in the integrated soil pedon.

In contrast to the conclusions of Fitzgerald and coworkers regarding Coweeta, a recent model of sulfur transformation kinetics that considers sorption, immobilization, and mineralization rates suggests a different conclusion for two northeastern sites. Fuller et al. (1986a) concluded that overall uptake and mineralization of sulfur are of comparable magnitude, and that the overall net sulfur budgets at Huntington Forest, NY, and at Hubbard Brook, NH, are near steady state (i.e., sulfur input equals output). Separate analyses of sulfur isotope data for the Hubbard Brook Experimental Forest led Fuller et al. (1986b) to conclude again that Hubbard Brook soils have negligible net sulfur retention. A broader evaluation of sulfur input/output budgets for the NE (Rochelle and Church, 1987; see also Section 7.3) showed that watershed sulfur budgets for the region are, on average, at or near steady state, suggesting little or no net retention as organic or other forms of sulfur in typical watersheds of the region.

3.3.3.5 Sulfate Adsorption by Soils

Adsorption has long been recognized as an important process affecting sulfate mobility in soils and availability to plants (early research on sulfate retention focused on sulfate deficiencies in agricultural soils). Pioneering work by Chao and coworkers in the early 1960s identified adsorption as a principal retention mechanism, identified key soil variables affecting adsorption capacity, and used nonlinear isotherms (Freundlich) to describe partitioning between dissolved and adsorbed phases (Chao et al., 1962a,b; 1964a,b).

Research during the late 1960s and 70s suggested two distinct mechanisms of adsorption, commonly referred to as (1) non-specific adsorption, an electrostatic bonding at positive charge sites on the soil surface, and (2) specific adsorption, which involves ligand exchange (with OH^- or OH_2) and ionic bonding (Hingston et al., 1967, 1972). Subsequent work by Rajan (1978, 1979) and by Parfitt and Smart (1978) demonstrated that specific sorption could involve exchange of one or two surface ligands, with the latter resulting in "bridging" and formation of an M-O-S(O_2)-O-M ring, in which M is a metal ion, usually iron or aluminum, incorporated in a polymeric hydrous oxide or on the edge of a clay lattice.

3.3.3.5.1 Factors affecting adsorption by soils -

Adsorption capacity of soils is influenced by a variety of physical and chemical variables. The amount of adsorbing substrate (iron and aluminum hydrous oxides, clay), soil organic content, and pH is usually regarded as the most important of these variables. Hydrous oxides of iron and aluminum are probably the most important substrates for sulfate adsorption in soils. These materials are precipitated as amorphous or poorly crystalline coatings on particle surfaces in the soil and are positively charged at low pH, providing anion adsorption sites. Adsorption occurs by exchange with OH^- or OH_2, and can involve a single ligand or pair of ligands, depending on surface charge and the abundance of one-coordinated (i.e., linked to a single metal atom) hydroxyl or aquo ligands (Parfitt and Smart, 1978). Several studies, under field and laboratory conditions, have demonstrated high positive correlations between sulfate adsorption and iron and/or aluminum content of soils (e.g., Chao et al., 1964b; Johnson and Todd, 1983; Fuller et al., 1985).

Clay content of soils has been correlated with sulfate adsorption by soils, although it is regarded as a minor adsorber (Johnson and Todd, 1983). In part, the correlations result from occurrence of positive charge sites for anion adsorption on clay edges. Perhaps more important, clay content is often highly correlated with non-silicate iron and aluminum content of soils and can serve as a surrogate for the oxides in regression analyses. Several investigators (e.g., Neller, 1959; Chao et al., 1962b; Johnson et al., 1980) have found positive correlations between clay content (or surface area, which is in turn correlated with both clay content and hydrous oxide content) and adsorbed sulfate. Others (e.g., Haque and Walmsley, 1973; Johnson and Todd, 1983; Fuller et al., 1985) failed to find such a correlation, although, as noted above, significant correlations have been observed between adsorbed sulfate and hydrous oxides.

Interactions of soil organic matter, sulfate, and adsorbing substrates have received increasing attention in recent years. Chao et al. (1964a) noted that the presence of a variety of organic acids reduced sulfate adsorption in laboratory studies; the most pronounced reduction was by those acids forming very strong complexes with metals (i.e., oxalate, tartrate). Negative correlations between soil organic matter and sulfate adsorption have also been noted by Barrow (1967; correlation was with soil organic nitrogen) and Haque and Walmsley (1973). More recently, organic "blocking" of sulfate adsorption has been hypothesized to occur in forest soils and has been suggested as a major factor contributing to regional differences in sulfate mobility and surface water acidification in forest systems receiving acidic deposition (Johnson et al., 1980; Johnson and Todd, 1983). This hypothesis is consistent with observed regional (NE vs. SBRP) differences in sulfur budgets. Northeastern soils typically have higher organic content than those from the Southeast, but have lower adsorption capacities despite having iron and aluminum concentrations comparable to those of southeastern soils (Johnson and Todd, 1983).

Fitzgerald and Johnson (1982) have suggested that blocking is a result of competition for anion adsorption sites by fulvic acids. Similarly, Davis (1982) noted that introduction of fulvic acids resulted in reduced anion phosphate adsorption by alumina in laboratory studies. He concluded that preferential sorption of the organic acids was the principal blocking mechanism. Although the occurrence of blocking is now widely accepted and sorption of organic acids is the most likely process, there has not been a rigorous evaluation of this or other hypothesized blocking mechanisms (e.g., coating of iron and aluminum surfaces; Couto et al., 1979).

Along with the amounts of adsorbing substrates and of competing anions, pH is a major, albeit indirect, control on sulfate adsorption by soils. Chao et al. (1964b) initially demonstrated effects of pH on adsorption, using fresh hydrous oxides of iron and aluminum, and demonstrated that adsorption increased as soil pH was lowered. Subsequent investigators (e.g., Hingston et al., 1967, 1972; Couto et al., 1979; Nodvin et al., 1986) showed similar effects of soil pH on adsorption. Surface charge on iron and aluminum hydrous oxides is amphoteric. The ratio of OH_2 to OH^- ligands increases as pH is reduced, resulting in increased positive surface charge and enhanced anion adsorption capacity. Reduced pH also decreases dissociation of organic acids (Stevenson, 1982), minimizing the interference or blocking effect of organic matter on sulfate adsorption.

The specific soil properties cited above, as well as sulfate adsorption, have been associated with a variety of qualitative variables. Shriner and Henderson (1978) suggested that differences in net sulfate retention at Coweeta, NC (high), Walker Branch, TN (intermediate), and Hubbard Brook, NH (negligible), were related to cumulative acidic (sulfur) deposition, or more specifically to relative saturation of sulfate adsorption sites. Barrow et al. (1969) noted significant differences in sulfate adsorption by soils formed over different parent rock. They also noted that the soils had different pH, texture, and hydrous oxide properties related to mineralogy of the parent material. Barrow et al. (1969), Hasan et al. (1970), and Johnson and Henderson (1979) have also noted correlations between adsorbed sulfate and degree of soil weathering, which were in turn related to age and/or annual rainfall. Those investigators pointed out that differences in composition of the parent material and/or degree of weathering lead to differences in soil pH and hydrous oxide content, which are probably actually controlling sulfate adsorption. Although it is important to remember that the quantitative soil properties (iron and aluminum hydrous oxides, organics, pH, etc.) that control sulfate adsorption are the end products of their environment, and therefore reflect parent material, weathering history, vegetation, climate, and the influences of man.

3.3.3.5.2 Sorption kinetics -

Kinetics of sulfate adsorption have usually been reported to be very rapid, with soil solution sulfate concentrations reaching 95-97 percent of steady state within 5 to 15 minutes after addition of sulfate to soil-water slurries, and steady state within one to three hours (Rajan, 1979; Chao et al., 1962a; Bolan et al., 1986). In a few cases, slower equilibration has been reported, with gradual changes in sulfate for 50 days or more (Barrow and Shaw, 1977; Singh, 1984; Hayden, 1987). Hayden (1987) attributed the slow changes in her batch experiments to physical alteration (grinding) of surfaces (because no equivalent "slow" equilibration was observed in concurrent column experiments using the same soils). In the other reported cases, it appears likely that slow "adsorption" was similarly attributable to treatment effects and/or to microbially mediated sulfate uptake.

3.3.3.5.3 Desorption -

Although adsorption of sulfate has been extensively studied, relatively little attention has been paid to desorption. Reported reversibility of sorption ranges widely, from less than 10 percent (Bornemisza and Llanos, 1967) to complete desorption (e.g., Weaver et al., 1985; Sanders and Tinker, 1975). Several factors influencing reversibility have been identified: aging of sulfate on the soil (decreased desorption with time since adsorption), temperature (less desorption for soils held at higher temperatures), and characteristics of the adsorbing substrate. Other factors, especially the mechanism of adsorption and number of ligands, also may contribute to the effects noted above. Desorption kinetics have not been extensively characterized, but are apparently similar to those for adsorption (Barrow and Shaw, 1977; Rajan, 1979). The extent of sorption reversibility for soils from the NE and SBRP is currently being evaluated as part of an ongoing EPA-funded project. Results of that project will contribute significantly to our understanding of sorption processes and to our ability to project rates of soil and surface water sulfate response to changes in atmospheric deposition.

3.3.4 Models of Sulfur Retention

Several models have been developed to describe components of watershed sulfur cycles, but to date there has not been a single model that incorporates all the major terrestrial and aquatic processes of concern. Both equilibrium and kinetic expressions are incorporated in existing models. Baker et al. (1986b) and Kelly et al. (1987) developed essentially identical kinetic models to describe in-lake alkalinity generation. Both models include equations that describe rates of sulfate retention (principally reduction) as a first-order process with respect to sulfate concentration, and annual percent sulfur retention as a function of lake hydrologic retention time. The models use a sulfur mass transfer coefficient based on an average of field measurements from a variety of sites in North America and Europe. Neither model considers terrestrial or wetland processes, and both are limited to in-lake retention.

Fuller et al. (1986a) have developed a relatively complete kinetic model to describe soil sulfur transformations. The model includes reversible sorption reactions and reversible, first-order immobilization/mineralization reactions for both ester sulfate and carbon-bonded sulfur. Although this model was developed in part to provide a set of sulfur-cycling subroutines for incorporation in integrated watershed chemistry models, there are at present insufficient data for its general usage. Rate constants have been defined for only a few sites under very limited conditions, and supporting soil chemistry data (e.g., quantification of soil organic sulfur pools) do not exist except for a few research sites.

Several dynamic watershed chemistry models have been developed to describe or project watershed acidification, and all consider sulfate retention in some way. Jenne et al. (in press) have recently evaluated and compared process representation, including sulfur processes, for the three models used in the DDRP. The Model for Acidification of Groundwater in Catchments (MAGIC), developed by Cosby et al. (1985a,b; 1986b), uses a nonlinear isotherm (Langmuir) to partition sulfate between dissolved and sorbed phases in the soil; phase equilibrium is assumed at each time step. For simulations of lake chemistry, MAGIC optionally incorporates the Baker et al. (1986b) model of in-lake retention. The Integrated Lake/Watershed Acidification Study (ILWAS) model (Chen et al., 1983; Gherini et al., 1985) can use either a linear or Langmuir function to describe inorganic partitioning in the soil; a first-order in-lake retention component also can be included as appropriate. The Enhanced Trickle Down (ETD) model of Schnoor and coworkers (Schnoor et al., 1986b; Lee, 1987) was originally developed for seepage lakes in the Upper Midwest; early versions assumed steady state for sulfate in the terrestrial system and used an empirically defined zero-order function for in-lake retention. Current versions of the model include a linear isotherm to describe adsorption by soils. Application of these models in DDRP Level III Analyses is discussed in Section 10.

Along with the models used in the DDRP, the Birkenes model (Christophersen and Wright, 1981; Christophersen et al., 1982) has been used for simulation of watersheds in Norway and Canada. The Birkenes model was developed by Christophersen and coworkers for a catchment in Norway having thin soils with high organic content and low adsorption capacity. Sulfate transformations in soils are represented by empirically derived equations (fit to stream sulfate concentrations). The upper soil horizon includes a constant net mineralization term, while transformations in the lower soil compartment are described by an exponential function with an empirically derived half-time (45 days) and equilibrium value. The exponential function was not designed to describe a specific process, but is believed to represent some combination of adsorption and microbially mediated transformations.

3.3.5 Summary

Sulfur input/output budgets for individual sites and for regional lake or stream populations indicate major differences in sulfur mobility in watersheds of the NE and the SBRP (Rochelle et al., 1987; Rochelle and Church, 1987). Although several terrestrial and in-lake processes may contribute to the observed differences in budget status, two processes are believed to dominate sulfate control. The first process, accumulation of soil organic sulfur, apparently does not contribute significantly to net sulfur retention in most northeastern watersheds (Fuller et al., 1986a,b; Rochelle et al., 1987), but may be a net sulfur sink in the SBRP. Due to a lack of data describing soil organic sulfur pools and a paucity of kinetic data, however, the actual importance of organic transformations as sulfur sinks cannot be evaluated at regional scales for regions with significant net sulfur retention.

The second process presumed to have significant influence on sulfate mobility in the two regions is adsorption. Until recently, it was often assumed that differences in regional sulfur budget status resulted from differences in soil age between the Northeast and Southeast (young, glaciated northern soils are developed to only a relatively shallow depth, have few hydrous oxides and secondary clay minerals, and thus low sorption capacity; in contrast, older southeastern soils are often developed to a depth of several meters and have abundant secondary minerals, hydrous oxides and clay). Recent data (e.g., Johnson et al., 1980; Johnson and Todd, 1983) suggest the previous assumption was partly correct. The glaciated northern soils have much lower clay content and poorer development of the C horizons than typical southeastern soils, but B horizons of many northern soils have iron and aluminum contents and adsorbed sulfate concentrations comparable to those of southern soils and have significant capacity to adsorb additional sulfate (Johnson et al., 1980; Johnson and Todd, 1983; Fuller et al., 1985). An important, but more recently recognized difference between the regions is the higher organic content of many northern soils, which acts to inhibit or "block" adsorption (Couto et al., 1979, Johnson et al., 1980; Johnson and Todd, 1983).

Differences in soil physico-chemical variables related to adsorption, coupled with significant differences in historic sulfur loadings to the two regions (Gschwandtner et al., 1985), probably account for most of the observed difference in sulfate mobility between the NE and SBRP. Although many SBRP watersheds are retaining a major portion of incident sulfur deposition, soils have a finite sorption capacity, and there are recent observations of increasing sulfate in many streams of the region (e.g., Smith and Alexander, 1983; Swank and Waide, 1988). These trends suggest that effects of acidic deposition are likely to increase in softwater systems of the region over the next few decades. Conversely, because most northeastern systems are already at or very near steady state for sulfur, changes in sulfate concentration under current deposition loadings will be small. If deposition were to change in the NE, the relatively low sorption capacity of typical soils in the region suggests that resulting increases or decreases in surface water sulfate would also occur quickly, probably within a few decades or less. Predicted responses of watersheds in the two regions to continued loading at current or altered levels of deposition are addressed in both Level II and III Analyses in the DDRP, and are described in Section 9.2 (sulfate only) and Section 10 (sulfate and associated changes in cations).

3.4 BASE CATION SUPPLY PROCESSES

3.4.1 Introduction

The second major group of processes affecting surface water acidification is composed of those processes or reactions responsible for supplying base cations (i.e., Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) to surface waters. Recently, Driscoll et al. (1989b) have demonstrated that a good correlation exists between changes in base cation deposition at Hubbard Brook Experimental Forest and changes in cation fluxes in streams. Based on these results, these authors have hypothesized that the deposition of base cations may be a primary factor in regulating surface water acidification. However, we (Holdren and Church, in review) feel that the processes that have previously been suggested as primary factors controlling surface water composition (Galloway et al., 1983a; Reuss and Johnson, 1986) are sufficient to explain the results of Driscoll et al. (1989b). As such, the focus of the remainder of this section is on primary mineral weathering and cation exchange (Figure 3-2). The weathering of primary minerals is the ultimate source for base cations. Cations released during weathering, especially K^{+}, Ca^{2+}, and Mg^{2+} are extensively

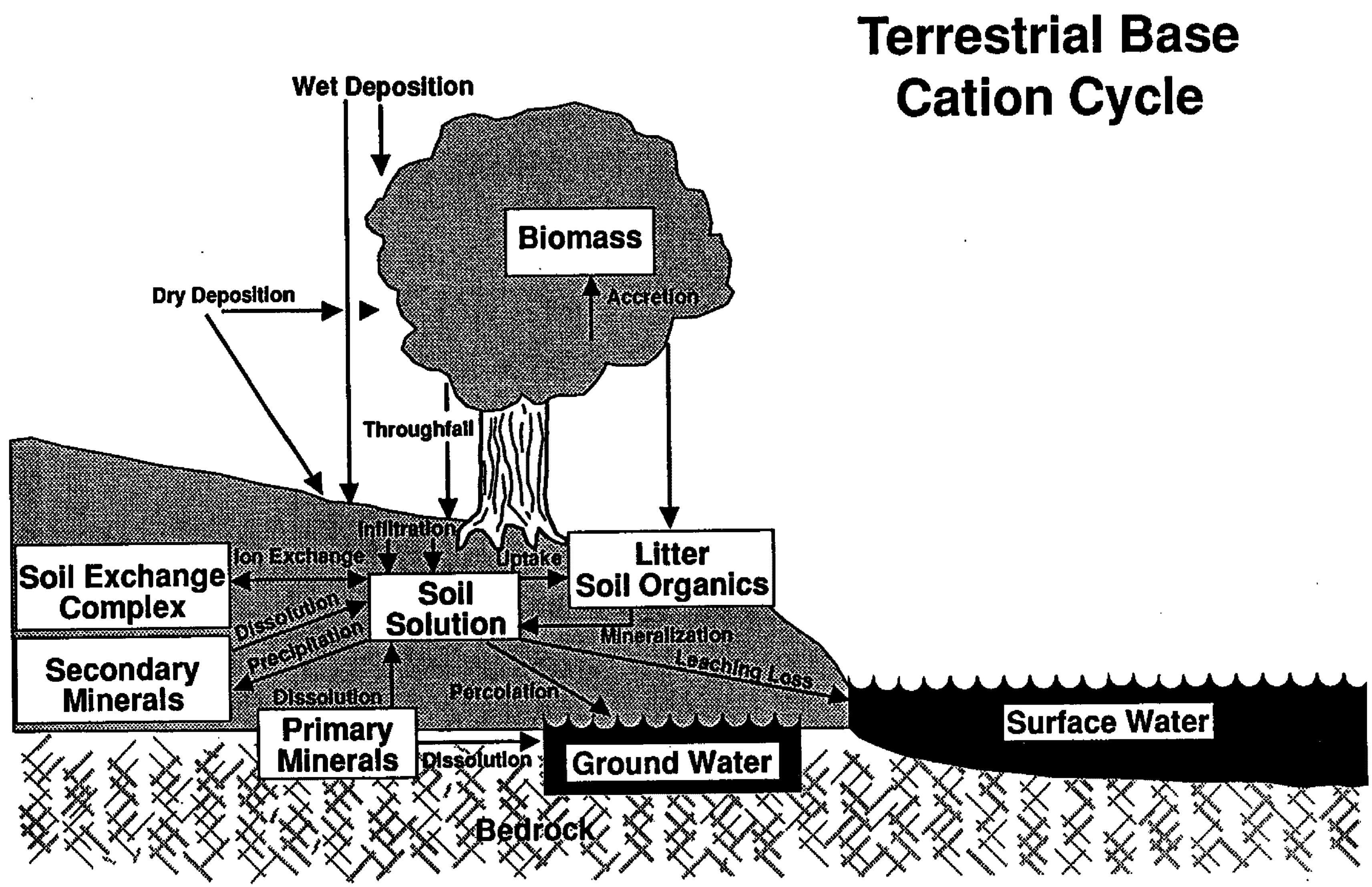


Figure 3-2. Diagram of terrestrial base cation cycle.

cycled between the actively growing biomass and the forest litter layer. Within the solum, cations may precipitate as secondary minerals. The extent to which the base cations are released into solution plays a major role in determining the response of a system to acidic deposition.

In evaluating the potential for weathering or cation exchange to neutralize incident deposition, it is critical to be aware of the time frames over which the two processes operate and to understand the potential for depletion of buffering capacity. In general, weathering is a slow process that releases base cations and silica to soil and surface waters at a more or less constant rate over long periods of time. The capacity for weathering to supply base cations is dictated by the exposed surface area of cation release is large. The primary concern about weathering, therefore, is not capacity, but rather the rate at which the reactions occur. The rate of weathering depends on the exposed surface areas of reactive minerals in soils or aquifers and on the hydraulic contact between minerals and soil waters. Rates can vary widely and, in some watersheds, may not be sufficient to neutralize incident deposition. These systems are thus potentially susceptible to adverse effects of acidic deposition.

In those systems in which the weathering rates are low, cation exchange reactions can ameliorate, at least transiently, the effects of acidic deposition. Unlike weathering, exchange reactions are rapid, usually approaching steady-state conditions within several hours in static systems. The ability of exchange processes to neutralize incident deposition depends both on the size of the exchange reservoir and on its exchange properties. In the regions of interest to this study, the exchange reservoir is probably small. The northeastern soils are young and have low clay mineral content, and soils in the SBRP are highly weathered. While the organic horizons of soils in these regions do have substantially larger cation exchange capacity (CEC) values than do their underlying mineral horizons, these organic components of the soils tend to be quite acidic (i.e., pH $<$ 4.0). As such, exchange reactions involving organic horizons do not contribute substantially to the ANC-generating capacity of the soils as integrated systems. In soils with low weathering rates, base cations will be depleted from the exchange complex as a direct consequence of acidic deposition.

The exchange reaction, in which acid cations (H^+ or Al^{3+}) replace base cations on the exchange complex, is essentially a buffering process. This reaction affords some degree of protection on soil and surface waters in terms of limiting changes in pH and ANC. If the cation resupply rate from weathering is less than the rate at which the increased acidic deposition removes cations from the exchange complexes, then through time, as the reservoir of base cations is depleted, the observable effects on the soils and associated surface waters increase. Initially, when base saturation is high, changes in the projected surface water ANC are relatively small. When the base saturation for the soils is reduced to only a few percent, however, the projected changes in ANC are much greater (resulting in extremely low projected ANC) per unit change in base saturation (Cosby et al., 1985b; 1986a).

In the regions examined in DDRP, certain soils could experience significant depletions of base cations over the next 50 to 100 years. If soils undergo a significant reduction in base saturation, the associated soils and surface waters will experience parallel declines in pH and ANC. Such changes have already been well documented in the northeastern United States, eastern Canada, and Scandinavia. The major concerns, then, focus not on whether changes have occurred, but rather on the possible extent of changes anticipated to occur in selected regions over the next several decades.

3.4.2 Factors Affecting Base Cation Availability

Base cations actively cycle through virtually all ecosystems. In forested watersheds, the cations can be delivered via deposition, both wet deposition and various forms of dry deposition. Alternatively, cations can be derived by the weathering of bedrock underlying these systems. In the ecosystem, base cations actively participate in a number of cycles. Vegetation actively cycles Ca^{2+}, Mg^{2+}, and K^+ through the upper portion of the soil (Likens et al., 1977; Johnson et al., 1988a). Easily observable changes in the concentrations of cations in the exchange pools occur on a seasonal basis as a result of these processes. On a slower time scale, the base cations participate in the formation (and, subsequently, the degradation) of secondary minerals (Garrels and Mackenzie, 1967). Although in young soils these secondary minerals might represent only a small fraction of the mass of cations cycling through the ecosystem, they serve as a reasonably accessible reservoir for cations on time scales of weeks to months. Cations can be removed from watersheds by any of a number of processes. Surface water runoff and deep groundwater percolation both export cations from watersheds, and cations can be transported fluvially via suspended solids loads. Aggrading forests also act as a sink for base cations, and, as such, have an acidifying effect in forest soils (Nilsson et al., 1982; Johnson et al., 1988a).

Two processes provide primary buffers against adverse effects of acidic deposition: mineral weathering and base cation exchange. Other processes (e.g., cation uptake by vegetation), however, can be quantitatively important aspects of the elemental cycles in watersheds (Likens et al., 1977). Perturbations or disruptions, such as logging, to the biogeochemical cycles not only have dramatic effects on the cation balances in these systems, but also play a major role in soil acidification (Nilsson et al., 1982).

3.4.2.1 Mineral Weathering

The weathering of rock-forming minerals is the primary source for base cations in surficial environments. Because of differences in composition and reactivity, different minerals contribute in varying degrees to the ability of soils or watersheds to neutralize incident deposition. A summary of some the principal factors and processes is given below.

3.4.2.1.1 Primary rock-forming minerals and their rates of weathering -

A list of the major rock-forming minerals is provided in Table 3-1 along with information on their relative weathering rates and responsiveness of the rates to changes in pH. Reactions involving the primary minerals listed in Table 3-1 are, for all practical purposes, unidirectional. These minerals are unstable in soil environments. They weather to form secondary phases, such as the clay minerals, that are thermodynamically more stable and kinetically favored for formation.

Secondary minerals, such as kaolinite, smectites, or allophane, are not included in the table. The clays may contribute to ANC through both the degradation of their silicate frameworks and their ion

Table 3-1. Major Rock Forming Minerals and Their Relative Reactivities

Mineral	Reaction Rate (moles m^{-2} s^{-1})	Hydrogen Ion Rate Coefficient
Olivine	1.2×10^{-12}	$(a^{H+})^{0.6}$
Pyroxenes	1.0×10^{-10}	$(a^{H+})^{0.8}$
Amphiboles	1.4×10^{-10}	$(a^{H+})^{0.7}$
Muscovite	2.6×10^{-13}	$(a^{H+})^{0.10}$
Feldspars		$(a^{H+})^{0.25}$
Albite	1.2×10^{-10}	
Oligoclase	2.0×10^{-11}	
Anorthite	5.6×10^{-9}	
Microcline	5.0×10^{-11}	
Orthoclase	1.7×10^{-12}	
Quartz	4.1×10^{-14}	$(a^{H+})^{0}$

exchange properties. Discussion about how these minerals contribute to the transient buffering of soil pH and ANC in the absence of primary mineral weathering is presented in Section 3.4.3.

As indicated in Table 3-1, different minerals weather at different rates. Some, such as calcite, weather rapidly and provide considerable ANC to soils and surface waters. Watersheds underlaid by limestone, therefore, are rarely at risk to acidification (Hendrey et al., 1980). Conversely, some rocks/minerals are slow to weather and generate little or no ANC. For example, watersheds underlaid by the quartzites are usually considered to be sensitive to the adverse effects of acidic deposition (Hendrey et al., 1980; Rapp et al., 1985; Shilts, 1981).

The rates listed in Table 3-1 were obtained from laboratory studies. As such, these rates are the maximum values expected to occur in field settings. In most cases, rate estimates obtained from field studies are one to three orders of magnitude slower than those listed in the table (Velbel, 1986b; Paces, 1973). Although up to about one order of magnitude might be due to temperature effects, reasons for these discrepancies are currently not well understood. Other potential processes contributing to rate suppression include poisoning of active surfaces by organic coatings or mineral precipitates and non-continuous reactions caused by the wetting/drying cycles in soils (Velbel, 1986a).

Given that it is difficult to infer rates of weathering of primary minerals from field studies, it is virtually impossible to obtain information concerning how changes in the soil environment influence estimated rates. Essentially all of the data available on the effects of pH, organic interactions, and temperature are derived from laboratory studies. The major results from these efforts are summarized below.

3.4.2.1.2 Laboratory studies on rates and mechanisms -

Over the past three decades, considerable efforts have been made to determine the rates and mechanisms of weathering of most of the major rock-forming minerals. Of the factors affecting observed rates, pH, organic interactions, and temperature probably exert the most significant influence in determining the rates that are realized in the field. Other factors, specifically the nature and extent of mineral surface complexation by inorganic anions and the postulated presence (or lack thereof) of leached layers on weathered mineral surfaces, are likely to be important determinants of dissolution rates in soil environments. At this point, however, there is not sufficient information concerning these processes to understand how changing environmental conditions would influence observed rates through these processes.

3.4.2.1.2.1 Dependence on pH --

Over the past two decades a number of laboratory studies have been undertaken to determine changes in the reaction rates of various common rock-forming minerals as functions of hydrogen ion activity (e.g., Wollast, 1967; Helgeson et al., 1984; Chou and Wollast, 1985; Holdren and Speyer, 1985). Results from these studies are summarized in Table 3-1. As might be expected, different minerals respond differently to changes in solution pH. Reaction rates for some minerals, such as quartz, are only marginally affected by pH in acidic to circumneutral solutions. At the other extreme, calcite and dolomite reaction rates are quite responsive to changes in hydrogen ion activity. For the major soil-forming minerals present in the study regions, i.e., the feldspars, various micas, and hornblende, observed reaction rates tend to vary as functions of $(a^{H+})^{0.2}$ to $(a^{H+})^{0.5}$. Therefore, since soil pH values are expected to change by only a few tenths of a pH unit in response to acidic deposition, the magnitude of this pH effect on the rates of mineral weathering in soils should be affected by less than a factor of about 2.

3.4.2.1.2.2 Organic interactions --

One of the more poorly understood aspects of weathering has to do with the effects of organic ligands on the rates of reaction. Comparisons between laboratory-generated data and field observations have resulted in a clear understanding of the role of organics in the weathering process. If the role of organics on the rates of weathering is poorly understood, then our understanding of how acidic deposition will affect these rates is even less understood. With the information currently available, two reasonable hypotheses can be developed.

First, if organics do not have a major influence on the reaction rates of primary minerals (Mast and Drever, 1987), then the effect of acidic deposition on the reaction rates will be limited to the direct effects caused by changes in the hydrogen ion activities of the solutions bathing the soil particles. Under these conditions, weathering rates would most likely increase slightly in response to imposed environmental conditions.

On the other hand, if organics play an active role in weathering, then the interaction between acidic deposition and the organics could suppress mineral weathering. It has recently been hypothesized (Krug and Frink, 1983; Krug et al., 1985; Sullivan et al., in press) that the mobility of natural organics is depressed in more acidic environments. The decreased mobility, and hence concentration, coupled with their effect on reaction rate could conceivably cause net decreases in weathering rates in certain environments. It should be stressed that little is actually known about the effects of organics on weathering rates under field conditions. The above scenarios are, at best, speculative, but they do present the range of expected effects under different conditions.

3.4.2.1.2.3 Temperature --

The third major environmental influence on observed reaction rates is temperature. Very little experimental work has been undertaken at environmentally representative temperatures (i.e., in the 0 °C to 10 °C range). Results from a number of studies suggest, however, that the activation energies for dissolution for most common silicate minerals are in the range of 60 to 80 kJ mol^{-1}. Assuming activation energy in this range and a mean average annual temperature of 4 °C, dissolution rates are probably seven to eight times slower in the field than those observed in laboratory settings (see Table 3-1).

3.4.2.2 Cation Exchange Processes

The second major base cation-related process contributing to watershed buffering is base cation exchange. Exchange pools are dynamic reservoirs. Under steady-state conditions, the base cation content of the exchange pool represents a dynamic balance between supply from mineral weathering and organic matter mineralization and removal processes, including uptake by vegetation and leaching to ground and surface waters. On annual time scales, the soil exchange complex is in equilibrium with the soil solutions. Hence, the net uptake or net desorption of cations from soil exchange complexes should change only slowly in response to long-term weathering processes. In the absence of system perturbations and under steady-state conditions, base cations derived from weathering should be effectively passed through, either to accreting biomass or to ground or surface waters. The exchange pool reflects the concentrations observed in soil solutions, but again, in the absence of a system perturbation, is neither a source nor sink for the base cations on a long-term basis.

With increased levels of H^+ inputs, this balance changes. The increased acidity of the deposition increases the leaching of base cations from the exchange complex, replacing them with acid cations, namely H^+ or Al^{3+} (Reuss et al., 1987). In addition, the increase in the total anionic content of the soil water requires an increased total cationic flux from the soil (Johnson and Cole, 1980; Seip, 1980). The increased leaching resulting from the increased acidity is a transient phenomenon. Eventually, a new steady state is attained that reflects the properties of the exchange complex and the increased anionic concentrations in soil solutions. In the short term, then, the surface water pH and ANC are buffered by the increased leaching of base cations from the soil exchange complex. Concurrently, the soil pH and base saturation of the soil are reduced. As the exchange approaches the new steady state, the balance between the flux of H^+ to the ecosystem and the average primary mineral weathering rate will determine the final pH and ANC values for soils and the associated surface waters.

3.4.2.2.1 Types of exchangers -

The soil exchange complex is composed of essentially three types of exchangers: clay minerals, organics, and metal oxides. Within each of these broad categories of exchangers, several types of sites can actively participate in exchange reactions. For example, clay minerals can have both pH-dependent surface charges and permanent, structurally based sites acting as exchange sites. The two types of exchangers that are of most concern are the clays and the organic exchangers. The metal oxides, at the pH values of forested soils, typically have positively charged surface sites. As such, they represent sites for anion exchange (see discussion in Section 3.3) rather than for cation exchange.

3.4.2.2.2 Factors affecting the exchange process -

A number of factors that affect exchange processes can be most easily described when the process is conceived in terms of an exchange reaction. For example, for the reaction:

$$3Ca^{2+} + 2(=S-)Al = 2Al^{3+} + 3(=S-)Ca \qquad \text{(Equation 3-1)}$$

where the (=S-) indicates the surface exchange site, the reaction characteristics can be estimated in terms of a mass action equation:

$$K_{ex}^{ac} = \{Al^{3+}\}^2 [X_{Ca}]^3 / \{Ca^{2+}\}^3 [X_{Al}]^2 \qquad \text{(Equation 3-2)}$$

where the species in braces, {x}, are the activities of the aqueous species, and those in the bracket, [x], are the mole fractions of the associated solid exchangers. The selectivity coefficient, K_{ex}^{ac}, is not a thermodynamic constant because no attempts have been made to include the rational activity coefficients for the solid phase exchangers. Nevertheless, this expression can be used to understand the effects that various perturbations might have on the system.

It should also be pointed out that, in the above expressions, aluminum is being used as a surrogate for the hydrogen ion. In soils, Al^{3+} comprises the bulk of the acid cations on exchange sites. In addition, Al^{3+} activities, while having a major role in exchange reactions, are frequently regulated by other reactions such as the dissolution of gibbsite-like phases (Reuss, 1983).

Soils exposed to increased hydrogen ion activities undergo a number of possible changes. For example, aluminum activities increase at lower soil pH values simply because the solubility of gibbsite increases with decreasing pH. In response to the changing hydrogen ion regime, the activity of calcium in soil solutions would have to increase, or the ratio of calcium to aluminum on the exchange sites would have to decrease (i.e., there would be a net replacement of aluminum for calcium on exchange sites).

In addition to acidic deposition, other anthropogenic activities can affect the cation balance of soil exchange pools. Perhaps one of the better documented activities is the effect of whole tree harvesting (Johnson et al., 1988a; Reynolds et al., 1988). Biomass is a major and dynamic reservoir for base cations in most watersheds. Cations are absorbed from the solum during the spring and summer growing seasons and then partially recycled to the soil in the fall and winter with leaf fall and organic matter mineralization. Afforestation places an increased demand on the cation supply in soils as cations are retained in the aggrading biomass. This process has an additional acidifying effect on forest soils.

3.4.3 Modelling Cation Supply Processes

3.4.3.1 Modelling Weathering

In general, weathering models used to describe watershed-scale processes have been developed along one of two conceptual lines: whole watershed/mass balance and kinetics. The most commonly used models are the watershed/mass balance-type models (Bricker et al., 1968; Cleaves et al., 1970; Garrels and Mackenzie, 1967; Clayton, 1986; Creasey et al., 1986; Velbel, 1985, 1986a; Dethier, 1986). These models are based on selected sets of reactions and are calibrated to specific systems. The models work best in systems with simple mineralogies. However, the application of this type of model for studying the impacts of acidic deposition is limited because, in general, the models do not distinguish between primary mineral weathering and transient, enhanced leaching of base cations from soil exchange sites. Therefore, watershed models are most applicable to systems at steady state with regard to incident deposition.

More recently, kinetic models have begun to appear (e.g., Furrer et al., 1989). As discussed previously, application of these models to field situations is only now becoming possible. Discrepancies between laboratory and apparent field rates of weathering for individual primary minerals result in poorly constrained models. As more is learned about processes controlling rates of weathering in the field, kinetic models should play an increasing role in projecting the effects of acidic deposition.

In spite of the state of weathering models, several integrated watershed-type models (e.g., Cosby et al., 1985a,c; Gherini et al., 1985; Nikolaidis et al., 1988) incorporate weathering "modules" within their frameworks. In some models, primary mineral weathering reactions are lumped with exchange processes to yield net cation transfer rates (Nikolaidis et al., 1988). Other models treat the processes independently (Cosby et al., 1985a,c; Gherini et al., 1985). In either case, the weathering modules tend to be used primarily in calibrating stream or lake compositions, because data needed to determine these parameters for individual soils and watersheds are not generally available in sufficient detail to set the values a priori.

3.4.3.2 Modelling Cation Exchange Processes

In contrast to the situation with mineral weathering, cation exchange processes have been examined in detail and have been modelled extensively. Two types of models have been used in describing exchange processes: mass action models and heuristic models. Both types of models, it should be stressed, are empirical and depend on obtaining appropriate descriptive data from the field sites being studied.

The mass action models are based on specific reactions such as the one illustrated in Equation 3-1. For example, Reuss (1983) and Reuss and Johnson (1985, 1986) have developed soil exchange models incorporating the effects of soil gas pCO_2 and soil solution ionic strength as well as the properties of the exchange reactions. Reuss's approach has the advantage of being responsive to a wide range of environmental conditions. The models, however, generally tend to be data intensive.

Heuristic models, in contrast, are based on known or observed relationships between various soil parameters. For example, Bloom and Grigal (1985) developed a model based on the relationship between soil pH and base saturation in selected Minnesota soils. These models have the advantage of providing reasonably accurate descriptions of closely related soils or horizons, and they are less data intensive than the mass action-type models. They are not as flexible, however, in modelling the effects of perturbations to a soil (e.g., changes in soil pCO_2).

In DDRP, both types of models are being used to examine the effects of acidic deposition on the base saturation status of soils in forested watersheds in the NE and SBRP of the United States. Details regarding model formulations are presented in Section 9.

SECTION 4

PROJECT APPROACH

4.1 INTRODUCTION

As H.B.N. Hynes (1975) once noted, "We must not divorce the stream from its valley in our thoughts at any time. If we do we lose touch with reality." Although surface waters can be affected by acidic deposition originating from emissions many miles distant, the concept of the watershed as a unit is critical in understanding current and future aquatic effects. Indeed, for drainage lake and reservoir systems in the Northeast, Upper Midwest, and Southern Blue Ridge Province, most ANC production occurs as a result of biogeochemical processes within the surrounding watershed (Section 7.2; Shaffer et al., 1988; Shaffer and Church, 1989).

Because of the importance of watershed processes (especially those occurring in soils) in determining future aquatic effects, new data on these processes and on related soil pools and capacities were required. Initially, we considered using existing regional soils data in the DDRP analyses. Existing soils databases, however, have serious deficiencies with respect to the needs of the Project. First, because of the economic importance of croplands, such data are available primarily for lowland agricultural regions; surface water acidification, however, occurs principally in relatively undisturbed upland systems. Second, such databases generally do not include chemical characterizations of a number of key variables relevant to soil chemical interactions with acidic deposition (e.g., sulfate adsorption capacity and unbuffered cation exchange capacity).

After consideration of these factors, we decided that a new regional soils database was required, thus necessitating a major soil survey effort (Sections 5.1 - 5.5; also see Lee et al., 1989a; Church, in press). We further concluded that this survey should enable the specific soils (and specific soil types) to be linked with the NSWS databases that describe the chemistry of low ANC lakes and streams. Accordingly, we adopted the approach outlined in this section and illustrated in Figure 4-1.

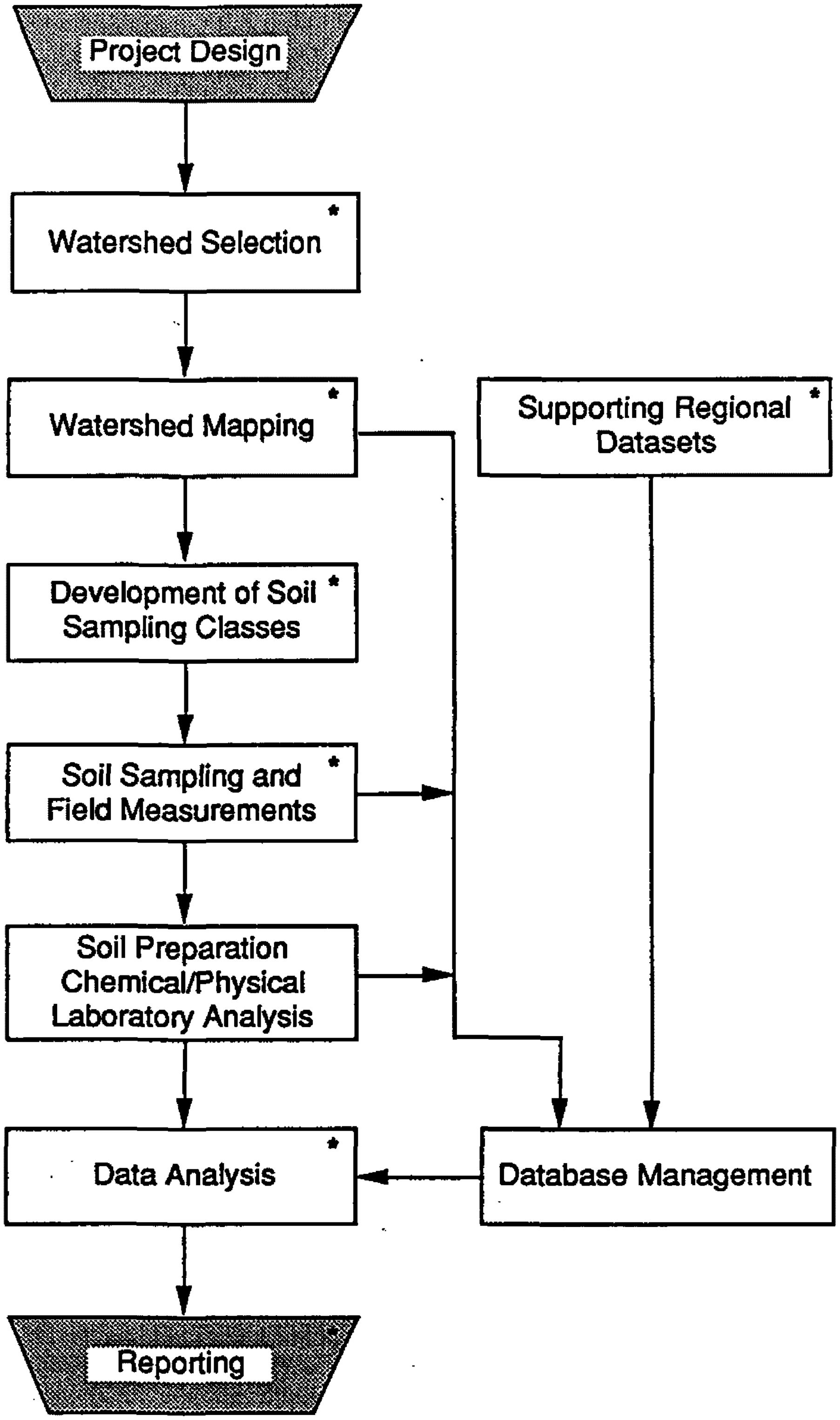


Figure 4-1. Steps of the Direct/Delayed Response Project (DDRP) approach. Asterisks denote steps that received significant support from Geographic Information Systems (GIS)-based activities (Campbell and Church, 1989; Campbell et al., in press).

4.2 SOIL SURVEY

4.2.1 Watershed Selection

The selected DDRP watersheds comprise a high interest subset of lake and stream systems surveyed in the NSWS. A sufficient number of watersheds was selected to allow for (1) reasonably broad regional coverage and (2) statistical examination of interrelationships (deposition:watershed characteristics:surface water chemistry) and model projections of response. Because watersheds were selected as probability samples, results can be extrapolated to a specified population of interest. Further details on watershed selection are provided in Section 5.2 (also see Lee et al., 1989a). Regional population estimation is discussed in Section 6.

4.2.2 Watershed Mapping

Maps of soils, vegetation, land use, and depth to bedrock were prepared for each DDRP watershed by the USDA Soil Conservation Service (SCS). Bedrock geology was obtained from existing state geology maps. SCS mapping was at a scale of 1:24,000 and was at a "second order" intensity (comparable to most county soil surveys). An important part of this mapping was the regional correlation of map unit names and definitions, a common procedure at the county or state level but a much greater challenge at the regional scales of this Project. Additional maps of land use and wetlands were developed by interpreting infrared stereo aerial photographs at a scale of 1:12,000, with land use delineated to 2.5 ha and wetlands to 0.4 ha (Liegel et al., in review). Watershed mapping is discussed in detail in Section 5.4.

4.2.3 Sample Class Definition

Because many soil components were mapped in the study regions (e.g., about 600 in the NE), characterizing each one physically and chemically was not feasible. Instead, sample classes were defined for each region, and individual soils were assigned to those classes based on (1) expert knowledge of the soils mapped and (2) expectations of the potential responses of those soils to acidic deposition. Soils selected from these classes were sampled across the study regions. Soils were aggregated within sampling classes to develop characterizations (e.g., class means and variances) that were used to "rebuild" or represent (e.g., by mass or area weighting) the characteristics of study watersheds. Details of the sample class selection are provided in Section 5.5.1 and by Lee et al. (1989b).

4.2.4 Soil Sampling

We developed a procedure that allowed random selection of soil sampling sites within the context of expert classification. This procedure was designed to ensure that adequate and complete coverage was obtained of both the sampling classes and the watersheds across the regions. Details are given in Sections 5.5.2 and 5.5.3.

4.2.5 Sample Analysis

Samples were analyzed by independent soil laboratories under contract through EPA's Environmental Monitoring and Systems Laboratory - Las Vegas (EMSL-LV). A rigorous quality assurance program was implemented to ensure the quality of these analyses. Sample analyses are discussed in Section 5.5.4.

4.2.6 Database Management

Management of the soil survey databases involved operations at the Environmental Research Laboratory - Corvallis (ERL-C), EMSL-LV, and Oak Ridge National Laboratory (ORNL). Centralized database management was maintained at ORNL with backup at ERL-C. Database management activities in the DDRP are further discussed in Sections 5.4 and 5.5.

4.3 OTHER REGIONAL DATASETS

Because of the regional nature of the Project, we required estimates of precipitation, atmospheric deposition (wet and dry), and surface water runoff (as runoff depth) that were generated in a standardized manner across the eastern United States. Study sites for the DDRP were selected statistically, and most sites had no direct information for the above variables. Furthermore, time and budgetary constraints precluded the instrumentation of sites and, thus, the direct acquisition of such data. These estimates, therefore, had to be developed within the Project.

4.3.1 Atmospheric Deposition

The acquisition/development of internally consistent regional datasets on atmospheric inputs was a challenging task. In effect, two types of datasets were developed. One dataset representing "long-term average annual" conditions was constructed for use in the correlative analyses in the Project (Section 4.4.1). The temporal resolution of this dataset is annual. A second atmospheric deposition dataset was constructed for use in the watershed modelling analyses of the Project (Section 4.4.3). This dataset provides daily estimates of precipitation (to "drive" the hydrologic subroutines of the watershed models) and monthly inputs of atmospheric deposition.

For both datasets, precipitation amount and chemical concentrations were estimated from the Acid Deposition System (ADS) network (Wampler and Olsen, 1987). Wet deposition was determined as the product of these measures. Dry sulfur deposition was estimated from simulations using the Regional Acid Deposition Model (RADM) (R. Dennis and S. Seilkop, personal communication and unpublished internal report, 1987; Clark et al., 1989). Estimates of dry deposition for other ions were not directly available from any source and had to be developed within the Project. The atmospheric data acquisition and development are described in Section 5.6. To our knowledge, this is the first time that such a complete deposition database has been developed on such an extensive regional basis.

4.3.2 Runoff Depth

Because direct runoff measurements were lacking for the selected watersheds, we relied upon regional maps of annual runoff depth. Investigation of the maps available at the start of the Project yielded no single map with a resolution finer than five inches of runoff depth. We therefore enlisted the U.S. Geological Survey (Madison, WI) to produce an annual runoff map for the period 1951-80 (Krug et al., in press), corresponding to long-term precipitation records used to estimate deposition. As part of this work we performed a quantitative uncertainty analysis of estimates of long-term runoff from the Krug et al. map (Rochelle et al., in press-b). Details of the development and application of these runoff data within the Project are given in Section 5.7.1.

4.4 DATA ANALYSIS

A variety of analyses have been undertaken within the Project. Many analyses were performed by the EPA and contractor staff at ERL-C. Others were performed by extramural cooperators in close coordination with ERL-C staff. Data analyses within the Project are classified into three "levels", according to the complexity of the analyses and the degree of reliance upon knowledge, or hypotheses, of process interaction within watersheds. For example, Level I Analyses presuppose the least about our knowledge of the way watersheds "operate", whereas Level III Analyses depend upon more comprehensive knowledge of system behavior.

4.4.1 Level I Analyses

Level I Analyses include constituent input/output budget estimates and statistical analyses. The leaching of the mobile anion sulfate is considered to be a key process in long-term acidification. Accordingly, one part of the Level I Analyses is to determine retention of atmospherically deposited sulfur within watersheds. We examined annual watershed input/output budgets for sulfur, based on detailed studies at a few sites and relatively sparse data from many sites. These analyses and results are presented in Section 7 (for interim results see Rochelle et al., 1987; Rochelle and Church, 1987).

The other part of Level I Analyses is the statistical evaluation of interrelationships among atmospheric deposition, mapped watershed characteristics, soil chemistry, and current surface water chemistry (e.g., see Rochelle et al., in press-a). One goal of this evaluation is to verify that the processes and relationships incorporated in the Level II and III Analyses reasonably represent the systems under study. These analyses (presented in Section 8) are complicated by the fact that the ANC range of the study systems is relatively narrow.

4.4.2 Level II Analyses

The Level II Analyses use relatively restricted models of key processes that regulate the dynamics of (1) base cation supply and (2) watershed retention of atmospherically deposited sulfur. The models are used to project how these processes might affect conditions in the DDRP watersheds and in the surface waters that drain them under continuing or altered future levels of atmospheric sulfur deposition. The models used to investigate and project base cation supply are the "Bloom-Grigal" model (Bloom and Grigal, 1985) and the "Reuss-Johnson" model (Reuss and Johnson, 1985, 1986). Watershed sulfur retention is modeled as sulfate adsorption according to the approach presented by Cosby et al. (1986b). The models are run independently of one another and of other watershed factors, such as forest accretion, that might affect watershed response. The analyses and results are given in Section 9.

4.4.3 Level III Analyses

In the DDRP Level III Analyses, integrated watershed models are used to project future effects of atmospheric sulfur deposition on surface water chemistry. Three models specifically developed to investigate the effects of acidic deposition on watersheds and surface waters are being applied: (1) the Model for Acidification of Groundwater in Catchments (MAGIC) (Cosby et al., 1985a,b,c; Cosby et al., 1986a,b); (2) the Enhanced Trickle Down (ETD) Model (Lee, 1987; Nikolaidis et al., 1988; Schnoor et al., 1986a); and (3) the Integrated Lake-Watershed Acidification Study (ILWAS) Model (Chen et al., 1983; Gherini et al., 1985).

These three models were selected on a competitive, externally peer-reviewed basis via EPA's standard Cooperative Agreement funding mechanism. A sequence was followed that included a public announcement of the Request for Proposals, committee review of pre-proposals, and external peer review of full proposals. Candidates were requested to submit for review only those models that met the following criteria:

> The model to be applied must be capable of time-variable predictions of the effects of acidic deposition on the chemistry of waters delivered from terrestrial systems to streams and lakes. A simplified mechanistic or process-oriented approach is preferred. As such, the model should include representation of those processes commonly considered to be the most important within soil systems (e.g., anion retention, cation exchange, mineral weathering, CO_2 dynamics). It is not required that interactions of deposition within vegetative canopies be simulated, nor is it required that within-lake or within-stream interactions be included (e.g., sulfate reduction in anoxic hypolimnia or in sediments, exchange reactions within sediments). The model must contain its own soil hydrologic component, but significant lumping within this component is allowable (e.g., a standard two-compartment representation).

Although further testing and refinement of the model structure and application is encouraged and expected during the course of the project, the model to be used must be reasonably complete and tested, and in the possession of the applicant at the time of proposal submission.

The three models are run using common datasets for forcing functions (e.g., rainfall, runoff, atmospheric deposition) and state variables (e.g., soil physical and chemical variables). Projections of changes in annual average surface water chemistry are being made for the Northeast (NE) and the Southern Blue Ridge Province (SBRP) for at least 50 years for two scenarios of atmospheric sulfur deposition: (1) continued deposition at current levels (for both regions) and (2) altered deposition over the next 50 years, i.e., a decrease in the NE and an increase in the SBRP (see Section 5.6). Because the models are being applied to watersheds having sparse, but internally consistent regional datasets, reliability checks are being performed using much more complete (in terms of time and space) data from intensively studied watersheds. Such analyses for three of the ILWAS/RILWAS lakes in the NE (Chen et al., 1983) are presented in Section 10. Additionally, confirmation activities continue for White Oak Run, VA (Cosby et al., 1985c) and Coweeta watersheds 34 and 36 (Swank and Crossley, 1987) and will be presented in the DDRP Mid-Appalachian Report. The Level III Analyses and results are presented in Section 10.

4.4.4 Integration of Results

To a large extent, de facto integration of interim results has taken place during the course of the Project with feedback occurring among all levels of analyses. As noted in Section 2, the principal "bottom line" of the DDRP (i.e., time dynamic projections of the long-term effects of sulfur deposition on regional surface water chemistry) comes from the dynamic watershed simulations performed in the Level III Analyses. The manner in which the results from the Level I and II Analyses support and expand upon the Level III findings is presented in Section 11 of this report.

4.4.5 Use of a Geographic Information System

A Geographic Information System (GIS) has played an integral part in the DDRP (Campbell and Church, 1989; Campbell et al., in press). Initial GIS-based activities were data entry (Section 5.4.1.7), display, and spatial analysis of the watershed mapping data from the Soil Survey. Activities have been greatly expanded, however, to include data aggregation, analysis, and display at a variety of scales and projections. The GIS outputs are particularly useful in communicating results to a variety of audiences.

SECTION 6

REGIONAL POPULATION ESTIMATION

6.1 INTRODUCTION

The purpose of this section is to describe the procedures used to extrapolate analyses on individual watersheds to the target populations in the study regions. This process of extrapolation is called population estimation.

6.2 PROCEDURE

6.2.1 Use of Variable Probability Samples

Probability samples were selected for lake watersheds in the Northeast and stream watersheds in the Southern Blue Ridge Province (SBRP). Any quantity that can be defined for a sample unit (i.e., for each watershed) can be extended to a corresponding population quantity through the probabilistic structure of the sample. The quantity can be a measured variable or a model-based estimate. It can be a number, a vector, or a function. In the Eastern Lake Survey (ELS), most quantities were measured values, and the measurement error tended to be small relative to the sampling variation. In contrast to the ELS, many of the quantities produced in the DDRP are model outputs believed to have significant uncertainty associated with them. The population estimation techniques provided below apply to any probability sample with defined inclusion probabilities. Thus, they are applicable to any identifiable subset of the DDRP sample. Explicit provision is made for including uncertainty associated with the quantity that is extended to the regional population.

In the ELS and, hence, the DDRP, the size of the target population is not precisely known. The sampling frame for the ELS consisted of designated lakes on USGS maps. In some cases during field sampling in the ELS, a field visit to the sample lakes selected from this frame indicated that some water bodies designated as lakes on the map actually were not lakes, but rather marshes or old beaver ponds, for example. When these "non-lakes" were subsequently excluded from the sample, a similar proportion of lakes also had to be excluded from the target population, effectively reducing its size. Thus, the size of the target population is estimated from the sample size. This presents no particular difficulty as long as each unit in the sample has a known inclusion probability.

The design of the surface water surveys and the DDRP also permits arbitrary subsetting of the sample. In some cases, the subsetting would correspond to a redefinition of the target population (e.g., the exclusion of seepage lakes). In such cases, the inclusion probabilities for the remaining sample units do not change, which, as can be seen from Equation 6-1 below, implies a smaller target population. In other cases, the subset should be viewed as a subsample. In these cases, a smaller sample is being used to make an inference about the same target population, and the inclusion probabilities do change. This might occur if a selected lake could not be sampled or simulated for some reason. Inferences can still be made about the same target populations, but the inclusion probabilities would change.

6.2.2 Estimation Procedures for Population Means

The structure of the DDRP sample is almost identical to the structure of the ELS Phase II sample. The differences are primarily in the conditional probability of inclusion in the second phase of the sample: the DDRP sample was reduced by exclusion of lakes with large watersheds and the Phase II sample was reduced at random. The estimation procedures are parallel to those detailed in the ELS Phase II Data Analysis Plan (Overton,1987). Let n be the size of the sample selected from the target population, let p_i be the probability that sample unit i was included in the sample, and let p_{ij} be the joint inclusion probability of units i and j. For sample unit i, let y_i be the "true" quantity, and let z_i be the observed quantity, i.e., the unknown true value with an associated error e_i. The error may be an observation error or a measurement error; it could also be a prediction error. In each case we assume that the characteristics of the error distribution are known, and that the uncertainty in the observed values is characterized by that error distribution. The basic estimation procedures will follow the Horvitz-Thompson estimator (Cochran, 1977) for variable probability samples; some details, however, will depend on assumptions made about the observation error. Several distinct error models are treated below.

In one case, the uncertainty is due to an additive error term, so that the magnitude of the uncertainty is constant over the range of the response. The observation is related to the true value through the equation $z_i = y_i + e_i$. Two distributions were available to handle this case: the error term was assumed to have either a normal distribution with mean 0 and variance σ^2 or a uniform distribution over the interval (-a,a). For this uniform distribution, the mean is 0 and $\sigma^2 = a^2/3$.

In a second case, the magnitude of the uncertainty depends on the magnitude of the response. This can be modelled with a multiplicative error term, where the uncertainty is proportional to the response, so that $z_i = y_i e_i$. We assumed that the uncertainty followed a log-normal distribution with a mean value of 1 and a variance $\sigma^2 = RSD^2$, where RSD was the relative standard deviation.

An implication of the above multiplicative model is that the uncertainty goes to 0 along with the response. In some instances, however, there was appreciable uncertainty even when the response was 0. For these cases, we assumed that the uncertainty was proportional to the sum of the response plus an offset (h), so that the observation equation was $z_i = y_i + (y_i + h)e_i = y_i(e_i + 1) + he_i$. The mean value of the error term was 0, and the $\sigma^2 = RSD^2$. As above, a log-normal distribution was used for this case.

The error structure affects only the variance of the population total, the variance of the population mean, and the estimator of the cumulative distribution function and its associated variance. The estimator of the target population size and population total take the same form under all of the above error structures.

Estimator of population total, $\hat{T}$:

$$\hat{T} = \sum_{1}^{n} z_i/p_i \qquad \text{(Equation 6-1)}$$

Estimator of the size of the target population, $\hat{N}$.

$$\hat{N} = \sum_{1}^{n} 1/p_i \qquad \text{(Equation 6-2)}$$

Estimator of population average, $\bar{Y}$:

$$\bar{Y} = \hat{T}/\hat{N} \qquad \text{(Equation 6-3)}$$

Both $\hat{T}$ and $\hat{N}$ are random variables, and both are unbiased estimators of the respective population quantities. However, $\bar{Y}$, similar to most ratio estimators, is a slightly biased estimator of the population average.

6.2.3 Estimators of Variance

For all three error models, the estimator of the variance of $\hat{T}$ has the form

$$\mathrm{Var}(\hat{T}) = \sum_{i}^{n} \frac{(1 - p_i)z_i^2}{p_i^2} + \sum_{i}^{n}\sum_{j>i}^{n} \left(\frac{(p_{ij} - p_i p_j) z_i z_j}{p_i p_j p_{ij}} \right) + g(e,z) \qquad \text{(Equation 6-4)}$$

where g(e,z) is a function that depends on the error model and the sample data. For the additive model, $g(e,z) = \sigma^2 \hat{N}$; for the multiplicative model, $g(e,z) = \sigma^2 \Sigma z_i^2/p_i$, and for the multiplicative model with offset, $g(e,z) = \sigma^2 \Sigma(z_i + h)^2/p_i$, where h is the offset.

The variance of $\hat{N}$ is estimated by

$$\mathrm{Var}(\hat{N}) = \sum_{i}^{n} \frac{(1 - p_i)}{p_i^2} + \sum_{i}^{n}\sum_{j>i}^{n} \left(\frac{(p_{ij} - p_i p_j)}{p_i p_j p_{ij}} \right) + g(e,z) \qquad \text{(Equation 6-5)}$$

The joint inclusion probabilities p_{ij} are determined by the structure of the DDRP sample. They are computed according to the algorithm in the ELS Phase II Analysis Plan (Overton, 1987).

Finally, the variance of the estimator of the population average was obtained from a first-order variance propagation using Equations 6-4 and 6-5:

$$Var(\bar{Y}) = Var(\hat{T})/\hat{N}^2 + \hat{T}^2 Var(\hat{N})/\hat{N}^4 - \hat{T}Cov(\hat{T},\hat{N})/\hat{N}^2, \qquad \text{(Equation 6-6)}$$

where

$$Cov(\hat{T},\hat{N}) = \sum_{i}^{n} \sum_{i>j}^{n} (p_i p_j - p_{ij})(1/p_i - 1/p_j)(z_i/p_i^2 - z_j/p_j^2)$$

Confidence intervals will be derived from the usual normal theory, e.g., a 95 percent CI on the population average is given by

$$\bar{Y} \pm 1.96\sqrt{Var(\bar{Y})}.$$

6.2.4 Estimator of Cumulative Distribution Function

Let N(y) be the total number in the population with the value of Y less than or equal to y, so that the cumulative distribution function of Y is $F_Y(y) = N(y)/N$. An estimator of N(y) is

$$\hat{N}_z(y) = \sum_{z_i \leq y}^{n} 1/p_i = \sum_{i=1}^{n} v_i(y)/p_i,$$

where

$$v_i(y) = \begin{cases} 1, & z_i \leq y \\ 0, & z_i > y \end{cases}$$

An estimator of the cumulative distribution function of Y is

$$\hat{F}_Y(y) = \hat{N}(y)/\hat{N}$$

The variance of $\hat{F}_Y$ has both a sampling component and a component due to measurement uncertainty. The variance of the $\hat{N}(y)$ and covariance of $\hat{N}(y)$ and $\hat{N}$ are needed to calculate the sampling variance of $\hat{F}_Y$. These are given by

$$Var(\hat{N}(y)) = \hat{F}_Y(y)(1-\hat{F}_Y(y))\Sigma\ 1/p_i^2 + \hat{F}_Y^2(y)Var(\hat{N})$$

and

$$Cov(\hat{N},\hat{N}(y)) = \hat{F}_Y(y)Var(\hat{N}).$$

Then a first order variance propagation formula gives

$$Var(\hat{F}_Y) = Var(\hat{N}(y))/\hat{N}^2 + \hat{N}^2(y)Var(\hat{N})/\hat{N}^4 - \hat{N}(y)Cov(\hat{N}(y),\hat{N})/\hat{N}^2$$

for the sampling variance. A Monte Carlo procedure was used to calculate the measurement variance. The sampling variance and the measurement variance were added to obtain total variance. The median and quintiles of the distribution of Y were estimated by the linear interpolation of $\hat{F}_Y$.

6.3 UNCERTAINTY ESTIMATES

The quantities displayed in this report are the end result of a sequence of operations, beginning with collection of a physical sample in the field and ending with the production of a table or graph. A variety of steps were conducted, including chemical analyses, data aggregation, data reduction, and processing of the data through various mathematical models. The final result contains an element of uncertainty that has its origin in the design, in the implementation of the field protocol, and in the precision of the basic measurement process (e.g., the chemical analytic precision). The uncertainty on the final result can be quantified by propagating the uncertainty (or its mathematical analog) through the same sequence of operations as were the data.

In the DDRP, several techniques have been used to propagate uncertainty through a functional relationship (which could be a complex simulation model as well as an explicit function). Let $f(x_1, x_2, \ldots, x_n)$ be a function of the variables $x_1, x_2, \ldots, x_n$ with uncertainties $e_1, e_2, \ldots, e_n$, respectively. The probability distributions (or at the least the variances) of the uncertainties are presumed known. If the functional relationship is such that partial derivatives can be easily obtained, then the variance of functional values can be estimated using a first-order linear approximation to the functional relationship:

$$Var(f) = \Sigma(\partial f/\partial x_i)^2 \sigma_i^2$$

In the case of a simulation model, the function is the model itself, and the partial derivatives cannot be calculated explicitly. An approximation to the partials can be obtained by perturbing the x_i's in turn. If a suitably small perturbation is chosen, then the ratio of the change in output to the perturbation is an estimate of the partial derivative. These estimates can then be used in a first-order propagation as above.

A disadvantage of both of the above techniques is that they ignore possible correlations among the uncertainties. One way to account for such correlations is to propagate not only variances but also covariance terms. The "first-order, second-moment" technique used in the Enhanced Trickle Down uncertainty analysis is a means of doing exactly that. A first-order approximation is made to the model, and Kalman filtering techniques are used to build up an estimate of the state variable variance-covariance matrix. A final method that was used in uncertainty assessment was Monte Carlo. The Monte Carlo method is applied by repeatedly calculating the value of f, each time perturbing the value of each x_i by a random quantity drawn from the respective uncertainty distribution. Monte Carlo is most easily applied when uncertainties are statistically independent, but can also be applied when correlations exist. A variant of Monte Carlo, called "fuzzy optimization", was used in the uncertainty analyses for the Model of Acidification of Groundwater in Catchments.

6.4 APPLICABILITY

This section discusses the procedures for the Level I, II, and III population estimation approaches for DDRP, including the statistical formulas that will be used to estimate population means, variances, and cumulative frequency distributions. The population estimation procedures are generic and do not depend on the level of analysis. The specific target populations for inference, however, do depend on the analyses performed. Not all DDRP watersheds were used at each level of analysis so the target population will vary. The explicit target populations being considered in the analysis are discussed in Sections 8, 9, and 10. The generic uncertainty estimation procedures introduced in this section also are more explicitly discussed for each of the individual analyses in Sections 8, 9, and 10.

SECTION 5

DATA SOURCES AND DESCRIPTIONS

5.1 INTRODUCTION

The purpose of Section 5 is to present sufficient information concerning the design of the Project and data acquisition within the DDRP to familiarize the reader with the characteristics of the regions studied and to allow the reader to evaluate the analyses performed in Sections 7-10. Many data have been generated and used by the Project during its course. Although a complete listing of the data is not presented here, descriptions of the way the data were gathered within the Project or obtained from other sources are presented along with pertinent examples or summaries of the data. As indicated in Section 2.6, a complete listing of the DDRP databases will be presented late in 1989.

5.2 STUDY SITE SELECTION

In selecting study sites, the intent was to focus on regions with watersheds potentially sensitive to acidic deposition (Section 2.3), but exhibiting a wide contrast in both soil and watershed characteristics and levels of deposition.

5.2.1 Site Selection Procedures

The procedures for selecting the DDRP sample watersheds differed somewhat between the NE and the SBRP, primarily because of the differences in the Eastern Lake Survey (ELS) and Pilot Stream Survey sampling designs. Some background on the design of these two surveys is provided here because of their influence on the DDRP design. Complete details are provided by Linthurst et al. (1986a) and Messer et al. (1986a).

5.2.2 Eastern Lake Survey Phase I Design

The ELS Phase I, conducted in the fall of 1984, sampled over 1,600 lakes in the eastern United States, including over 760 lakes in the NE. The sampling approach of the ELS was to use a stratified design with about 50 lakes per stratum. For purposes of the survey, the Northeast Region was divided into subregions based on physiographic features. Each subregion, in turn, was divided into three mapped strata based on the surface water ANC expected to dominate different areas (Figure 5-1). The expected values for ANC in each stratum were based on a national map of surface water ANC that indicated areas with low ANC and, therefore, areas potentially susceptible to acidic deposition (Omernik and Powers, 1983). Stratum 1 had projected ANC < 100 μeq L^{-1}, stratum 2 had projected ANC of 100-200 μeq L^{-1}, and stratum 3 had projected ANC > 200 μeq L^{-1}. A probability sample of about 50 lakes in each stratum was selected from a list of all lakes identifiable on USGS 1:250,000-scale maps using a systematic sample with a random start. Some of the sample lakes were subsequently classified as non-target and eliminated from the sample. The ELS strata included lake populations of differing sizes and, therefore, the inclusion probability for any given lake in the target population varied among strata (Table 5-1).

5.2.3 Pilot Stream Survey Design

The National Stream Survey (NSS) began with a Pilot Survey in the SBRP, the purpose of which was to establish the methodology for conducting a broad regional survey of streams. The Pilot Stream Survey framed the target population by defining a stream reach as the length of "blue-line" stream on USGS 1:250,000-scale maps that lies between the downstream and upstream confluences with other blue-line streams, or the upper stream boundary if no upper confluence is present (Figure 5.2.3-1).

A two-stage sampling approach was used for selecting NSS streams. In the first stage, a point frame was used to select the sample of stream reaches. A rectangular grid of points, separated by a scaled distance of approximately 13 km (8 mi), was positioned at random over a 1:250,000 topographic map. The first stream reach intersected by a line from each point drawn downslope perpendicular to the contour lines was included in the first stage sample. If any portion of the reach extended outside the study region, if the reach drained into a reservoir, or if a watershed was too large (> 155 km^2 (60 mi^2)), the reach was designated non-interest and dropped from the sample. The inclusion probability for a reach in the target population was proportional to the watershed area that drains directly into the reach compared to the total area of the grid square (i.e., ~164 km^2) (Figure 5-2). This is the area in which a grid point had to fall for the reach to be selected.

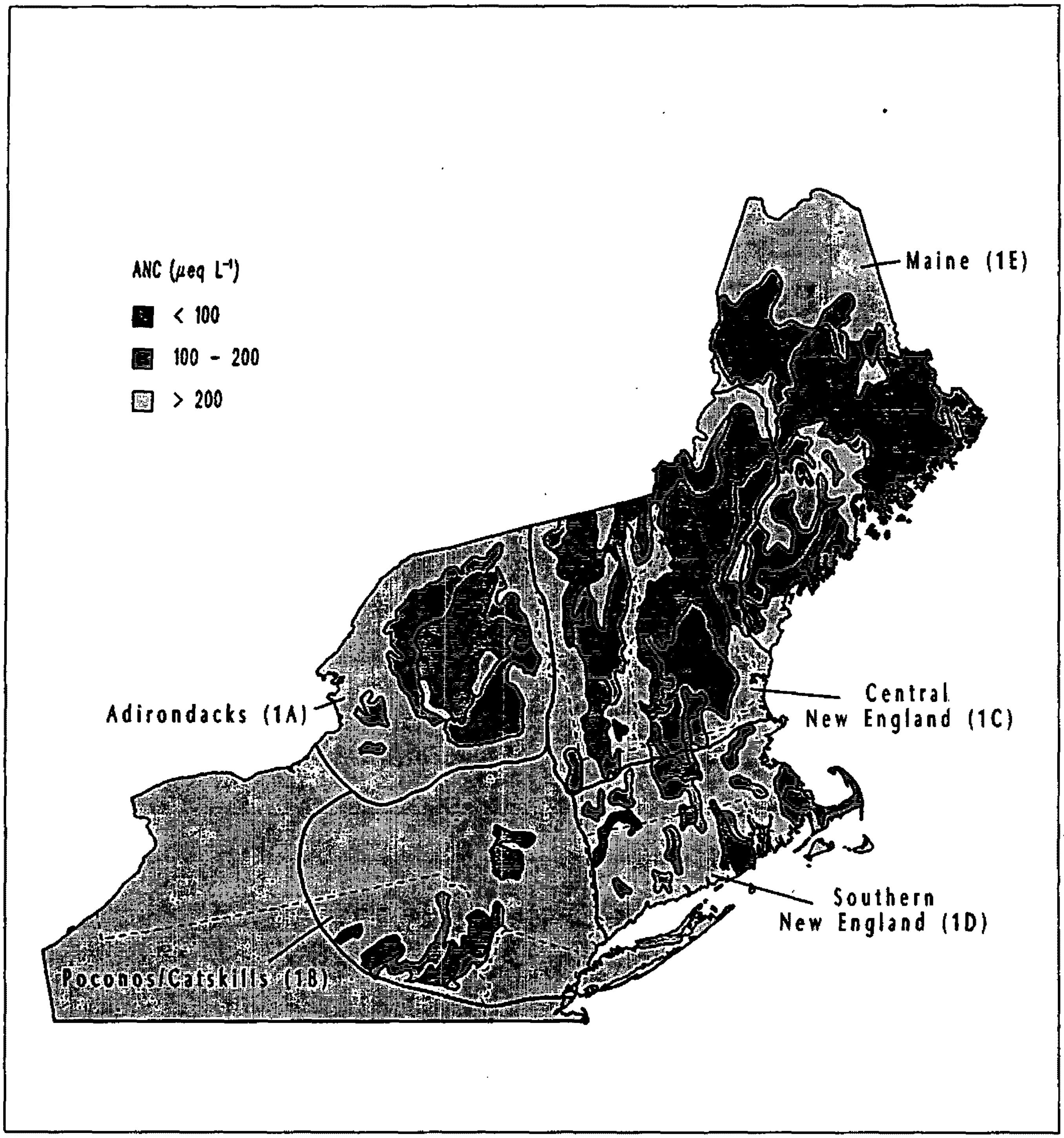


Figure 5-1. Northeastern subregions and ANC map classes, Eastern Lake Survey Phase I (Linthurst et al., 1986a).

Table 5-1. Sampling Structure for Phase I, Region 1 (Northeast), Eastern Lake Survey

Stratum	N*	n	p	w	N̂	SE
A1	711	57	0.1038	9.633	549.08	33.08
A2	542	51	0.1199	8.338	425.24	26.13
A3	431	47	0.1488	6.719	315.79	22.13
B1	208	49	0.3133	3.192	156.41	9.29
B2	96	48	0.6770	1.477	70.90	3.00
B3	1682	47	0.0368	27.209	1278.82	90.37
C1	631	63	0.1278	7.822	492.79	27.31
C2	752	54	0.0931	10.743	580.12	36.20
C3	650	47	0.1117	8.953	420.79	34.59
D1	443	47	0.1522	6.572	308.88	23.00
D2	656	43	0.1448	6.905	296.92	31.14
D3	1568	37	0.0515	19.426	718.76	85.22
E1	1038	89	0.1239	8.070	718.23	39.71
E2	606	48	0.1198	8.344	400.51	31.80
E3	744	41	0.0968	10.333	423.65	41.55

N* = No. of lakes identified on the maps
n = No. of lakes sampled
p = Inclusion probability for each lake in stratum
W = Weight or no. of lakes in the target population ^ represented by that lake. Defined as 1/p.
N̂ = Estimated no. of lakes in the stratum (n*w)
SE = Standard error of the estimate

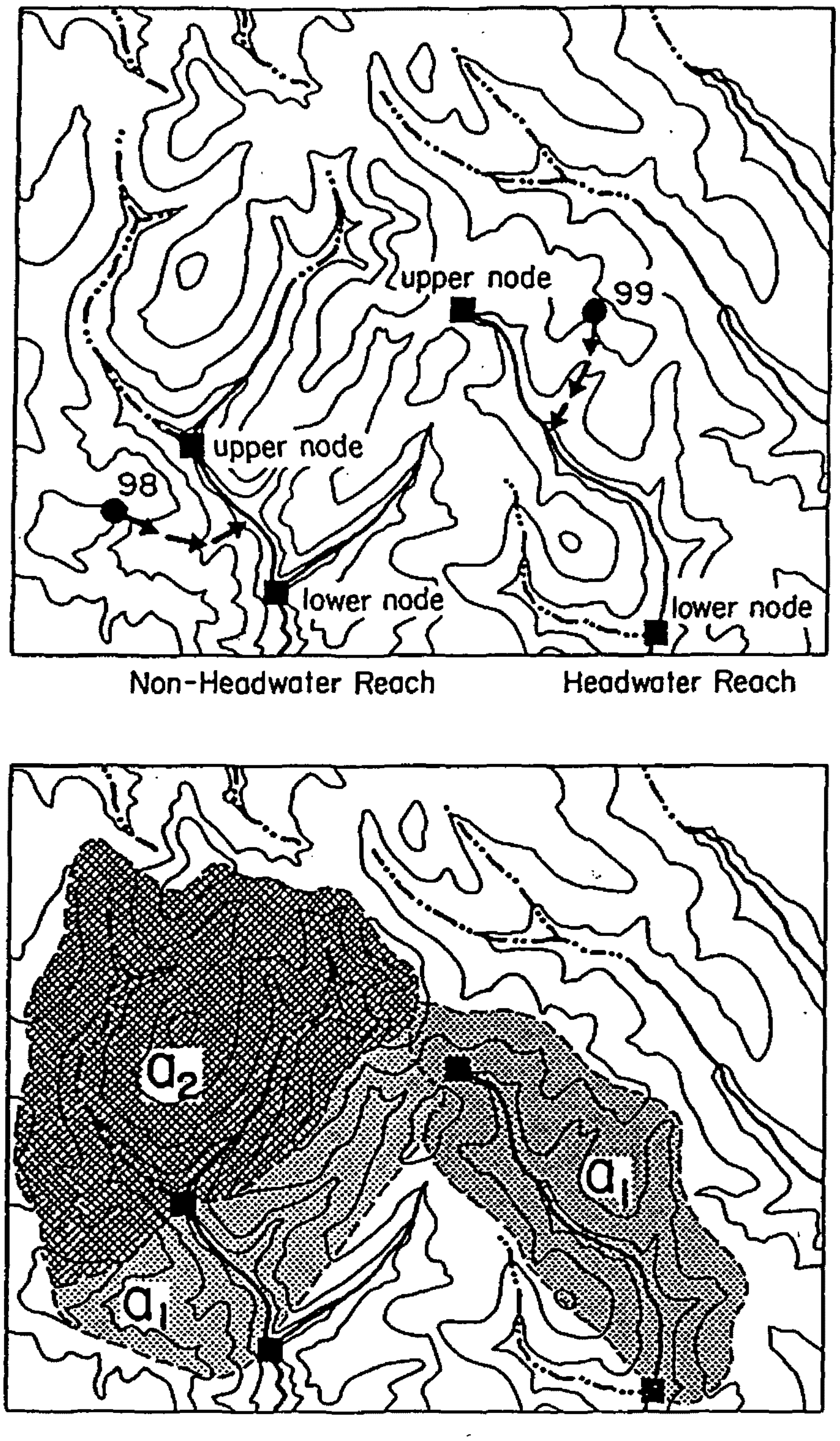


Figure 5-2. Representation of the point frame sampling procedure for selecting NSS Stage I reaches. Area a_1 represents the direct drainage area to the lower node of non-headwater reaches, or the total drainage area to the lower node of headwater reaches. Area a_2 is the total drainage area to the upper node of non-headwater reaches.

The first-stage sample was used to establish physical characteristics of the stream reach population (e.g., distribution of reach lengths and drainage areas). A second-stage sample for chemical sampling was chosen by selecting reaches corresponding to every other grid point.

5.2.4 DDRP Target Population

The DDRP data were obtained from 145 lake watersheds in the NE (a subsample from the ELS Phase I) and 35 stream watersheds in the SBRP (a subset of the streams surveyed in the NSS Pilot Survey).

5.2.4.1 Northeast Lake Selection

At the time the DDRP subsample was selected, lakes for the detailed sampling phase (Phase II) of the ELS also were being chosen. Preliminary data from the ELS Phase I were used to identify lakes of low interest, such as high ANC lakes (ANC > 400 μeq L^{-1}), shallow lakes (<1.5 m deep), or anthropogenically disturbed lakes. These lakes were excluded from consideration as DDRP or Phase II lakes. Very large lakes (surface area > 2000 ha) were placed in a reserved category and also excluded from sampling for the present ELS Phase II or DDRP studies. Logistical considerations for both the DDRP and the Phase II sample limited the number of lakes/watersheds that could be adequately characterized to a total of about 150 lakes. Statistical precision requirements indicated that a sample size of about 50 lakes was required for any subset for which estimates were desired. In order to satisfy these constraints, the remainder of the ELS Phase I sample was split into three groups using cluster analysis on the Phase I chemical data. After examination of the clusters using variables that described the chemical, physical, and pollution status of the lake, the lakes were split into groups based only on ANC. The final division defined the three groups as (1) ANC < 25 μeq L^{-1}; (2) 25 - 100 μeq L^{-1}; and (3) 100 - 400 μeq L^{-1}.

Although the DDRP and Phase II both required a sample size of about 50 lakes per cluster, the DDRP had an additional constraint: watersheds with an area greater than 3000 ha could not be adequately mapped during the DDRP soil survey phase (Section 5.4). To accommodate this constraint, 60 lakes were selected from each of the three ANC groups. The lakes were selected from the clusters using a fixed size, variable probability systematic sampling scheme that resulted in approximately equal inclusion probabilities within groups. The selection probabilities were inversely proportional to Phase I inclusion probabilities, so that the total inclusion probabilities were nearly uniform within groups. (Some Phase I sample lakes had inclusion probabilities sufficiently small, relative to group size and sample size, that they were entered with probability one. These lakes disrupted the within-group uniformity.) Additionally, the Phase II selection was made before final disposition of the ELS Phase I sample lakes, and some lakes were subsequently reclassified. Because this step changed the Phase I inclusion probabilities, it also changed the total DDRP inclusion probabilities. The conditional selection probabilities were fixed by the list at the time of selection and did not change. After the sample was selected, lakes with large watersheds were dropped from the DDRP sample, which resulted in a redefinition of the DDRP target population. The 60-lake sample was randomly reduced to 50 for the Phase II sample. Thus, although there is considerable overlap of DDRP and Phase II (ca. 85 percent), there are lakes in ELS Phase II whose watersheds were not studied by DDRP, and vice versa.

Several lakes also were eliminated from the sample because access was denied to the watershed for mapping or soil sampling. This process was treated as a random deletion, which decreased the sample size but left the target population unchanged. This step resulted in a total sample size of 145 lakes. Subsequent to this sample determination the NSWS recalculated lake ANC values because of some slight errors in the original fitting of the Gran's titration data (J. Eilers, personal communication). The resultant recalculation generally decreased the computed lake ANC values resulting in a shift in sample size for the ANC groups. Again, this affected the sample size but not the target population. The final structure for the DDRP sample is given in Table 5-2; lake ID's, inclusion probabilities, and weights are given in Table 5-3. Further identification of the NE DDRP lake/watersheds is given in Tables 5-4 and 5-5, Figures 5-3 through 5-7, and Plate 5-1.

Table 5-2. Sample Structure for the Direct/Delayed Response Project - Northeastern Sample

ANC Group[a]	n	$\hat{N}$
1	55	796
2	46	1100
3	44	1772
Subtotal	145	3368
Reserved[b]	262	
Total	768	

n = No. of DDRP lakes sampled from the ANC group.
$\hat{N}$ = Estimated no. of lakes in the DDRP target population.

[a] Group 1 = ANC < 25 μeq L^{-1},
Group 2 = 25-100 μeq L^{-1}
Group 3 = ANC > 100 μeq L^{-1}
based on recalculated ANC values (see text for explanation) from the ELS - Phase I (Linthurst et al., 1986a)

[b] Reserved lakes in the ELS - I population that were of low interest (e.g. ANC > 400 μeq L^{-1}) and were placed in a reserved category

Table 5-3. ANC Group, Lake Identification, ELS-I Phase I ANC, Weight and Inclusion Probabilities for the Direct/Delayed Response Project Northeast Sample Watersheds

ANC Group	Lake ID	Phase I ANC (μeq L^{-1})[a]	Weight	Inclusion Probability
1	1A1-003	-21.7	12.2850	0.08140010
1	1A1-012	11.4	12.2850	0.08140010
1	1A1-017	-7.4	12.2850	0.08140010
1	1A1-020	6.0	12.2850	0.08140010
1	1A1-028	1.8	12.2850	0.08140010
1	1A1-039	-1.7	12.2850	0.08140010
1	1A1-049	-30.3	12.2850	0.08140010
1	1A1-057	-18.0	12.2850	0.08140010
1	1A1-061	-53.0	12.2850	0.08140010
1	1A1-066	1.8	12.2850	0.08140010
1	1A1-073	-28.1	12.2850	0.08140010
1	1A2-002	1.8	12.2850	0.08140010
1	1A2-004	-32.0	12.2850	0.08140010
1	1A2-041	22.4	22.4929	0.04445860
1	1A2-042	6.2	12.2850	0.08140010
1	1A2-045	7.8	12.2850	0.08140010
1	1A2-046	12.9	12.2850	0.08140010
1	1A2-048	-5.3	12.2850	0.08140010
1	1A2-052	1.1	12.2850	0.08140010
1	1A2-054	-14.7	12.2850	0.08140010
1	1A3-028	-4.3	12.2850	0.08140010
1	1A3-046	18.2	22.4929	0.04445860
1	1A3-048	7.3	12.2850	0.08140010
1	1A3-065	0.5	12.2850	0.08140010
1	1B1-010	-23.9	12.2850	0.08140010
1	1B1-043	12.1	12.2850	0.08140010
1	1B2-028	14.6	12.5230	0.07985310
1	1B3-052	16.4	27.2090	0.03675250
1	1B3-056	-6.0	27.2090	0.03675250
1	1B3-059	-4.4	27.2090	0.03675250
1	1C1-068	-43.1	12.2850	0.08140010
1	1C2-037	5.5	12.2850	0.08140010
1	1C2-041	2.2	12.2850	0.08140010
1	1C2-048	11.5	22.4929	0.04445860
1	1C2-054	-6.9	12.2850	0.08140010
1	1C2-057	19.6	22.4929	0.04445860
1	1C3-055	-35.2	12.2850	0.08140010
1	1D1-031	2.9	12.2850	0.08140010
1	1D1-034	9.8	12.2850	0.08140010
1	1D1-037	5.3	12.2850	0.08140010
1	1D1-046	13.1	12.2850	0.08140010
1	1D1-056	3.5	12.2850	0.08140010
1	1D1-067	3.6	12.2850	0.08140010
1	1D1-068	-16.9	12.2850	0.08140010
1	1D2-027	-6.0	12.0620	0.08290500

continued

Table 5-3. (Continued)

ANC Group	Lake ID	Phase I ANC (μeq L^{-1})[a]	Weight	Inclusion Probability
1	1D2-036	0.1	12.0620	0.08290500
1	1D2-094	-5.6	12.0620	0.08290500
1	1D3-002	1.6	19.4260	0.05147740
1	1D3-029	-15.2	19.4260	0.05147740
1	1E1-009	11.1	12.4160	0.08054120
1	1E1-011	19.5	22.7327	0.04398960
1	1E1-106	22.7	22.7327	0.04398960
1	1E1-111	6.3	12.4160	0.08054120
1	1E2-038	9.4	12.0540	0.08296000
1	1E2-049	-3.7	12.0540	0.08296000
2	1A1-014	30.0	22.4929	0.04445860
2	1A1-038	97.2	40.4692	0.02471010
2	1A1-046	56.3	22.4929	0.04445860
2	1A1-064	82.9	22.4929	0.04445860
2	1A2-006	33.5	22.4929	0.04445860
2	1A3-001	76.9	22.4929	0.04445860
2	1A3-040	69.2	22.4929	0.04445860
2	1A3-042	30.0	22.4929	0.04445860
2	1B1-023	33.3	22.4929	0.04445860
2	1B1-055	52.9	22.4929	0.04445860
2	1B3-025	30.4	27.7643	0.03601750
2	1B3-041	89.7	27.7643	0.03601750
2	1C1-031	62.9	22.4929	0.04445860
2	1C1-050	63.6	22.4929	0.04445860
2	1C1-084	41.7	22.4929	0.04445860
2	1C1-086	25.7	22.4929	0.04445860
2	1C2-002	69.2	22.4929	0.04445860
2	1C2-012	71.5	22.4929	0.04445860
2	1C2-028	51.7	22.4929	0.04445860
2	1C2-033	97.3	40.4692	0.02471010
2	1C2-035	64.7	22.4929	0.04445860
2	1C2-050	45.0	22.4929	0.04445860
2	1C2-062	36.4	22.4929	0.04445860
2	1C2-064	86.2	22.4929	0.04445860
2	1C2-066	67.7	22.4929	0.04445860
2	1C3-030	86.8	22.4929	0.04445860
2	1D1-027	67.1	22.4929	0.04445860
2	1D1-054	63.4	22.4929	0.04445860
2	1D2-025	71.8	22.0837	0.04528230
2	1D2-074	80.3	22.0837	0.04528230
2	1D3-044	41.5	22.0031	0.04544820
2	1E1-025	98.0	40.9000	0.02444990
2	1E1-040	36.8	22.7327	0.04398960
2	1E1-050	43.8	22.7327	0.04398960
2	1E1-054	33.4	22.7327	0.04398960

continued

Table 5-3. (Continued)

ANC Group	Lake ID	Phase I ANC (μeq L^{-1})[a]	Weight	Inclusion Probability
2	1E1-061	66.0	22.7327	0.04398960
2	1E1-062	86.2	22.7327	0.04398960
2	1E1-073	52.3	22.7327	0.04398960
2	1E1-074	70.2	22.7327	0.04398960
2	1E1-077	81.0	22.7327	0.04398960
2	1E1-082	89.0	22.7327	0.04398960
2	1E1-092	77.5	22.7327	0.04398960
2	1E1-123	74.0	22.7327	0.04398960
2	1E2-007	75.4	22.0694	0.04531160
2	1E2-056	58.8	22.0694	0.04531160
2	1E2-063	25.6	22.0694	0.04531160
3	1A1-029	111.9	40.4692	0.02471010
3	1A1-033	183.2	40.4692	0.02471010
3	1A2-037	161.2	40.4692	0.02471010
3	1A2-039	140.9	40.4692	0.02471010
3	1A2-058	391.6	40.4692	0.02471010
3	1A3-043	238.4	40.4692	0.02471010
3	1B1-029	166.0	40.4692	0.02471010
3	1B3-004	342.7	40.4692	0.02471010
3	1B3-012	342.2	40.4692	0.02471010
3	1B3-019	218.5	40.4692	0.02471010
3	1B3-021	380.8	40.4692	0.02471010
3	1B3-032	332.5	40.4692	0.02471010
3	1B3-043	143.0	40.4692	0.02471010
3	1B3-051	275.3	40.4692	0.02471010
3	1B3-053	245.8	40.4692	0.02471010
3	1B3-060	190.9	40.4692	0.02471010
3	1B3-062	376.4	40.4692	0.02471010
3	1C1-009	105.7	40.4692	0.02471010
3	1C1-017	325.9	40.4692	0.02471010
3	1C1-018	173.3	40.4692	0.02471010
3	1C1-021	122.5	40.4692	0.02471010
3	1C2-016	128.8	40.4692	0.02471010
3	1C2-056	213.0	40.4692	0.02471010
3	1C2-068	285.5	40.4692	0.02471010
3	1C3-031	122.4	40.4692	0.02471010
3	1C3-063	325.9	40.4692	0.02471010
3	1D2-049	107.8	39.7325	0.02516830
3	1D2-084	142.5	39.7325	0.02516830
3	1D2-093	221.1	39.7325	0.02516830
3	1D3-003	154.4	39.5892	0.02525940
3	1D3-020	104.0	39.5892	0.02525940
3	1D3-025	162.1	39.5892	0.02525940
3	1D3-033	368.5	39.5892	0.02525940
3	1E2-002	256.7	39.7075	0.02518420
3	1E2-030	174.3	39.7075	0.02518420
3	1E2-054	228.9	39.7075	0.02518420

continued

Table 5-3. (Continued)

ANC Group	Lake ID	Phase I ANC (μeq L^{-1})[a]	Weight	Inclusion Probability
3	1E2-069	238.1	39.7075	0.02518420
3	1E3-022	222.1	40.4692	0.02471010
3	1E3-040	229.1	40.4692	0.02471010
3	1E3-041	349.4	40.4692	0.02471010
3	1E3-042	162.5	40.4692	0.02471010
3	1E3-045	141.7	40.4692	0.02471010
3	1E3-055	299.5	40.4692	0.02471010
3	1E3-062	153.7	40.4692	0.02471010

[a] Recalculated values (see text for explanation)

Table 5-4. Lake Identification (ID) and Name, and State and Latitudinal/Longitudinal Location of the Northeast Sample Watersheds, Sorted by Lake ID

Lake ID	Lake Name	State	Latitude °	'	"	Longitude °	'	"
1A1-003	Hawk Pond	NY	43	57	25	74	57	30
1A1-012	Whitney Lake	NY	43	35	15	74	33	45
1A1-014	Wilmurt Lake	NY	43	25	45	74	43	30
1A1-017	Constable Pond	NY	43	50	0	74	47	45
1A1-020	Fourth Lake (Bisby Lakes)	NY	43	34	15	74	58	15
1A1-028	Dry Channel Pond	NY	44	21	10	74	26	15
1A1-029	Middle Pond	NY	44	20	20	74	22	45
1A1-033	Kiwassa Lake	NY	44	17	45	74	9	30
1A1-038	Nicks Pond	NY	44	8	35	74	58	5
1A1-039	John Pond	NY	44	6	45	74	45	50
1A1-046	Partlow Lake	NY	44	0	15	74	50	0
1A1-049	Middle South Pond	NY	43	59	22	75	1	6
1A1-057	Hitchcock Lake	NY	43	51	0	75	2	30
1A1-061	Wolf Lake	NY	43	37	45	74	39	15
1A1-064	Mt. Arab Lake	NY	44	11	18	74	36	3
1A1-066	Woodhull Lake	NY	43	35	30	74	59	13
1A1-073	Gull Lakes (South)	NY	43	51	22	74	49	15
1A2-002	St. John Lake	NY	43	26	30	74	3	40
1A2-004	Duck Lake	NY	43	14	8	74	27	9
1A2-006	Lake Frances	NY	44	41	45	74	19	30
1A2-037	Fish Ponds (Northeast)	NY	43	32	50	74	3	40
1A2-039	Oxbow Lake	NY	43	26	30	74	29	0
1A2-041	Mud Lake	NY	43	20	26	74	27	14
1A2-042	North Branch Lake	NY	43	18	45	74	47	40
1A2-045	Woods Lake	NY	43	15	10	74	19	0
1A2-046	Nine Corner Lake	NY	43	11	45	74	33	0
1A2-048	No Name	NY	43	7	39	74	35	20
1A2-052	Chub Lake	NY	43	15	30	74	31	50
1A2-054	Trout Lake	NY	43	20	48	74	42	50
1A2-058	Trout Lake	NY	44	21	47	75	16	8
1A3-001	Nate Pond	NY	43	51	30	74	5	30
1A3-028	Curtis Lake	NY	43	20	10	74	57	40
1A3-040	Zack Pond	NY	43	56	0	74	11	0
1A3-042	Cheney Pond	NY	43	52	40	74	9	45
1A3-043	Unknown Pond	NY	43	49	10	74	17	0
1A3-046	Long Pond	NY	43	38	15	74	17	20
1A3-048	Grass Pond	NY	43	41	35	75	3	40
1A3-065	South Lake (East Branch)	NY	43	30	38	74	53	32
1B1-010	Ganoga Lake	PA	41	21	30	76	19	15
1B1-023	Twin Lakes (Brink P)	PA	41	23	0	74	54	15
1B1-029	No Name (Wilson Creek Dam)	PA	41	17	30	75	14	20
1B1-043	Penn Lake	PA	41	6	45	75	46	10
1B1-055	Rock Hill Pond	PA	41	18	49	75	0	58
1B2-028	Mill Creek Reservoir	PA	41	15	45	75	45	0
1B3-004	Guilford Lake	NY	42	24	45	75	30	0
1B3-012	Little Butler Lake	PA	41	51	45	75	37	40
1B3-019	Hartley Pond	PA	41	39	30	75	42	30
1B3-021	Cord Pond	PA	41	39	10	75	51	0

continued

Table 5-4. (Continued)

Lake ID	Lake Name	State	Latitude °	'	"	Longitude °	'	"
1B3-025	Trout Lake	NY	41	35	10	74	40	50
1B3-032	Wixon Pond	NY	41	23	45	73	44	5
1B3-041	East Stroudsburg Reservoir	PA	41	4	0	75	10	0
1B3-043	Trout Lake	PA	41	0	15	75	20	30
1B3-051	Barrett Pond	NY	41	26	4	73	44	25
1B3-052	No Name	NY	41	29	23	74	32	20
1B3-053	No Name (Snowflake Lake)	PA	41	54	18	75	24	37
1B3-056	Riga Lake	CT	42	1	18	73	29	0
1B3-059	Island Pond	NY	41	15	26	74	8	25
1B3-060	Sly Lake	PA	41	49	25	75	20	14
1B3-062	Bassett Pond	PA	41	35	33	75	42	40
1C1-009	Upper Baker Pond	NH	43	54	30	71	59	30
1C1-017	Welhern Pond	ME	45	12	45	70	29	40
1C1-018	Decker Ponds (Eastern)	ME	45	11	45	69	56	15
1C1-021	Clear Pond	ME	45	6	30	69	59	15
1C1-031	Hunt Pond	ME	44	5	0	71	0	0
1C1-050	Billings Pond	NH	43	17	0	71	56	30
1C1-068	Lincoln Pond	MA	42	40	10	71	54	45
1C1-084	Upper Beech Pond	NH	43	38	54	71	12	15
1C1-086	Star Lake	NH	43	27	43	72	3	20
1C2-002	Iron Pond	ME	45	27	30	70	22	30
1C2-012	Black Pond	ME	44	8	45	70	48	0
1C2-016	Trafton Pond	ME	43	50	45	70	53	30
1C2-028	Sunset Lake	NH	43	28	15	71	18	0
1C2-033	Long Pond	NH	43	12	14	71	48	43
1C2-035	Smith Pond	NH	43	9	15	72	1	45
1C2-037	Mendums Pond	NH	43	10	30	71	4	0
1C2-041	Juggernaut Pond	NH	42	57	35	72	0	45
1C2-048	Cranberry Pond	NY	42	44	40	73	26	0
1C2-050	Moores Pond	MA	42	39	20	72	20	50
1C2-054	Lake Wamponoag	MA	42	37	2	71	57	45
1C2-056	Drury Pond	ME	44	42	15	70	14	30
1C2-057	Babbidge Reservoir	NH	42	56	5	72	13	0
1C2-062	Pemigewasset Lake	NH	43	36	55	71	35	45
1C2-064	Hancock Pond	ME	44	57	20	69	59	10
1C2-066	Turtle Pond	NH	43	15	15	71	31	0
1C2-068	Quimby Pond	ME	44	59	27	70	44	31
1C3-030	Pelham Lake	MA	42	42	0	72	53	30
1C3-031	Sadawaga Lake	VT	42	47	0	72	52	30
1C3-055	Darrah Pond	NH	42	49	52	71	26	40
1C3-063	Martin Meadow Pond	NH	44	26	30	71	36	30
1D1-027	School House Pond	RI	41	24	0	71	40	0
1D1-031	Kings Pond	MA	41	54	40	70	42	15
1D1-033	Rocky Pond	MA	41	53	10	70	41	45
1D1-037	Ezekiel Pond	MA	41	48	15	70	36	45
1D1-046	Robbins Pond	MA	41	42	20	70	6	40
1D1-054	Upper Millpond	MA	41	43	51	70	7	0
1D1-056	Little West Pond	MA	41	55	17	70	42	24
1D1-067	Round Pond	RI	41	58	17	71	46	20

continued

Table 5-4. (Continued)

Lake ID	Lake Name	State	Latitude °	'	"	Longitude °	'	"
1D1-068	Little Sandy Pond	MA	41	47	47	70	36	13
1D2-025	Little Quittacas Pond	MA	41	47	30	70	55	0
1D2-027	Sandy Pond	MA	41	46	20	70	39	15
1D2-036	Micah Pond	MA	41	38	20	70	22	45
1D2-049	Spring Grove Pond	RI	41	54	35	71	39	0
1D2-074	Stetson Pond	MA	42	1	40	70	49	39
1D2-084	Goose Pond	MA	41	41	38	70	0	28
1D2-093	Ashland Reservoir	MA	42	14	22	71	27	52
1D2-094	Snows Pond	MA	41	45	30	70	51	10
1D3-002	Dykes Pond	MA	42	36	15	70	43	46
1D3-003	Sandy Pond	MA	42	33	45	71	33	15
1D3-020	Little Alum Pond	MA	42	7	45	72	9	15
1D3-025	Long Pond	CT	42	1	15	71	49	0
1D3-029	Killingly Pond	CT	41	51	45	71	47	45
1D3-033	No Name	CT	41	39	30	73	11	30
1D3-044	Middle Farms Pond	NY	41	16	30	71	58	40
1E1-009	Peep Lake	ME	44	54	30	67	53	30
1E1-011	Fourth Davis Pond	ME	45	15	30	69	23	40
1E1-021	Bean Ponds (Middle)	ME	45	48	45	69	11	30
1E1-040	Lt. Greenwood Pond (West)	ME	45	22	0	69	24	30
1E1-050	Lower Oxbrook Lake	ME	45	17	0	67	50	30
1E1-054	Duck Lake	ME	45	9	0	68	6	0
1E1-061	Little Seavey Lake	ME	44	56	15	67	38	0
1E1-062	Long Pond	ME	44	55	0	68	16	11
1E1-073	Georges Pond	ME	44	37	0	68	14	30
1E1-074	Craig Pond	ME	44	35	0	68	40	0
1E1-077	Parker Pond	ME	44	22	20	68	42	30
1E1-082	Stevens Pond	ME	44	22	0	69	18	0
1E1-092	Great Pond	ME	44	36	3	68	17	0
1E1-106	Greenwood Pond	ME	45	32	7	69	13	58
1E1-111	Long Pond	ME	44	32	2	68	10	13
1E1-123	First Pond	ME	44	22	10	68	36	0
1E2-002	No Name	ME	45	59	40	69	47	0
1E2-007	Fairbanks Pond	ME	44	23	21	69	49	52
1E2-030	Round Lake	ME	45	1	0	67	16	0
1E2-038	Nelson Pond	ME	44	24	55	70	15	45
1E2-049	Gross Pond	ME	44	3	30	69	23	35
1E2-054	Brettuns Pond	ME	44	23	30	70	15	0
1E2-056	Peabody Pond	ME	43	56	32	70	41	13
1E2-063	Kalers Pond	ME	44	6	29	69	25	22
1E2-069	No Name	ME	46	7	27	68	46	45
1E3-022	Number Nine Lake	ME	46	25	0	68	3	0
1E3-040	Nokomis Pond	ME	44	52	15	69	18	0
1E3-041	Round Pond	ME	44	44	20	69	13	30
1E3-042	Sand Pond	ME	44	34	10	70	7	10
1E3-045	McClure Pond	ME	44	29	0	68	57	50
1E3-055	Togue Pond	ME	46	56	2	68	53	31
1E3-062	Cain Pond	ME	44	29	32	68	58	3

continued

Table 5-5. Lake Identification (ID) and Name, Sorted by State – Northeast Sample Watersheds

State	Lake ID	Lake Name
CT	1B3-056	Riga Lake
CT	1D3-025	Long Pond
CT	1D3-029	Killingly Pond
CT	1D3-033	No Name
MA	1C1-068	Lincoln Pond
MA	1C2-050	Moores Pond
MA	1C2-054	Lake Wamponoag
MA	1C3-030	Pelham Lake
MA	1D1-031	Kings Pond
MA	1D1-034	Rocky Pond
MA	1D1-037	Ezekiel Pond
MA	1D1-046	Robbins Pond
MA	1D1-054	Upper Millpond
MA	1D1-056	Little West Pond
MA	1D1-068	Little Sandy Pond
MA	1D2-025	Little Quittacas Pond
MA	1D2-027	Sandy Pond
MA	1D2-036	Micah Pond
MA	1D2-074	Stetson Pond
MA	1D2-084	Goose Pond
MA	1D2-093	Ashland Reservoir
MA	1D2-094	Snows Pond
MA	1D3-002	Dykes Pond
MA	1D3-003	Sandy Pond
MA	1D3-020	Little Alum Pond
ME	1C1-017	Welhern Pond
ME	1C1-018	Decker Ponds (Eastern)
ME	1C1-021	Clear Pond
ME	1C1-031	Hunt Pond
ME	1C2-002	Iron Pond
ME	1C2-012	Black Pond
ME	1C2-016	Trafton Pond
ME	1C2-056	Drury Pond
ME	1C2-064	Hancock Pond
ME	1C2-068	Quimby Pond
ME	1E1-009	Peep Lake
ME	1E1-011	Fourth Davis Pond
ME	1E1-025	Bean Ponds (Middle)
ME	1E1-040	Lt. Greenwood Pond (West)
ME	1E1-050	Lower Oxbrook Lake
ME	1E1-054	Duck Lake
ME	1E1-061	Little Seavey Lake
ME	1E1-062	Long Pond
ME	1E1-073	Georges Pond
ME	1E1-074	Craig Pond
ME	1E1-077	Parker Pond
ME	1E1-082	Stevens Pond
ME	1E1-092	Great Pond

continued

Table 5-5. (Continued)

State	Lake ID	Lake Name
ME	1E1-106	Greenwood Pond
ME	1E1-111	Long Pond
ME	1E1-123	First Pond
ME	1E2-002	No Name
ME	1E2-007	Fairbanks Pond
ME	1E2-030	Round Lake
ME	1E2-038	Nelson Pond
ME	1E2-049	Gross Pond
ME	1E2-054	Brettuns Pond
ME	1E2-056	Peabody Pond
ME	1E2-063	Kalers Pond
ME	1E2-069	No Name
ME	1E3-022	Number Nine Lake
ME	1E3-040	Nokomis Pond
ME	1E3-041	Round Pond
ME	1E3-042	Sand Pond
ME	1E3-045	McClure Pond
ME	1E3-055	Togue Pond
ME	1E3-062	Cain Pond
NH	1C1-009	Upper Baker Pond
NH	1C1-050	Billings Pond
NH	1C1-084	Upper Beech Pond
NH	1C1-086	Star Lake
NH	1C2-028	Sunset Lake
NH	1C2-033	Long Pond
NH	1C2-035	Smith Pond
NH	1C2-037	Mendums Pond
NH	1C2-041	Juggernaut Pond
NH	1C2-057	Babbidge Reservoir
NH	1C2-062	Pemigewasset Lake
NH	1C2-066	Turtle Pond
NH	1C3-055	Darrah Pond
NH	1C3-063	Martin Meadow Pond
NY	1A1-003	Hawk Pond
NY	1A1-012	Whitney Lake
NY	1A1-014	Wilmurt Lake
NY	1A1-017	Constable Pond
NY	1A1-020	Fourth Lake (Bisby Lakes)
NY	1A1-028	Dry Channel Pond
NY	1A1-029	Middle Pond
NY	1A1-033	Kiwassa Lake
NY	1A1-038	Nicks Pond
NY	1A1-039	John Pond
NY	1A1-046	Partlow Lake
NY	1A1-049	Middle South Pond
NY	1A1-057	Hitchcock Lake
NY	1A1-061	Wolf Lake
NY	1A1-064	Mt. Arab Lake
NY	1A1-066	Woodhull Lake

continued

Table 5-5. (Continued)

State	Lake ID	Lake Name
NY	1A1-073	Gull Lakes (South)
NY	1A2-002	St. John Lake
NY	1A2-004	Duck Lake
NY	1A2-006	Lake Frances
NY	1A2-037	Fish Ponds (Northeast)
NY	1A2-039	Oxbow Lake
NY	1A2-041	Mud Lake
NY	1A2-042	North Branch Lake
NY	1A2-045	Woods Lake
NY	1A2-046	Nine Corner Lake
NY	1A2-048	No Name
NY	1A2-052	Chub Lake
NY	1A2-054	Trout Lake
NY	1A2-058	Trout Lake
NY	1A3-001	Nate Pond
NY	1A3-028	Curtis Lake
NY	1A3-040	Zack Pond
NY	1A3-042	Cheney Pond
NY	1A3-043	Unknown Pond
NY	1A3-046	Long Pond
NY	1A3-048	Grass Pond
NY	1A3-065	South Lake (East Branch)
NY	1B3-004	Guilford Lake
NY	1B3-025	Trout Lake
NY	1B3-032	Wixon Pond
NY	1B3-051	Barrett Pond
NY	1B3-052	No Name
NY	1B3-059	Island Pond
NY	1C2-048	Cranberry Pond
NY	1D3-044	Middle Farms Pond
PA	1B1-010	Ganoga Lake
PA	1B1-023	Twin Lakes (Brink P)
PA	1B1-029	No Name (Wilson Creek Dam)
PA	1B1-043	Penn Lake
PA	1B1-055	Rock Hill Pond
PA	1B2-028	Mill Creek Reservoir
PA	1B3-012	Little Butler Lake
PA	1B3-019	Hartley Pond
PA	1B3-021	Cord Pond
PA	1B3-041	East Stroudsburg Reservoir
PA	1B3-043	Trout Lake
PA	1B3-053	No Name (Snowflake Lake)
PA	1B3-060	Sly Lake
PA	1B3-062	Bassett Pond
RI	1D1-027	School House Pond
RI	1D1-067	Round Pond
RI	1D2-049	Spring Grove Pond
VT	1C3-031	Sadawga Lake

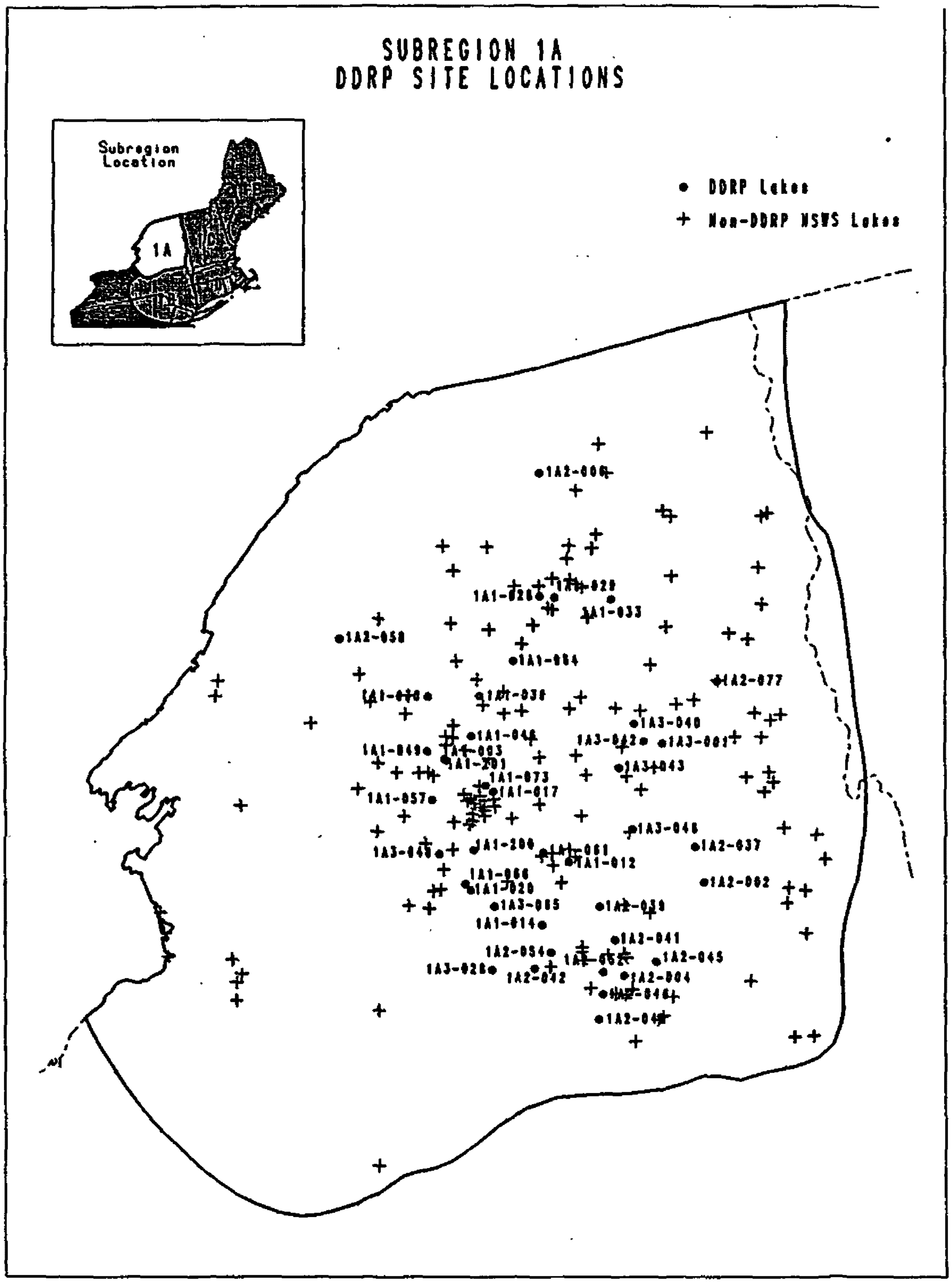


Figure 5-3. DDRP site locations for Subregion 1A.

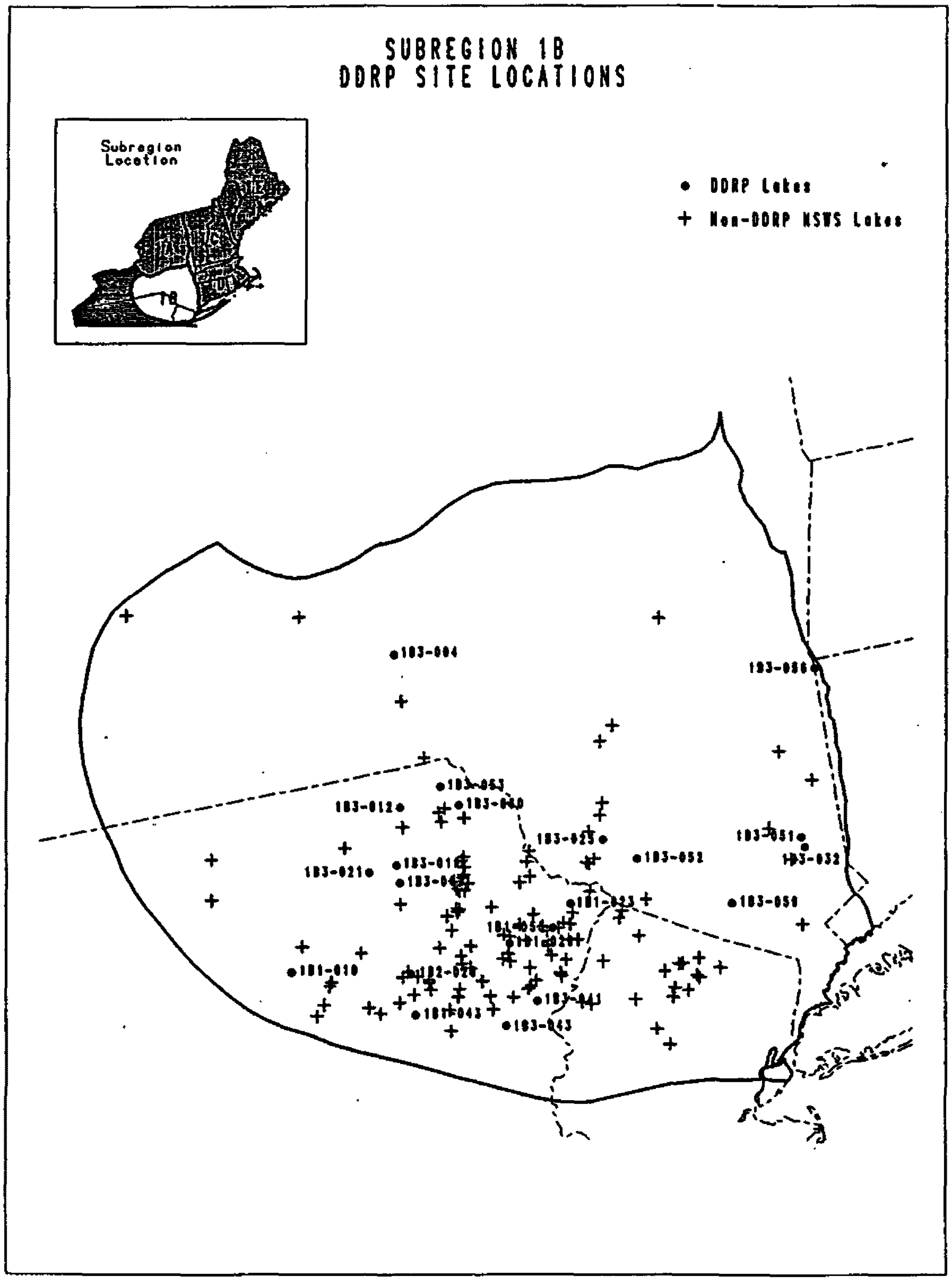


Figure 5-4. DDRP site locations for Subregion 1B.

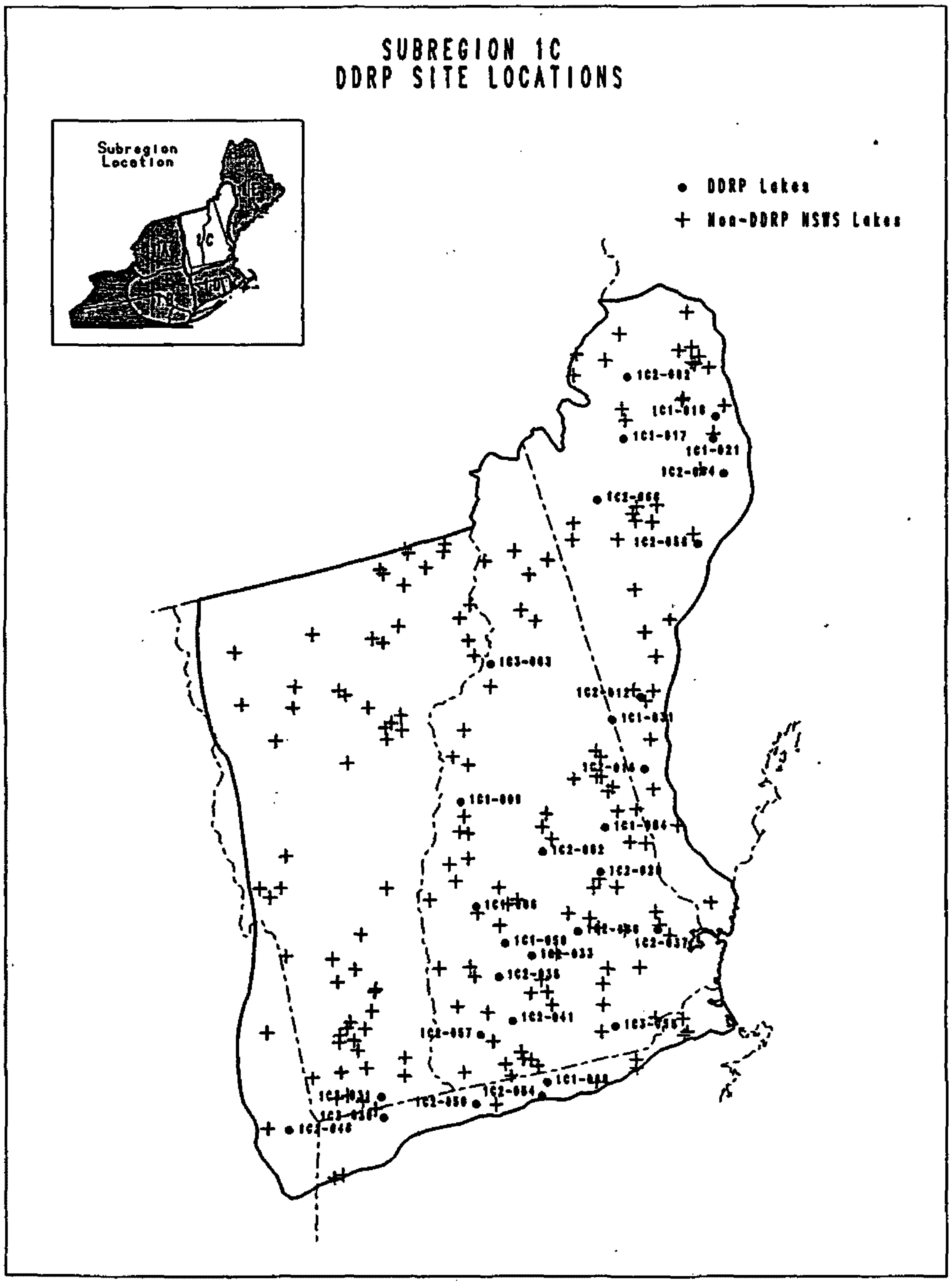


Figure 5-5. DDRP site locations for Subregion 1C.

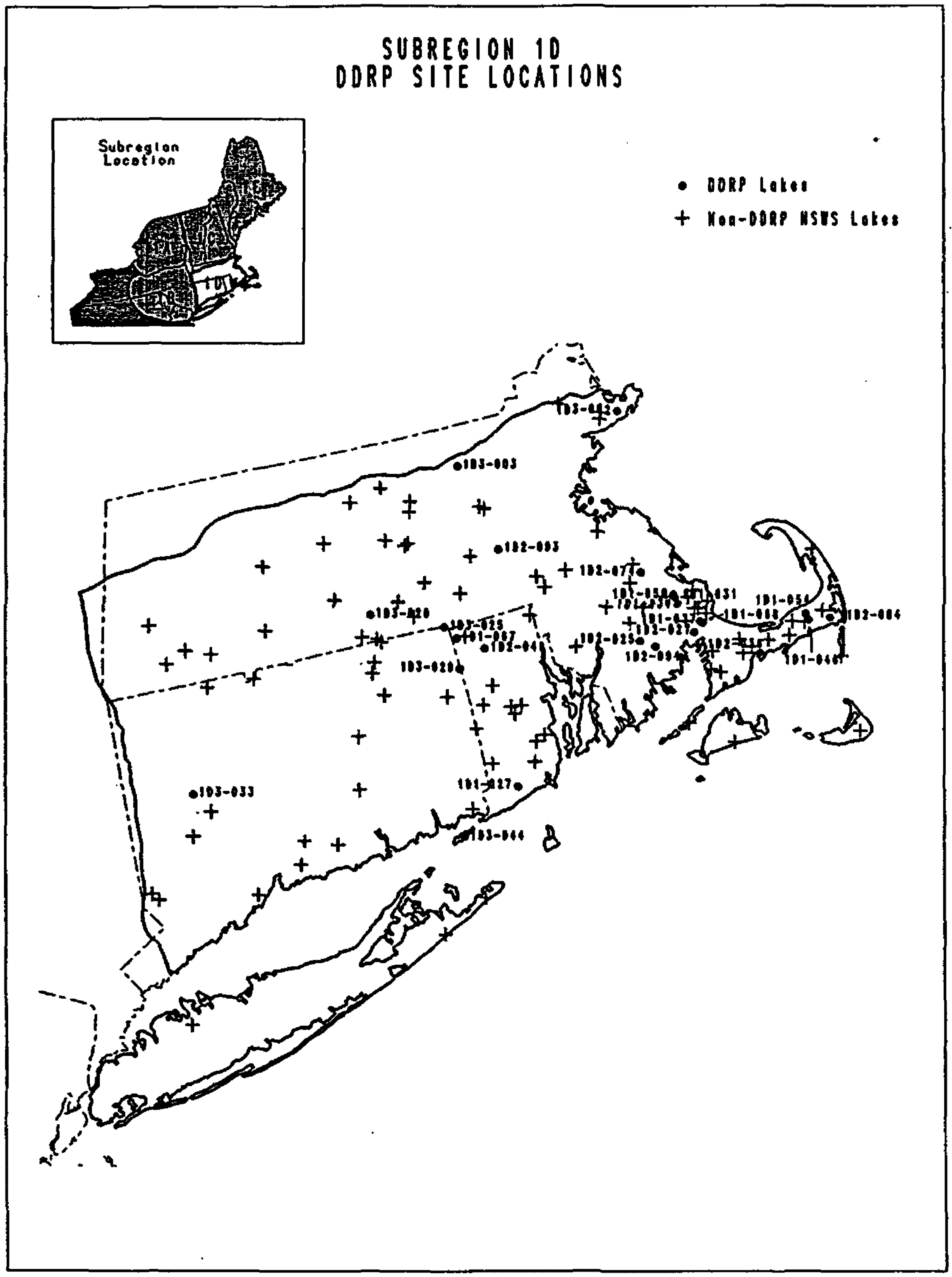


Figure 5-6. DDRP site locations for Subregion 1D.

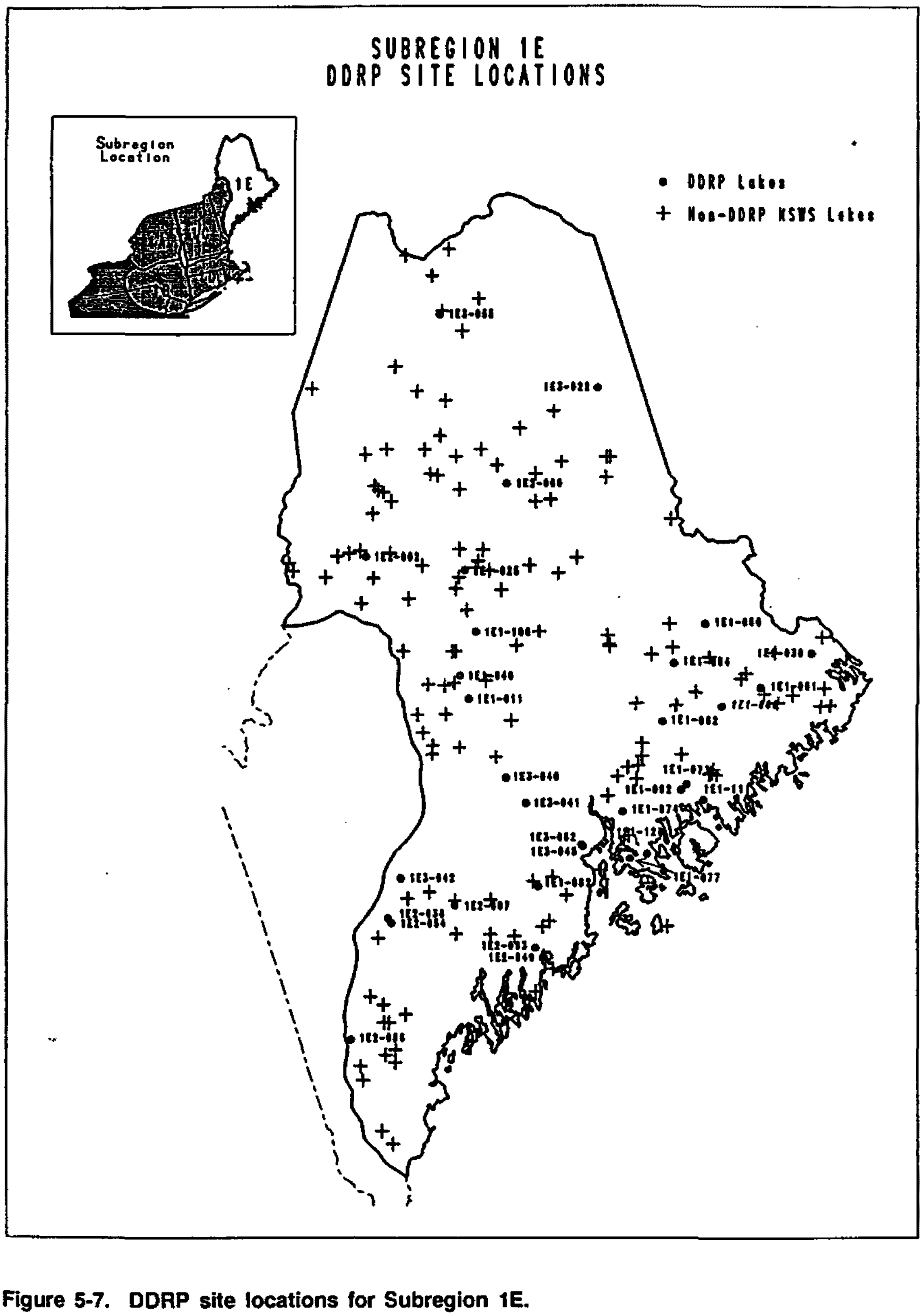
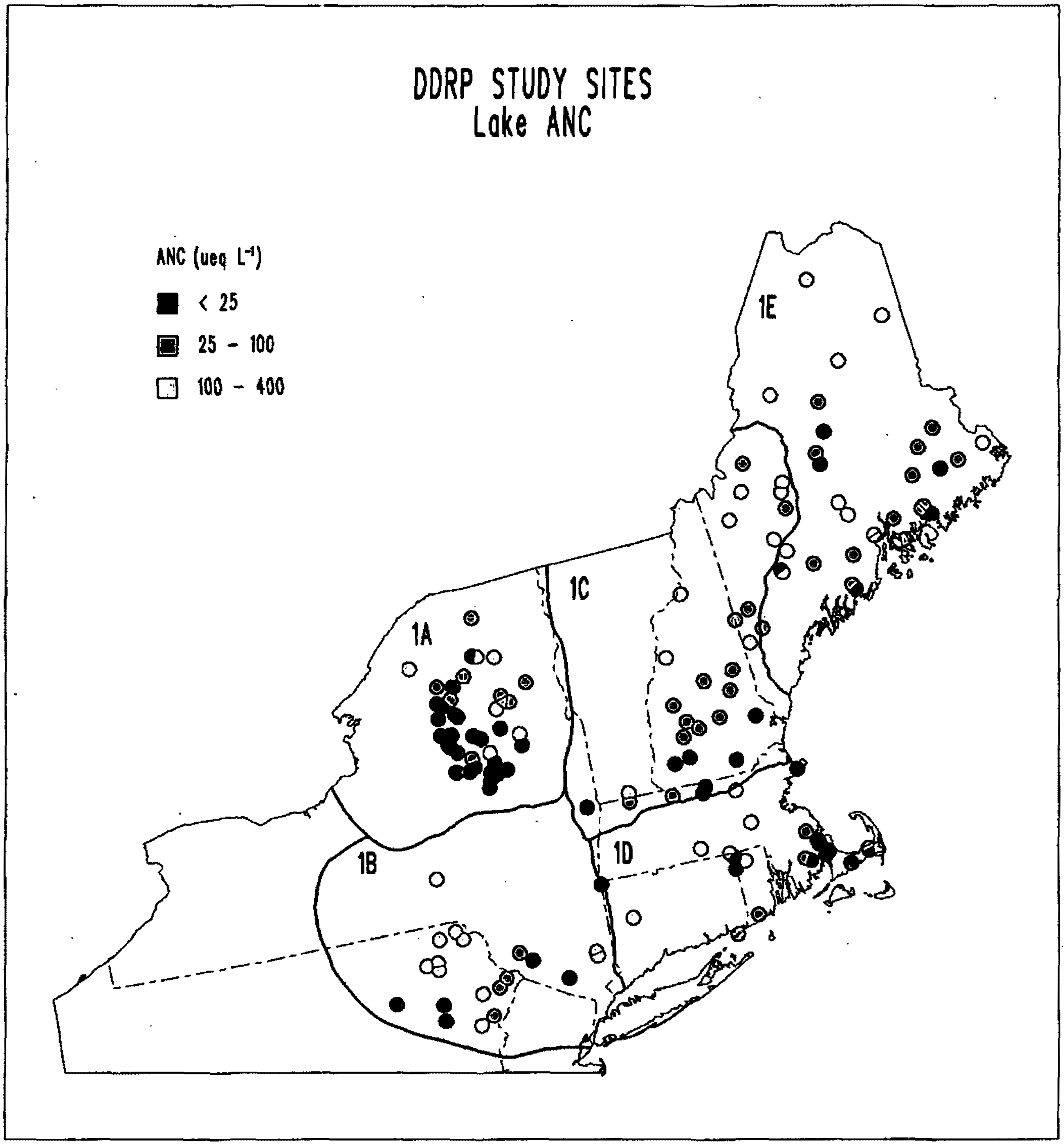


Figure 5-7. DDRP site locations for Subregion 1E.

Plate 5-1. ANC of DDRP lakes by ANC group.



DDRP STUDY SITES
Lake ANC
ANC (ueq L-1)
< 25
25 - 100
100 - 400
1A
1B
1C
1D
1E

5.2.4.2 Southern Blue Ridge Province Stream Selection

Fifty-one stream reaches were sampled for water chemistry in the Pilot Stream Survey. Of these, only 35 had watersheds less than 3000 ha (as defined based on the downstream sampling node), the maximum size suitable for mapping within the DDRP. All of these 35 stream reaches were included in the DDRP. As for the NE, eliminating streams with large watersheds has the effect of re-defining the target population. The sampling structure stream ID's, inclusion probabilities, and weights for DDRP SBRP streams are given in Table 5-6. Further information is provided in Tables 5-7 and 5-8 and in Figure 5-8.

5.2.4.3 Final DDRP Target Populations

5.2.4.3.1 Northeast -

The final DDRP target population for the northeastern lakes represents 3,668 lakes, based on a sample size of 145 lakes subsampled from the ELS Phase I target population. The target population represents lakes with watershed areas greater than 4 ha and less than 3,000 ha and ANC concentrations less than 400 $\mu eq\ L^{-1}$. The comparable ELS Phase I target population represented 7,157 lakes.

5.2.4.3.2 Southern Blue Ridge Province -

The final DDRP target population for the SBRP represents 1,531 streams based on a sample size of 35 watersheds from the NSS Pilot Survey that satisfied the DDRP selection criteria. The SBRP target population represents stream reaches with watershed areas less than 3,000 ha and ANC concentrations less than 400 $\mu eq\ L^{-1}$. The comparable NSS Pilot target population represented 2,021 stream reaches.

5.3 NSWS LAKE AND STREAM DATA

5.3.1 <u>Lakes in the Northeast Region</u>

5.3.1.1 Lake Hydrologic Type

The NSWS classified lakes of the NE by hydrologic type, as described in the following paragraph.

> "Lakes were classified by hydrologic type (Wetzel, 1983) through visual examination of their morphology on the largest-scale topographic maps available. "Seepage" lakes were defined as those lakes having no inlet or outlet. "Closed" lakes

Table 5-6. Stream Identification (ID), Weight, and Inclusion Probabilities for the Southern Blue Ridge Province Direct/Delayed Response Project Sample Watersheds

Stream ID	ANC (μeq L^{-1})	Weight	Probability
Inclusion			
2A07701	89.3	15.44026	0.06477
2A07702	1,218.8	30.33178	0.03297
2A07703	145.2	32.65306	0.03063
2A07802	219.5	17.46253	0.05727
2A07803	1710.5	64.64653	0.01547
2A07805	98.8	93.43066	0.01070
2A07806	104.4	22.85709	0.04375
2A07811	16.2	26.72230	0.03742
2A07812	102.7	43.68692	0.02289
2A07813	371.7	13.34720	0.07492
2A07816	56.5	10.82906	0.09234
2A07817	30.4	12.36710	0.08086
2A07821	126.5	50.39373	0.01984
2A07823	102.5	16.93120	0.05906
2A07826	347.7	31.37254	0.03188
2A07827	234.7	32.32320	0.03094
2A07828	48.2	17.39136	0.05750
2A07829	64.8	15.12998	0.06609
2A07830	217.2	23.65990	0.04227
2A07833	211.8	21.47648	0.04656
2A07834	43.2	28.44442	0.03516
2A07835	96.3	11.99629	0.08336
2A07882	106.5	57.65760	0.01734
2A08801	1497.7	75.73965	0.01320
2A08802	87.8	58.44749	0.01711
2A08803	171.1	50.39373	0.01984
2A08804	58.6	129.29292	0.00773
2A08805	118.2	38.67072	0.02586
2A08806	164.3	213.33337	0.00469
2A08808	202.8	39.87533	0.02508
2A08810	138.0	68.08512	0.01469
2A08811	121.3	99.22483	0.01008
2A08901	120.5	17.08941	0.05852
2A08904	186.5	25.49798	0.03922
2A08906	72.7	25.19680	0.03969

[a] Recalculated values (see text for explanation)

Table 5-7. Stream Identification (ID) and Name, and State and Latitudinal/Longitudinal Location of the Southern Blue Ridge Province Sample Watersheds, Sorted by Stream ID

Stream ID	Stream Name	State	Latitude °	'	"	Longitude °	'	"
2A07701	Sugar Cove Creek	TN	35	19	20	84	6	1
2A07702	Childers Creek	TN	35	11	25	84	29	23
2A07703	Hall Creek	NC	35	5	44	84	19	32
2A07802	Puncheon Creek	NC	35	54	36	82	32	56
2A07803	Chestnut Flats Branch	NC	35	46	48	83	47	47
2A07805	Cosby Creek	NC	35	47	37	83	14	22
2A07806	Roaring Fork	NC	35	49	17	82	53	33
2A07811	False Gap	NC	35	41	59	83	23	2
2A07812	Correll Branch	NC	35	40	33	83	5	19
2A07813	Little Sandymush	NC	35	42	12	82	45	38
2A07816	Eagle Creek	TN	35	29	54	83	45	49
2A07817	Forney Creek	NC	35	30	48	83	33	28
2A07821	Grassy Creek	NC	35	27	51	82	16	55
2A07823	Brush Creek	NC	35	19	8	83	31	0
2A07826	Henderson Creek	NC	35	22	42	82	23	5
2A07827	Welch Mill Creek	NC	35	11	6	83	53	38
2A07828	White Oak Creek	NC	35	13	33	83	37	7
2A07829	Catheys Creek	NC	35	12	48	82	47	9
2A07830	Mud Creek	NC	35	15	17	82	30	2
2A07833	Allison Creek	NC	35	7	17	83	28	28
2A07834	Brush Creek	NC	35	6	50	83	15	28
2A07835	Middle Saluda River	SC	35	7	14	82	32	19
2A07882	Little Branch Creek	NC	35	26	59	83	3	50
2A08801	Perry Creek Tributary	GA	34	57	37	84	44	13
2A08802	Dunn Mill Creek	GA	34	56	57	84	26	18
2A08803	Owenby Creek	GA	34	59	13	84	8	47
2A08804	Bear Creek	GA	34	49	28	84	33	58
2A08805	Weaver Creek	GA	34	52	16	84	18	0
2A08806	Kiutuestia Creek Trib.	GA	34	51	32	84	1	25
2A08808	White Path Creek	GA	34	44	15	84	25	59
2A08810	Bryant Creek	GA	34	36	35	83	59	57
2A08811	Hinton Creek	GA	34	29	7	84	25	17
2A08901	Persimmon Creek	GA	34	54	47	83	30	7
2A08904	She Creek	GA	34	50	6	83	20	42
2A08906	Deep Creek	GA	34	40	37	83	27	22

Table 5-8. Stream Identification (ID) and Name, Sorted by State – Southern Blue Ridge Province Sample Watersheds

State	Stream ID	Stream Name
GA	2A08801	Perry Creek Tributary
GA	2A08802	Dunn Mill Creek
GA	2A08803	Owenby Creek
GA	2A08804	Bear Creek
GA	2A08805	Weaver Creek
GA	2A08806	Kiutuestia Creek Tributary
GA	2A08808	White Path Creek
GA	2A08810	Bryant Creek
GA	2A08811	Hinton Creek
GA	2A08901	Persimmon Creek
GA	2A08904	She Creek
GA	2A08906	Deep Creek
NC	2A07703	Hall Creek
NC	2A07802	Puncheon Creek
NC	2A07805	Cosby Creek
NC	2A07806	Roaring Fork
NC	2A07811	False Gap
NC	2A07812	Correll Branch
NC	2A07813	Little Sandymush
NC	2A07817	Forney Creek
NC	2A07821	Grassy Creek
NC	2A07823	Brush Creek
NC	2A07826	Henderson Creek
NC	2A07827	Welch Mill Creek
NC	2A07828	White Oak Creek
NC	2A07829	Cathey's Creek
NC	2A07830	Mud Creek
NC	2A07833	Allison Creek
NC	2A07834	Brush Creek
NC	2A07882	Little Branch Creek
SC	2A07835	Middle Saluda River
TN	2A07701	Sugar Cove Creek
TN	2A07702	Childers Creek
TN	2A07803	Chestnut Flats Branch
TN	2A07816	Eagle Creek

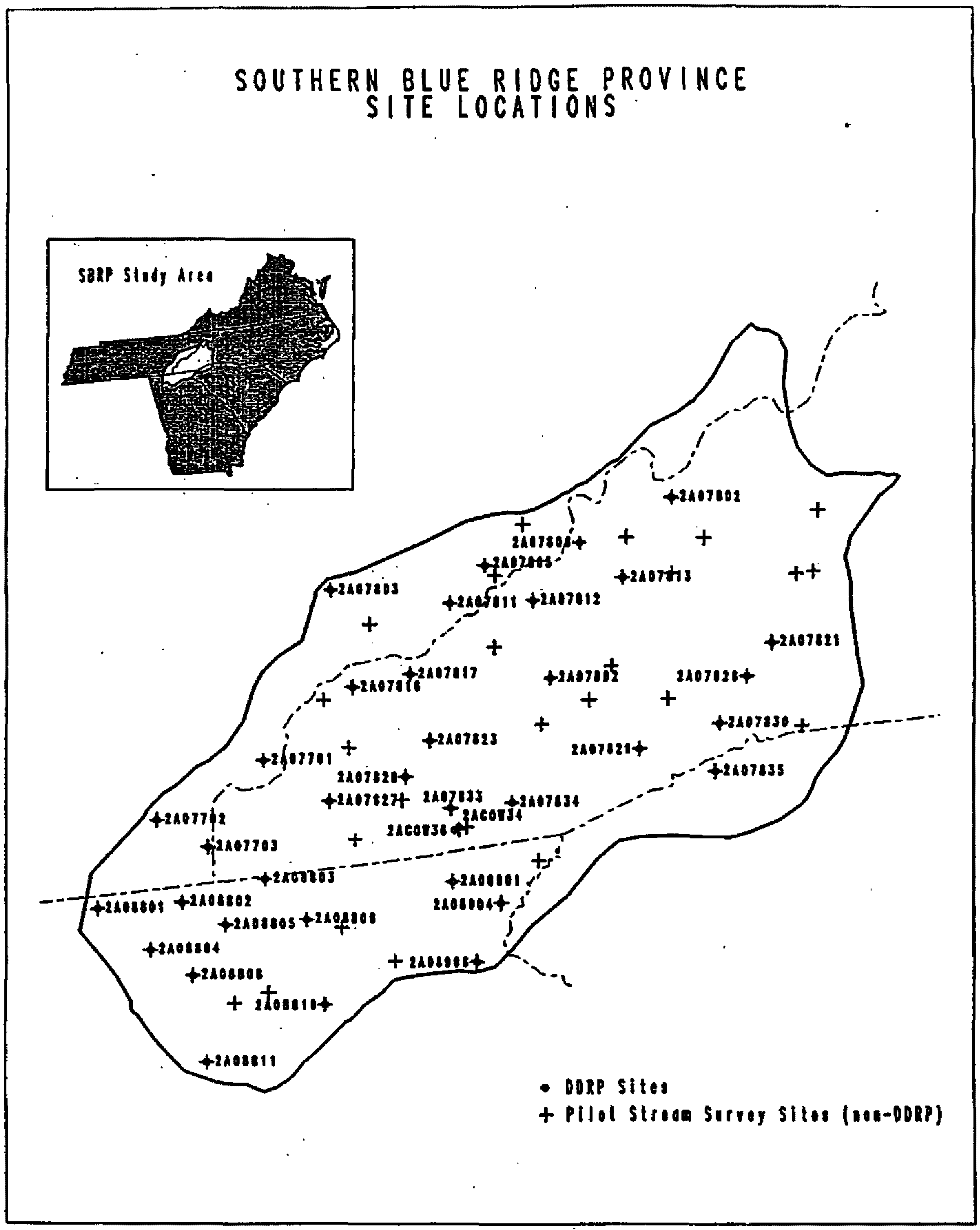


Figure 5-8. DDRP stream reach study sites in the Southern Blue Ridge Province.

were those with inlets and no outlets. Lakes with outlets but no inlets or with both were termed "drainage" lakes. A fourth category comprised artificial lakes or "reservoirs"." (From Linthurst et al., 1986a; Section 2.4.3 "Lake Type")

During the course of DDRP field mapping, aerial photo-interpretation, and field auditing and checking (see Section 5.4), we found that numerous lakes classified by the NSWS as seepage or closed actually fit the NSWS classification of drainage lakes. Lakes falling in the DDRP sample that were originally classified by the NSWS as seepage or closed are indicated in Table 5-9 along with their final classification by the DDRP. The final DDRP classification of lake hydrologic type for the entire DDRP sample is shown in Plates 5-2 through 5-6. This classification is often important in determining to which lakes or watersheds certain analyses are applied (e.g., see Section 7.2.2).

5.3.1.2 Fall Index Sampling

As discussed in Section 5.2, the DDRP was designed in a manner consistent with and dependent upon the NSWS sampling of lakes and streams. The ELS Phase I was based on the concept of "index" sampling. This conceptual basis was the result of much consultation among chemical limnologists and statisticians specializing in sampling statistics. The approach was exhaustively reviewed prior to the NSWS sampling and has proven to be a very powerful tool for answering the types of regional questions posed by the NSWS. The NSWS index sampling approach is described below.

> "A critical issue in the design of the ELS-I was the representation of a selected lake. If a single water sample can adequately represent the chemistry of a lake to satisfy the specific objectives of a study, a large number of lakes can be sampled. If multiple water samples are needed on a single occasion, then a reduction in the number of sample lakes must be considered. If multiple occasions are needed to represent the chemistry of a single lake, the number of sample lakes must be reduced proportionally.
>
> It is obvious that one sample, from one location, at one time of the day, in a specific season of a particular year, cannot characterize the complex chemical dynamics of a lake. Such a sample is justified only in the sense that it is an *index* to the essential characteristics of the lake.. But even if two samples are taken, or three, they remain only indices because understanding the dynamics of a single lake requires far more detailed study. This study was designed to describe populations of lakes. Therefore, each lake must be represented in that population description in a manner that captures its essence, but such that the number of lakes that can be sampled is maximized. The single index sample maximizing both lake number and spatial coverage on a large geographic scale was therefore deemed the most appropriate choice for addressing the collective objectives of the ELS-I.
>
> To enhance the utility of the index sample, careful consideration was given to location and season. The sampling window was designated as the fall season, just after turnover. Spatial variation within the lake is reduced at this time. Sampling at the apparently deepest part of the lake was intended to provide a sample from the dominant water mass. Therefore,

Table 5-9. DDRP Reclassification of Northeastern Lakes Classified as "Seepage" or "Closed" by the NSWS

Lake ID	Original NSWS Class	Final DDRP Class
1A1-039	S	D
1A1-066	C	D
1A2-006	S	S
1A2-058	C	D
1A3-028	S	S
1C1-018	S	D
1C1-031	S	D
1C1-050	S	D
1C1-068	C	D
1C2-056	C	D
1C2-066	S	D
1C3-055	S	S
1D1-027	S	D
1D1-034	S	D
1D1-037	S	S
1D1-068	S	S
1D2-036	C	D
1D2-084	S	S
1D3-044	S	D
1E1-009	S	S
1E2-007	S	S
1E2-049	S	D
1E2-069	S	D

S = Seepage lake
C = Closed lake
D = Drainage lake

Plate 5-2. Final DDRP classification of lake hydrologic type - Subregion 1A.

SUBREGION 1A
LAKE HYDROLOGIC TYPE

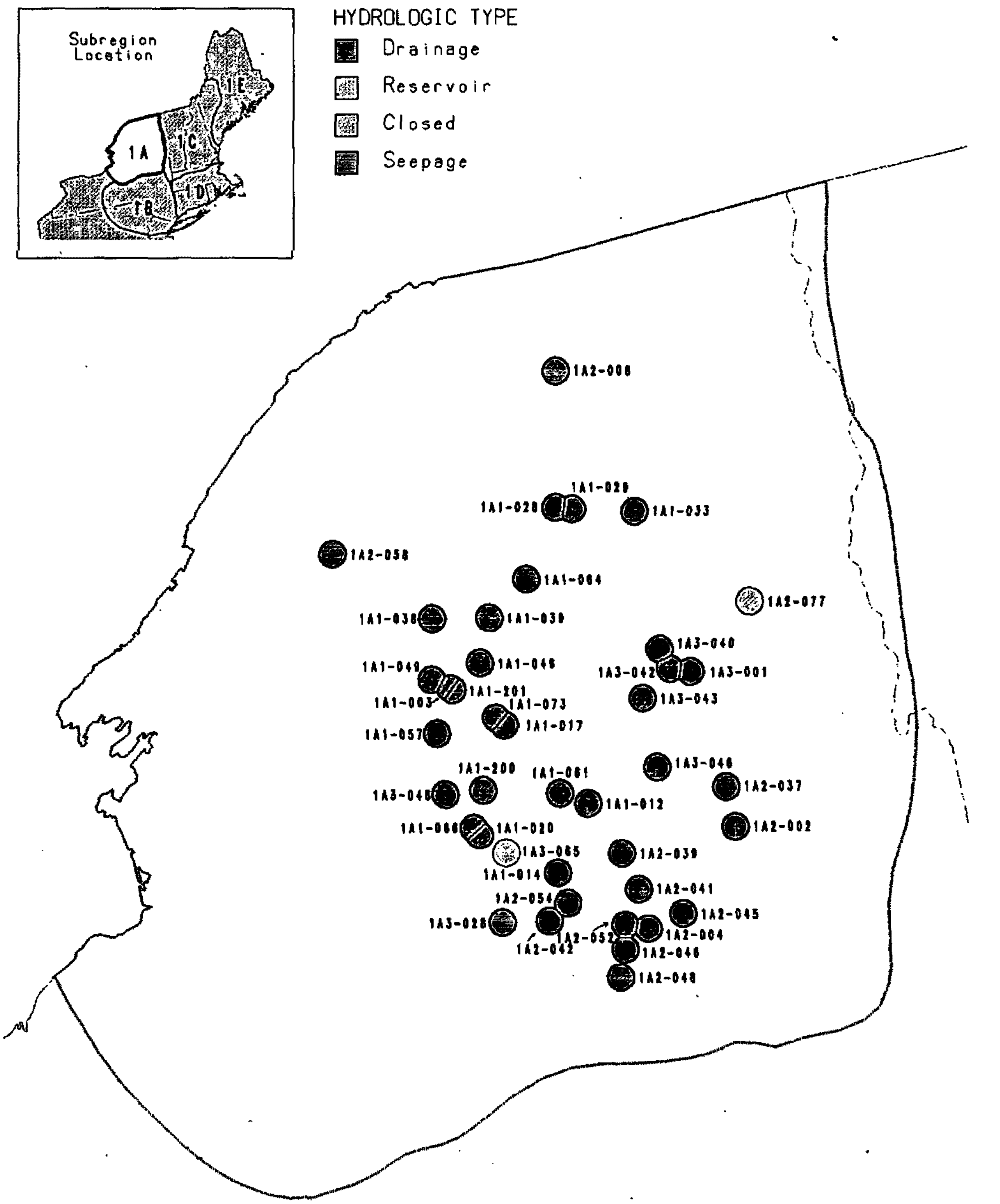


Plate 5-3. Final DDRP classification of lake hydrologic type - Subregion 1B.

SUBREGION 1B
LAKE HYDROLOGIC TYPE

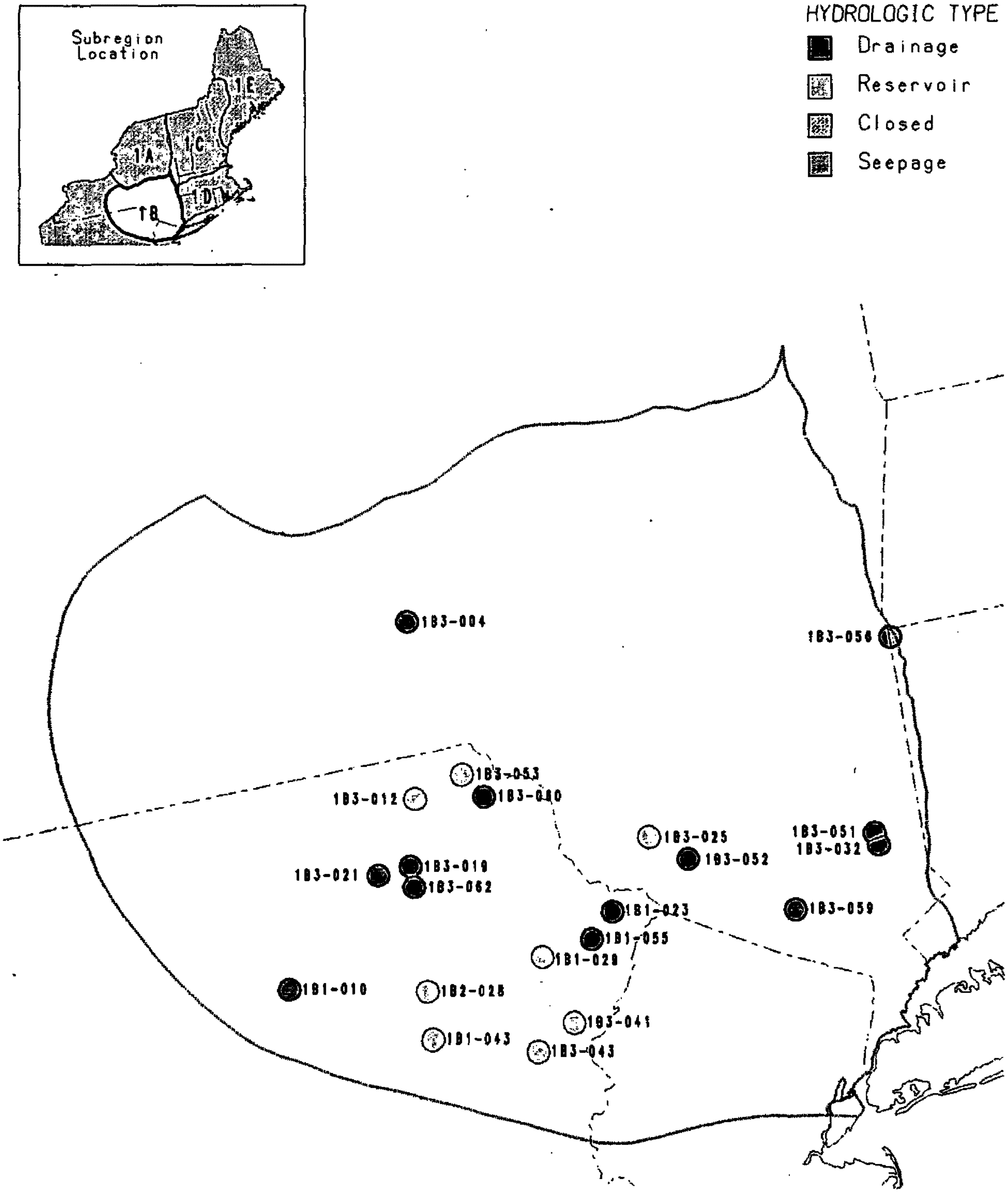


Plate 5-4. Final DDRP classification of lake hydrologic type - Subregion 1C.

SUBREGION 1C
LAKE HYDROLOGIC TYPE

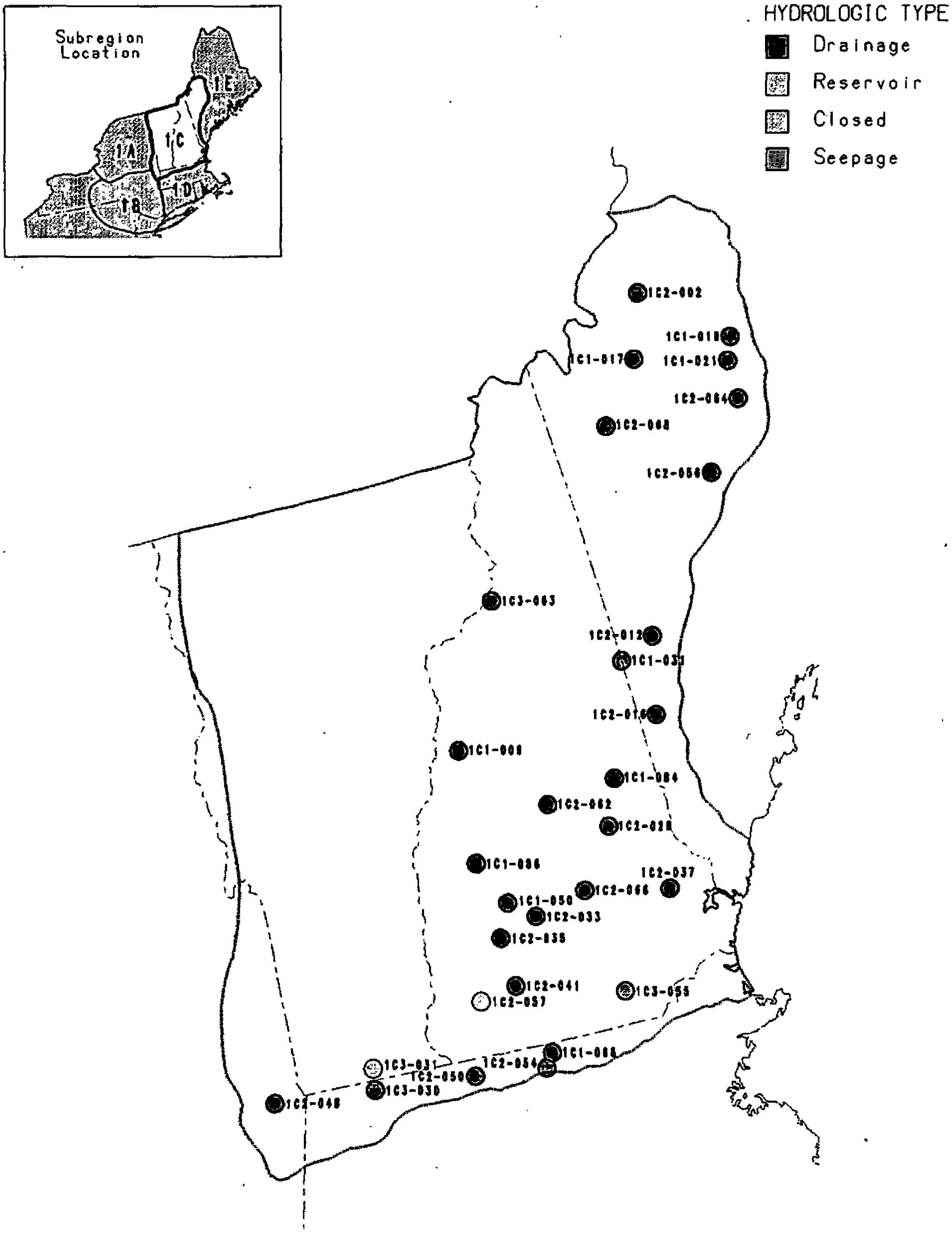


Plate 5-5. Final DDRP classification of lake hydrologic type - Subregion 1D.

SUBREGION 1D
LAKE HYDROLOGIC TYPE

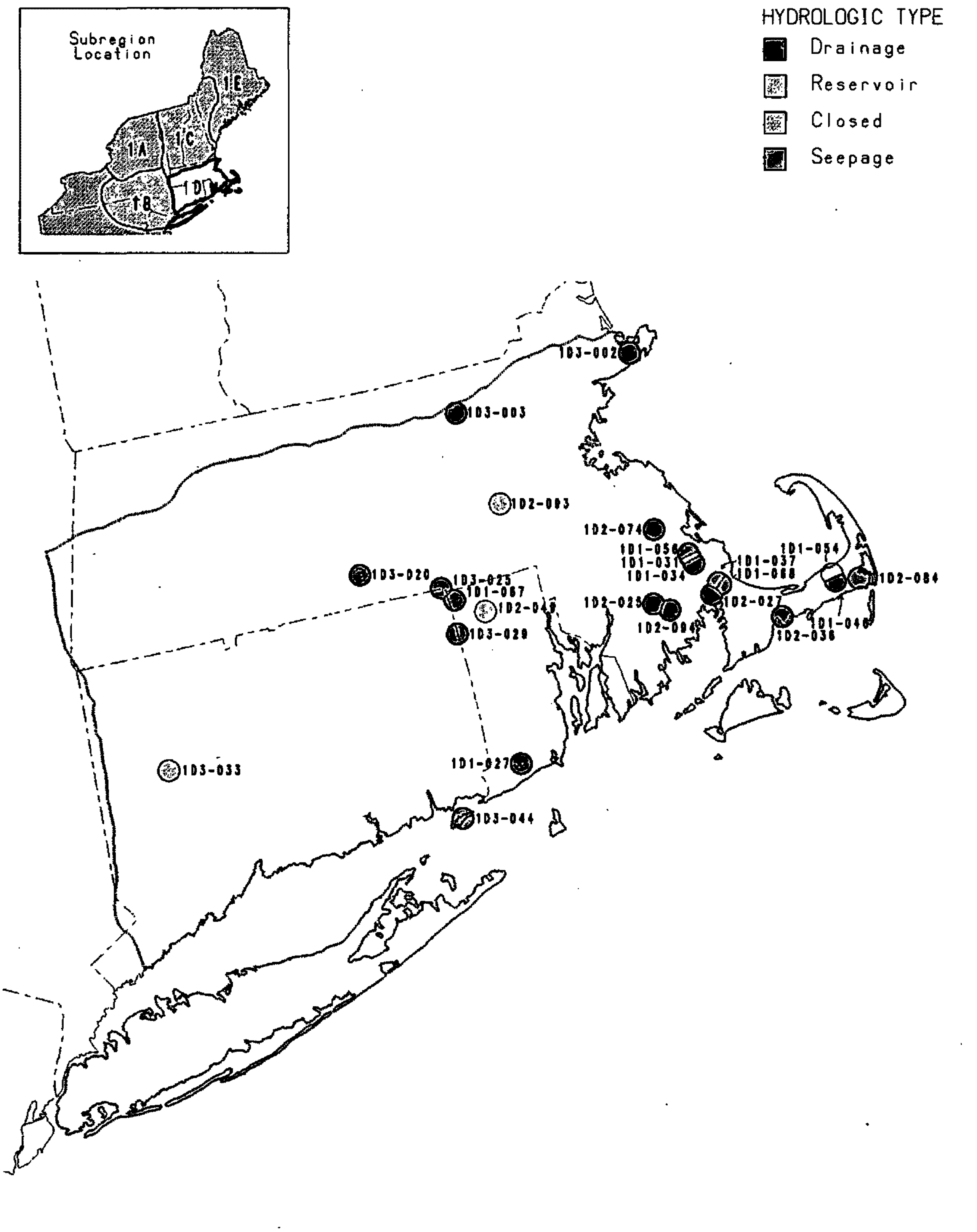
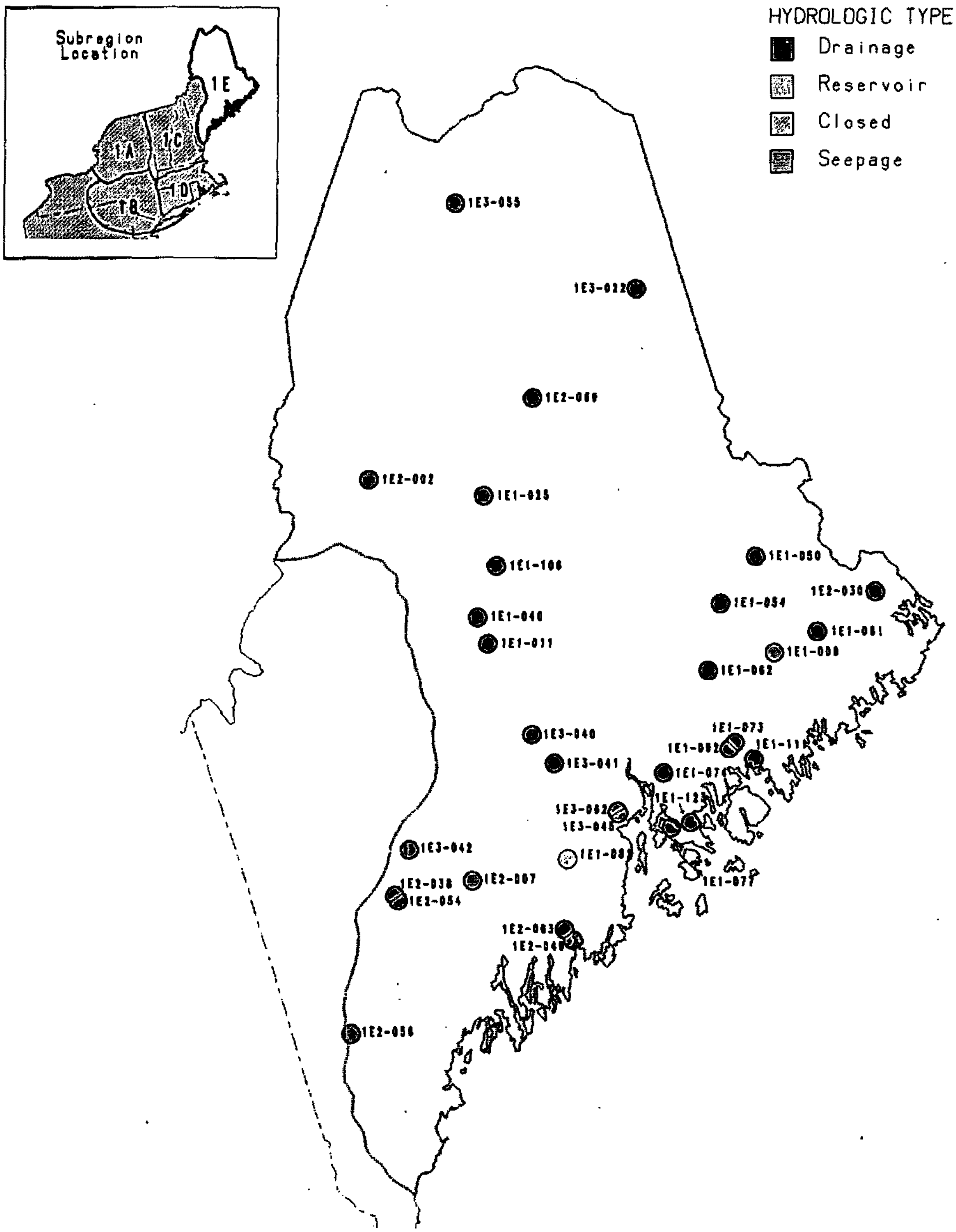


Plate 5-6. Final DDRP classification of lake hydrologic type - Subregion 1E.

SUBREGION 1E
LAKE HYDROLOGIC TYPE



the combination of a fall season sampling period and collecting a sample near the lake center at the apparently deepest part, appeared to be the best protocol to provide the needed sampling characteristics.

The perspective that each lake is represented by an index chemistry, rather than, for example, mean chemistry or some other integration over time and space, is important in interpreting the results presented in this report. The population descriptions represent and characterize the chemistry of a population of lakes, as though every lake in the population had been sampled in the same manner as the sampled lakes. Thus the resulting frequency and areal distributions for the chemical parameters (Sections 4.2 and 4.3) represent an index to water mass chemistry for the population of lakes that can be interpreted only through study of the predictive capacity of that index." (From Linthurst et al., 1986a; Section 2.1.2 "Lake Representation").

5.3.1.3 Chemistry of DDRP Lakes

The complete chemistry of the lakes of the DDRP watersheds in the NE has been given by Kanciruk et al. (1986a) and will not be repeated here. The pH-ANC relationship for ELS Phase I lakes falling in the DDRP target population (i.e., ANC < 400 μeq L^{-1}, Section 5.2.4.1) is shown in Figure 5-9. Also shown in Figure 5-9, for comparison, is the pH-ANC relationship for the DDRP study lakes by themselves. The ANC referenced for DDRP lakes is the modified Gran for ANC.

5.3.2 Streams in the Southern Blue Ridge Province Region

5.3.2.1 Spring Baseflow Index Sampling

The index sampling concept for Phase I of the NSS is described in the following paragraphs.

"Like the ELS-I components of the NSWS, the NSS-I relied on samples taken during an appropriate season from a representative sample of water bodies to provide an index of the chemical characteristics of the target population (Messer et al., 1986). In the Eastern and Western Lake Surveys (Linthurst et al., 1986; Landers et al., 1987), a single mid-lake sample taken during well-mixed conditions at fall turnover provided a reasonably good spatial representation of the nonlittoral lake water volume. Furthermore, this fall index sample for lakes can be related to water quality during other seasons of the year when chemical conditions may be more critical for biota (Driscoll and Newton, 1985; Newell, 1987). In lakes, relatively long hydraulic residence times (low flushing rates) tend to integrate the inputs of water and dissolved materials from the lake watershed, which reduces that portion of the chemical variability caused by changes in input rates. Streams generally exhibit greater within- and among-season variability than do lakes. Since streams have little temporal integrative capacity within their channels, it is necessary to draw an index sample during a period of the year that is expected to exhibit chemical characteristics most closely linked to acidic deposition or to its most deleterious effects. Sampling the relatively stable chemistry of late summer baseflows dominated by groundwater, for example, would provide a poor index of potentially limiting conditions during winter and spring periods when the stream water is poorly buffered against pH changes. The choice of the spring index sampling period for streams was based on a literature search followed by a series of meetings with hydrologists, biochemists, and fishery experts in Pennsylvania, Virginia, North Carolina, Florida, and

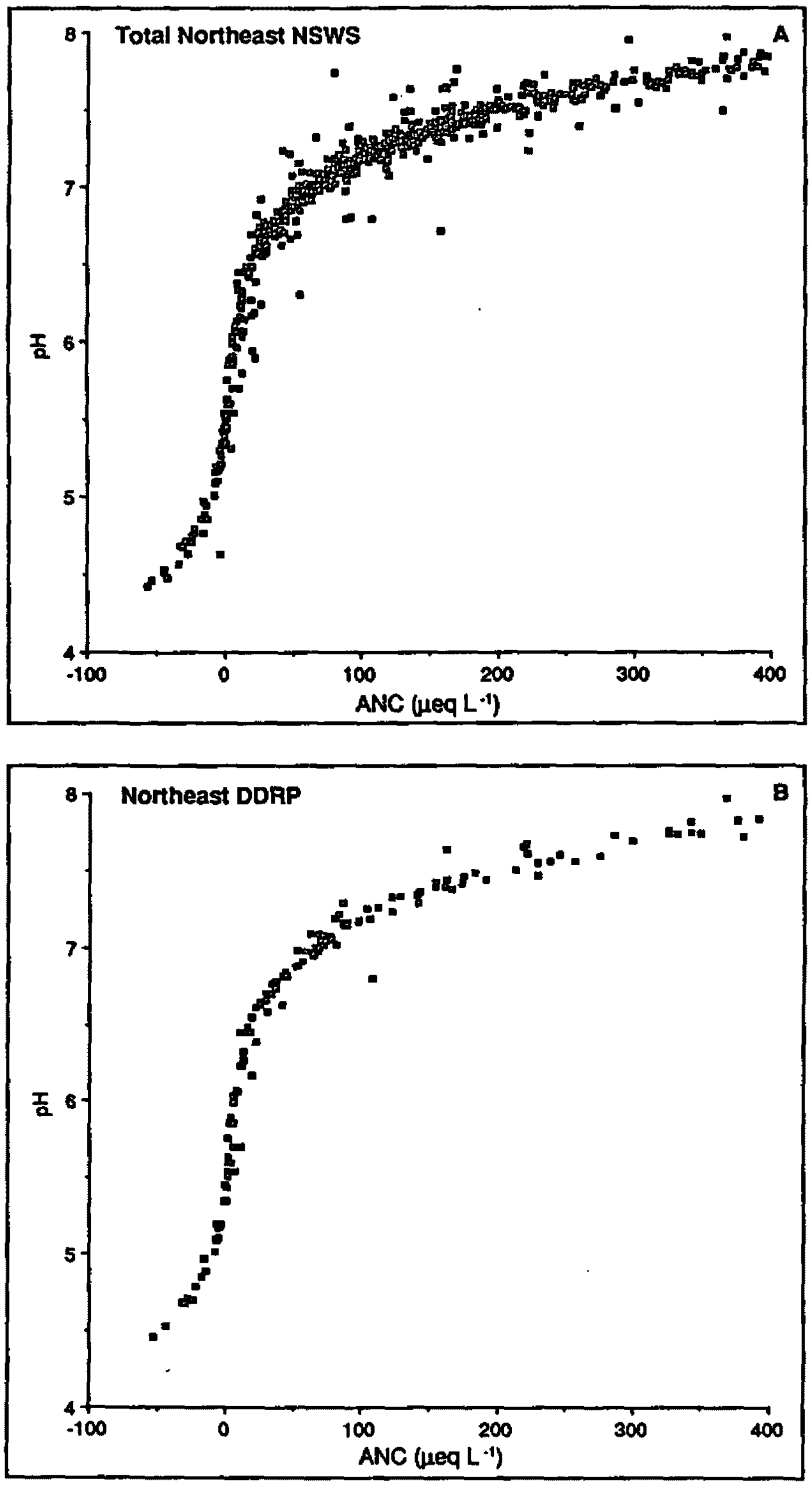


Figure 5-9. The pH-ANC relationship for (A) lakes of the ELS Phase I sampling in the Northeast and (B) DDRP study lakes in the Northeast.

Arkansas to discuss ongoing projects involving stream chemistry and fisheries in the proposed NSS-I study areas (U.S. EPA, 1984b). The choice involved a trade-off between minimizing within-season and episodic chemical variability and maximizing the probability of sampling during chemical conditions potentially limiting for aquatic organisms.

A number of sources of stream chemistry data from several geographic areas support the choice of a spring index sampling period for observing prolonged periods of low pH and ANC. Ford et al. (1986), for example, summarized the results of four recent (1984-1985) studies of seasonal and short-term variability in six second- and third-order streams in the Catskill Mountains of New York (Murdoch, 1986), the Laurel Hills of Pennsylvania (Witt and Barker, 1986), the Southern Blue Ridge Province of North Carolina and Tennessee (Olem, 1986), and the Ouachita Mountains of Arkansas (Nix et al., 1986). Minimum flow-weighted pH values and concentrations of base cations and ANC occurred during the spring at almost all sites. Those sites with minimum values during the winter had spring values nearly as low.

For a spring index sampling period to be biologically relevant, however, sensitive life-stages of aquatic biota must also be present during the sampling period. Studies have indicated that all life stages of fish are not equally sensitive to acidity and chemical constituents that accompany low pH conditions in surface waters. Some of these studies involved observations of acidic lakes and streams in which viable eggs were found together with older age classes of fish that appeared to be spawning successfully, but in which young age classes were absent (e.g., Beamish et al., 1975; Muniz and Leivestadt, 1980; Kelso and Gunn, 1982; Gunn and Keller, 1984; Sharpe et al., 1984). Such a population structure suggests more pronounced effects of acidity on larval fish than on egg hatching or adult survival. These field observations are in agreement with laboratory bioassays that also indicate greater sensitivity of fry to low pH conditions, relative to other fish life stages (Schofield, 1976; Haines, 1981). Fry of the most important sport fish are present in the NSS-I study area during the March 15 - May 15 period. Fry of some trout (Salmo spp.) populations may also be present at other times of the year.

In summary, spring appears to be the most appropriate index sampling period for streams, because ANC is typically low, and life stages of aquatic biota that are sensitive to low pH are likely to be present at this time. The low ANC during the season minimizes buffering against episodic pH changes accompanying high runoff. Although pH and ANC depressions can also occur during other seasons, they may be more pronounced during the spring because short hydraulic residence times in the soil during the spring minimize acid neutralization. Also, acid-sensitive, swim-up fry of key fish species are typically present in streams during the spring in many parts of the United States. The index sampling period for the NSS-I thus was chosen as the time period following snowmelt but prior to leafout (mid-March to mid-May, depending on the subregion). Results of the NSS-I Pilot Survey in the Southern Blue Ridge showed very little difference in separate population distributions of pH, ANC, and major cations and anions based on three successive spring baseflow samples during this sampling window (Messer et al., 1986, 1988). The occurrence of large episodic chemical changes over the course of hours or days during storm runoff, however, makes the use of spring samples for indexing water chemistry difficult, unless sampling during such events is avoided (Messer et al., 1986). To avoid alterations in index chemistry caused by atypical stormflow samples, the NSS-I avoided sampling within 24 hours following significant rain events (> 0.2 inches).

Unlike lakes, for which a single mid-lake sample taken during well-mixed conditions at fall turnover can provide a reasonably good spatial representation of the nonlittoral lakewater volume, a sample taken at a single point on a stream reach would not adequately describe chemistry for the whole length of the reach (Messer et al., 1986). Streams were expected to exhibit substantial trends in chemistry over their length at any given time during the spring index period. To incorporate this variability and to establish a basis for quantifying relationships between upstream and downstream chemistry on sample reaches, samples from both ends of the reaches were collected in the NSS-I." (From Kaufmann et al., 1988; Section 2.5 "Index Sampling")

As discussed in Section 5.2.4.2, DDRP study watersheds in the SBRP were defined based upon the downstream nodes of the reaches sampled.

5.3.2.2 Chemistry of DDRP Stream Reaches

The complete chemistry at the downstream nodes of the stream reaches used to define the DDRP study watersheds in the SBRP has been given by Messer et al. (1986a) and Sale et al. (1988) and will not be repeated here. The pH-ANC relationship for samples taken at the downstream nodes of the reaches for ANC < 400 $\mu eq\ L^{-1}$ is given in Figure 5-10. Also given, for comparison, is the pH- ANC relationship for the samples taken at the downstream nodes of the DDRP reaches. Only the relationship for ANC < 400 $\mu eq\ L^{-1}$ is shown. The ANC referenced for the stream reaches is the modified Gran for ANC.

5.4 MAPPING PROCEDURES AND DATABASES

The first step in gathering the terrestrial information required to characterize the study watersheds was to map them. This mapping was designed to include all the major characteristics thought to be important in determining the response of surface waters to acidic deposition for watersheds selected to represent the study region. Existing terrestrial databases were examined and found to be highly limited (Lee et al., 1988a).

Specific resource inventories of soils, geology, depth to bedrock, drainage, forest cover type, and land use were designed within the Project and implemented through the assistance of the USDA Soil Conservation Service (SCS) in the NE and SBRP Regions.

The performance and direction of field activities in the Soil Survey were modelled after the organization of the National Cooperative Soil Survey (Soil Survey Staff, 1983). The Mapping Task Leader for the DDRP, located at the ERL-C, had overall responsibility for mapping and coordinated all mapping activities. A Regional Coordinator/Correlator (RCC), an independent contractor, provided quality assurance/quality control (QA/QC) for the field mapping. The RCC maintained a uniform, consistent

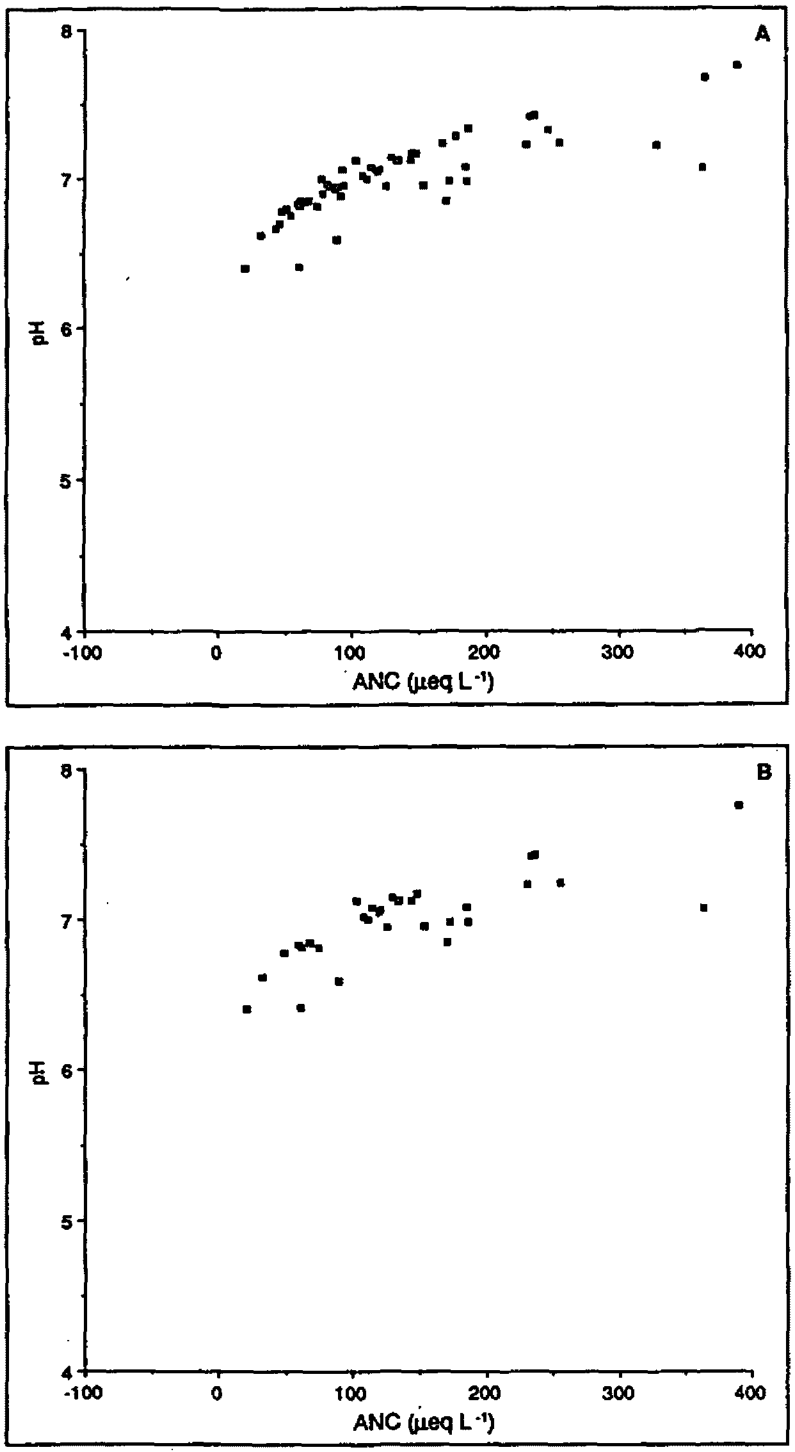


Figure 5-10. The pH-ANC relationship for samples with ANC < 400 μeq L^{-1} taken at the downstream nodes of stream reaches sampled in the NSS. Shown are the relationships for all such samples from the NSS and samples for the downstream nodes of DDRP study reaches in the SBRP. Samples are the average of either two or three samples each, with samples taken during events excluded.

regional mapping legend, participated in at least one field review of mapping procedures for each state, ensured regional consistency of field procedures, and evaluated mapping activities to assure quality.

Each State Soil Scientist (USDA-SCS), with the support of the State Soils Staff, was responsible for mapping activities in that state. This included supervising and coordinating field and support crews, forwarding maps and notes to the Mapping Task Leader, performing at least one field review of each field crew, and working with the RCC to ensure regional consistency. The field crews, led by an experienced soil scientist, mapped the watersheds, described the soils and soil map units, and transected each watershed to determine the correctness of the mapping.

Map products delineated at a scale of 1:24,000 were digitized in separate layers and entered into a Geographic Information System (GIS) as described in Sections 5.4.1.7 and 5.4.2.8 of this report. The soil map legend, map unit composition, characteristics of the soils, and soil transect data described from the mapping were entered into an interactive microcomputer data management system. The survey of each region was independent, in that a single unified and consistent legend was developed and correlated within each individual region.

5.4.1 Northeast Mapping

Mapping of soils, watershed drainage, geology, forest cover type, and depth to bedrock on 145 watersheds in the NE was initiated on April 15, 1985, and completed before July 5, 1985; the total area mapped was about 75,000 ha (185,000 acres). Soil mapping activities and quality assurance of the mapping data were described in depth by Lammers et al. (1987b).

Before field work started, mapping protocols were written, a preliminary regional soil legend was developed, and a plan of operations was prepared for each state. Mapping protocols, used by personnel involved in the mapping to maintain quality and consistency, were described in detail by Lammers et al. (1987b, Appendix C). The preliminary soil legend was based on soil map units that had been mapped within the region. These map units, therefore, had established soil-landscape relationships and were expected to be applicable to much of the area to be mapped. A plan of operations was prepared by the SCS State Soil Scientist in each state to direct the flow of personnel and mapping products. USGS topographic quadrangle maps at a scale of 1:24,000 were acquired for the watershed areas and prepared for field use. For areas where 7.5' maps were not available, 15' topographic quadrangle maps were photographically enlarged to an approximate scale of 1:24,000. When available at SCS field offices, aerial photographs were used to assist with landscape interpretation and map delineation. Just prior to the start of mapping, State Soils Staff, Field Soil Scientists, and Mapping Task Leaders met at a workshop to review mapping protocols and to clarify instructions.

5.4.1.1 Soils

Soils were mapped using standards and procedures specified in the National Soils Handbook (Soil Survey Staff, 1983) and Soil Survey Manual (Soil Survey Staff, 1981). Soils were classified according to Soil Taxonomy (Soil Survey Staff, 1975). Soils map units were delineated directly on topographic quadrangle base maps and identified with a unique map symbol. Each map unit represented a collection of areas defined and named the same in terms of their soil components, miscellaneous areas, or both. Units that consisted of one dominant component (consociation) and units with two or more dominant components (complexes) were mapped. Although most soil components of map units were phases of soil series, some components were phases of soil families or higher categories of taxonomic classes. The soil map units and soil components that make up the map units were described with the following characteristics:

- name and symbol of the map unit
- regional landform
- local landform
- geomorphic position
- slope configuration
- percent composition of map unit components
- characteristics of the soil components
    - name of the soil component
    - phase (i.e., slope, texture, rock fragments)
    - drainage class
    - parent material, origin and mode of deposition
    - depth to bedrock
    - depth to impermeable layer
    - taxonomic classification

Soil map units were cartographic delineations of the landscape that reflected the dominant soil conditions of a landscape element or segment. Soil mapping was based on enough observations to determine soil/landscape relationships and confirm predictions of soil occurrence established from these relationships. Each map delineation was visited in the field. The minimum size of individual map delineations was 2.7-4.5 ha (6-10 acres). Inclusions may have been larger if the soils were similar and there were no readily observable landscape features to use for delineation. The proportion of small areas, inclusions in map unit delineations, were estimated to the nearest 5 percent and were, thereby, included in aggregated values for a watershed. Soil map unit boundaries were delineated directly on USGS topographic quadrangle base maps at a scale of 1:24,000. Perennial and intermittent drainages not indicated on the USGS maps were drafted onto the base maps.

5.4.1.1.1 Soil Correlation -

Soil correlation is the process of maintaining consistency in naming, classifying, and interpreting soils and units delineated on maps. Thus, there are two main elements of soil correlation: (1) the correlation of an individual soil pedon or groups of soil pedons with a soil series, or with some higher level soil taxonomic class, and (2) the correlation of map units. Correlation requires consistent methods of observation and measurement among all participants, as well as the use of consistent conventions and terminology. The Soil Survey Manual (Soil Survey Staff, 1981) and Soil Taxonomy (Soil Survey Staff, 1975) provide the conventions and guidelines for defining and naming map units, and for defining diagnostic properties and taxonomic classes of soils used in the National Cooperative Soil Survey. Soil series are defined by official soil series descriptions.

The soil correlation process started with the development of the preliminary regional identification legend and continued throughout the progress of the mapping phase. The preliminary identification legend was based on soil map units that had been mapped previously within the NE. These map units, therefore, had been tested for soil-landscape relationships and were expected to be applicable to much of the area to be mapped. Consistent breaks for slope phases for map units and the use of the most common soil texture phase for a soil series were established by the preliminary legend, in which 623 units were listed. Soil map units were not limited to those in the preliminary legend and map units were redefined and added as necessary during the progress of the field mapping; 89 map units were added to the identification legend during the field mapping. From the total of 712 map units in the preliminary legend and those added to the legend, 398 map units were used in the mapping.

The soil scientist responsible for mapping each watershed performed the first level of correlation of the soils and map units. The descriptions of official soil series were adopted to represent those soil series for the region. At each point along a traverse, the soil was examined and evaluated for characteristics that were within the range of a soil series or that were similar to an established series. Soils that were dissimilar to all recognized soil series were classified at the family level of Soil Taxonomy (Soil Survey Staff, 1975). Brief descriptions were made of the different kinds of soil to document what was observed and to compare or correlate with the official series description or other field descriptions. The descriptions of the different recognized kinds of soil were further evaluated by the State Soils Staff during the progress field review for consistent correlation within each state.

In addition to the proper recognition and classification of soils observed, the soil scientist also determined the relative proportion of each kind of soil on a landscape segment. In this manner, soil map units were defined. The soil scientist then correlated the composition of soils with one of the map units in the preliminary legend or proposed an additional map unit. The map units were reviewed by the State Soils Staff to correlate map units on all watersheds within each state. The RCC controlled the mapping legend and correlated soil map units throughout the NE Region.

During the week of July 8-12, 1985, soil scientists representing the SCS from all of the states involved in mapping the DDRP NE Region met at Saranac Lake, NY, with the RCC, task leaders from the ERL-C, and the Data Management Leader from ORNL. Objectives of the meeting were to correlate soils and soil map units for the region and to complete descriptions of the map units. Each of the 398 map units used during the mapping was reviewed. Descriptions of the map units and the characteristics and taxonomic classification of the major components of each map unit were checked and completed.

A few units mapped in more than one state were found to be similar, and they were combined. Other map units were represented by just a few hectares and were combined with the most similar map unit in the legend. When transect data or field notes indicated that the map unit was not correct, the description was adjusted or the map unit was combined with another that better fit the soils recognized. Map unit descriptions, defined during the mapping and correlated within states, and summaries of the mapping transects were the basis for correlation and map unit description decisions. The state with the greatest area of each map unit took the lead responsibility for providing a description of the map unit. Transect summaries from every state mapped were summarized on a regional basis to determine a consensus description. When transect data did not appear to accurately represent the map unit, soil scientists with experience in mapping that unit were asked to alter the description. Most often, the alterations were based on the kinds and percentages of minor soil components in the map unit. Following the regional correlation review, 356 map units remained in the regional soils legend. After the area of each map unit was more precisely determined from the digitized data in the GIS, additional map units with only a few acres were combined with other similar map units by the Mapping Task Leader. This resulted in a final soil map legend of 338 map units. A few small map units remained in the legend, if there were no similar map units with which they could be combined.

The soil taxonomic class, drainage class, depth to bedrock, and estimated depth to a slowly permeable or impermeable layer were obtained from the official soil series for the major components of each map unit.

5.4.1.1.2 Soils database -

The mapping phase of the DDRP NE Soil Survey generated vast amounts of data. In order to verify, validate, and analyze these data, the data were entered into computer database files. Data products generated by the mapping included the identification legend, descriptions of the soil map units, descriptions of the soil taxonomic units (components of the map units), soil transect information, and the map products. The map products included maps of the soils, vegetation, depth to bedrock, and geology of the 145 watersheds. This section describes the database files developed for the DDRP mapping data and the procedures and QA/QC checks used during the computerization of the DDRP data. Both ORNL and EPA's ERL-C were involved with management of the mapping data. Most of the data were double entered by ORNL, using the Statistical Analysis System (SAS) installed on tandem IBM 3033 computers. ORNL also performed most of the data checking. ERL-C had overall responsibility for the quality of the data and contributed to the development of the database files. The maps were digitized for input to a GIS at ERL-C. An overview of mapping databases is provided by Turner et al. (in review).

The preliminary soil identification legend, including additions and corrections to the legend made during the mapping, was reviewed by the RCC during the regional correlation workshop held in Saranac Lake, NY, in July 1985. Map units not used were marked for deletion, and map units that were combined were noted on the legend. The legend data were input using dBase III software on an IBM PC at ERL-C and also double entered at ORNL by in-house data entry center personnel, with the resulting files transferred to SAS files on the IBM 3033 system. Legends from each watershed map also were entered into the GIS as the maps were digitized at ERL-C.

The legend data from the GIS were transferred to a dBASE III file where they were summarized for the region and then compared to the regional soil identification legend. Discrepancies were then resolved and the map unit names were checked with the descriptions of the map units for validity. Map units from the GIS database showing less than 8 ha (20 acres) were then combined with another similar map unit where possible. Usually this procedure involved either including the major component of the minor map unit with another slope phase of the same soil and adjusting the slope range or showing an inclusion of the soil on the different slope. The ERL-C version of the identification legend was then compared with the ORNL version and discrepancies were resolved.

The soil identification legend database file for the DDRP NE Soil Survey, NEIDLGD, contained the following information for each map unit: map symbol; map unit name, including the name of major soil component(s), texture modifier (e.g., gravelly, mucky), texture phase, slope phase, and other phase (e.g., very stony, rocky); regional landform; local landform; geomorphic position; slope shape across; slope shape down; and area in acres (determined from the GIS database). This file contains 338 records, one for each map symbol in the soils legend.

A soil map unit worksheet was used to record information about each map unit. This worksheet included the map symbol, map unit name, information about the landscape, major soil components, minor soil components, the proportion of each component in the map unit, and information about the major components including the taxonomic classification. Originally the minor components or inclusions were only listed by name and percent composition. After the soil correlation workshop at Saranac Lake, NY, the map unit worksheet data were entered into a database file using dBASE III software on an IBM PC. Inasmuch as soil data analyses must be made on kinds of soil or classes of soils, it was immediately evident that individual components of map units must be recognizable in the database, not the map units themselves. In some map units, the minor components (inclusions) collectively made up more than 30 percent of the map unit and were found to be important for data analyses. Also, a major soil component in a consociation may have the same attributes as a major component in a complex or minor component in another map unit. The information from the map unit worksheet was therefore separated into two files, a map unit composition file and a soil components file. Each unique soil component was assigned a component code to aid in accessing all the attributes of a soil component with one code. The map unit composition file, NECMPOS contains the map symbol, the component code for every component in the map unit, and the percent composition of each of the components. There are 1381 data records in the NECMPOS file.

The soil components file was named NECMPON and has 594 records. Each record includes the component code; soil name, texture, and slope of the component; five characteristics of the soil: drainage, depth to bedrock, depth to impermeable layer, origin, and mode of deposition of the parent material; and the taxonomic class. The sampling class code for the class with which the soil component was grouped for sampling was also included in the record for each component in this database file.

The records from the three database files, NEIDLGD, NECMPOS, and NECMPON, were merged for printout of a computer-generated map unit worksheet. Copies of these computer-generated worksheets were sent to the SCS State Soil Scientist in each of the northeastern states for review. Instructions were to review the map units used in their respective states, make corrections, and fill in data blanks wherever possible. Data from these corrected map unit worksheets were entered into the SAS files at ORNL. The updates were entered into a change file containing the record identifier, variable name, and old value for each record in the database. Only when all three items matched an observation in the database was the old value updated. This method of correcting the database virtually eliminated the possibility of updating the wrong observation or variable.

After the updates were completed, ORNL generated frequency tables of the coded variables and compared these tables with lists of valid codes. The frequency tables were also used to build code translation tables containing the codes and definitions. These translation tables were stored as SAS format libraries and are a part of the database. The final step in editing the map data files involved labeling variables and, where necessary, modifying variable names and labels to ensure consistency among the various mapping data files.

5.4.1.2 Depth to Bedrock

Depth to bedrock maps were prepared on mylar overlays of base maps at a scale of 1:24,000 during soil mapping. Soil depth was observed while traversing all map unit delineations and at an average of 100 transect stops in each watershed. Soil scientists usually examined the soil to a depth of 1.5 m, or depth to bedrock or dense till. Because of this direct observation, soil scientists were highly confident in the reliability of depth-to-bedrock estimates within the depth of observation. Estimates of depths greater than 2 m were based on road cuts, stream incisements, and knowledge of the landscape; the confidence in the reliability of these estimates was lower. Each soil map delineation was assigned to one of six depth classes and a depth-to-bedrock map was prepared by combining contiguous delineations of the same class. The six depth-to-bedrock classes and qualitative estimated reliability in determining the correct class are shown in Table 5-10.

Table 5-10. Depth-to-Bedrock Classes and Corresponding Level of Confidence

Class	Depth	Midpoint	Estimated Reliability
I	< 0.5 m	-	High
II	0.5 - 1 m	0.75	High
III	1 - 2 m	1.50	High
IV	2 - 5 m	3.50	Moderate
V	5 - 30 m	17.50	Low
VI	> 30 m	-	Low

Standard seismic refraction techniques were employed to estimate depth to bedrock along selected transects in 15 of the 145 watersheds. Depth to bedrock estimated from soil mapping and from seismic techniques could not be directly compared due to differences in the two approaches. Of the 696 seismic readings, 83 percent were within one class of that on the depth-to-bedrock map. Means of the seismic determined depths increased with increasing mapped depth class for all classes.

The extent of depth-to-bedrock classes on a watershed could also be estimated directly from the soils database. This approach, is described in Section 8.7.2 and was used in the regression analysis reported in that section. The percent (in intervals of 5 percent) of exposed bedrock or soil having a designated depth to bedrock was estimated for each soil map unit and recorded with the map unit composition in the soils database. In this manner, areas of rock outcrop or of soil with a depth different depth than that of the major component of the map unit and too small to be delineated at the scale of mapping were accounted for in the analysis.

5.4.1.3 Forest Cover Type

During the soil mapping, soil scientists also made vegetation cover type maps, at a scale of 1:24,000 for each watershed. The vegetation map units were based on Society of American Foresters (SAF) cover types described by Eyre (1980). Open areas containing poorly drained soils were delineated as "open areas-wet," while other open areas were delineated simply as "open." Delineation was made by air photo imagery and topographic and landscape features. Delineations were confirmed by field observation during the course of soil mapping.

5.4.1.4 Bedrock Geology

Field soil scientists obtained the best available bedrock geology map and sketched delineations of the formations on an overlay of the base map for each watershed. Geology data extracted from several different sources were found to be extremely difficult to correlate; therefore, bedrock geology was digitized from state geology maps as discussed in Section 5.4.1.7.

5.4.1.5 Quality Assurance

A rigorous plan for QA/QC was implemented from the beginning of the mapping and maintained at every level of authority. QA/QC activities included field review, point transects of the watersheds, and independent evaluation of mapping on selected watersheds. The transect data were evaluated to determine the correctness of the soil map units.

5.4.1.5.1 Field reviews by the Soil Conservation Service -

Field reviews were conducted by the SCS, the State Soil Scientist, or another member of the State Soils Staff for each soil mapping crew in their respective states. During a review, the watershed was visited and a number of map unit delineations were traversed. The mapping was evaluated and the following items were checked: adherence to protocols, identification of soils, placement of map unit boundaries, identification of soil map units, and clarity and legibility of the field notes and maps. There were 34 different soil mapping crews responsible for the mapping, and field reviews were conducted on watersheds mapped by 32 of the crews. A written field review report was submitted to the Mapping Task Leader and the RCC following the field review. Field review reports for each of the watersheds are summarized by Lammers et al. (1987b, Appendix E).

None of the field review reports indicated that the mapping was unacceptable. Field reviews clearly resulted in improved mapping on the watersheds in which the reviews were conducted. Although it cannot be quantified, undoubtedly the communication and feedback resulting from the field reviews improved mapping on the other study watersheds.

5.4.1.5.2 Field reviews by the Regional Coordinator/Correlator -

The RCC participated in a field review of at least one watershed in each state (except Vermont for which there was only one watershed). The purpose of the RCC participation was to coordinate the mapping throughout the region and to control the quality of the mapping. The RCC facilitated better communication among states to ensure consistency and improve correlation of the soils and map units.

The RCC participated in 13 field reviews and submitted an independent narrative report of the results of each review to the Mapping Task Leader. The mapping was judged acceptable on all of the watersheds after discrepancies were corrected. Field review reports by the RCC are contained in Appendix F of Lammers et al. (1987b).

5.4.1.5.3 Evaluation of mapping by the Regional Coordinator/Correlator -

The RCC independently evaluated the mapping of 15 of the 145 watersheds in the Northeast Soil Survey. These 15 watersheds were selected from the top of a random list of all 145 watersheds, with the constraints that watersheds visited by the RCC for progress field reviews during the mapping would not be revisited for independent evaluation, and no more than one watershed would be evaluated for each mapping team.

Mapping was evaluated by examining stereoscopic pairs of aerial photographs, when available. Relationships between soils and landform segments were scrutinized and questionable areas marked for further examination on the ground by traversing and transecting. About one-third of the delineations on the soil map were evaluated on the ground and about one-half as many transect points as in the routine mapping were examined. A report of the results of the mapping evaluation was submitted to the EPA ERL-C.

The soil mapping activity carried out by soil scientists within the framework of the National Cooperative Soil Survey was in reality the art of sketching the landscape portrait to show a location of areas with defined kinds and distribution of soils, the soil map units. Although map correctness was judged by how well the map unit descriptions fit the soils in the mapped areas, the utilitarian correctness had to be judged with the DDRP in mind. For this project, depth to bedrock, depth to slowly permeable or impermeable layer, drainage class, taxonomic family, slope, and stoniness were selected as important soil characteristics.

Of the 15 watersheds evaluated by the RCC, the mapping was judged acceptable on 13 and unacceptable on the other 2. Mapping that was unacceptable did not mean that all the mapping on that watershed was incorrect, but of the delineations checked, nearly one-half had an inappropriate map symbol. Mapping in both of the unacceptable watersheds was corrected by the mapper and the State Soils Staff.

The number of watersheds, other than the 15 evaluated by the RCC, that might have unacceptable mapping errors could not be determined. Mapping errors were most likely associated with individual soil scientists, with watersheds where soil mapping was dominantly based upon published soil surveys, or with soils that were difficult to map.

Summaries of mapping evaluation results of the 15 watersheds selected for evaluation by the RCC were reported in Appendix G by Lammers et al. (1987b). Significant watershed boundary errors were identified on 3 watersheds during the mapping evaluation. The mapped area was adjusted as appropriate to correct these errors. Watershed boundaries were difficult to determine in topography common to the glaciated region of the Northeast.

5.4.1.5.4 Evaluation of soil transect data -

As specified in the mapping protocols (Lammers et al., 1987b), point observations were made at 30-m (100-ft) intervals along transects across each watershed. Transects were located to pass through as many map unit delineations as was practical. A "yes" response was recorded when the soil was similar to a named soil of the map unit in which the transect stop was located. In complex map units, the name of the major soil was recorded with a "yes" response and the name of a dissimilar soil was recorded with a "no" response. "Routine" transects were conducted by soil scientists with the soil survey party; and additional "RCC" transects were made by the RCC in 15 of the 145 watersheds. The transect data were entered into a SAS database at ORNL and were verified at ERL-C.

A number of analyses could be made with the transect data, which were used to evaluate the correctness of the described map units. For both the routine and RCC transect data, the proportion of major components in map units, "yes" responses in the transect data, was compared to the estimated percent composition in the map unit description, NECMPOS file. Routine transects were compared to RCC transects of the same map unit for watersheds in common. Finally, soil components observed at transect points were assigned the proper class for sampling, and map unit correctness was evaluated with respect to the sampling class composition. This evaluation of the proportion of sampling classes in map units was especially relevant to judging the "correctness" of map units for the purposes of the DDRP.

5.4.1.5.4.1 Analysis of major components in map units with routine transects –

Transect data "yes" responses, representing 274 of the 338 map units in the regional legend, were compared to the proportion of major map unit component(s) in the map unit descriptions. Of these 274 map units, 39 were found to have significantly different proportions. Seven of the 39 map units had 100 or more transect observations and had a difference between the proportion from the transect and the proportion estimated in the NECMPOS database of less than .09, or 9 percent.

Another 18 of the 39 map units had significantly different proportions, but fewer than 30 observations. These differences could be indicative of unrepresentative transects, rather than incorrect expected proportions of major components. Given that transect points were not independent random observations and that individual transect segments had not yet been analyzed for problems, the number of map units with significantly different composition was reasonable.

A transect segment union was defined as all transect stops in the same map unit on a watershed. Fifty-two transect segment unions, about 3 percent of all transect segment unions in the database, had proportions significantly different from that estimated. When these 52 transect segment unions were excluded from the dataset and map unit composition was analyzed, 29 map units were found to have a significantly different proportion of "yes" responses compared to the estimated proportion of major component(s). Of these 29 map units, 13 had fewer than 30 observations and 9 had a proportion difference of 9 percent or less.

5.4.1.5.4.2 Analyses of major components in map units with RCC transects –

As with the routine transects, the proportion of major map unit components from the "yes" responses on transects conducted by the RCC on 15 watersheds was compared to the estimated proportion in the NECMPOS data file. Of the 47 map units examined, 12 map units had proportions that were significantly different. Ten of the 12 map units had less than 30 transect observations.

Similarly, the RCC transects were examined for transect segment unions with significantly different proportions at the .01 level of significance. After significant transect segment unions were excluded, there were five map units with significantly different proportions. Two of these were based on fewer than five observations for which the power of the hypothesis test was limited. The percent of map units with significantly different proportions was about the same for routine transects as for RCC transects.

These comparisons suggest that the correctness of the estimated composition of major map unit components was about the same when analyzed with routine transects as when analyzed with transects conducted by the RCC.

5.4.1.5.4.3 Comparison of the routine and RCC transects –

The analyses in the previous section compared the proportion of major components predicted from the routine transects and those of the RCC with the proportion estimated in the NECMPOS data file. The analysis in this section compares the proportion of "yes" responses in the routine dataset with the proportion of "yes" responses in the RCC dataset for the same watershed and map unit.

There were 94 watershed/map unit combinations, of which 47 had observations from both RCC and routine transecting that could be compared. Five map units were found to have significantly different proportions. If the true proportions were the same for each of the 47 comparisons, about two or three combinations would still appear to be significant. Furthermore, some of these significant combinations were based on few observations, and RCC transects were not in the same places on the watersheds as the routine transects. For these reasons, the RCC and routine transects are considered reasonably consistent.

5.4.1.5.4.4 Analysis of the map units by sampling class –

The soil series in the transect data were assigned the appropriate sampling class. Sampling class composition of the map units predicted from the transect data was compared to sampling class composition estimated during the mapping by soil scientists and entered in the NECMPOS data file. (Sampling classes are described in Section 5.5.1.3.) The Bonferroni (Johnson and Wichern, 1982) inequality was used to handle the error rate of the simultaneous hypothesis tests within each map unit.

There were 38 map units, analysis for which the proportion of one or more sampling class(es) differed significantly from the proportion estimated in the NECMPOS data file. Of these 38 map units, 17 had fewer than 30 transect observations, and 3 more map units, all with more than 100 observations, had a difference of less than 9 percent. These 20 map units were therefore removed from the analysis, leaving 18 map units with 30 or more transect observations, for which the difference in proportion of at least one sampling class in the map unit was 15 percent or greater. At the .05 level of significance, we would expect about 14 map units to have at least one sample class with a significantly different proportion, suggesting that the sample class proportion from the NECMPOS data file was not noticeably different from to that predicted from the transect data for most map units.

5.4.1.5.4.5 Summary of the transect analyses –

For the most part, the routine transect data were used to make estimates of map unit composition in the NECMPOS data file. The RCC transects were independent of the NECMPOS data file estimates; map unit component proportions, however, were consistent with proportions from routine transects. The proportion of each sampling class in the map units, estimated in the NECMPOS data file, was within reasonable mapping precision for more than 95 percent of the map units. Although transects were used as a measure of map unit composition correctness, it was recognized that soil scientist experience may in some cases provide the better composition estimate.

5.4.1.6 Land Use/Wetlands

5.4.1.6.1 Data acquisition -

Information on land use and wetlands for the NE DDRP watersheds was obtained via interpretation of aerial photography. Details of the procedures used and evaluation of the results are presented by Liegel et al. (in review).

During April and May 1986, leaf-off color infrared (CIR) stereo photography, 1:12,000 scale, was obtained for 145 watersheds from Lockheed Engineering and Sciences Company, Las Vegas, NV (LESC-contract no. 68-03-3245). The selected film, Kodak aerochrome 2443 or equivalent, was kept frozen until a few hours before actual use. Two subcontractors were responsible for the actual photography; Zeiss cameras and Zeiss B and D filters were used. Exposed film was packed in styrofoam mailers and shipped to the contractor by next-day air courier service. The contractor used Kodak 1594 film processing to make 23 x 23 cm contact prints.

Contractor staff made overlays of land use and wetlands from office photointerpretation of CIR stereo film positive negatives. Information was transferred to 1:24,000-scale (7.5') USGS topographic base map overlays. When 7.5' maps did not exist, photographic enlargements of 15' maps were used. On the land use overlay, 12 general land use classes (Table 5-11) were mapped to a resolution of 2.5 ha. On the second overlay, detailed wetlands, using modified National Wetland Inventory (Cowardin et al., 1979) subcategories, were mapped to a resolution of 0.4 ha; greater resolution for wetlands was tied to the suspected greater influence of wetlands on ameliorating surface water chemistry in areas of high acidic deposition. Also, five point classes summarizing beaver activity were included (Table 5-11).

Table 5-11. Interpretation Codes for Northeast Map Overlays -- Land Use/Land Cover, Wetlands, and Beaver Activity

Overlay Type	Class	Subclass	Map Unit
Land use/ land cover	Cropland	-	C
	Forest land	-	E
	Pasture land	-	G
	Horticulture land	-	H
	Cemeteries	-	M
	Waste disposal land	-	L
	Barren land	-	N
	Gravel pits/quarries	-	P
	Urban-commercial	-	U_c
	Urban-industrial	-	U_i
	Urban-residential(#)	-	U_y
	Wetlands	-	W
Detailed wetlands	Aquatic bed	algal	AB1
		aquatic moss	AB2
		rooted vascular	AB3
		floating vascular	AB4
		unknown submergent	AB5
		unknown surface	AB6
	Emergent	persistent	EM1
		nonpersistent	EM2
	Forested	broad-leaved deciduous	FO1
		needle-leaved deciduous	FO2
		broad-leaved evergreen	FO3
		needle-leaved evergreen	FO4
		dead	FO5
		deciduous	FO6
		evergreen	FO7
		open water/unknown	OW
		rocky bottom	RB
		rocky shore	RS

continued

Table 5-11. (Continued)

Overlay Type	Class	Subclass	Map Unit
	Scrub/Shrub	broad-leaved deciduous	SS1
		needle-leaved deciduous	SS2
		broad-leaved evergreen	SS3
		needle-leaved evergreen	SS4
		dead	SS5
		deciduous	SS6
		evergreen	SS7
Beaver activity		unbreached dam	U
		breached dam	B
		old beaver dam	O
		beaver lodge	Δ
		impounded water	IM
		open water	OW

5.4.1.6.2 Field check protocols -

Independent QA/QC activities were required to evaluate both base map and air photo overlays and to assess inherent photointerpretation discrepancies. To meet this requirement, field checks were made of office interpretations for 15 watersheds, a 10 percent subsample (Figure 5-11, Table 5-12). Sample watersheds were representative of DDRP watershed sizes and maximized mapped land use, wetland, beaver activity, and stream variability found across the 145 NE watersheds. For example, for several similar-sized watersheds, those with diverse land uses and wetlands were chosen over ones that had a few wetlands or forest cover as the sole land use.

Staff from the Center for Earth and Environmental Science, State University of New York, Plattsburgh (SUNY-P), performed the field QA/QC check of office-generated land use and wetland maps. The QA/QC work involved two distinct phases (Bogucki et al., 1987): Phase I, field checks, and Phase II, photointerpretation and evaluation. In Phase I, SUNY-P staff verified existing point and area land use delineations at 5 to 12 sites per watershed that had been targeted for field checking by ERL-C staff. Between specific check points, detailed observations also were made to characterize land use, wetlands, and beaver activity existing across the landscape. Field checking was conducted during October and November 1986, when most leaves had fallen from the trees.

In Phase II, SUNY-P staff independently mapped land use and wetlands on CIR stereo pair overlays. Notes also were made on imagery quality factors that adversely affected photointerpretation, watershed disturbances that could affect surface water chemistry (e.g., recent or historical logging), and interpretation problems that were encountered.

ERL-C staff analyzed differences between office and field maps by Chi-square goodness-of-fit tests to determine those categories that were significantly more difficult to map. The null hypothesis for each test was that differences between office and field maps were proportional over all classification categories used in the tests (Sokal and Rohlf, 1969). In the first test, the null hypothesis was that all general land use categories were likely to have equal differences in interpretation. In the second test, the null

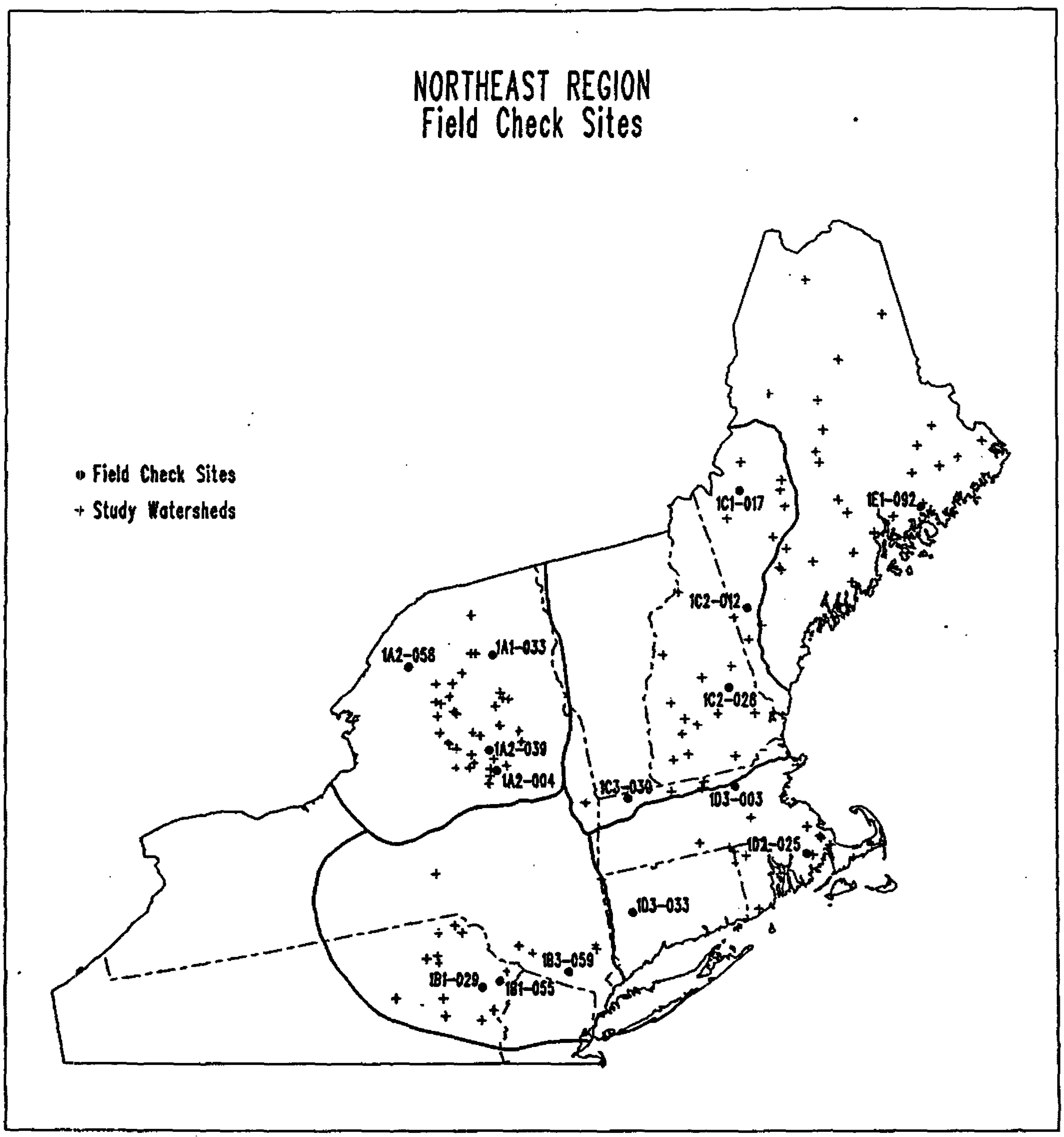


Figure 5-11. Location of Northeast field check sites and other DDRP watersheds.

Table 5-12. Northeast Watersheds Studied for Independent Field Check of Land Use and Wetland Photointerpretations

Lake ID	Name/State	Size (ha)	Topo Name	Scale (min)	County
1A1-033	Kiwassa, NY	415	Saranac Lake	15'	Franklin
1A2-004	Duck Lake, NY	111	Caroga Lake	7.5'	Hamilton
1A2-039	Oxbow Lake, NY	1165	Lake Pleasant	15'	Hamilton
			Piseco Lake		
1A2-058	Trout Lake, NY	444	Edwards	7.5'	St. Lawrence
			Bigelow		
			S. Edwards		
			Hermon		
1B1-029	No Name, PA	486	Promised Land	7.5'	Pike
1B1-055	Rock Hill, PA	194	Peck's Pond	7.5'	Pike
1B3-059	Island Pond, NY	330	Monroe	7.5'	Rockland
			Sloatsburg		
1C1-017	Welhern Pond, ME	341	Tim Mtn.	7.5'	Franklin
			Stratton	15'	
1C2-012	Black Pond, ME	460	Pleasant Mtn.	7.5'	Oxford
			N. Waterford		
1C2-028	Sunset Lake, NH	1348	Gilmantown	15'	Belknap
			Winnepesaukee		
1C3-030	Pelham Lake, MA	1082	Rowe	7.5'	Franklin
			Heath		
1D2-025	Little Quittacus, MA	298	Assawompset	7.5'	Plymouth
1D3-003	Sandy Pond, MA	531	Ayer	7.5'	Middlesex
1D3-033	No Name, CT	337	Litchfield	7.5'	Litchfield
1E1-092	Great Pond, ME	2511	Hancock	7.5'	Hancock
			Eastbrook		

hypothesis was that all detailed wetland categories were likely to have equal differences in interpretation. This method is probably more appropriate than using a simple contingency table to measure how well office map units matched the field landscape (George, 1986).

5.4.1.6.3 Results and discussion -

For general land use, differences in interpretations between office and field maps were significant (Table 5-13). The forest class (E) had the highest percentage (87 percent) of matches, whereas the least percentages of matches were for wetlands (W), 50 percent, and for an aggregated "disturbance" class that included waste disposal sites (L), gravel pits and quarries (P), barren land (N), horticulture (H), and cemeteries (M), 52 percent (Table 5-14). Mismatches might have been unusually high for several general land use classes. First, the high discrepancy in wetland matches was due to field check identification of more very small ($\pm$ 0.4 ha) wetland areas than were mapped by office procedures. Second, matches for the combined/cropland pasture (C/G) class were low because both unimproved and improved pasture were often confused with plowed land on the leaf-off imagery taken during the very wet spring. Third, a high percentage of mismatches for the disturbed class (L/P/N/H/M) probably reflects the very intensive field check work done by SUNY-P staff who classified specific land use that appeared different on aerial photos [e.g., horticulture (cranberries, H) instead of wetland (W); waste disposal land (L) instead of urban land (U); and forest land (E) instead of barren land (N)].

For detailed wetlands, differences between field check and office determinations were also significant (Table 5-15). The easiest subclasses to identify were emergents (EM), broad-leaved evergreen shrubs (SS3), and open water (OW), which all had about 80 percent matches (Table 5-16). Forest subclasses (FO1/FO2, FO4, and FO5) were the most difficult to map. Office maps usually had only one National Wetlands Inventory (NWI) subclass for each wetland delineation; SUNY-P field maps had a greater number of dual NWI subclass modifiers for wetland delineations.

Table 5-13. Chi-Square Test for General Land Use Categories

	Land Use Classes[a]					
	C/G	E	L/P/N/H/M	W	U	OW
Totals						
O=Match	46	109	11	170	300	25
E=Exp.	47.030	80.531	13.529	220.977	278.960	19.972
$(O-E)^2/E$	0.023	10.064	0.473	11.760	1.587	1.266
O=Mismatch	27	16	10	173	133	6
E=Exp.	25.970	44.469	7.471	122.022	154.039	11.028
$(O-E)^2/E$	0.041	18.226	0.056	21.297	2.874	2.293
	73	125	21	343	433	31

Chi-squared, $\Sigma_i(O_i-E_i)^2/E_i$ = 70.759
d.f. = 5
Table value = 16.748 (for p = 0.005)

[a] See Table 5-11 for explanation of land use codes.

Table 5-14. Comparison of Field Check (Matched) General Land Use Determinations with Office Photointerpretations

	Land Use Classes[a]					
	C/G	E	P/P/N/H/M	W	U	OW
Matched	46	106	11	170	300	25
Totals	73	125	21	343	433	31
Matched Percent	63	87	52	50	69	81

[a] See Table 5-11 for explanation of land use codes.

Table 5-15. **Chi-Square Test for Detailed Wetland Categories**

	Wetland Categories[a]							
	FO1/FO2	FO4	FO5	SS1	SS3	SS4/SS5	EM	OW
Totals								
O=Match	50	26	6	142	55	17	102	37
E=Exp.	88.865	50.466	14.810	127.260	38.398	15.908	74.054	25.2
$(O-E)^2/E$	16.998	11.861	5.241	1.706	7.178	0.075	10.545	5.4
O=Mismatch	112	66	21	90	15	12	33	9
E=Exp	73.135	41.533	12.189	104.730	31.601	13.092	60.945	20.8
$(O-E)^2/E$	20.654	14.412	6.369	2.073	8.721	0.091	12.814	6.7
	162	92	27	232	70	29	135	46

Chi-squared, $\Sigma_i(O_i - E_i)^2/E_i$ = 130.89
d.f. = 7
Table value = 20.276 (for $p = 0.005$)

[a] See Table 5-11 for explanation of detailed wetland codes.

Table 5-16. Comparison of Field Check (Matched) Detailed Wetland Determinations with Office Photointerpretations

	Wetland Categories[a]							
	FO1/FO2	FO4	FO5	SS1	SS3	SS4/SS5	EM	OW
Matched	50	26	6	142	55	17	102	37
Totals	162	92	27	232	70	29	135	46
Matched Percent	31	28	22	61	79	59	76	80

[a] See Table 5-11 for explanation of detailed wetland codes.

Open water matches were lower than expected because SUNY-P delineations followed CIR imagery water body boundaries shown on CIR aerial photos, whereas office map delineations tended to follow shorelines shown on USGS topographic maps. Topographic maps ranged from 15 to more than 40 years old and included a large number of smaller scale, less detailed 15' base maps. A low percentage of matches for forest and shrub subclasses was probably due to the combined effects of (1) office photointerpreters less familiar with northeastern forest and wetland vegetative patterns and (2) the poor quality CIR imagery used.

Based on the overall mapping accuracy observed, general land use data, but not detailed wetland data, were digitized for all 145 DDRP NE watersheds. Two factors influenced this decision. First, although the office maps excluded many small wetlands, they did include large wetlands that generally coincided with field delineations; such wetlands were primarily adjacent to lakes or along major streams that flowed into them. Small wetlands excluded on office maps were usually in remote parts of the watershed and not adjacent to either the perimeter of lakes or major streams flowing into them. The larger wetlands contiguous to lakes and streams are probably much more important in influencing surface water chemistry (Johnston et al., 1984; Cooper et al., 1986; Osborne and Wiley, 1988). Second, although office maps had delineations with one rather than two or three NWI wetland subclasses, total wetland area on office maps agreed well with that found on field maps.

5.4.1.6.3.1 Beaver activity --

Three of the 15 field check watersheds had no beaver activity, 2 had ancient or recent dams not mappable from photo imagery, and 10 had many examples of unbreached (U) and breached (B) dams and in-lake lodges (L). Generally, office maps identified beaver activity in watersheds where it existed but underestimated the total number of dams present (Table 5-17). Field work characterized extent of beaver activity, identified bank lodges not seen on aerial photos, verified two roads mistaken for beaver dams, and identified a large rock mapped as an in-lake lodge. Based on experiences from prior studies (Bogucki et al., 1986), some discrepancies in beaver activity between office and field maps were probably

Table 5-17. Comparison of Beaver Dam Number (#), Breached (B) and Unbreached (U) Status, and Lodges (L), Identified via Field Check and Office Photointerpretation Methods

Lake ID/Name	Office				Field			
	#	B	U	L	#	B	U	L
1A2-004/Duck Lake, NY	4	1	3	2	6	0	6	3
1A2-039/Oxbow Lake, NY	4	0	4	1	15	12	3	1
1A2-058/Trout Lake, NY	1	1	0	0	3	0	3	0
1B3-059/Island Pond, NY	1	1	0	0	0	-	-	-
1C1-017/Welhern Pond, ME	7	0	7	0	14	14	0	1
1C2-012/Black Pond, ME	2	0	2	1	2	1	1	1
1C2-028/Sunset Lake, NH	27	4	23	5	42	32	10	5
1C3-030/Pelham Lake, MA	9	1	8	1	22	22	0	2
1D3-033/No Name, CT	1	0	1	0	2	2	0	2
1E1-092/Great Pond, ME	20	4	16	5	42	32	10	5
Totals	76	12	64	5	148	115	33	20

due to (1) the five- to six-month time difference between photography and field check dates and (2) variability in photointerpreter experience in distinguishing beaver dam activity on large-scale photography.

5.4.1.6.3.2 Map scale and imagery quality --

The CIR 1:12,000 scale imagery was ideal for mapping land use, wetlands, and water bodies. Detailed NWI wetland subclasses were readily identifiable as were beaver dams and lodges. Compared to 1:24,000-scale photography, however, the 1:12,000 scale was somewhat undesirable for mapping watershed boundaries, particularly in large areas of the NE where local relief is either minimal or very great. Also, although lots of wetland detail was seen on the 1:12,000-scale photos, considerably greater time and money were spent on photointerpretation time and map control to prepare photo and base map overlays. Imagery quality was generally poor (e.g., excessive shadows, variable color quality, excessive vignetting, and considerable tonal variation) on photos for 9 of the 15 field check watersheds. Only in a few instances, however, did imagery quality seriously affect mapping quality at the NWI subclass and land use discrimination levels used in the Project. Limiting photo acquisition to one subcontractor and imposing stricter quality control on "minimally acceptable" photo products would have improved image quality for all photos.

5.4.1.6.4 Land use digitization -

Photointerpretation of 1:12,000 CIR photographs allowed characterization of land use and land cover found across the NE. Thus, general land use data from all 145 NE watersheds were digitized via GIS (Section 5.4.1.7). Finally, some watershed land use attributes (e.g., particularly small beaver dams and some pasture/cropland distinctions) were only detectable by conscientious ground-truthing rather than careful photointerpretation of large-scale conventional imagery.

5.4.1.6.5 Land use/land cover summaries -

More urban land exists in Subregion 1D, which includes the heavily built-up portions of Connecticut and Massachusetts (Table 5-18). Subregion 1B, northeastern Pennsylvania and southeastern New York, had the second highest amount of urban land as well as the highest amount of agricultural land. These

Table 5-18. Aggregated[a] Land Use Data for Northeast Watersheds

Land Use	Subregions 1A (38)	1B (20)	1C (30)	1D (24)	1E (32)
Water (ha)	44	29	44	31	104
Urban (%)	1	6	0.5	15	0.5
Agriculture (%)	-	11	2.5	4.5	4
Forest (%)	96	78	91	75	91
Wetlands (%)	3	5	6	5	4.5
Sum (%)	100	100	100	99.5	100.0

[a] Aggregated land use classes, as described in Table 8-27. Percents are based on terrestrial areas of watersheds.

Water	=	all OW
urban	=	$P + L + U_V + U_i + U_c + M$
agriculture	=	C + G + H
forest	=	E
wetlands	=	W

areas comprise the Pocono and Catskill Mountains, respectively, both of which have large commercial and private retreat camps for East Coast city residents. Valleys between rolling hills contain gentle topography and fertile soil that is suited to agriculture. Three subregions had forest land $\geq$ 91 percent; even Subregions 1B and 1D, with the highest urban areas, had forest percentages $\geq$ 75 percent. These results are not surprising because NE watersheds were selected to eliminate very urbanized and/or disturbed watershed systems.

Although the mean size of water bodies in Subregion 1E, Maine, was two or three times greater than mean lake size in the other subregions, average percent of area in wetlands was not greater. In all subregions, total wetlands averaged 5 percent. The range in wetland was also fairly constant, 0 to 16 percent for all but Subregion 1C, comprising Vermont/New Hampshire. Although much of Subregion 1A includes the mountainous and heavily forested Adirondack State Park, work by Bogucki et al. (1986) showed a 34 percent increase in beaver activity between 1978 to 1985. We therefore expected mean wetland percent for the subregion to be greater. However, in another study covering 10 watersheds in the Adirondacks, mean wetland cover was also low: 2 percent (Cronan et al., 1987).

5.4.1.7 Geographic Information Systems Data Entry

5.4.1.7.1 Introduction -

Upon receipt from the mapping contractors, the mapped watershed information was entered into a GIS. The GIS is designed to automate, manipulate, analyze, and display geographical data in digital form, and was used in the DDRP as a spatial tool for technical analysis and for effective communication (Campbell et al., 1989).

5.4.1.7.2 Northeast databases -

The DDRP obtained data from contract mappers and from existing information. The USDA-SCS, in cooperation with the U.S. EPA, mapped soils, vegetation, and depth to bedrock at a scale of 1:24,000 for each watershed (Lammers et al., 1987b; Lee et al., 1989a) (see Sections 5.4.1.1 through 5.4.1.5). Land use was mapped at the same scale by the U.S. EPA - EMSL-LV (Liegel, in review) (Section 5.4.1.6).

Streams and bedrock geology were extracted from existing maps published by the USGS: streams from 7.5' or 15' topographic maps and geology from appropriate state geology maps. Contour lines for the elevational buffers (Section 5.4.1.7.5.1) were obtained from the same topographic maps as the streams. These data were all entered in a GIS using ARC/INFO software. Examples of GIS maps of watershed characteristics are given for a specific watershed (1E1-062, Little Seavey Lake) in Plates 5-7 through 5-11 (see also Plate 5-13).

Upon receipt of the SCS and EMSL-LV manuscript maps, the map overlays were prepared for GIS entry. A minimum of four registration marks were placed on each overlay to geographically coordinate the watershed to the surface of the earth. These registration marks also ensure manuscript-to-manuscript registration.

Because the topographic reference maps used for the manuscript maps were produced differently by the SCS and EMSL-LV, separate datasets were developed. The SCS primarily used diazo prints of topographic maps, and EMSL-LV used original or photographically enlarged topographic maps. This made the scaling of the reference maps somewhat different. In addition, the two sources were mapped during different years; thus, the lake delineations were inherently slightly different. The same geographic coordinates for registration within each watershed were used for both sources, however, and were drafted onto each manuscript map. These registration marks were independently checked by another technician before the map was digitized.

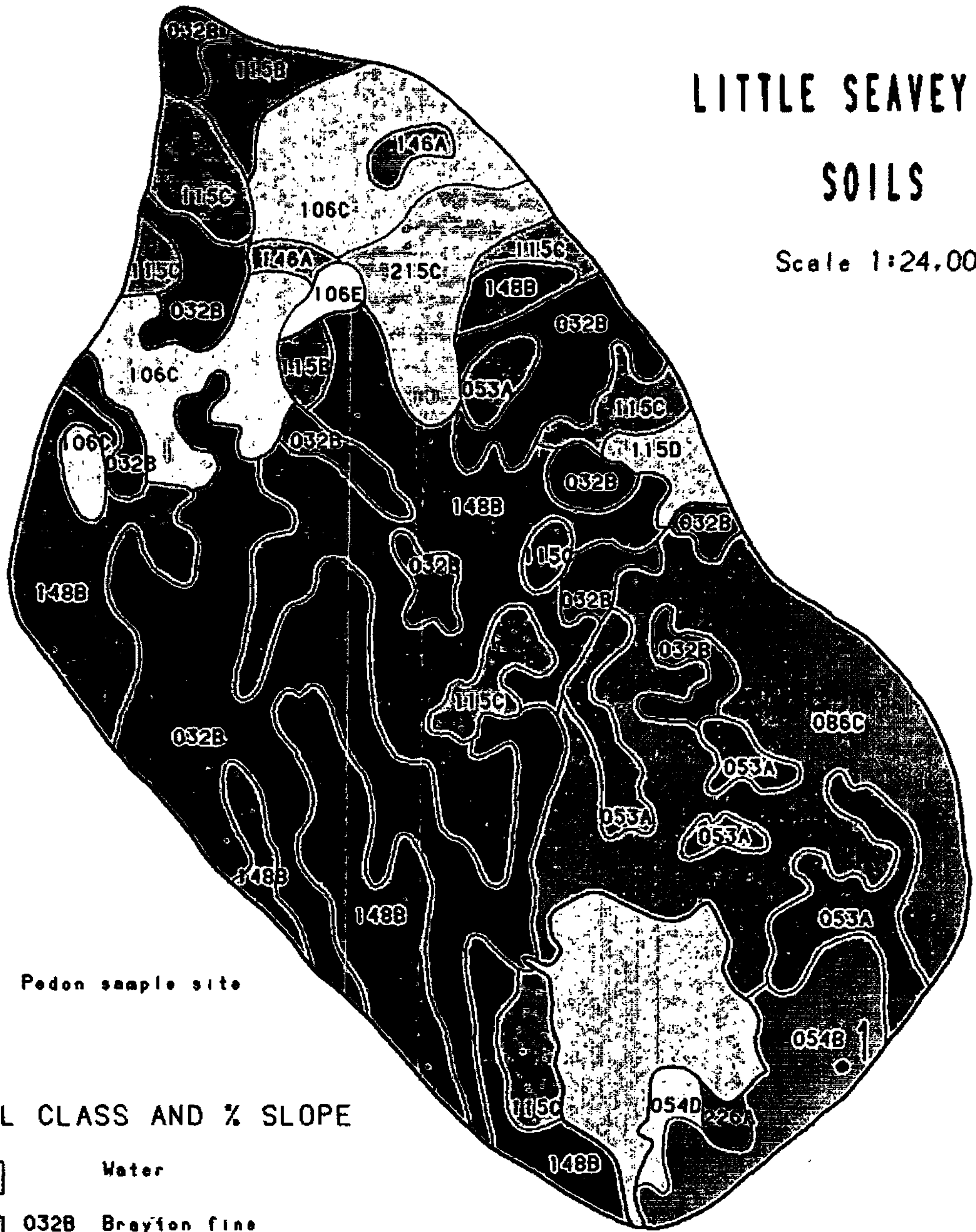
5.4.1.7.2.1 Digital entry of manuscript maps –

The manuscript maps were digitally entered into the computer using two basic steps -- digitization and attribute entry. Once entered, the digitized map is referred to as a coverage in ARC/INFO. The digitization process enters the lines (arcs) of each layer into separate coverages. Attribute entry relates the map classifications to a specific polygon area.

Plate 5-7. Example of watershed soil map (including pedon site location).

LITTLE SEAVEY LAKE SOILS

Scale 1:24,000

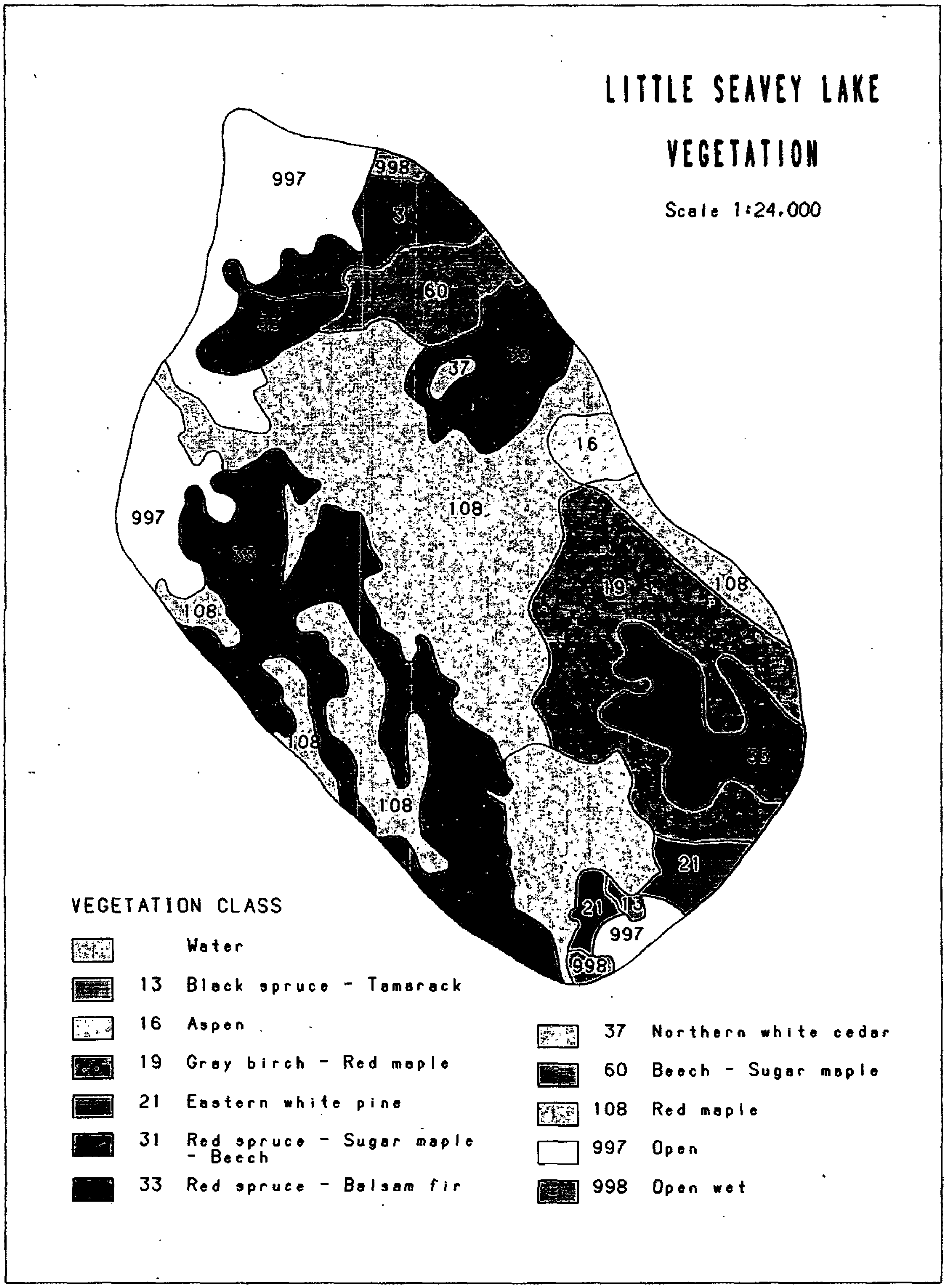


● 1 Pedon sample site

SOIL CLASS AND % SLOPE

		Water	
	032B	Brayton fine sandy loam	3-8%
	053A	Chocorua mucky peat	0-3%
	054B	Colton gravelly loamy sand	3-8%
	054D	Colton gravelly loamy sand	15-25%
	086C	Hermon sandy loam	8-15%
	106C	Lyman-Rock outcrop complex	3-15%
	106E	Lyman-Rock outcrop complex	15-45%
	115B	Marlow fine sandy loam	3-8%
	115C	Marlow fine sandy loam	8-15%
	115D	Marlow fine sandy loam	15-25%
	146A	Peacham muck	0-3%
	148B	Peru fine sandy loam	3-8%
	215C	Tunbridge-Lyman complex	8-15%
	226A	Waskish peat	0-3%

Plate 5-8. Example of watershed vegetation map.



LITTLE SEAVEY LAKE
VEGETATION
Scale 1:24,000
997
998
60
37
16
108
997
19
108
108
108
108
21
21
13
997
998
VEGETATION CLASS
Water
13 Black spruce - Tamarack
16 Aspen
19 Gray birch - Red maple
21 Eastern white pine
31 Red spruce - Sugar maple - Beech
33 Red spruce - Balsam fir
37 Northern white cedar
60 Beech - Sugar maple
108 Red maple
997 Open
998 Open wet

Plate 5-9. Example of depth-to-bedrock map.

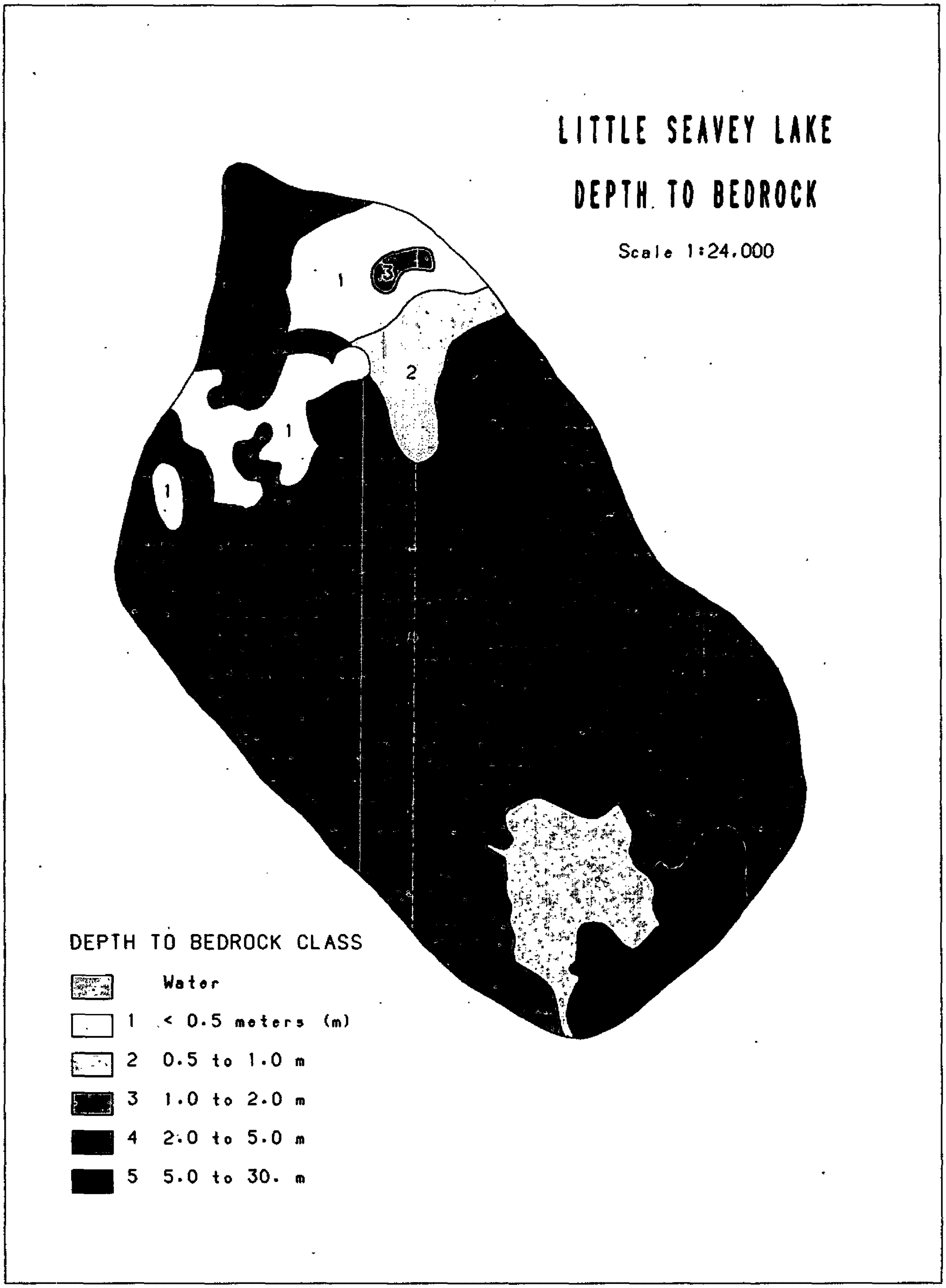

LITTLE SEAVEY LAKE
DEPTH TO BEDROCK
Scale 1:24,000
1
3
2
1
1
DEPTH TO BEDROCK CLASS
Water
1 < 0.5 meters (m)
2 0.5 to 1.0 m
3 1.0 to 2.0 m
4 2.0 to 5.0 m
5 5.0 to 30. m

Plate 5-10. Example of watershed land use map.

LITTLE SEAVEY LAKE
LAND USE

Scale 1:24,000

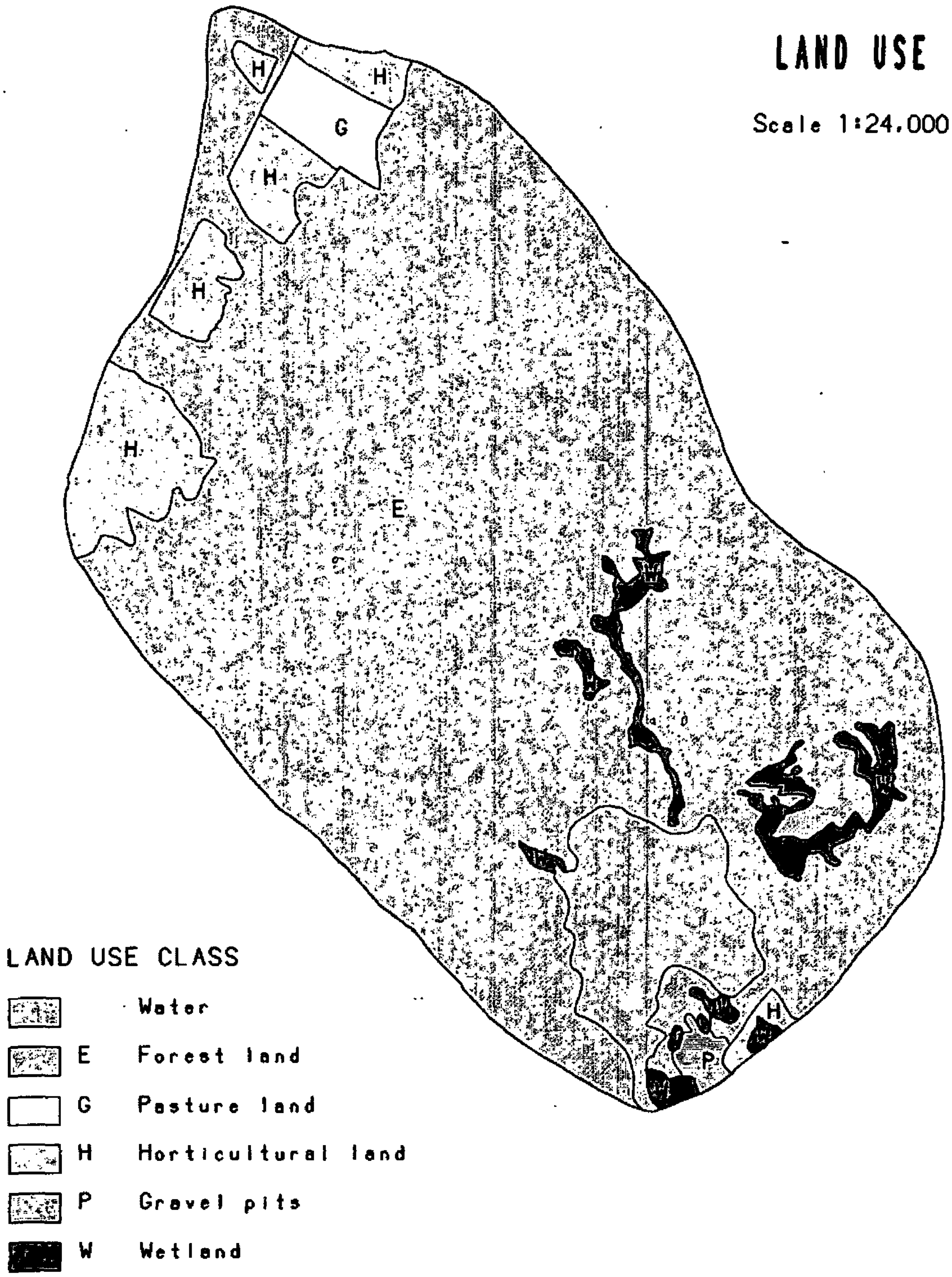
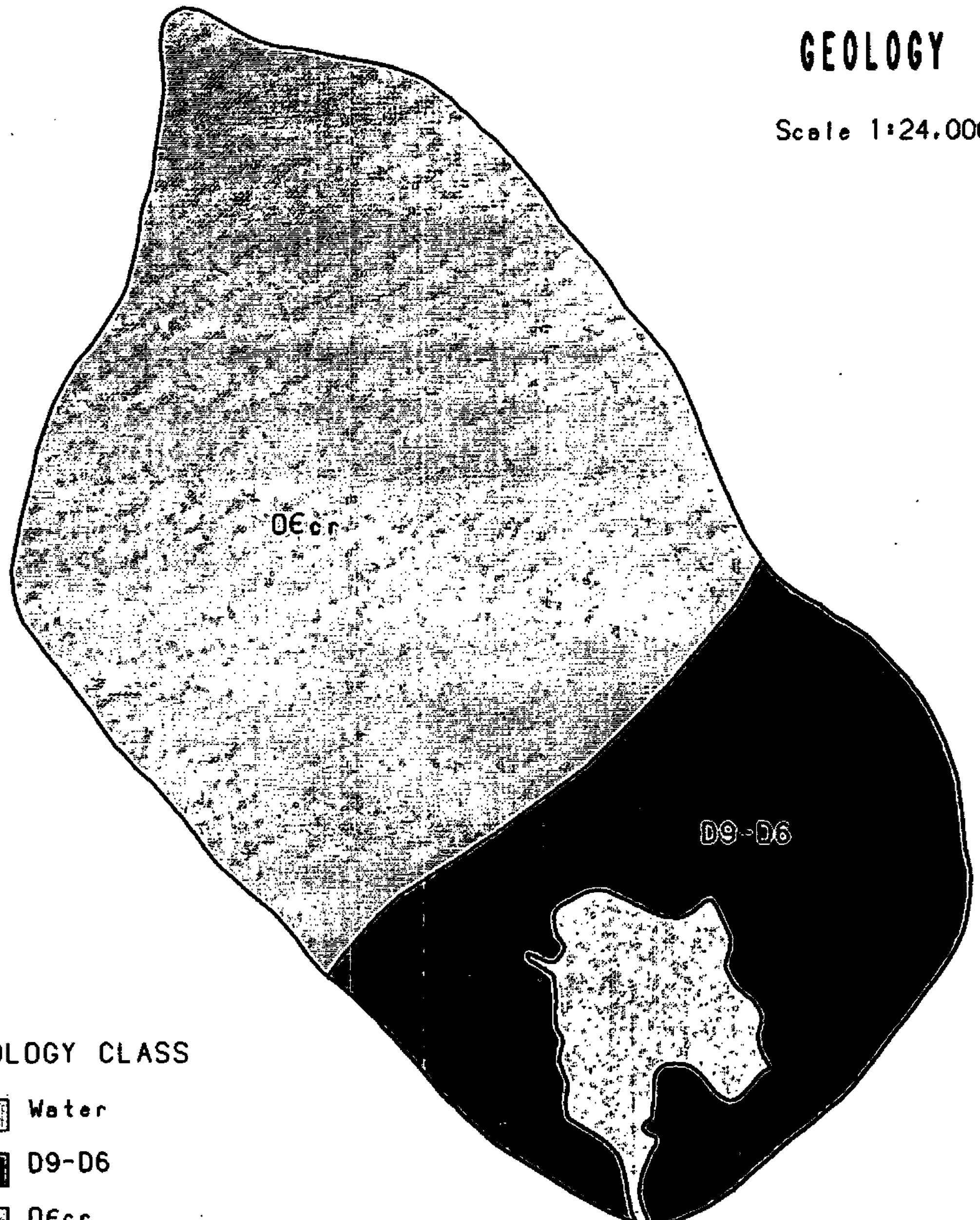


Plate 5-11. Example of watershed geology map.

LITTLE SEAVEY LAKE
GEOLOGY

Scale 1:24,000



GEOLOGY CLASS

- Water
- D9-D6
- O€cr

To ensure consistency in data entry among personnel over the course of the Project, a log sheet of the steps necessary to create each of the coverages was developed. These steps were (1) sequentially digitizing the arcs of each layer into separate coverages, (2) adding labels to each polygon, (3) editing any necessary changes, and (4) establishing the coverage into a workable database. Upon completion of each task, the log sheet was initialed by the operator (Figure 5-12).

5.4.1.7.2.1.1 Digitization

To ensure consistent delineation among the SCS coverages, a template coverage with only the lake and watershed boundaries was created. This template was used as a starting base for the soil, vegetation, and depth-to-bedrock coverages. Because of the watershed and lake boundary differences discussed previously, the EMSL-LV land use did not use this template. The remaining polygons and labels were then digitized into their corresponding coverages, using the specified criteria for high quality digitizing.

5.4.1.7.2.1.2 Polygon error and digitizing quality check

After the coverages had been completely digitized, a plot of any polygon errors was made using an internal editing function of ARC/INFO. These plots indicated polygon errors, including unclosed polygons, unlabeled polygons, or polygons with more than one label point. Any errors found were corrected before continuing. A new plot displaying all the digitized polygons and labels was then made at the same scale as the manuscript maps. This plot was used as the first quality check of the digitized arcs. The plot was overlaid with the mylar or acetate manuscript maps on the light table. If any light appeared between the digitized line and the drafted line, the digitized line was corrected, and the polygon error check was repeated. If there were no line errors, the attributes were written on the map next to the polygon identification number for attribute entry.

5.4.1.7.2.1.3 Attributes entry and quality control procedures

Log sheets listing the ARC/INFO commands were created (Figure 5-13) to promote consistency in adding attributes. The attributes for each polygon were added, in code form, into an ASCII file.

WATERSHED NO.__________ Date________ INITIALIZE UPON COMPLETION

1.	$ CREATE/DIR [DDELAY.------] i.e., CREATE/DIR [DDELAY.1A1003]	
2.	$ SET DEF [DDELAY.------]	
3.	$ ARC	
4.	ARC: ADS BASEDG Digitized tics, watershed boundary, and all water bodies.	BASEDG________
5.	ARC: CLEAN BASEDG BASECN .25	BASECN________
6.	ARC: EDITPLOT BASECN BASE.PLT	BASE.PLT______
7.	ARC: ARCEDIT Make corrections, as needed. Repeat steps 5 - 7, as needed.	BASECN________
8.	ARC: COPY BASECN BASE	BASE__________
9.	ARC: COPY BASE (SOILDG) (VEGDG) COPY SOIL (DEPDG)	SOILDG________ VEGDG_________ DEPDG_________
10.	ARC: ADS (SOILDG) (VEGDG) Digitize the remaining arcs and labels.	SOILDG________ VEGDG_________
11.	ARC: ARCEDIT Delete arcs from SOIL to create DEPDG. Add polygon IDs.	DEPDG_________
12.	ARC: CLEAN (SOILDG) (SOILCN) .25 (VEGDG) (VEGCN) (DEPDG) (DEPDG)	SOILCN________ VEGCN_________ DEPCN_________
13.	ARC: EDITPLOT (SOILCN) (SOIL.PLT) (VEGCN) (VEG.PLT) (DEPCN) (DEP.PLT)	SOIL.PLT______ VEG.PLT_______ DEP.PLT_______
14.	ARC: ARCEDIT Make corrections, as needed. Repeat steps 12 - 14, as needed.	SOILCN________ VEGCN_________ DEPCN_________
15.	ARC: COPY (SOILCN) (SOIL) (VEGCN) (VEG) (DEPCN) (DEP)	SOIL__________ VEG___________ DEP___________

Figure 5-12. Example of digitization log sheet.

```
WATERSHED NO.____________ DATE___________          INITIALIZE UPON
                                                   COMPLETION
                                                   ____________________

1.  $ SET DEF [DDELAY.------]

2.  $ COPY [DDELAY]BASE.DAT (SOIL.DAT)            SOIL.DAT_______
                            (VEG.DAT)             VEG.DAT________
                            (DEP.DAT)             DEP.DAT________

3.  $ VP (SOIL.DAT)                               SOIL.DAT_______
         (VEG.DAT)                                VEG.DAT________
         (DEP.DAT)                                DEP.DAT________
          type in data
          cntl/z

4.  $ ARC

5.  ARC: INFO
    USER NAME> ARC
    ENTER COMMAND> ADIR [DDELAY.SKELETON.INFO]
    ENTER COMMAND> TAKE ARC *
    ENTER COMMAND> SEL SOILTAB
    ENTER COMMAND> ADD FROM [DDELAY.------]SOIL.DAT
                                                   SOILTAB_________
6.  ENTER COMMAND> SEL VEGTAB
    ENTER COMMAND> ADD FROM [DDELAY.------]VEG.DAT
                                                   VEGTAB__________
7.  ENTER COMMAND> SEL DEPTAB
    ENTER COMMAND> ADD FROM [DDELAY.------]DEP.DAT
                                                   DEPTAB__________
    ENTER COMMAND> Q STOP

8.  ARC: JOINITEM SOIL.PAT SOILTAB SOIL.PAT SOIL-ID SOIL-ID
                                                   SOIL.PAT________

9.  ARC: JOINITEM VEG.PAT VEGTAB VEG.PAT VEG-ID VEG-ID
                                                   VEG.PAT_________

10. ARC: JOINITEM DEP.PAT DEPTAB DEP.DAT DEP-ID DEP-ID
                                                   DEP.PAT_________

11. ARC: INFO
    USER NAME> ARC
    ENTER COMMAND> SEL (SOIL.PAT)                  SOIL.PAT________
                       (VEG.PAT)                   VEG.PAT_________
                       (DEP.PAT)                   DEP.PAT_________
    ENTER COMMAND> LI
                   check .PAT files
    ENTER COMMAND> Q STOP
```

Figure 5-13. Example of attribute entry log sheet.

This list was rechecked for accuracy. The file was then merged with the corresponding coverage file and scanned for errors. Corrections were made, and any necessary QC procedures were repeated.

5.4.1.7.2.2 Quality control plotting –

The final plots containing the arcs and attributes of each coverage for each watershed were produced. These plots were then compared with the original manuscript maps over a light table and checked for accuracy. If any light passed between the digitized arc and the drafted line, the arc was corrected and the necessary QC procedures were repeated. If the arcs appeared to be correct, the attributes were checked for accuracy. Each individual attribute was checked against the drafted map, thereby double checking for any attributes that might have been misunderstood due to plotting resolutions (e.g., 1's and "I"s, 0's and "O"s, "G"s and "C"s). This procedure was performed independently by two individuals. Agreement, by signature, was required before the coverage was accepted.

5.4.1.7.2.3 Projection –

Following digitization, the coverages were projected into Universal Transverse Mercator (UTM) coordinates relating the watersheds to the surface of the earth and enabling comparison of databases. A series of procedures was used to ensure accurate transformation from the original digitized coordinates. First, the projected DDRP coverages were interactively displayed and visually checked for consistent location with coordinates of each lake corresponding to the NSWS (Linthurst et al., 1986a; Landers et al., 1988). The NSWS point locations data represent NSWS sites estimated independently from 1:24,000 topographic maps and projected into a UTM projection, and should appear near the center of the lake for each DDRP coverage. Next, the original digitized coverages were overlaid with the projected coverages and checked for consistency in area representation. Watershed areas were then calculated for the original digitized coverages versus the projected coverages. Variations of greater than 5 percent were flagged and rechecked for accuracy. Finally, to detect locational errors or any major differences in watershed or lake delineations, the SCS template coverage was visually compared to the EMSL-LV land use coverage. No errors were found during this final check.

5.4.1.7.3 Databases derived from existing maps -

Additional information was obtained from existing maps. The bedrock geology and streams databases were collected directly from published USGS maps.

5.4.1.7.3.1 Bedrock geology --

State bedrock geology maps were used to generate the bedrock geology coverages. These were the only maps available that provided a consistent geologic classification scheme within each state. The scale of the geology maps is 10-20 times smaller than the other coverages previously described (1:125,000 for Connecticut and Rhode Island; 1:250,000 for Massachusetts, New Hampshire, New York, Pennsylvania, and Vermont; 1:500,000 for Maine) (Billings, 1980; Doll et al., 1961; Isachsen et al., 1970; Miles, 1980; Osberg et al., 1985; Quinn et al., 1971; Rodgers, 1985; Zen, 1983). The SCS attempted to map the geology, but the map legends for the various reference maps used were inconsistent, and it was difficult to distinguish the classes into a single, usable map legend (see Section 5.4.1.4).

It was only necessary to digitize portions of the state geology maps corresponding to each particular watershed. A state scale map containing the template coverage and watershed identification number for all watersheds within that state was plotted. This plot was used as an overlay to the state geology maps to focus on the DDRP watershed areas.

Following digitization, the geology coverages were clipped, or "cookie cut", with the template coverage. This process creates a geology coverage with the same watershed delineation as the template coverage. Each new coverage was examined individually to ensure that the geology was complete for the entire watershed area. If it was incomplete, the missing area was added and clipped again. All water bodies from the template coverage were then added to the geology coverage.

To check the digitized arcs against the original map, the geology coverages within each state were plotted at the scale of the original state maps. The plots were then overlaid onto the state geology map and independently compared by two technicians. Enlargement of the geology coverages were also plotted to increase the visibility of all polygons. Attributes were written on the enlarged versions and checked independently for accuracy. Attributes were added into the coverage file, checked, and plotted at a scale of 1:24,000. The final QC procedure consisted of two independent comparisons of the new plots for accuracy. If there were any discrepancies in the attributes, they were corrected, plotted, and, again, checked twice independently until agreement was reached that the information was correct.

5.4.1.7.3.2 Streams –

The USGS topographic maps provided the most consistent drainage information available. (Independent interpretation of aerial photos was attempted as a means of identifying perennial and intermittent streams, but was not successful (see Section 5.4.1.1).) The 7.5' maps were used whenever possible; otherwise 15' maps were used. Because the resolution of 15' maps defines very few intermittent streams, only perennial streams were digitized for the entire stream dataset.

A log sheet was created for consistency in stream data entry. Four classes were used to categorize the streams: perennial inflow streams, perennial inflow streams through wetlands, outlet streams of the lake, and outlet streams of the lake draining through wetlands.

The stream coverages were plotted with the template coverage, and were overlaid with the topographic map on a light table and checked for discrepancies. If any light passed between the digitized arc and the stream on the map, the digitized arc was corrected. Stream classification was also checked for accuracy. This QC procedure was performed independently by two individuals until both agreed that the information was accurate.

5.4.1.7.4 Final quality control check and output generation -

After the mapped information was digitized and checked for accuracy, computer programs were written in ARC/INFO to check for consistency and to calculate a usable output for the data. These programs created lists of the classifications used and the calculated area, and also generated reports. This information was then transferred to other computer systems for data analysis within the project.

5.4.1.7.4.1 Classification –

A sorted list of all the attributes used to classify map units was generated to check for consistency in data entry from watershed to watershed. Any unnecessary spaces or data entry errors (e.g., 0's and "O"s, or capital letters used in one watershed and lower case letters used in another) were easily detected. Corrections were made within the coverage file.

5.4.1.7.4.2 Area –

The total watershed and lake areas were calculated and compared on a per-watershed basis for all the polygon coverages. Soils, vegetation, depth-to-bedrock, and geology coverages were exactly the same within a particular watershed, because these coverages used the same template coverage. Because land use was digitized independently of the template coverage, its coverage was similar, but not identical. If the differences were greater than 5 percent, the watershed was re-examined, and any necessary changes were made. When a change occurred after the original QC check, the watershed was subjected to an additional independent quality check until agreement was reached that the information was accurate. Additional changes were recorded.

5.4.1.7.4.3 Reports –

When all the QC requirements were met, the data were used to create land area summaries, or reports, using programming within INFO software. These reports list the classification, description of that class, area in hectares, and percentage for each watershed (see Table 5-19 as an example). Water bodies were not included in the percentage calculation. This output was then released for data analysis within the Project.

5.4.1.7.5 Buffers -

Low lying areas adjacent to the lakes and streams potentially have a more direct influence on the chemistry and response of the study lakes than upland areas. To examine this phenomenon, elevational

Table 5-19. Watershed No. 1E1062 Soil Mapping Units

Class	Soil Mapping Unit	Slope (%)	Hectares	Percent
000W	Water		42.1	0.0
032B	Brayton Fine Sandy Loam	3-8	170.3	24.9
053A	Chocorua Mucky Peat	0-3	38.7	5.7
054B	Colton Gravelly Loamy Sand	3-8	29.2	4.3
054D	Colton Gravelly Loamy Sand	15-25	4.4	0.6
086C	Hermon Sandy Loam	8-15	108.5	15.9
106C	Lyman-Rock Outcrop Complex	3-15	59.7	8.7
106E	Lyman-Rock Outcrop Complex	15-45	3.3	0.5
115B	Marlow Fine Sandy Loam	3-8	14.6	2.1
115C	Marlow Fine Sandy Loam	8-15	43.7	6.4
115D	Marlow Fine Sandy Loam	15-25	6.8	1.0
146A	Peacham Muck	0-3	6.2	0.9
148B	Peru Fine Sandy Loam	3-8	172.1	25.2
215C	Tunbridge-Lyman Complex	8-15	23.8	3.5
226A	Wakish Peat	0-3	2.4	0.4
			725.7	100.0

buffers were digitized for study lakes and generated linear buffers around streams and wetlands to capture the most proximal characteristics. [The wetlands information was mapped in the land use coverage (see Section 5.4.1.6)]:

5.4.1.7.5.1 Elevational buffers --

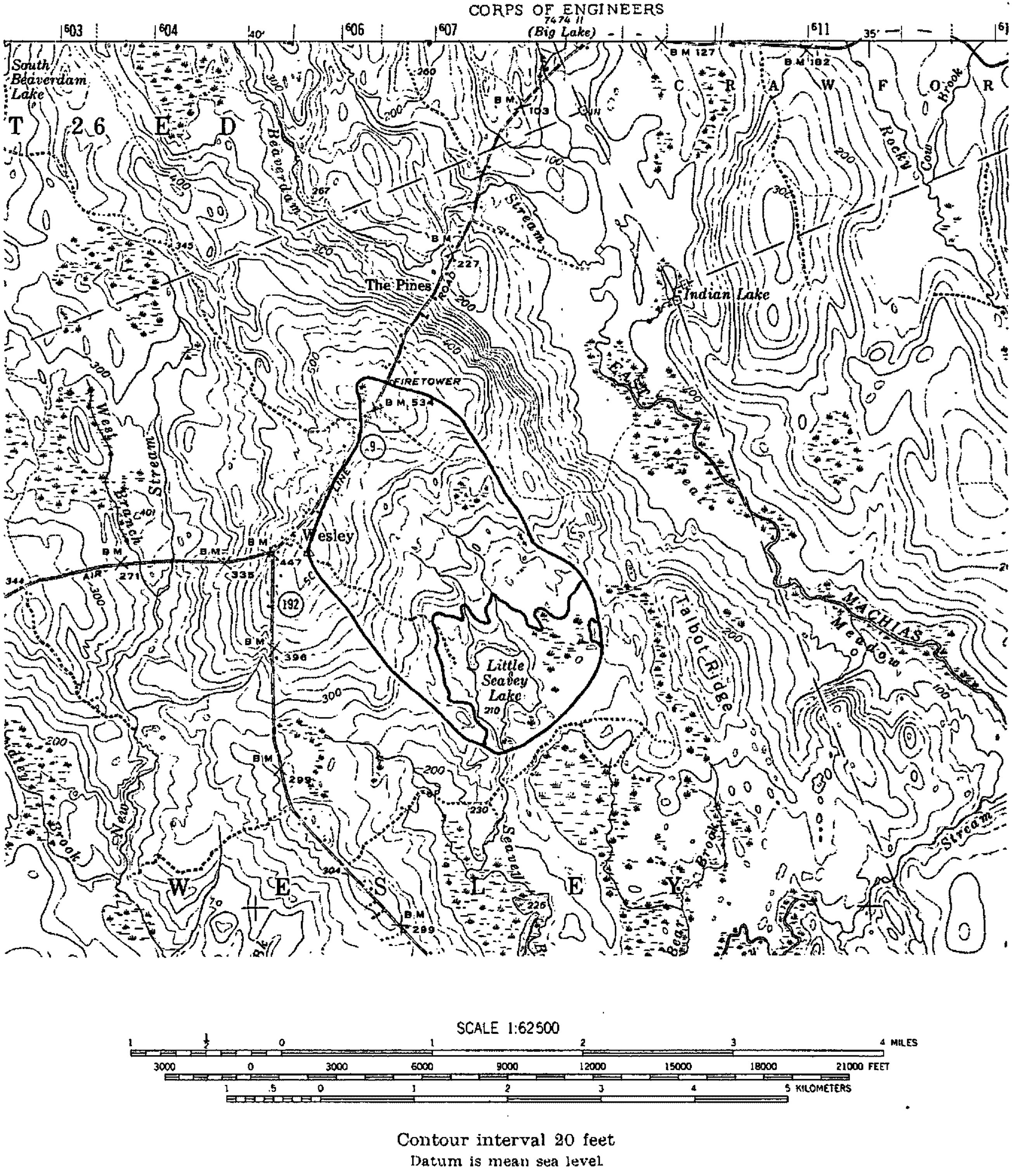
An elevational buffer was developed to provide a topographically and hydrologically meaningful buffer around each lake. Such buffers tend to include low lying wetlands areas and exclude sheer cliffs. The 40-foot contour above the outlet lake and any other lake connected to the outlet lake by a perennial stream was selected and digitized using topographic maps (Plate 5-12). The contour interval for the maps was 6 m, 10 ft, or 20 ft. Depending on the elevation of the lake, the actual elevation change from the lake to the digitized contour varied from 7 to 12 m (23 ft to 39 ft) on 6-m interval maps, 31 to 40 ft on 10-ft interval maps, and 21 to 40 ft on 20-ft interval maps. For example, if the elevation of the lake was 1219 ft on a 20-ft contour interval map, the digitized contour was 1240 ft, making the elevation change only 21 ft. If the elevation of the lake was 1200 ft, the digitized contour was still 1240 ft, making the elevation change 40 ft.

A log sheet of the steps necessary to create this coverage was designed to promote consistency in digitizing among personnel. It also provided additional information, such as lake elevation, the digitized contour, the contour interval of the map, and the number of islands or hills over 40 ft within the contour. The 40-ft contour was digitized into a copy of the template coverage for consistent lake delineation and registration.

When digitization of the contours and labels was completed, the coverage was plotted. The plot was overlaid with the topographic map on a light table. Any discrepancies were corrected, and the QC procedure repeated. As described previously for the other coverages, two technicians independently checked the plot for accuracy.

Plate 5-12. Example of 40-ft contour delineations on a 15' topographic map.

UNITED STATES
DEPARTMENT OF THE ARMY
CORPS OF ENGINEERS



SCALE 1:62500

Contour interval 20 feet
Datum is mean sea level

5.4.1.7.5.2 **Combination buffers** –

The 40-ft contour buffers, 30-m linear stream buffers, and 30-m linear wetlands buffers were combined to make a continuous hydrologic buffer. The 30-m stream and wetlands buffers were generated using ARC/INFO software (Environmental Systems Research Institute, 1986). No digitizing was necessary to develop this coverage. Extensive editing was required because isolated buffers needed to be deleted and areas surrounded by buffers needed special labeling so that these areas were not included in the buffer (Plate 5-13).

The combination buffer coverages were plotted, overlaid with the topographic map on a light table, and checked for the inclusion of pertinent buffers, exclusion of irrelevant buffers, and any special labeling. To check the wetlands information, the plots were also overlaid with the land use manuscript map. Discrepancies were corrected, and the QC procedure repeated. Two independent checks were made of each plot to ensure consistency.

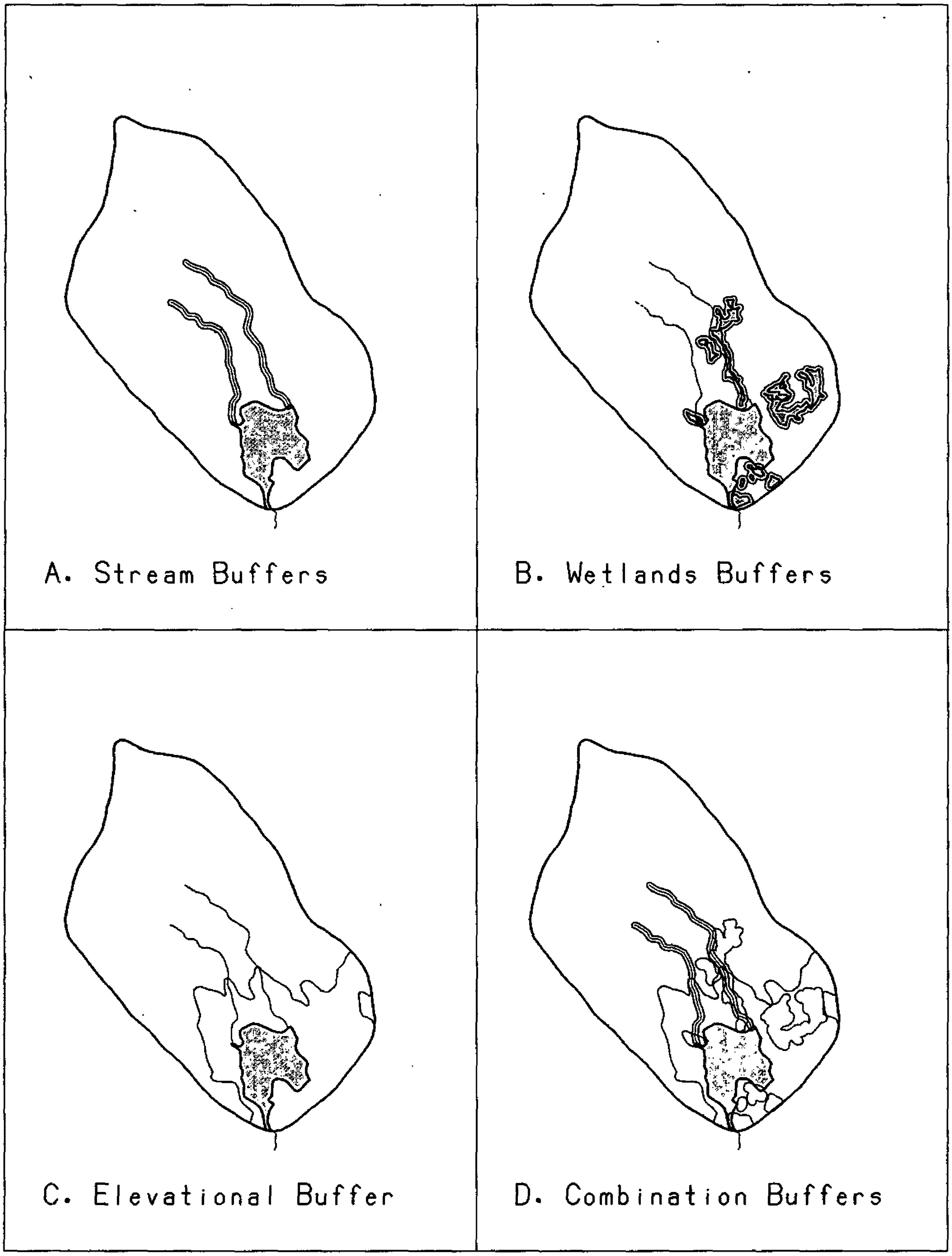
5.4.1.7.6 **Summary** -

The DDRP has a complex geographic database and uses a GIS to store, manipulate, analyze, and display these data. Extensive QC procedures were developed to ensure the data were entered as consistently and accurately as the original mapped information allowed. These procedures included checking the accuracy of the information before, during, and after digitizing. Two independent checks were performed before any data were accepted for use within the DDRP. (For more extensive details concerning the GIS, see Mortenson (1989a).)

5.4.2 Southern Blue Ridge Province Mapping

Mapping of soils, forest cover type and land use, depth to bedrock, geology, and watershed drainage was initiated in the SBRP during the week of October 15, 1985. Thirteen field soil scientists were responsible for mapping 35 watersheds, an area of about 46,730 ha (115,430 acres). Soil mapping activities and quality assurance of the mapping data were described in depth in a report by Lammers et al. (1987a).

Plate 5-13. Example of combination buffer: (A) stream and 30-m linear buffer for streams, (B) wetlands and 30-m linear buffer for wetlands, (C) elevational buffer for lake, and (D) combination of all preceding buffers.


A. Stream Buffers
B. Wetlands Buffers
C. Elevational Buffer
D. Combination Buffers

The survey was implemented through interagency agreements between the EPA and the SCS. The SCS has a professional staff of trained soil scientists located throughout the DDRP region, who are capable of producing high quality mapping products over large geographical regions within a short time frame.

Mapping protocols were developed in cooperation with soil scientists who worked in the SBRP and were familiar with standards and procedures used in the National Cooperative Soil Survey. The mapping phase was scheduled for October 15, 1985, to December 20, 1985, in order to accomplish compilation and correlation tasks before the sampling phase, scheduled to begin in April 1986. A preliminary regional soils identification legend was developed from existing soil survey legends within major land resource areas in the region. The State Soil Scientist in each state prepared a work plan to arrange for personnel and equipment to conduct the mapping. National high altitude aerial photographs at a scale of 1:24,000 were ordered for most of the watersheds, to be used as field base maps.

Prior to the start of mapping, the Mapping Task Leader, Regional Coordinator/Correlator, State Office Soils Staff and Field Soil Scientists involved in the mapping attended a workshop in order to review and practice the mapping protocols. The purpose of the workshop was to promote more consistent interpretation and application of the protocols.

Start of field work was delayed in North Carolina due to other mapping commitments, and an early fall snow storm terminated work in high elevation watersheds until spring. Field mapping continued through the winter months, and all watersheds except one (2A07816) were completed before the soil correlation workshop on March 3-6, 1986. Mapping was accomplished on most of the watersheds by two-person teams, each led by an experienced soil scientist. The soil scientist responsible for the mapping of each watershed, along with the watershed identification number, the name of the watershed, and the state responsible for the mapping, are listed in Lammers et al. (1987a). Because wilderness restrictions prohibited the use of any type of motorized vehicle in some watersheds, and several of the watersheds did not have roads, these watersheds could only be accessed by hiking. Access to some small areas within watersheds was denied by private landowners, but was not a major problem during the mapping phase of the survey. Generally, some other part of the landscape or a similar landscape was accessible and could be investigated. The mapping was extrapolated to the inaccessible areas by aerial photograph interpretation, other soil maps, or observation from a distance.

Map cartography and map compilation usually occurred in a field office. Some of the states arranged for the final cartography and compilation work to be performed by one person at a central location. Area of each map unit was estimated by a dot grid or with a planimeter. The map symbol, map unit name, and area of each map unit in acres was listed in a legend on each watershed map. Rough estimates of the area of map units were used during correlation and selection of classes of soils for sampling. A more precise measurement of the area of the map units was obtained when the maps were digitized and entered into the computerized GIS.

Aerial photographs at a scale of 1:20,000 were used for mapping one watershed (2A07826). Three watersheds (2A07828, 2A07833, and 2A07834) were mapped using 1:12,000-scale orthophotographs. Map overlays were rectified to 1:24,000-scale film positives of orthophotographs on scale stable film after mapping was completed. Film positives of 7.5', 1:24,000-scale topographic quadrangle maps were used for the rectified base where orthophotographs were not available.

5.4.2.1 Soils

Soils were mapped using the same standards and procedures described in Section 5.4.1.1 and the mapping protocols in Appendix A of the report by Lammers et al. (1987a). Soil scientists made soil maps on mylar overlays of base maps at a scale of 1:24,000.

5.4.2.1.1 Soil correlation -

The soil correlation process was described in Section 5.4.1.1.1 of this report.

A preliminary identification legend was developed based on soil map units that had been mapped within the SBRP. There were 210 map units listed in the preliminary legend, and about 90 map units were added during the field mapping. From the total of 300 map units, about 200 were actually used in the mapping. During the week of March 3-6, 1986, soil scientists representing the SCS from all of the states involved in mapping the DDRP SBRP Region met in Corvallis, OR, with the RCC and task leaders from ERL-C and ORNL. The objectives of the meeting were to correlate the soils and soil map units for the region and to complete descriptions of the map units. Each one of the 200 map units used during the mapping was reviewed. The characteristics and taxonomic classification of the major components of each map unit were checked and completed.

A few map units mapped in more than one state were found to be similar and were combined. Other map units were represented by just a few hectares and were combined with the most similar map unit in the legend.

Fifty of the map units were randomly selected for collection of transect data. Four available transects were randomly selected to represent each of the 50 map units. A transect consisted of examining and documenting the kind of soil or miscellaneous area at 10 points at equally spaced intervals across the map unit delineation.

Map unit descriptions were again reviewed during an Exit Meeting held at Park City, UT, on July 15-17, 1986. Transect data, available at that time, were examined and used for making adjustments to map unit composition and for correlation. When transect data did not appear to accurately represent the map unit, soil scientists with experience in mapping that unit were asked to make a "best estimate" of the composition. Most often, the alterations were based on the kinds and percentages of minor soil components in the map unit. After the area of each map unit was more precisely determined from the digitized data in the GIS, additional map units with only a few acres were combined with other similar map units by the Mapping Task Leader. This resulted in a final soil map legend of 176 map units. A few small map units remained in the legend, if there were no similar map units with which they could be combined.

The soil taxonomic class, drainage class, depth to bedrock, and estimated depth to a slowly permeable or impermeable layer were compared to the official soil series for the major components of each map unit.

5.4.2.1.2 Soils database -

The mapping phase of the DDRP SBRP Soil Survey generated vast amounts of data. In order to verify, validate, and analyze these data, they were entered into computer database files. Data products generated by the mapping included the identification legend, descriptions of the soil map units, descriptions of the soil taxonomic units (components of the map units), soil transect information, and the map products. The map products included maps of the soils, land use/vegetation, depth to bedrock, geology, and drainage of the 35 watersheds. This section describes the database files developed for the DDRP mapping data and the procedures and QA/QC checks used during the computerization of the DDRP data. Both ORNL and EPA's ERL-C were involved with management of the mapping data. Most of the data were entered at ERL-C using a Mapping Data Management program with dBase III plus software. Correlation corrections to the mapping data were also entered at ORNL using SAS. ORNL performed most of the data comparisons to identify discrepancies. ERL-C had overall responsibility for the quality of the data and validation of data. The maps were digitized for input to a GIS at ERL-C as described in Section 5.4.2.6. An overview of mapping databases is presented by Turner et al. (in review).

5.4.2.1.2.1 Soil identification legend –

A preliminary soil identification legend was developed from existing soil survey legends within the major land resource area of the Southern Blue Ridge Mountains. Map symbols were assigned to map units in the legend by the RCC. Corrections and additions were approved by the State Soil Scientist and RCC and then entered into the identification legend (SE_MP_UN) file at ERL-C. Map unit symbols used in the mapping as shown on individual watershed maps were entered into a dBASE III file during a regional correlation workshop. Map units not used were marked for deletion, and map units that were combined due to small extent or similar soils were noted on the legend. Legends from each watershed map were also entered into the GIS as the maps were digitized at the ERL-C.

The legend data from the GIS were transferred to a dBASE III file where they were summarized for the region and then compared to the regional soil identification legend. Discrepancies were then resolved, and the map unit names were checked with the descriptions of the map units for validity. The soil identification legend database file for the DDRP SBRP Soil Survey named SE_MP_UN contained the following information for each map unit: map symbol; map unit name, including the name of dominant soil component(s), texture modifier (e.g., gravelly, mucky), texture phase, slope phase, and other phase (e.g., very stony, rocky); regional landform; local landform; geomorphic position; slope shape across; slope shape down; and area in acres (determined from the GIS database). This file was accessed through the Southern Blue Ridge Mapping Database Management (SEDBMNT) program developed at ERL-C, as demonstrated by Lammers et al. (1987c). The initials of the person making changes to the legend, the date the changes were made, and records marked for deletion were automatically recorded.

5.4.2.1.2.2 Soil map units and soil taxonomic units --

In some map units, the minor components (inclusions) collectively made up more than 30 percent of the map unit and were found to be important for project analyses. Also, a major soil component in a consociation may have had the same attributes as a major component in a complex or minor component in another map unit. The information from the map unit worksheet was, therefore, separated into two files, a map unit composition file and a soil components file. Each unique soil component was assigned a component code to aid in accessing all the attributes of a soil component with one code. The map unit composition file named SE_MP_CM contains the map symbol, the component code for every component in the map unit, and the percent composition of each of the components.

The soil components file was named SECMPNT. Each record in the SECMPNT file includes the component code; soil name, texture, and slope of the component; five characteristics of the soil:

permeability, drainage, depth to bedrock, origin, and mode of deposition of the parent material; and the taxonomic class. The sampling class code for the class with which the soil component was grouped for sampling was also included in the record for each component in this database file. The records from the three database files, SE_MP_UN, SE_MP_CM, and SECMPNT, were merged in the SEDBMNT, to display information about each map unit on a soil map unit worksheet. This worksheet included the map symbol, map unit name, information about the landscape, major soil components, minor soil components, the proportion of each component in the map unit, and information about the major components including the taxonomic classification.

Copies of these computer-generated worksheets were reviewed by soil scientists in each of the Southern Blue Ridge states. Corrections to these map unit data sheets were reviewed at the Exit Meeting in Park City, UT, in July 1986. Data from these corrected map unit worksheets were entered into the SAS files at ORNL and corrections entered into the SEDBMNT files at ERL-C. The two databases were compared to identify discrepancies. This method of correcting the database virtually eliminated the possibility of updating the wrong observation or variable.

After the updates were completed, ORNL generated frequency tables of the coded variables and compared these tables with lists of valid codes. The frequency tables were also used to build code translation tables containing the codes and definitions. These translation tables were stored as SAS format libraries and are a part of the database. The final step in editing the map data files involved labeling variables and, where necessary, modifying variable names and labels to ensure consistency among the various mapping data files.

5.4.2.2 Depth to Bedrock

Depth-to-bedrock maps were made during the course of soil mapping on mylar overlays of base maps at a scale of 1:24,000. Bedrock was in some cases weathered bedrock designated as a Cr horizon in the soil description. Each delineation on the soil map was assigned to one of the six depth classes. Complexes in which depth of soil over bedrock spans two depth classes were described with dual classes, with the dominant depth to bedrock listed first. Such dual classes were used where the soils were in adjacent depth classes, e.g., classes II and III, III and IV. From this information, a depth-to-bedrock map on a mylar overlay was made by combining contiguous delineations of the same class. Depth to bedrock was estimated from all available information, including soils data, road cuts, and stream incisements.

5.4.2.3 Forest Cover Type/Land use

Forest cover type and land use were mapped together on overlays of base maps at a scale of 1:24,000. The forest cover types mapped were those published by the Society of American Foresters and described by Eyre (1980). Open areas not having a forest cover type were designated by the land use. Land use was designated by one of the land use codes used by the SCS for soil site description, as listed in Table 5-20.

Forest cover and land use were delineated from interpretation of aerial photograph imagery and from observation of topographic and landscape features. Delineations were confirmed by field observation during the course of soil mapping.

5.4.2.4 Bedrock Geology

Bedrock geology maps were made on a mylar overlay of USGS topographic quadrangle or National High Altitude Photography (NHAP) base maps at a scale of 1:24,000. Bedrock geology was obtained from current geology maps. Field crews noted any obvious departures from mapped bedrock geology (Section 5.4.2.8.3.1).

5.4.2.5 Drainage

Watershed drainage was drafted on a mylar overlay of USGS topographic or NHAP base maps at a scale of 1:24,000. Drainages not shown on topographic maps were added to the drainage overlay (Section 5.4.2.8.3.2).

Table 5-20 Land Use Codes Used as Map Symbols

C cropland	I cropland, irrigated
E forest land, grazed	F forest land, not grazed
G pasture land	H horticultural land
L waste disposal land	N barren land
P rangeland, grazed	S rangeland, not grazed
R wetlands	Q wetlands, drained
T tundra	U urban and built-up land

5.4.2.6 Quality Assurance

A rigorous plan for QA/QC, similar to that used in the NE mapping, was implemented during all phases of mapping activities. QA/QC activities included field reviews, independent evaluation of the mapping, and random transecting of selected soil map units in the watersheds. The approach used in the transecting was different than that used in the NE. The transect data were evaluated to determine the correctness of the soil map units.

5.4.2.6.1 Field reviews by the Soil Conservation Service -

Field reviews were conducted by the SCS State Soil Scientist, or another member of the SCS State Soils Staff, for each soil mapping crew in their respective states. There were 11 different soil mapping crews responsible for the mapping, and field reviews were conducted on watersheds mapped by all 11 crews.

The purpose and conduct of the field reviews were the same as described for the NE Region in Section 5.4.1.5.1 of this report, and the same aspects of the mapping were evaluated. Field reviews were conducted at various stages of mapping; on some the mapping had been completed, and on others the mapping was just beginning. A written progress review report was submitted to the RCC and Mapping Task Leader following each field review. Field review reports from Georgia, North Carolina, and Tennessee are in Appendix D of the QA/QC report on soil mapping activities by Lammers et al. (1987a).

The field review reports documented about 45 problems or mapping errors on 32 watersheds. Problems included understanding of mapping protocols, identification of available transects, and correlation with the regional legend. Mapping errors included use of the wrong map symbol, inappropriate map unit, poor location of the map delineation, mapping of small areas of less than 2.7 ha (6 acres), incorrect depth-to-bedrock class, and incorrect vegetation cover type. Most of the problems were resolved during the review and mapping errors were corrected, or the responsible soil scientists agreed to make corrections or conduct additional investigations to resolve the discrepancies.

Mapping was judged acceptable for the purposes of the survey on all watersheds for which a review was conducted.

5.4.2.6.2 Field reviews by the Regional Coordinator/Correlator -

The RCC was required to participate in the field review of at least one watershed in each of the three states responsible for the mapping. Eight watersheds - three in Georgia, three in North Carolina, and two mapped by Tennessee - were reviewed by the RCC. The purpose of the RCC participation was to coordinate the mapping throughout the region and to control the quality of the mapping. The RCC facilitated better communication among states to effect consistency and improve correlation of the soils and map units.

A narrative report on the findings and the discussion resulting from the field reviews for each of the states was submitted to the Mapping Task Leader at ERL-C. After discrepancies were corrected, the mapping was judged acceptable on all of the watersheds. Field review reports by the RCC are in Appendix E of the report by Lammers et al. (1987a).

5.4.2.6.3 Evaluation of mapping by the Regional Coordinator/Correlator -

The RCC evaluated the mapping on 7 of the 35 watersheds in the SBRP Soil Survey. These 7 watersheds were selected from the top of a random list of all 35 watersheds with the constraint that no more than one watershed would be evaluated by the RCC for each mapping team.

Mapping was evaluated by examining stereoscopic pairs of aerial photographs. Relationships between soils and landform segments were scrutinized and questionable areas marked for further examination on the ground by traversing and transecting. About one-third of the soil map delineations were traversed on the ground and the soils in five map units on each watershed were documented at 10 points along a transect. A report of the results of the mapping evaluation was submitted to the Mapping Task Leader at ERL-C. Mapping was judged "acceptable" on all 7 watersheds that were evaluated. Summaries of the mapping evaluation by the RCC are reported by Lammers et al. (1987a, Appendix E).

5.4.2.6.4 Evaluation of soil transect data -

Observations were made at 10 equally spaced stops along transects across selected map unit delineations in each watershed. Of the 176 map units, 50 were selected for transecting by soil mappers. Four transects were randomly selected from the list of available transects for all of the 50 map units except for 5 for which there were only 3 available transects. The RCC conducted five 10-point transects in 7 of the 35 watersheds. At each transect stop, the soil name and a few important differentiating characteristics were recorded.

5.4.2.6.4.1 Management of the transect data –

The watershed number, transect number, map symbol, soil name, slope, and notes at each transect stop were entered into a database file at ERL-C and into a SAS file at ORNL. The two files were compared and discrepancies resolved. Due to correlation of soils and soil map units, soil names and map unit symbols were different on the final regional soils legend than on the transect data forms. The transect soil name and map symbol entries were corrected to agree with the final correlation.

5.4.2.6.4.2 Analyses of the transect data –

The transect data were used to evaluate the correctness of the described map units. The correctness of the map units was evaluated by comparing the proportions of soils transected with the expected proportions in the map unit composition (SE_MP_CM) database. Routine transect results were compared to RCC transects for watersheds mapped by both. Finally, soil components observed at transect points were assigned the proper sampling class, and map unit correctness was evaluated with respect to the sampling class composition. The latter evaluation was especially relevant to judging the correctness of map units for the purposes of DDRP. All hypothesis tests were conducted using two-sided alternative hypotheses.

5.4.2.6.4.2.1 Analysis of major components in map units with routine transects

The soils that were major (named) components of each map unit were pulled from the map unit file (SE_MP_UN). For the major components of each map unit, the transect points were treated as observations from a binomial distribution with the population proportion p, where p was calculated from the SE_MP_CM data file. The sample proportion used was the total number of transect points containing a major component, divided by the total number of transect points. This analysis was similar to the analysis described in Section 5.4.1.5.4.1 and subject to the same conditions.

The proportion of major components was significantly different than the estimated proportion in the SE_MP_CM file for 25 of the 188 transects used in the analysis. Corrections made during correlation accounted for differences in 13 of these transects. At the 0.01 level of significance, we would expect about 10 transects to have a significantly different proportion.

These significantly different transects were excluded from the dataset, and the variability in proportion of major components between transects was calculated, to determine if some soils were uniformly different from the expected proportions or just highly variable. The proportion of major components was calculated for each transect that was not significantly different. The variance of these proportions was then calculated for each map unit with two or more transects. Since the distribution of these variances was asymmetric, a robust data analysis technique was used.

A boxplot (also called a box-and-whiskers plot; Velleman and Hoaglin, 1981) of the variances of proportions was drawn. Boxplots use the interquartile range (IQR) (i.e., the distance between the 75th and 25th percentiles). Points more than 1.5 times the IQR away from the median are considered outliers, and points more than 3 times the IQR away from the median are considered strong outliers. For this dataset, there were no map units with variance of proportion outside the 1.5 IQR and only seven above the 75th percentile.

5.4.2.6.4.2.2 Analysis of major components with RCC transects

RCC transects were examined, at the 0.01 level of significance, for the proportion of major map unit components significantly different from the proportion estimated in the SE_MP_CM data file. There were 4 transects out of 31 that were found to have significantly different proportions. Two of the transects had names of soils recorded that were similar to the major components. which most likely results from difference in soil scientists rather than a difference in map unit composition.

These comparisons suggest that the quality of the mapping evaluated by the routine transects was about the same as when evaluated from transects performed by the RCC. About 7 percent of the transects were as significantly different at a significance level of 0.01.

5.4.2.6.4.2.3 Comparison of the routine and RCC transects

When routine and RCC transects were compared, as in Section 5.4.1.5.4.3, five map units were found to have significantly different proportions. Three of the map units were due to significantly different RCC transects, and the other two map units were situations in which the routine transect proportion was slightly above the expected proportion and the RCC transect proportion was slightly below it. Neither the RCC proportion nor the routine proportion was significantly different from the expected proportion, but in both cases, they were far enough apart to be observed. This strong agreement suggested that the routine transecting and transecting done by the RCC were comparable.

5.4.2.6.4.2.4 Analysis of the map units by sampling class

Because soils were grouped into 12 classes for sampling and analytical characterization, the correctness of mapping these classes was important to evaluate the mapping for project assessment. The soil at each transect stop was assigned the appropriate sampling class (described in Section 5.5.1.3.2) to compare transect-determined sampling class composition with map unit description sampling class composition. Because there were several hypothesis tests for each map unit, the Bonferroni inequality was used to handle the error rate of the simultaneous hypothesis tests within each map unit.

There were nine map units in which the sampling class proportion differed significantly from the proportion estimated by soil scientists. Six of the nine map units had an estimated sampling class proportion of 100 percent. Five of these units had an actual difference of less than 7 percent, due to the estimated proportion being 100 percent. All five were actually quite close to the estimated proportion. At the .05 significance level we would expect about five significant map units, if the null hypothesis were true throughout and no estimated proportions were equal to 100 percent. This observation suggests that the estimated sampling class proportions are accurate for most map units.

5.4.2.6.4.2.5 Summary of the transect analyses

For the most part, the transect analysis indicated that the mapping was good. There were a few map unit delineations that may have been mismapped. On the other hand, the differences between transect data and estimated map unit composition could have been due to unrepresentative transects, incorrect estimated proportions, or soils that were difficult to map. No map units had unusually high variability that may have indicated problems with the transecting or the map unit definitions. After the significant transects were removed, the map units were reasonably consistent, suggesting that some of the problem may have been the estimated proportions. The sampling classes matched the estimated proportions very well, indicating that there were few problems in the mapping as far with regard to the needs of DDRP.

5.4.2.7 Land Use/Wetlands

5.4.2.7.1 Data acquisition -

Information on land use and wetlands was obtained via interpretation of existing, but older, NHAP photography (1:24,000) and field observations during soil mapping (Section 5.4.2.3). Current photography was not required nor were specialized photointerpretation/field checking activities performed as they were for the NE watersheds (Section 5.4.1.6). General land use, forest cover type, and wetland data for all SBRP watersheds were digitized via GIS (Section 5.4.2.8).

5.4.2.7.2 **Land use/land cover summary -**

The predominant land use in all but one watershed was ungrazed forest; in the one exception (2A07826), the predominant land use was horticulture (Table 5-21). Hardwood forests, ranging from 50 to 98 percent, predominated over mixed and coniferous forest. Coniferous vegetation (42 to 44 percent) was predominant only in two watersheds. Wetlands were absent in all but one watershed (2A07802).

Urban development was absent or minimal in all but one watershed and ranged from 1 to 6 percent; watershed 2A07802 had 19 percent of its area in urban land use. Agricultural development was also limited. Little area was devoted to cropland in any watershed except 2A07826. However, all but 10 watersheds had managed or unimproved native pasture and 10 watersheds had pasture percentages $\geq$ 10 percent.

5.4.2.7.3 **Regional comparisons --**

Although methods for determining land use and wetlands were different for the NE and SBRP Regions, certain generalizations are possible. Similarities between NE lake and SBRP stream watersheds are the predominance of forest land use and little agricultural or urban development - both are results of the overall DDRP field design to work with "undeveloped" watersheds. The greatest dissimilarity is the overall lack of wetlands, beaver activity, and (lowland) horticulture in the SBRP region, reflecting large differences in physiography and landform features of the two regions.

5.4.2.8 Geographic Information Systems Data Entry

5.4.2.8.1 **Southern Blue Ridge Province databases -**

The DDRP obtained data from contract mappers and from existing information. The SCS, in cooperation with the EPA, mapped soils, vegetation/land use, depth to bedrock, and streams at a scale of 1:24,000 for each watershed (Lammers et al., 1987a; Lee et al., 1989a) (see Sections 5.4.2.1 through 5.4.2.6). Bedrock geology and additional stream information were extracted from existing maps published by the USGS, geology from appropriate state geology maps, and streams from 7.5' or 15' topographic maps. These data have been entered into the GIS.

Table 5-21. Percent Land Use Data for Southern Blue Ridge Province Watersheds

) lo.	St.	C	E	F	G	H	K	L	M	N	O	R	U	Z
01	TN	0.0	0.0	100	0.0	0.0	0	0	0.0	0	0	0	0.0	0
02	TN	0.0	0.0	91	9	0.0	0	0	0.0	0	0	0	0.3	0
03	TN	0.0	18	63	16	0.0	0	0	0.0	0	0	0	2.7	0
13	TN	0.0	0.0	74	24	1.7	0	0	0.0	0	0	0	0.0	0
16	TN	0.0	0.0	99	0.0	0.0	0	0	0.0	0	0	0	0.0	.4
35	SC	0.0	0.0	94	0.8	0.0	4	0	0.0	0	0	0	1.6	0
01	GA	0.0	0.0	96	4.3	0.0	0	0	0.0	0	0	0	0.0	0
02	GA	0.0	3.5	86	10	0.0	0	0	0.0	0	0	0	0.0	0
03	GA	1.2	2.6	91	5	0.0	0	0	0.0	0	0	0	0.0	0
04	GA	0.0	0.0	100	0	0.0	0	0	0.0	0	0	0	0.0	0
05	GA	0.0	0.0	84	16	0.0	0	0	0.0	0	0	0	0.0	0
06	GA	0.0	0.0	80	20	0.0	0	0	0.0	0	0	0	0.0	0
08	GA	0.0	0.0	95	2	0.0	0	0	0.0	3	0	0	0.0	0
10	GA	0.0	0.0	100	0	0.0	0	0	0.0	0	0	0	0.0	0
11	GA	0.0	0.0	100	0	0.0	0	0	0.0	0	0	0	0.0	0
01	GA	1.8	0.0	94	4	0.0	0	0	0.0	0	0	0	0.9	0
04	GA	3.8	0.0	89	3	0.0	0	0	0.0	0	0	0	4.0	0
06	GA	0.0	0.0	85	13	1.4	0	0	0.0	0	0	0	0.6	0
03	NC	0.0	0.0	94	6	0.0	0	0	0.0	0	0	0	0.0	0
02	NC	0.0	0.0	63	15	0.0	0	0	0.0	0	0	2	19	0
05	NC	0.0	0.0	95	0	0.0	0	0	0.0	0	5	0	0.0	0
06	NC	0.0	3.2	88	9	0.0	0	0	0.0	0	0	0	0.0	0
11	NC	0.0	0.0	99	0	0.0	0	0	0.0	0	1	0	0.0	0
12	NC	0.0	0.0	100	0	0.0	0	0	0.0	0	0	0	0.0	0
17	NC	0.0	0.0	98	2	0.0	0	0	0.0	0	0	0	0.0	0
21	NC	0.1	0.0	87	12	0.6	0	0	0.0	0	0	0	0.0	0
23	NC	0.0	0.0	95	5	0.0	0	0	0.0	0	0	0	0.0	0
26	NC	11	0.0	34	8	42	0	0	0.0	0	0	0	3.6	0
27	NC	0.9	0.0	91	7	0.9	0	0	0.0	0	0	0	0.0	0
28	NC	1.0	0.0	97	2	0.0	0	0	0.0	0	0	0	0.0	0
29	NC	0.0	0.0	97	0.0	1.3	2	0	0.0	0	0	0	0.0	0
30	NC	11	0.0	75	13	0.4	0	1	0.1	0	0	0	0.1	0
33	NC	0.7	0.8	87	11	0.5	0	0	0.0	0	0	0	0.0	0
34	NC	0.0	0.0	98	2	0.0	0	0	0.0	0	0	0	0.0	0
82	NC	0.0	0.0	94	0.0	0.0	0	0	0.0	0	0	0	6.1	0

e: For explanation of land use symbols, consult Table 8-27.

Soils, vegetation/land use, depth to bedrock, and streams were mapped in the field by the SCS between fall 1985 and spring 1986. The SCS used 7.5' USGS orthophoto film positives or topographic film positives as their reference maps. These field maps were transferred onto mylar overlays following DDRP specifications (Lammers et al., 1987a; Lee et al., 1989a). These overlays are the final manuscript maps and were entered into the GIS.

When the SCS streams were overlaid with the topological maps, 14 of the watersheds were found to have been incorrectly transferred to the reference map. The field mapped information drawn on the areal photographs were traced directly onto the mylar without first adjusting, or "rectifying," the information to the reference map. Because the SCS was unavailable to make the corrections, these corrections were contracted to Oregon State University, Department of Geography. The overlays were hand transferred to the reference map using topographic features. For example, ridge top soils were placed on ridge tops, valley bottom soils were placed in valley bottoms. Because the soils overlay directly relates to the depth-to-bedrock overlay, the depth-to-bedrock overlay was adjusted by using the soils overlay as a mapping guide. Vegetation/land use information used features found on topographic maps and orthophotos such as open areas, vegetation changes, and riparian zones along with proximity to watershed boundaries and soil classes as guides.

Because the 14 unrectified watersheds were not identified until after the original database was completed, the corrections for these 14 watersheds were updated into the original database, making their entry procedure slightly different.

The original database followed the same digitizing procedures as the NE database. Because this information was completed and projected into Universal Transverse Mercator coordinates, the 14 unrectified watersheds were digitized directly into the same projection.

5.4.2.8.2 **Database preparation and digital entry** -

The SBRP databases were prepared and digitized similarly to the NE databases (see Sections 5.4.1.7.2.1 through 5.4.1.7.2.2), with two minor exceptions. First, as mentioned in the previous section, the remapped watershed information was digitized directly into the UTM projection. Secondly, the SCS combined the land use with the vegetation overlay. Codes depicting land use were entered as an attribute to the vegetation coverage, rather than as a separate coverage as in the NE.

5.4.2.8.2.1 **Projection** --

The same series of procedures was used in the SBRP as the NE to ensure accurate transformation from the original digitized coordinates to the UTM coordinates (see Section 5.4.1.7.2.3). Once the entire database was in UTM coordinates, the DDRP coverages were interactively displayed and visually checked for consistent location with coordinates of the downstream sampling node of each stream corresponding to the NSS (Messer et al., 1986a).

5.4.2.8.3 **Databases derived from existing maps** -

5.4.2.8.3.1 **Bedrock geology** --

As in the NE database, state bedrock geology maps were used to generate the bedrock geology coverages. These were the only maps available that provided a consistent geologic classification scheme within each state (see Section 5.4.1.7.3.1). The scale of the geology maps is 10-20 times smaller than the other coverages previously described (1:125,000 for South Carolina and Tennessee; 1:500,000 for Georgia and North Carolina) (Brown, 1985; Hardeman, 1966; Overstreet and Bell, 1965; Pickering and Murray, 1976). The same procedures were used to enter the geology information as in the NE (see Section 5.4.1.7.3.1).

5.4.2.8.3.2 Streams --

The streams manuscript maps provided by the SCS were used for the original database. In order to correct the streams for the unrectified watersheds, the streams and topological features from the USGS topographic maps were used as a guide. A log sheet was created for consistency in stream data entry.

The stream coverages were plotted with the template coverage. These plots were overlaid with the topographic map on a light table and checked for discrepancies. If any light was evident between the digitized line and the delineated stream, the digitized line was corrected. Stream classification was also checked for accuracy. This QC procedure was performed independently by two individuals until both agreed that the information was accurate.

5.4.2.8.4 Final quality control check and output generation -

After the mapped information had been digitized and checked for accuracy, computer programs similar to those used in the NE were written in ARC/INFO to check for consistency and to calculate a usable output for the data. These programs created lists of the classifications used and the calculated area, and also generated reports (see Sections 5.4.1.7.4.1 through 5.4.1.7.4.2). This information was then transferred to other computer systems for data analysis within the DDRP.

5.4.2.8.5 Summary -

Much of the SBRP database was developed similarly to the NE database. Unlike the NE, the SBRP received mapped information from one contractor rather than two. The SBRP did, however, follow the same QC procedures as the NE to ensure the data were entered as consistently and accurately as the original mapped information allowed. These procedures include checking the accuracy of the information before, during, and after digitizing. Two independent checks were performed at critical stages of the digitization before the data were accepted for use within the DDRP. (For more extensive details concerning the GIS, see Mortenson (1989b).)

5.5 SOIL SAMPLING PROCEDURES AND DATABASES

Soils were described and sampled to provide the morphological, physical, and chemical data needed for the three DDRP levels of analysis. In the NE, 306 pedons were described and 2000 samples (i.e., about six horizons per pedon) were taken. (A pedon is the smallest volume of soil that has all the characteristics by which a specific soil is defined. Operationally, it is usually taken to be about a meter square in cross section to depth of 1.5 m or to bedrock, whichever is shallower.) The corresponding numbers for the SBRP were 110 pedons and 1000 samples. Soil survey activities have been described in some detail by Lee et al. (1989a). Much of this section draws from that report and from the detailed description of sampling class development in the NE by Lee et al. (1989a).

5.5.1 Development/Description of Sampling Classes

5.5.1.1 Rationale/Need for Sampling Classes

In the NE, about 600 soils (mostly phases of soil series) were identified during mapping of 145 watersheds. In the SBRP, about 300 soils were identified on 35 watersheds. Because of the large number, it was impractical to sample each soil enough times to obtain statistically adequate estimates of the means and variances of the relevant soil properties. As a practical alternative, the soils identified during mapping were combined into a tractable number of groups, or sampling classes, that were either known or expected to have similar chemical and physical characteristics with respect to their responses to acidic deposition. The development and characteristics of these classes have been described by Lee et al. (1989b,c) and Lammers et al. (in review).

Each of these sampling classes was sampled across several watersheds, so that the mean and variance of the characteristics of each sampling class could be computed for the region. These regional means and variances are then used in conjunction with the soil maps to build area or volume weighted estimates, with error estimates, of the characteristics of each watershed. This same approach can be used for specific portions of watersheds, such as poorly drained soils near lakes. When using this approach, however, a given soil sample does not represent the specific watershed from which it was sampled. Instead, it contributes to a set of samples that, collectively, represent a specific sampling class on all

DDRP watersheds within the region for which the sampling class is defined. Because the DDRP is designed to estimate the uncertainties of its projections and conclusions, it is necessary to know the probable range of expression of a given characteristic for a sampling class within a region, and not just the value associated with the central concept of the class.

The soil sampling classes were used for statistical stratification for sampling, and for aggregation of data for analysis. Stratification and aggregation were necessary to obtain soils information on a very extensive area from sampling of only a limited number of pedons. If, for example, we had used a purely random scheme had been selected with each pedon representing 40 ha (larger than some DDRP watersheds), sampling would have been required on about 1700 pedons in the NE. By using soil mapping to determine the kinds of soils and their spatial distribution on the DDRP watersheds. Project objectives can be satisfied with approximately 300 sampled pedons in the NE.

5.5.1.2 Approach Used for Sampling Class Development

Sampling classes were developed at workshops (Lee et al., 1989b,c; Lammers et al., in review) by the field soil scientists responsible for soil mapping, in cooperation with the modelers and statisticians who would be using the data. Soils were split into different classes based on characteristics the soil scientists thought might be important for determining the responses of watersheds to acidic deposition. Characteristics considered included mineralogy, iron and aluminum oxides, organic matter content, texture, versus oxidizing chemistry, cation exchange capacity, base saturation, drainage (wetness), depth, hydraulic conductivity, role as a source area for surface waters. The schemes were tailored to each region to best distinguish these characteristics in the field.

Adequate resolution for the modelling and analysis tasks within the Project. The underlying rationale was that if the classes are in fact distinct, better resolution is attained by separating them. If, however, they turn out not to be distinct, then we have paid a small price in terms of precision; that is, the allocation of samples is not as efficient as it might have been. It is possible (and, in fact, expected) that soils were split into finer groups than were needed.

5.5.1.3 Description of Sampling Classes

5.5.1.3.1 Northeast -

The flowchart defining sampling classes in the NE is shown in Figure 5-14. Spodosols were separated because of the accumulation of aluminum oxides, iron oxides, and organic matter in spodic horizons. These would affect cation exchange capacity (CEC) and sulfate adsorption, two important processes that influence ANC (Section 3; Altshuller and Linthurst, 1984; NAS, 1984). Aluminum is also of interest as the toxin primarily responsible for the adverse effects of acidification on aquatic organisms (Altshuller and Linthurst, 1984).

The primary split on mode of deposition of parent material was glacial till versus glaciofluvial, implying differences in the degree of sorting of parent material. This distinction was made because particle-size distribution correlates with many properties of interest to DDRP, such as CEC and hydraulic conductivity.

The wettest soils (e.g., Aquods, Aquepts, aquic subgroups, non-folist Histosols) were separated because of their likely role as source areas for surface waters. They are also likely to differ from other soils in having a reducing rather than oxidizing chemical environment, which is especially important for sulfur retention. (Histosols were different from the other soils in most properties of interest.) Because approximately equal numbers of pedons were sampled for all sampling classes, separating the wettest soils resulted in more sampling of those soils in closest proximity to the surface waters.

The use of drainage classes to define sampling classes was considered by workshop participants. The consensus was to use aquic vs. non-aquic instead because these taxonomic terms are better defined and used more consistently by soil scientists than are the somewhat subjective drainage classes. The aquic vs. non-aquic split was made at the suborder (e.g., Aquepts vs. Ochrepts) and subgroup (e.g., Typic Dystrochrepts vs. Aquic Dystrochrepts) levels.

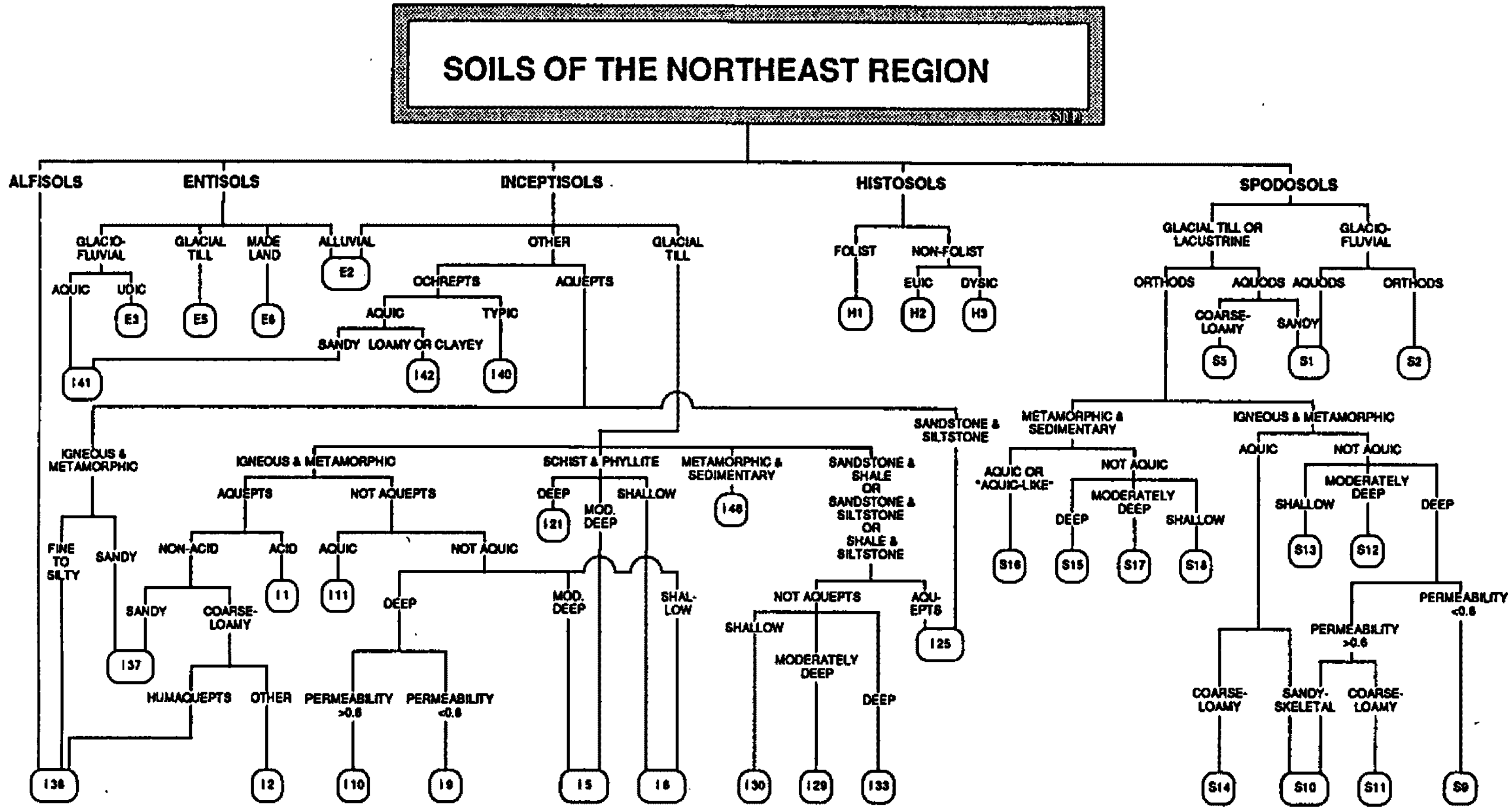


Figure 5-14. Definition of soil sampling classes for the DDRP Soil Survey in the Northeast.

One property used for defining groups was soil depth. This split reflects the ILWAS hypothesis (Gherini et al., 1985; Newton and April, 1982) that soil depth may be the most relevant soil property in the NE. For example, soils in groups S15, S17, and S18 are all non-aquic Orthods formed on similar parent materials, and are likely to have very similar chemical and physical properties, especially in the upper horizons. The distinction among them is soil depth: deep, moderately deep, and shallow, respectively. Aquic soils were not split by depth because the consensus was that these soils were hydrologically similar in that most water flow would be through the upper horizons; also, almost all of the aquic soils were deep.

As another example two classes I37 and I2, both contain wet, non-acidic Inceptisols formed from similar parent materials. They differ in family particle size: sandy vs. coarse-loamy. In other words, soils in I37 contain greater than 50 percent sand, and those in I2 less than 50 percent sand in the particle-size control section. If these soils range far from the 50 percent breakpoint, then these classes are likely to differ in properties of interest to DDRP. If, however, they cluster near the 50 percent breakpoint, the classes might not be separable; more importantly, there would be no reason to separate them. The latter case is an example of the conservative approach to defining classes.

5.5.1.3.2 Southern Blue Ridge Province -

The flowchart defining sampling classes in the SBRP is shown in Figure 5-15. The frigid soils occur only at the highest elevations in the region. They were separated because they have soil organic matter contents greater than average for the region, and might differ chemically because of the effects of temperature and vegetation on pedogenic processes. The calcareous soils occur only as inclusions in the SBRP. They were separated because their calcareous nature might have an effect on surface waters disproportionate to their small area of occurrence. Skeletal soils were separated because of the short residence time and limited amount of soil fines available for reaction with precipitation. The concave skeletal soils are the main conduits for waterflow, and represent the most probable path for the majority of water delivered to the streams. The convex skeletal soils occur at the upper extreme of watershed

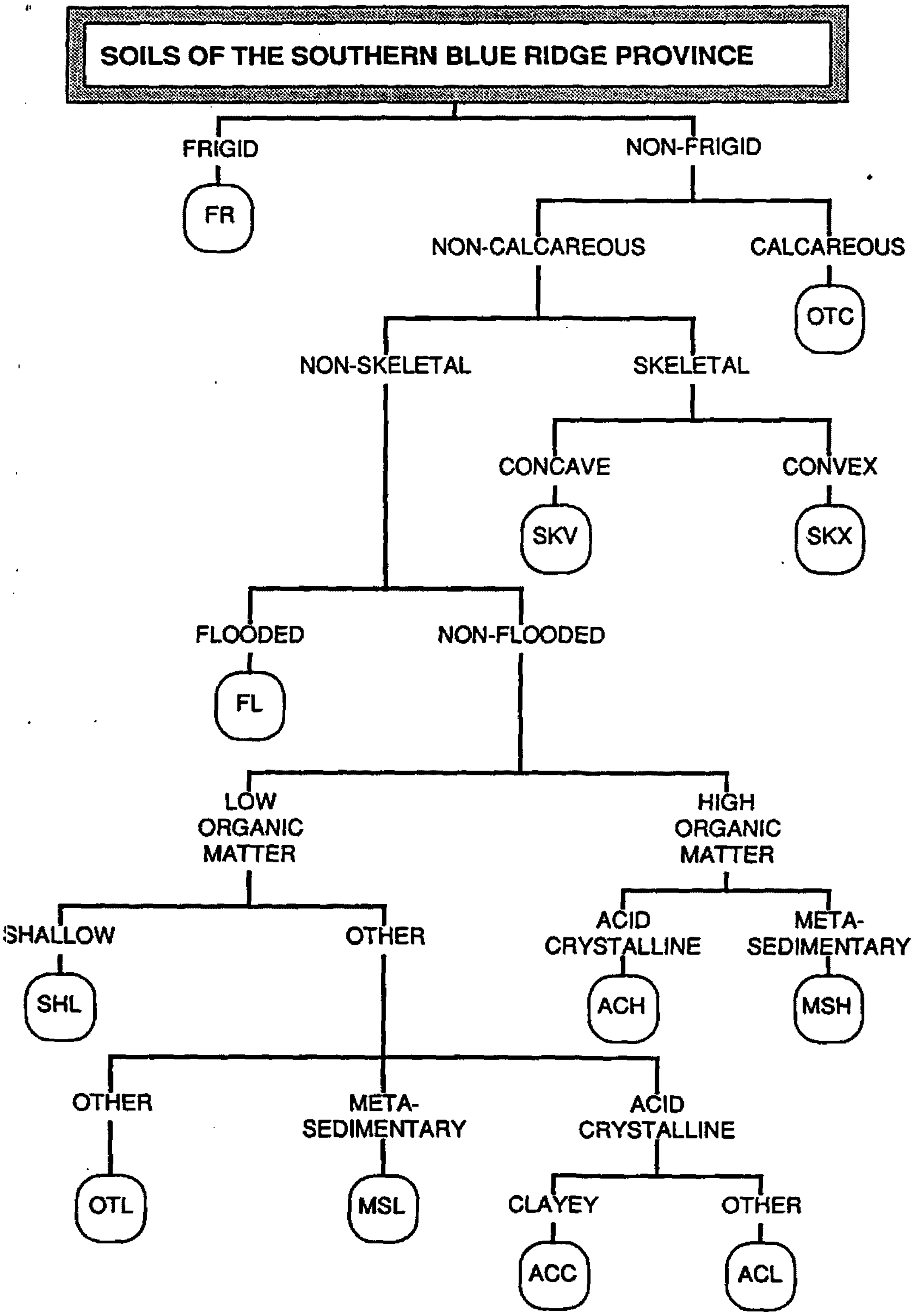


Figure 5-15. Definition of soil sampling classes for the DDRP Soil Survey in the Southern Blue Ridge Province.

slopes and serve as intakes of precipitation. Flooded soils were separated because of their proximity to surface waters. They serve as the final conduit of water from the watershed to the stream.

The break on high vs. low organic matter refers to the thickness of an organic rich surface horizon, which may affect organic content, aluminum forms, and other characteristics of the lower soil horizons. The break on soils formed from acid crystalline (e.g. light-colored, siliceous, granite, gneiss, and schist) vs. metasedimentary (e.g., phyllite, metasandstone, quartzite, slate) parent materials reflects a probable difference in the amounts of HIV clays; the latter group is likely to have the greater amounts. These clays can serve as sinks for aluminum in solution (Buol et al., 1980), an important consideration for the biological effects of acidification of surface waters. Gibbsite and kaolinite are common in soils from either parent material.

The separations on soil depth and family particle size in the SBRP were made for the same reasons as in the NE.

5.5.2 Selection of Sampling Sites

5.5.2.1 Routine Samples

There is a strong tendency for soil scientists to select typical soils for sampling. Although this is proper for most applications, it would not have been appropriate for the statistically based sampling scheme used by the DDRP. To ensure an unbiased sample for estimating means and variances of the characteristics of sampling classes over the regions, the DDRP used a unique three-part scheme of randomly selecting sampling sites for each sampling class: (1) random selection of watersheds from those in which the desired sampling class occurred (Figure 5-16); (2) random location of potential sampling sites on soils maps within delineations in which the class occurred (Figure 5-17); and (3) random selection of transect direction if the field crew found that the desired sampling class did not occur within 5 m of the potential sampling site (Figure 5-18).

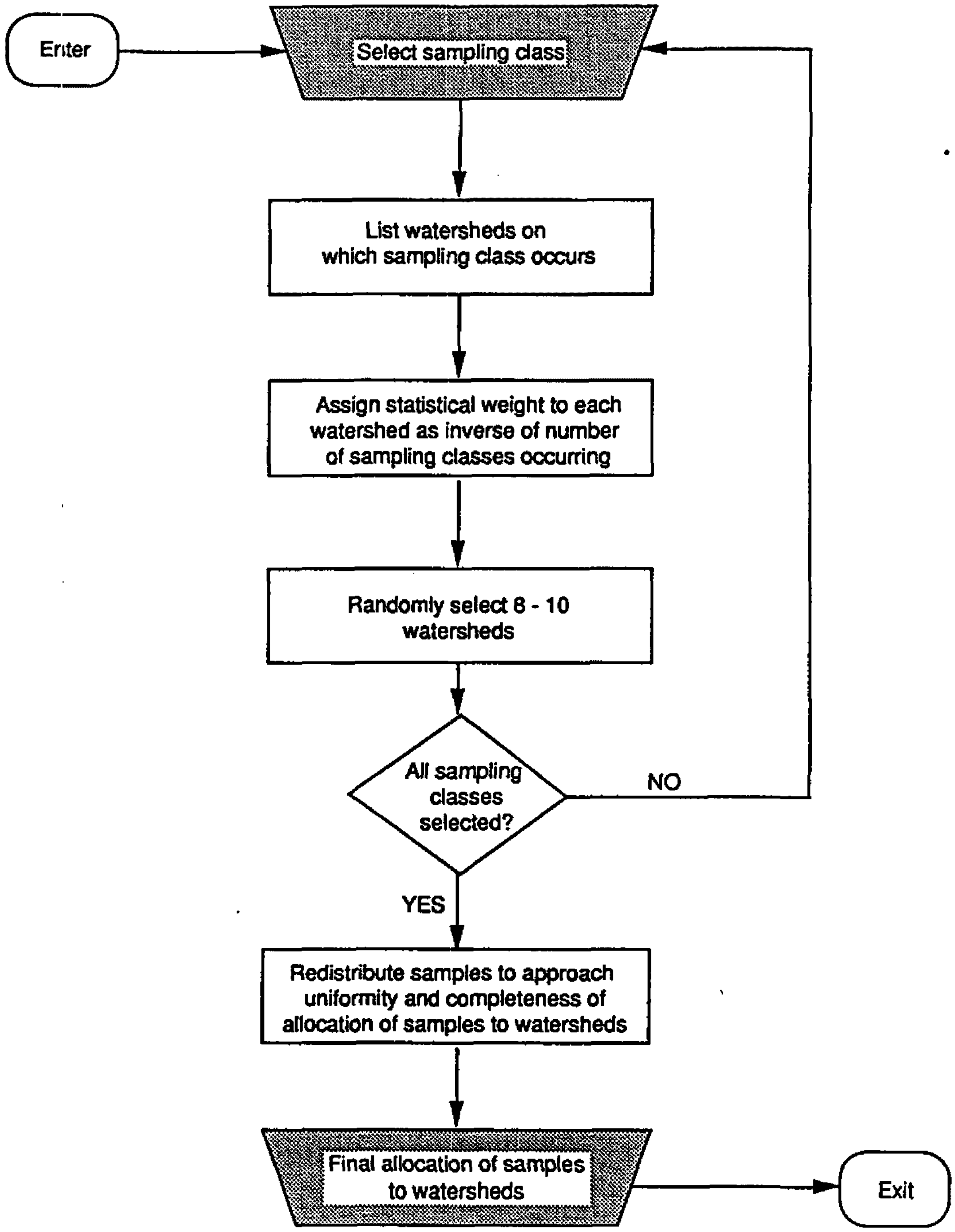


Figure 5-16. Selection of watersheds for sampling.

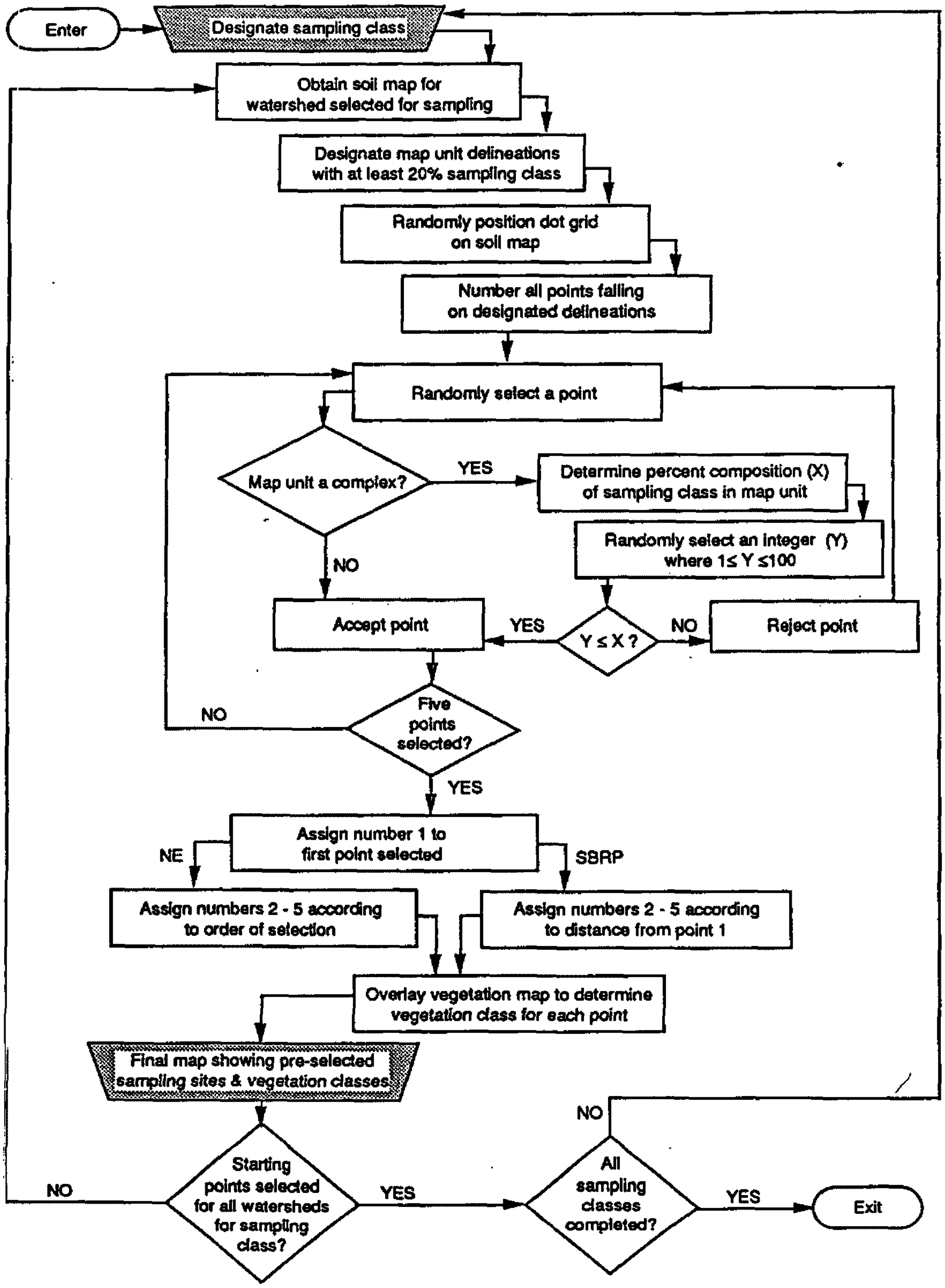


Figure 5-17. Selection of starting points for sampling.

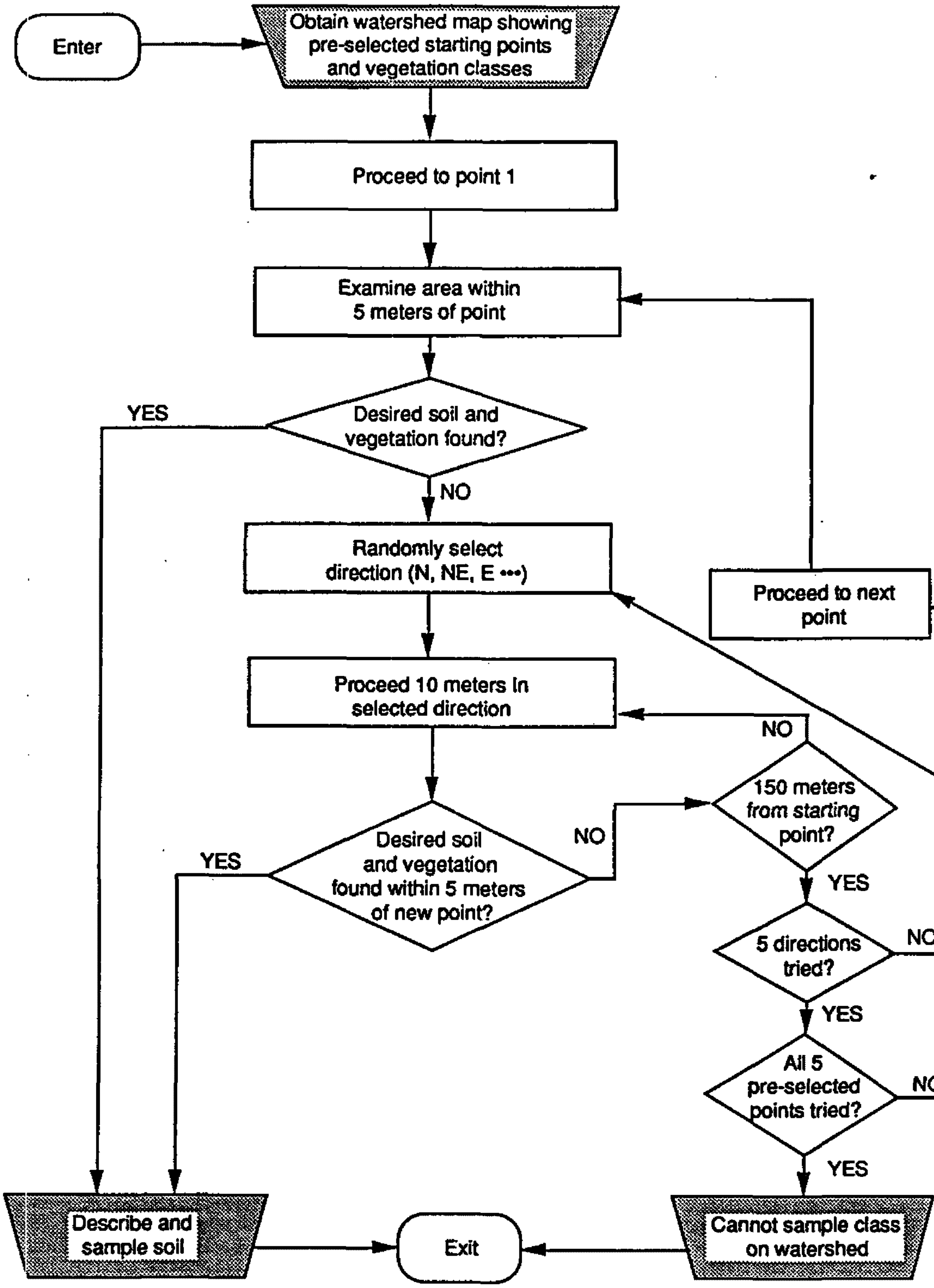


Figure 5-18. Field selection of a sampling point for sampling class on a watershed.

The first step in choosing sampling sites for a given class was to list every DDRP watershed in which that class occurred (Figure 5-16). Thus, watersheds were identified that had at least one delineation of any map unit for which soils in that class occupied at least 20 percent of the area. Watersheds for sampling were randomly selected from this list, at the rate of one watershed for each desired sample of that class (typically a total of 8-10 per class). For the purposes of this selection, each watershed was given a statistical weight equal to the inverse of the number of sampling classes occurring on the watershed. After watersheds were selected, samples were reallocated to approach the following conditions: (1) equal numbers of samples per watershed and (2) no more than one sample of a given sampling class in any watershed. Details of the selection process were described by Lee at al. (1989c).

After a watershed was selected for sampling of a particular class, potential sampling sites (usually five) were determined by random selection from grid points that fell on delineations of map units with at least 20 percent of their area occupied by soils within the class (Figure 5-17). The vegetation map unit (i.e., SAF cover type; Eyre, 1980) at each selected point was noted and classified into one of five broad groups (conifer, hardwood, mixed, open dryland, open wetland). A detailed description of the selection of potential sampling sites was documented by Lee et al. (1987b).

In each watershed selected for sampling, the field crews proceeded to the first of the potential sampling sites and determined whether a soil within the desired class occurred within 5 m (Figure 5-18). If there was any such soil, and if the vegetation at the site fell into the broad group identified from the vegetation map, the soil was sampled. Otherwise, the crew leader used a random number table to select a transect direction. The crew proceeded in this direction, stopping at regular intervals to determine if a suitable soil was present. They sampled the soil at the first site they found that met the criteria for the sampling class and for the broad vegetation class. If no such site was found on the first transect, another direction was selected (see Figure 5-18). If the desired combination of soil sampling class and broad vegetation group was not found after five transects, the crew proceeded to the second pre-selected potential sampling point, until all pre-selected points on the watershed were exhausted. The instructions given to the crews for selecting sampling sites were documented in Coffey et al. (1987a,b).

5.5.2.2 Samples on Special Interest Watersheds

The Special Interest Watersheds (SIW) serve a different purpose than the routine watersheds (Sections 4 and 11), so a different approach to soil sampling was taken. The five sampling sites in each SIW were selected to be representative of that watershed. DDRP scientists, in coordination with watershed modellers, located sampling sites on the soil maps based on hydrologic relation to the lake or stream, extent of soils in the watershed, and distribution of sampling sites across the watershed. Field crews went to each site and sampled a soil that they considered to be representative of soils in that portion of the watershed.

5.5.3 Soil Sampling

The USDA Soil Conservation Service conducted the soil sampling activities for the DDRP. State offices involved were Connecticut, Maine, Massachusetts, New Hampshire, New York, and Pennsylvania for the NE, and Georgia, North Carolina, Tennessee, and Virginia for the SBRP.

5.5.3.1 Soil Sampling Procedures

Protocols for DDRP soil sampling were developed for each region (Coffey et al., 1987a,b) by adapting the procedures of the National Cooperative Soil Survey (Soil Survey Staff 1975, 1983, 1984). To enhance regional consistency, standard supplies and equipment were provided to the field crews through regional centers, specifically the Soil Preparation Laboratories established in cooperation with Agricultural Experimental Stations. After the crews delivered soil samples to these laboratories, they obtained new supplies for the next sampling. Laboratory personnel inspected the samples for obvious problems (e.g., inadequate sample volume, poor labeling, possible contamination), thereby providing an additional check on regional consistency.

The protocols gave detailed instructions on the randomized procedure for locating sampling sites (see Figure 5-18), for excavating pedons in difficult situations, and for documenting the site and pedon with notes and photographs. Soil profile descriptions were entered onto a form (SCS 232) designed to facilitate entry into a database. Field estimates of percent rock fragments, included in the profile descriptions, were used to correct for non-soil volume during data aggregation (see Sections 8.8.3, 9.2, 9.3).

Crews sampled every horizon thicker than 3 cm thick down to bedrock or to 1.5 m (NE) or 2.0 m (SBRP). Thick horizons were split for sampling. Wherever possible (about 50 percent of horizons), clods were gathered and coated with Saran in the field, for subsequent determination of bulk density. Samples were cooled to 4°C within 12 hours, and then taken to the preparation laboratories.

5.5.3.2 Quality Assurance/Quality Control of Sampling

The purpose of the QA/QC tasks for sampling was to ensure and document that the samples were collected and handled in a consistent, proper manner, and that the chain of custody for each sample was properly tracked. The QA/QC procedures for sampling were described by Bartz et al. (1987); an evaluation sampling based on these procedures was documented by Coffey et al. (1987a,b).

Crews were trained at regional workshops prior to sampling. During sampling, every crew was audited by the State Soils Staff and the RCC, who were responsible for consistency within each state and within each region, respectively. At least one site per state was audited jointly by the State Soils Staff and the RCC.

Each crew also was audited by a member of the DDRP QA staff. As an independent evaluation, the EPA auditor used a detailed checklist to document adherence or deviation from protocols as given in the DDRP sampling manuals. As noted above, regional consistency was also promoted by feedback from the preparation laboratories.

The QC activities also provided unique information on the variability of pedon descriptions prepared by different soil scientists. The State Soils Staff and the RCC each performed independent descriptions of pedons that also had been described by the sampling crews. Thus, for some pedons, up to three independent descriptions were available. The primary purpose was not to decide which soil scientist was "right," but to document the variability inherent in a procedure that is somewhat subjective. Comparison of descriptions also was useful to promote consistent application of soils concepts within states and regions.

As an additional QA/QC check, the pedon descriptions were reviewed for consistency by the SCS state offices and by EMSL-LV staff. Discrepancies were documented and resolved by consulting the field crews.

Every day, each crew sampled one horizon in duplicate by placing alternate trowelfuls of soil into two sampling bags. Discrepancies in the laboratory analyses of these samples would indicate probable contamination at some point in the chain of custody (i.e., sampling, transportation, preparation laboratory, analytical laboratory). The variability of these samples was documented by Byers et al. (1989) and Van Remortel et al. (1988).

5.5.4 Physical and Chemical Analyses

The chemical and physical analyses performed on DDRP soil samples are summarized in Table 5-22.

5.5.4.1 Preparation Laboratories

Preparation laboratories acted as intermediaries between the sampling crews and the analytical laboratories. They were established at Agricultural Experiment Stations at locations within driving distance of the sampling sites. Four preparation laboratories were established in the NE, and two in the SBRP:

NE	SBRP
University of Connecticut	Clemson University
Cornell University	University of Tennessee
University of Maine	
University of Massachusetts	

Table 5-22. Laboratory Analysis of DDRP Soil Samples

Chemical Analyses

1. pH (distilled water; 0.01 M $CaCl_2$; 0.002 M $CaCl_2$)
2. Total carbon[a]
3. Total nitrogen
4. Total sulfur
5. Cation exchange capacity
    a. 1 N NH_4 OAc, pH = 7.0
    b. 1 N NH_4 Cl, unbuffered
6. Exchangeable bases (Na, K, Mg, Ca)
    a. extraction by 1 N NH_4 OAc, pH = 7.0
    b. extraction by 1 N NH_4 Cl, unbuffered
    c. extraction by 0.002 M $CaCl_2$
7. Exchangeable acidity
    a. $BaCl_2$ -TEA method, pH = 8.2
    b. 1 N KCl - effective acidity, exchangeable Al
8. Extractable iron and aluminum
    a. sodium pyrophosphate
    b. ammonium oxalate
    c. citrate-dithionite
    d. 0.0002 M $CaCl_2$
9. Extractable sulfate
    a. water soluble
    b. phosphate extractable
10. Sulfate adsorption isotherms (six points)
11. Specific surface area

Physical Analyses

1. Particle size (5 sand fractions, 2 silt fractions, clay)
2. Bulk density
3. Moisture content

[a] A qualitative test for inorganic carbon is also performed. In the two completed regions, only two samples (out of approximately 3000) tested positive.

5.5.4.1.1 Responsibilities -

The preparation laboratories received the samples from the crews and provided the crews with supplies. Soil samples were air dried, sieved (2 mm), subsampled, packaged, and shipped to the analytical laboratories by the preparation laboratories. Two to four audit samples supplied by the DDRP QA staff were included in each batch shipped to the analytical laboratories. In addition, one soil sample was split by the preparation laboratory and included as two samples, called "prep lab duplicates". The audit samples and preparation laboratory duplicates were packaged and labeled in the same way as routine samples, and were not identifiable by the analytical laboratories.

The preparation laboratories also were responsible for determining the coarse fragment and moisture content of samples, for performing a qualitative test for carbonates, and for determining bulk density from the clod samples. The procedures followed by the preparation laboratories were documented by Papp and Van Remortel (1987) and Haren and Van Remortel (1987).

5.5.4.1.2 Quality assurance/quality control of physical and chemical analyses -

Preparation laboratories were audited by DDRP QA staff before becoming operational and again while operational. The QA/QC procedures for the preparation laboratories were described by Bartz et al. (1987). QA/QC results were evaluated by Papp and Van Remortel (1987) and Haren and Van Remortel (1987), who concluded that soil sample integrity was maintained at the preparation laboratories.

5.5.4.2 Analytical Laboratories

5.5.4.2.1 Analyses -

The analytical laboratories were contracted to perform the physical and chemical analyses listed in Table 5-22 and described in Table 5-23. More complete descriptions of the procedures used by the analytical laboratories were given by Cappo et al. (1987).

In addition to the parameters listed in Table 5-23, a number of calculated variables were derived for use in various analyses. Derivation of these variables is described in sections where the variables

Table 5-23. Analytical Variables Measured in the DDRP Soil Survey (Van Remortel et al., 1988)

Variable	Description of Variable
MOIST	Percent air-dry soil moisture measured at the analytical laboratory and expressed as a percentage on an oven-dry weight basis. Mineral soils were dried at 105°C, organic soils at 60°C.
SP_SUR	Specific surface area determined by a gravimetric method of saturation with ethylene glycol monoethyl ether (EGME).
SAND	Total sand is the portion of the sample with particle diameter between 0.05 mm and 2.0 mm. It was calculated as the summation of percentages for individual sand fractions: VCOS + COS + MS + FS + VFS.
VCOS	Very coarse sand is the sand fraction between 1.0 mm and 2.0 mm. It was determined by sieving the sand which had been separated from the silt and clay.
COS	Coarse sand is the sand fraction between 0.5 mm and 1.0 mm. It was determined by sieving the sand which had been separated from the silt and clay.
MS	Medium sand is the sand fraction between 0.25 mm and 0.50 mm. It was determined by sieving the sand which had been separated from the silt and clay.
FS	Fine sand is the sand fraction between 0.10 mm and 0.25 mm. It was determined by sieving the sand which had been separated from the silt and clay.
VFS	Very fine sand is the sand fraction between 0.05 mm and 0.10 mm. It was determined by sieving the sand which had been separated from the silt and clay.
SILT	Total silt is the portion of the sample with particle diameter between 0.002 mm and 0.05 mm. It was calculated by subtracting from 100 percent the sum of the total sand and clay.
COSI	Coarse silt is the silt fraction between 0.02 mm and 0.05 mm. It was calculated by subtracting the fine silt fraction from the total silt.
FSI	Fine silt is the silt fraction between 0.002 mm and 0.02 mm. It was determined by the pipet method (USDA/SCS, 1984) and was calculated by subtracting the clay fraction from the less than 0.02 mm fraction.
CLAY	Total clay is the portion of the sample with particle diameter of less than 0.002 mm and is determined using the pipet method.
PH_H20	pH determined in a deionized water extract using a 1:1 mineral soil to solution ratio and 1:5 organic soil to solution ratio. The pH was measured with a pH meter and combination electrode.
PH_002M	pH determined in a 0.002M calcium chloride extract using a 1:2 mineral soil to solution ratio and 1:10 organic soil to solution ratio. The pH was measured with a pH meter and combination electrode.
PH_01M	pH determined in a 0.01M calcium chloride extract using a 1:1 mineral soil to solution ratio and 1:5 organic soil to solution ratio. The pH was measured with a pH meter and combination electrode.
CA_CL	Exchangeable calcium determined with an unbuffered 1M ammonium chloride solution. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
MG_CL	Exchangeable magnesium determined with an unbuffered 1M ammonium chloride solution. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
K_CL	Exchangeable potassium determined with an unbuffered 1M ammonium chloride solution. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Atomic absorption spectrometry was specified.
NA_CL	Exchangeable sodium determined with an unbuffered 1M ammonium chloride solution. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.

(continued)

Table 5-23. Continued

Variable	Description of Variable
CA_OAC	Exchangeable calcium determined with 1M ammonium acetate solution buffered at pH 7.0. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
MG_OAC	Exchangeable magnesium determined with 1M ammonium acetate solution buffered at pH 7.0. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
K_OAC	Exchangeable potassium determined with 1M ammonium acetate solution buffered at pH 7.0. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Atomic absorption spectrometry was specified.
NA_OAC	Exchangeable sodium determined with 1M ammonium acetate solution buffered at pH 7.0. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
CEC_CL	Cation exchange capacity determined with an unbuffered 1M ammonium chloride solution is the effective CEC which occurs at approximately the field pH when combined with the acidity component. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Samples were analyzed for ammonium content by one of three methods: automated distillation/titration; manual distillation/automated titration; or ammonium displacement/flow injection analysis.
CEC_OAC	Cation exchange capacity determined with 1M ammonium acetate solution buffered at pH 7.0 is the theoretical estimate of the maximum potential CEC for a specific soil when combined with the acidity component. A 1:26 mineral soil to solution ratio and 1:52 organic soil to solution ratio were used. Samples were analyzed for ammonium content by one of three methods: automated distillation/titration; manual distillation/automated titration; or ammonium displacement/flow injection analysis.
AC_KCL	Effective exchangeable acidity determined by titration in an unbuffered 1M potassium chloride extraction using a 1:20 soil to solution ratio.
AC_BACL	Total exchangeable acidity determined by titration in a buffered (pH 8.2) barium chloride triethanolamine extraction using a 1:30 soil to solution ratio.
AL_KCL	Extractable aluminum determined by an unbuffered 1M potassium chloride extraction using a 1:20 soil to solution ratio. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
CA_CL2	Extractable calcium determined by a 0.002M calcium chloride extraction. A 1:2 mineral soil to solution ratio and 1:10 organic soil to solution ratio were used. The calcium is used to calculate lime potential. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
MG_CL2	Extractable magnesium determined by a 0.002M calcium chloride extraction. A 1:2 mineral soil to solution ratio and 1:10 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
K_CL2	Extractable potassium determined by a 0.002M calcium chloride extraction. A 1:2 mineral soil to solution ratio and 1:10 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
NA_CL2	Extractable sodium determined by a 0.002M calcium chloride extraction. A 1:2 mineral soil to solution ratio and 1:10 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
FE_CL2	Extractable iron determined by a 0.002M calcium chloride extraction. A 1:2 mineral soil to solution ratio and 1:10 organic soil to solution ratio were used. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
AL_CL2	Extractable aluminum determined by a 0.002M calcium chloride extraction. A 1:2 mineral soil to solution ratio and 1:10 organic soil to solution ratio were used. The aluminum concentration obtained from this procedure is used to calculate aluminum potential. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.

(continued)

Table 5-23. Continued

Variable	Description of Variable
FE_PYP	Extractable iron determined by a 0.1M sodium pyrophosphate extraction using a 1:100 soil to solution ratio. The pyrophosphate extract estimates organically-bound iron. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
AL_PYP	Extractable aluminum determined by a 0.1M sodium pyrophosphate extraction using a 1:100 soil to solution ratio. The pyrophosphate extract estimates organically-bound aluminum. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
FE_AO	Extractable iron determined by an ammonium oxalate-oxalic acid extraction using a 1:100 soil to solution ratio. The acid oxalate extract estimates organic and amorphous iron oxides. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
AL_AO	Extractable aluminum determined by an ammonium oxalate-oxalic acid extraction using a 1:100 soil to solution ratio. The acid oxalate extract estimates organic and amorphous aluminum oxides. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
FE_CD	Extractable iron determined by a sodium citrate-sodium dithionite extraction using a 1:30 soil to solution ratio. The citrate dithionite extract estimates non-silicate iron. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
AL_CD	Extractable aluminum determined by a sodium citrate-sodium dithionite extraction using a 1:30 soil to solution ratio. The citrate dithionite extract estimates non-silicate aluminum. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry was specified.
SO4_H2O	Extractable sulfate determined with a double deionized water extract. This extraction approximates the sulfate which will readily enter the soil solution and uses a 1:20 soil to solution ratio. Ion chromatography was specified.
SO4_PO4	Extractable sulfate determined with a 0.016M sodium phosphate (500 mg P/L) extract. This extraction approximates the total amount of adsorbed sulfate and uses a 1:20 soil to solution ratio. Ion chromatography was specified.
SO4_0	Sulfate remaining in a 0 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio and 1:20 organic soil to solution ratio. The data are used to develop sulfate isotherms. Ion chromatography was specified.
SO4_2	Sulfate remaining in a 2 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio and 1:20 organic soil to solution ratio. The data are used to develop sulfate isotherms. Ion chromatography was specified.
SO4_4	Sulfate remaining in a 4 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio and 1:20 organic soil to solution ratio. The data are used to develop sulfate isotherms. Ion chromatography was specified.
SO4_8	Sulfate remaining in a 8 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio and 1:20 organic soil to solution ratio. The data are used to develop sulfate isotherms. Ion chromatography was specified.
SO4_16	Sulfate remaining in a 16 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio and 1:20 organic soil to solution ratio. The data are used to develop sulfate isotherms. Ion chromatography was specified.
SO4_32	Sulfate remaining in a 32 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio and 1:20 organic soil to solution ratio. The data are used to develop sulfate isotherms. Ion chromatography was specified.
C_TOT	Total carbon determined by rapid oxidation followed by thermal conductivity detection using an automated CHN analyzer. Total carbon can be used to characterize the amount of organic material in the soil.
N_TOT	Total nitrogen determined by rapid oxidation followed by thermal conductivity detection using an automated CHN analyzer. Total nitrogen can be used to characterize the organic material in the soil.
S_TOT	Total sulfur determined by automated sample combustion followed by infrared detection or titration of evolved sulfur dioxide.

are first used (e.g., sulfate adsorption isotherms in Section 9.2.3 and cation exchange selectivity coefficients in Section 9.3.2).

5.5.4.2.2 Selection of analytical laboratories -

The solicitation process (Van Remortel et al., 1988) began with preparation of a detailed statement of work that defined the analytical and QA/QC requirements in contractual format, followed by preparation and advertisement of an invitation for bid (IFB). All laboratories that responded to the IFB were sent performance evaluation soil samples (PE) to analyze according to DDRP procedures; these samples had been previously characterized for DDRP. PE bidding laboratories were rated using a scoring sheet developed by Bartz et al. (1987). All laboratories that passed the PE sample evaluation were then audited to verify their ability to meet the contractual requirements. Laboratories that passed these on-site evaluations were awarded contracts for analytical services.

5.5.4.2.3 Quality assurance/quality control of analytical laboratories -

The QA/QC procedures used for evaluating the analytical laboratories were described by Bartz et al. (1987). Evaluations of analytical laboratory performance were documented by Byers et al. (1989) and Van Remortel et al. (1988).

A priori data quality objectives (DQO) were established for all analyses performed by the analytical laboratories (Table 5-24). DQOs are statements of the levels of uncertainty that a data user is willing to accept for the planned purposes of the data. The wide variety of data uses planned by the DDRP made it difficult to set user-specific DQOs. The approach adopted was to set them at levels of precision that could be expected from good laboratory practices, based on review of available literature and the experience of DDRP scientists and cooperators. The DQOs were translated into detection limits and precisions that the analytical laboratories were required to meet (Tables 5-25 and 5-26).

Table 5-24. Data Quality Objectives for Detectability and Analytical Within-Batch Precision (Van Remortel et al., 1988)

		CRDL[a]		Precision[b]		
Variable	Reporting Units	Units	mg L^{-1}	Lower (SD)	Upper (RSD)	knot
MOIST	wt %	---	---	---	---	---
SP_SUR	m^2/g	---	---	---	---	---
SAND[c]	wt %	---	---	1.0	---	---
SILT[c]	"	---	---	1.0	---	---
CLAY	"	---	---	1.0	---	---
PH_H2O	pH units	---	---	0.15	---	---
PH_002M	"	---	---	0.15	---	---
PH_01M	"	---	---	0.15	---	---
CA_CL	meq/100g	0.003	0.05	0.03	15%	0.20
MG_CL	"	0.011	0.05	0.03	15%	0.20
K_CL	"	0.003	0.05	0.03	15%	0.20
NA_CL	"	0.006	0.05	0.03	15%	0.20
CA_OAC	meq/100g	0.006	0.05	0.03	15%	0.20
MG_OAC	"	0.011	0.05	0.03	15%	0.20
K_OAC	"	0.006	0.05	0.03	15%	0.20
NA_OAC	"	0.006	0.05	0.03	15%	0.20
CEC_CL	meq/100g	0.002	0.01[d,e]	0.25	10%	2.5
CEC_OAC	"	0.002	0.01[d,e]	0.25	10%	2.5
AC_KCL	"	0.11	0.40[e]	0.50	20%	2.5
AC_BACL	"	0.75	0.25[e]	0.50	20%	2.5
AL_KCL	"	0.80	0.10	0.50	20%	2.5
CA_CL2	meq/100g	---	---[f]	---	5%	---
MG_CL2	"	0.0007	0.05	---	10%	---
K_CL2	"	0.0002	0.05	---	10%	---
NA_CL2	"	0.0004	0.05	---	10%	---
FE_CL2	"	0.0005	0.05	---	10%	---
AL_CL2	"	0.0001	0.05	---	10%	---

continued

Table 5-24. (Continued)

Variable	Reporting Units	CRDL[a] Units	CRDL[a] mg L^{-1}	Precision[b] Lower (SD)	Precision[b] Upper (RSD)	Precision[b] knot
FE_PYP	wt %	0.005	0.50	0.05	15%	0.33
AL_PYP	"	0.005	0.50	0.05	15%	0.33
FE_AO	"	0.005	0.50	0.05	15%	0.33
AL_AO	"	0.005	0.50	0.05	15%	0.33
FE_CD	"	0.002	0.50	0.05	15%	0.33
AL_CD	"	0.002	0.50	0.05	15%	0.33
SO4_H2O	mg S/kg	2.0	0.10	1.0	10%	10.0
SO4_PO4	"	2.0	0.10	1.0	10%	10.0
SO4_0-32	mg S/L	0.10	0.10	0.05	5%	1.0
C_TOT	wt %	0.01[g]	0.010	0.05	15%	0.33
N_TOT	"	0.01[g]	0.010	0.01	10%	0.10
S_TOT	"	0.01[g]	0.010	0.01	10%	0.10

[a] Contract-required detection limit in reporting units and parts per million, respectively
[b] Precision objectives below and above the knot separating the lower tier (standard deviation in reporting units) and the upper tier (relative standard deviation in percent); the knot is in reporting units
[c] DQOs were not established for size fractions of this parameter
[d] Units are meq L^{-1} for this parameter for flow injection analysis
[e] Units in meq for this parameter for titration
[f] CRDL reported as standard deviation of ten non-consecutive blanks
[g] Units are weight percent (wt %) for this parameter

Table 5-25. Detection Limits for Contract Requirements, Instrument Readings, and System-Wide Measurement in the Northeast (Byers et al., 1989)

Variable	CRDL[a]	Calc IDL[b]	Conv IDL[c]	SDL[d]	%RS>SDL[e]
CA_CL	0.05 mg/L	0.0333 mg/L	0.0043 meq/100g	0.0237 meq/100g	88.5
MG_CL	0.05 "	0.0174 "	0.0037 "	0.0058 "	88.5
K_CL	0.05 "	0.0285 "	0.0019 "	0.0090 "	95.5
NA_CL	0.05 "	0.0343 "	0.0039 "	0.0149 "	71.7
CA_OAC	0.05 mg/L	0.0275 mg/L	0.0036 meq/100g	0.0215 meq/100g	89.5
MG_OAC	0.05 "	0.0278 "	0.0059 "	0.0126 "	83.0
K_OAC	0.05 "	0.0282 "	0.0019 "	0.0163 "	84.4
NA_OAC	0.05 "	0.0279 "	0.0032 "	0.0319 "	44.2
CEC_CL	0.01 meq/L	0.0861[f] meq/L	0.1722 meq/100g	0.6032 meq/100g	92.2
CEC_OAC	0.01 "	0.1086[f] "	0.2172 "	0.8541 "	96.5
AC_KCL	0.25 "	0.0693 "	0.1386 "	0.2400 "	82.1
AC_BACL	0.40 "	0.3374 "	1.0122 "	3.6072 "	78.3
AL_KCL	0.10 mg/L	0.1235 mg/L	0.0274 "	0.1267 "	84.0
CA_CL2	–[g] mg/L	0.0208 mg/L	0.0002 meq/100g	0.0939 meq/100g	99.9
MG_CL2	0.05 "	0.0144 "	0.0002 "	0.0023 "	93.7
K_CL2	0.05 "	0.0258 "	0.0001 "	0.0022 "	93.8
NA_CL2	0.05 "	0.0343 "	0.0003 "	0.0081 "	87.4
FE_CL2	0.05 "	0.0183 "	0.0002 "	0.0014 "	45.2
AL_CL2	0.05 "	0.0295 "	0.0007 "	0.0058 "	71.7
FE_PYP	0.50 mg/L	0.1941 mg/L	0.0020 wt %	0.0200 wt %	92.5
AL_PYP	0.50 "	0.2880 "	0.0029 "	0.0603 "	85.1
FE_AO	0.50 "	0.1972 "	0.0021 "	0.0193 "	96.9
AL_AO	0.50 "	0.2238 "	0.0022 "	0.0457 "	94.6
FE_CD	0.50 "	0.1739 "	0.0006 "	0.0653 "	95.4
AL_CD	0.50 "	0.2697 "	0.0009 "	0.0223 "	97.2
SO4_H2O	0.10 mgS/L	0.0250 mgS/L	0.1669 mgS/kg	1.1905 mgS/kg	99.1
SO4_PO4	0.10 "	0.0725 "	0.6050 "	3.2985 "	90.7
SO4_0	0.10 "	0.0306 "	—	0.1319 "	98.8
C_TOT	0.01 wt %	0.0387 wt %	—	0.0478 wt %	97.1
N_TOT	0.01 "	0.0776 "	—	0.0058 "	88.5
S_TOT	0.01 "	0.0045 "	—	0.0051 "	72.7

[a] Contract-required detection limit.
[b] Calculated instrument detection limit; estimated as three times the pooled standard deviation of a low level DL-QCCS.
[c] Converted instrument detection limit; based on the specified reporting units.
[d] System detection limit; estimated as three times the pooled standard deviations of the lowest 10 percent of field duplicates; independent of the CRDL.
[e] Percent of routine samples exceeding the system detection limit.
[f] Estimated by averaging laboratory-reported IDLs for incomplete DL-QCCS data.
[g] CRDL reported as standard deviation of ten non-consecutive blanks.

NOTE: Detection limits were not applicable for the physical parameters, soil pH, and the remainder of the sulfate isotherm parameters. Detailed discussions of the attainment of DQOs were given by Byers et al. (1989) and Van Remortel et al. (1988).

Table 5-26. Detection Limits for the Contract Requirements, Instrument Readings, and System-wide Measurement in the Southern Blue Ridge Province (Van Remortel et al., 1988)

Variable	CRDL[a]	Calc IDL[b]	Conv IDL[c]	SDL[d]	%RS>SDL[e]
CA_CL	0.05 mg/L	0.0524 mg/L	0.0068 meq/100g	0.0311 meq/100g	89.8
MG_CL	0.05 mg/L	0.0369 mg/L	0.0079 meq/100g	0.0328 meq/100g	92.4
K_CL	0.05 mg/L	0.0364 mg/L	0.0024 meq/100g	0.0423 meq/100g	90.0
NA_CL	0.05 mg/L	0.0415 mg/L	0.0046 meq/100g	0.0195 meq/100g	69.1
CA_OAC	0.05 mg/L	0.0314 mg/L	0.0041 meq/100g	0.0725 meq/100g	77.5
MG_OAC	0.05 mg/L	0.0121 mg/L	0.0026 meq/100g	0.0220 meq/100g	96.1
K_OAC	0.05 mg/L	0.0330 mg/L	0.0022 meq/100g	0.0363 meq/100g	92.2
NA_OAC	0.05 mg/L	0.0448 mg/L	0.0051 meq/100g	0.0098 meq/100g	92.0
CEC_CL	0.01 meq/L	0.0153 meq/L[e]	0.0306 meq/100g	1.0724 meq/100g	99.9
CEC_OAC	0.01 meq/L	0.0155 meq/L[e]	0.0311 meq/100g	0.5809 meq/100g	100
AC_KCL	0.25 meq/L	0.0060 meq/L[e]	0.0188 meq/100g	0.3870 meq/100g	92.1
AC_BACL	0.40 meq/L	0.1840 meq/L[e]	0.3681 meq/100g	3.7750 meq/100g	89.8
AL_KCL	0.10 mg/L	0.0840 mg/L	0.0186 meq/100g	0.4780 meq/100g	83.1
CA_CL2	-- mg/L[f]	0.6071 mg/L	0.0160 meq/100g	0.0565 meq/100g	99.6
MG_CL2	0.05 mg/L	0.0187 mg/L	0.0003 meq/100g	0.0041 meq/100g	99.7
K_CL2	0.05 mg/L	0.0335 mg/L	0.0002 meq/100g	0.0020 meq/100g	99.6
NA_CL2	0.05 mg/L	0.0560 mg/L	0.0005 meq/100g	0.0031 meq/100g	98.9
FE_CL2	0.05 mg/L	0.0402 mg/L	0.0004 meq/100g	0.0021 meq/100g	12.7
AL_CL2	0.05 mg/L	0.0616 mg/L	0.0014 meq/100g	0.0071 meq/100g	51.3
FE_PYP	0.50 mg/L	0.1434 mg/L	0.0015 wt %	0.0273 wt %	93.8
AL_PYP	0.50 mg/L	0.2278 mg/L	0.0023 wt %	0.0220 wt %	99.5
FE_AO	0.50 mg/L	0.1941 mg/L	0.0019 wt %	0.0509 wt %	93.7
AL_AO	0.50 mg/L	0.2282 mg/L	0.0023 wt %	0.0547 wt %	96.3
FE_CD	0.50 mg/L	0.1340 mg/L	0.0004 wt %	0.1449 wt %	98.5
AL_CD	0.50 mg/L	0.1998 mg/L	0.0006 wt %	0.0426 wt %	99.3
SO4_H2O	0.10 mgS/L	0.0141 mgS/L	0.2828 mgS/kg	1.7394 mgS/kg	92.0
SO4_PO4	0.10 mgS/L	0.0367 mgS/L	0.9186 mgS/kg	3.2539 mgS/kg	99.7
SO4_0	0.10 mgS/L	0.0494 mgS/L	—	0.0759 mgS/L	91.4
C_TOT	0.010 wt %	0.0105 wt %	—	0.0821 wt %	96.7
N_TOT	0.010 wt %	0.0114 wt %	—	0.0247 wt %	71.2
S_TOT	0.010 wt %	0.0026 wt %	—	0.0178 wt %	44.6

[a] Contract-required detection limit.
[b] Calculated instrument detection limit, estimated as three times the pooled standard deviation of a low level DL-QCCS.
[c] Converted instrument detection limit, based on the specified reporting units.
[d] System detection limit, estimated as three times the pooled standard deviations of the lowest 10 percent of field duplicates, independent of the CRDL; Percent of routine samples exceeding the system detection limit.
[e] Estimated by averaging laboratory-reported IDLs for incomplete DL-QCCS data.
[f] CRDL reported as standard deviation of ten non-consecutive blanks.

NOTE: Detection limits not applicable for the physical parameters, soil pH, and the remainder of the sulfate isotherm parameters

5.5.4.2.3.1 Audits --

Each analytical laboratory was audited twice. The first audit was conducted after evaluating the PE sample data, before the laboratories became operational. The second audit occurred after sample analysis had begun, and included review of data from audit and QC samples.

5.5.4.2.3.2 Quality control samples --

QC samples were created and used by the analytical laboratories to maintain random and systematic errors within specified limits (see Tables 5-25 and 5-26). They were used to evaluate the calibration and standardization of instruments and to identify problems such as contamination or analytical interference. QC samples included calibration blanks, reagent blanks, QC check samples, detection limit QC check samples, matrix spikes, analytical duplicates, and ion chromatography standards. Failure to meet the specified quality limits could result in rejection of a batch. Detailed descriptions of the use of QC samples was given by Byers et al. (1989) and Van Remortel et al. (1988).

5.5.4.2.3.3 Audit samples --

Audit samples differed from QC samples in that they were submitted as blind samples to the analytical laboratories. These were samples of soils that had been well characterized before the DDRP analyses began. The preparation laboratories inserted a pair of audit samples into batches so that their identities and composition were unknown to the analysts. Thus, data from these samples provided an independent assessment of data quality and a means for monitoring the QC procedures. As with the preparation laboratory duplicates and the field duplicates, the audit samples provided a measure of precision (i.e., standard deviation) that could be compared to the DQOs. Tables 5-27 and 5-28 summarize the attainment of DQOs in the Northeast and Southern Blue Ridge Province, respectively, as indicated by data from the audit samples.

Examples of cases in which DQOs were not attained are listed in Tables 5-27 and 5-28. Parameters for which the within-batch standard deviations exceeded their respective DQOs in both regions included SAND, SILT, K_CL2, NA_CL2, FE_CL2, SO4_0, and N_TOT. In retrospect, the DQOs for SAND

Table 5-27 Attainment of DQO's by the analytical laboratories as determined from blind audit samples for the Northeast.

Variable	Attainment of DQO	
	Lower limit	Upper limit
SAND	N	N/A
SILT	N	N/A
CLAY	S	N/A
PH_H20	Y	N/A
PH_002M	Y	N/A
PH_01M	Y	N/A
CA_CL	Y	Y
MG_CL	Y	Y
K_CL	Y	N
NA_CL	Y	Y
CA_OAC	Y	Y
MG_OAC	Y	Y
K_OAC	Y	S
NA_OAC	Y	Y
CEC_CL	N	Y
CEC_OAC	Y	Y
AC_KCL	Y	Y
AC_BACL	S	Y
AC_KCL	Y	Y
CA_CL2	N/A	N
MG_CL2	N/A	Y
K_CL2	N/A	N
NA_CL2	N/A	N
FE_CL2	N/A	N
AL_CL2	N/A	S
FE_PYP	Y	Y
AL_PYP	Y	Y
FE_AO	S	Y
AL_AO	Y	Y
FE_CD	Y	Y
AL_CD	Y	Y

Continued

Table 5-27. (Continued)

Variable	Attainment of DQO Lower limit	Upper limit
SO4_H20	Y	Y
SO4_PO4	N	N
SO4_0	N	N
SO4_2	N/D	Y
SO4_4	N/D	Y
SO4_8	N/D	Y
SO4_16	N/D	Y
SO4_32	N/D	Y
C_TOT	Y	Y
N_TOT	Y	N
S_TOT	Y	Y

Notes:
Y = Met DQO.
N = Did not meet DQO.
S = Slightly exceeded DQO.
N/A = Not applicable because no DQO set.
N/D = No data.

Table 5-28. Attainment of DQO's by the Analytical Laboratories as Determined from Blind Audit Samples for the Southern Blue Ridge Province.

Variable	Attainment of DQO	
	Lower limit	Upper limit
SAND	N	N/A
SILT	N	N/A
CLAY	Y	N/A
PH_H20	Y	N/A
PH_002M	Y	N/A
PH_01M	Y	N/A
CA_CL	N	Y
MG_CL	Y	Y
K_CL	Y	Y
NA_CL	Y	Y
CA_OAC	Y	Y
MG_OAC	Y	Y
K_OAC	Y	Y
NA_OAC	Y	Y
CEC_CL	Y	Y
CEC_OAC	Y	Y
AC_KCL	Y	Y
AC_BACL	S	Y
AC_KCL	Y	Y
CA_CL2	N/A	Y
MG_CL2	N/A	N
K_CL2	N/A	N
NA_CL2	N/A	N
FE_CL2	N/A	N
AL_CL2	N/A	Y
FE_PYP	Y	Y
AL_PYP	Y	Y
FE_AO	S	Y
AL_AO	Y	Y
FE_CD	Y	Y
AL_CD	Y	Y

Continued

Table 5-28. (Continued)

Variable	Attainment of DQO Lower limit	Attainment of DQO Upper limit
SO4_H20	Y	Y
SO4_PO4	Y	Y
SO4_0	S	S
SO4_2	N/D	Y
SO4_4	N/D	Y
SO4_8	N/D	Y
SO4_16	N/D	Y
SO4_32	N/D	Y
C_TOT	Y	Y
N_TOT	Y	N
S_TOT	Y	Y

Notes:
Y = Met DQO.
N = Did not meet DQO.
S = Slightly exceeded DQO.
N/A = Not applicable because no DQO set.
N/D = No data.

and SILT (± 1 percent SD) and for the CL2 cations (±10 percent RSD) seem excessively restrictive, especially for the extremely low concentrations in the extracts obtained with 0.002 M $CaCl_2$. For the latter, it would have been better to have specified a lower-limit DQO, as was done for the OAC and CL cations, rather than specifying a RSD to be applied for all concentrations.

5.5.5 Database Management

The DDRP database was developed by ORNL on IBM and VAX computers using the SAS statistical software system and the ARC/INFO GIS. Detailed descriptions of database development and management are contained in the DDRP Database Users' Guide (Turner et al., in review). This section quotes extensively from that document.

5.5.5.1 Database Structure

The data in the database consist of two fundamental types: alphanumeric (attribute) and geographic (map). The alphanumeric data were tabulated on IBM personal computers using dBase III and PC SAS software systems. All tabular data eventually were incorporated into a series of SAS files on mainframe computers. The map data were digitized and stored as ARC/INFO files (Section 5.4.1.7). In general, the database design and implementation used by the NSWS-ELS-I, described by Kanciruk et al. (1986b) was followed.

Figure 5-19 shows the major steps and datasets that led to the final validated database. The final database is composed of five groups of data files (mapping, field, laboratory, enhanced laboratory, and synthesis). The mapping, field (pedon description), and laboratory data files contain data that were collected specifically for this Project. The enhanced laboratory data files have missing, zero, and negative values replaced by duplicate values or imputed from the remainder of the data; this database was not used in the analyses presented in this report. The synthesis data files contain data that were summarized or calculated from the mapping, field, and Deposition Program/National Trends Network (atmospheric deposition), the USGS (runoff and topographic attributes), and the NSWS (lake and stream chemistry).

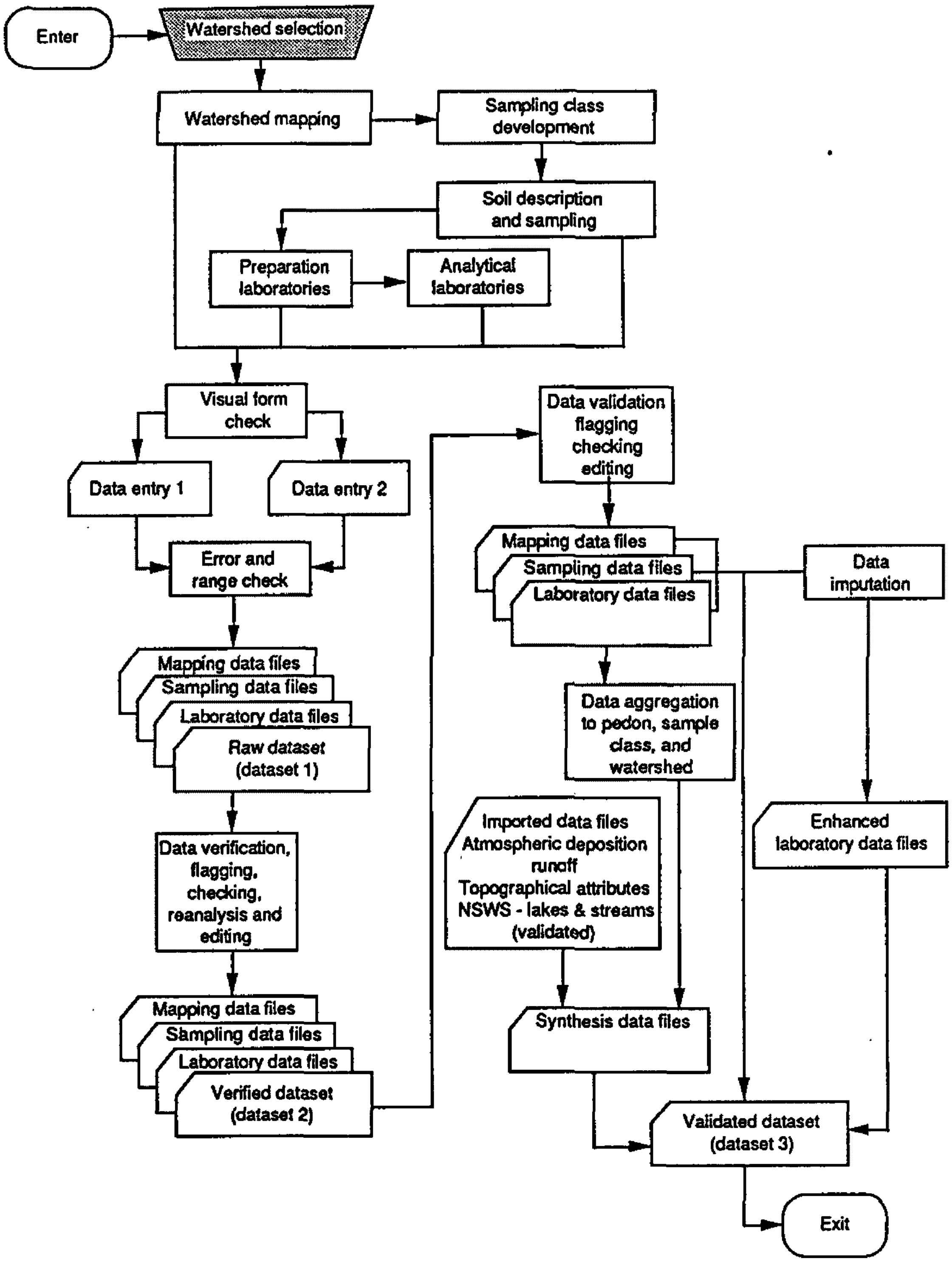


Figure 5-19. Major steps and datasets from the DDRP database.

The data acquired in each of the above activities were recorded on appropriate data input forms. The data forms were scanned visually for obvious errors; where possible, these were corrected before data entry through consultation with DDRP staff or the outside collaborators who had completed the forms. The data were double entered from the forms by two different keyboard operators and the files electronically compared and edited to produce one file with minimized input error. The edited files were then converted to SAS files as the "Raw Dataset" (Dataset 1).

Verification procedures were designed to ensure that QC goals were met and to evaluate and quantify sources of error in data collection and handling. Verification included evaluation of precision and accuracy, representativeness, completeness, and comparability. The specific checks varied with the type of data input. Data that did not meet the QA/QC criteria specified in the DDRP DQOs (Bartz et al., 1987; Coffey et al., 1987a,b) were flagged and then reviewed for field, laboratory, transcription, or data entry errors. Completion of the verification procedures resulted in the "Verified Dataset" (Dataset 2).

Validation of the data was an extension of verification, but from a larger perspective. For example, values that appeared reasonable in isolation or when compared with other values in the dataset for that variable could be distinct outliers within their particular pedon, sampling class, or watershed. Various graphical and statistical techniques were applied to the verified database to identify and check expected patterns within pedons, sampling classes, soil taxonomic classes, watersheds, and geographical regions. Flags assigned to the laboratory data during verification and validation were translated to a level of confidence for each laboratory data value to enable subsequent data analysis. The "Validated Dataset" was Dataset 3.

Data from the mapping, field, and laboratory files were linked and calculations made to aggregate the data into weighted-average values for each pedon, sample class, and watershed. These summary data are included in the synthesis data files. Aggregation methods are documented in Sections 8.8.3, 9.2, and 9.3. Data from outside sources, previously verified and validated, were also merged into the synthesis data files. These files were checked for transmission errors and compliance with documented format and contents as each file was merged into the database.

5.5.5.2 Database Operations

5.5.5.2.1 Field data (pedon descriptions) -

5.5.5.2.1.1 Entry of pedon descriptions --

Upon completion of field sampling in the NE, data from the field forms were entered into the database using ORNL in-house double-entry procedures and then converted to SAS files. For the SBRP field data, a custom dBase III data entry program was developed (Jones et al., 1986). The data were double entered, once by SCS staff and once by DDRP staff, using the dBase III program. The two versions of the data were converted into SAS files and compared using SAS procedures. Corrections were made to the data using the same transaction-checking procedure described for the mapping data (Section 5.4.1.2).

For all regions, the field data were entered as two linked files: base and horizon. The base file contained one record for each pedon. Data pertinent to the entire pedon, such as identifier, date sampled, location, taxonomic classification, and physiographic and other site information, were stored in this file. The horizon file contained the detailed horizon descriptions. Information such as horizon depth, thickness, color, structure, and other features specific to each horizon within each pedon was stored in this file. For the SBRP the log data (i.e., notes by field crews) were entered into a separate file. Log data for the NE were recorded in log books by the northeastern field teams. These data were not entered into the database.

5.5.5.2.1.2 Verification and validation of pedon descriptions --

When the pedon description forms (SCS 232 forms, Coffey et al., 1987a,b) (see Section 5.5.3.2) were returned from the field, they were evaluated by the QA staff for completeness, legibility, valid codes, and consistency of entries for each sampling team. After data entry, frequency tables of coded variables were generated and compared against lists of valid codes. With each of these steps, discrepancy forms were returned to the SCS state offices for resolution. Updates from the SCS were entered into a change file and integrated into the database in the manner described for the mapping files (Section 5.4.1.1.2). Pedon description data that still were questionable after these checks were flagged in the database.

5.5.5.2.2 Laboratory data -

5.5.5.2.2.1 Entry of laboratory data –

The soil samples were processed in batches consisting of up to 42 samples. The laboratory data were reported on two preparation laboratory forms and up to 67 analytical laboratory forms (see Cappo et al., 1987; Van Remortel et al., 1988; Byers et al., 1989). In addition, cover letters from the laboratories often contained pertinent data or data qualifiers. Some of these were added to the database as laboratory data tags accompanying the affected data and were considered in the verification process.

The laboratory data forms were sent concurrently to the DDRP data entry staff and the QA staff. The forms were logged into a tracking and filing system that facilitated entry of data into the computer as well as evaluation of progress. All forms were visually scanned for completeness, legibility, obvious errors of omission, and improper reporting units. Problems were noted and referred back to the laboratories for resolution.

The data were entered using a customized dBase III program (Schmoyer et al., in review) developed specifically for the DDRP. The double-entered data files were compared using a dBase III file comparison program. Discrepancies were corrected and the files were visually compared with the data sheets before being converted to SAS files.

The routine laboratory data were stored in three files containing 72 analytical and identifier variables. These in turn were linked to nine files of QA/QC data. Labels were assigned to all variables and, where necessary, variable names and labels were modified to ensure consistency among the various data files. A detailed listing of the laboratory data file contents is found in Chapter 7 of the DDRP Database Users' Guide (Turner et al., in review).

5.5.5.2.2.2 Verification of laboratory data –

Three types of data evaluation were performed for laboratory data verification: (1) QC samples were used by the laboratories and the QA staff to maintain systematic and random error within tolerable limits; (2) QA samples that were blind to the laboratories were used by the QA staff as an independent evaluation of laboratory performance; and (3) internal consistency checks of routine data were performed to identify outliers or potentially bad data.

Upon receipt by the QA staff, each data batch underwent the QA/QC checks shown in Table 5-29. QA and QC samples that did not meet the required limits were flagged in the database (these flags are listed in Chapter 7, Turner et al., in review). Based on the results of the QA/QC checks, the QA staff prepared a verification report for each batch of samples submitted. A letter was sent to each laboratory describing potential problems with the reported data. The letters suggested where errors such as transposed numbers, erroneous dilution factors, or improper calculations may have occurred. The laboratories were asked to respond with confirmation or reanalysis of the parameters in question. Reanalysis data were evaluated in the same manner as the original data and, if they met the required limits, were entered into the database during the verification process. QA and QC flags that remained in the database indicated data outside of specified limits, but the deviations were not considered serious enough to request reanalysis.

An internal consistency analysis was performed to identify outliers in the routine data (Byers et al., 1989; Van Remortel et al., 1988). A correlation matrix was generated for all laboratory variables measured. Highly correlated variables were regressed against one another using a weighted linear regression model. Outliers were identified using a variety of influence diagnostics. In some cases the outliers could be attributed to data entry errors, transcription errors, batch-wide calculation errors, and laboratory-specific calculation errors. If no discrepancies were found, the values were flagged with an "X4" flag (see Chapter 7, Turner et al., in review). In some cases, the values for one variable would not correlate well with values for any other variable. In those cases, the highest and lowest 10 percent of values for that variable were checked for errors.

Table 5-29. Quality Assurance and Quality Control Checks Applied to Each Data Batch (From Bartz et al., 1987; Byers et al., 1989)

1. Audit sample pairs were checked with a standard chart (template) that gave expected values and their acceptance windows.

2. The percent relative standard deviations (% RSD) of all duplicate pairs were checked.

3. The audit pairs were also subjected to consistency checks of the standard analyte relationships:

Soil pH	PH_H2O > PH_002M > PH_01M
CEC	CEC_OAC > CEC_CL
Extractable SO_4	SO4_PO4 > SO4_H2O
Acidity	AC_KCL < AC_BACL
SO_4 Isotherms	SO4_0 < 2 < 4 < 8 < 16 < 32
Particle Size	SAND + SILT + CLAY = 100 ± .1%
Organic Soil	> 12% C_TOT

4. Blank concentrations were checked for compliance with the Contract Required Detection Limits (CRDL).

5. Instrument Detection Limits (IDLs) were checked for contract compliance.

6. Matrix spikes were checked for compliance in preparation (i.e., concentrations were ten times the CRDL or twice the endogenous level, whichever was greater). Data were checked to ensure a recovery rate of 100% ± 15%.

7. QC Check Sample (QCCS) data were checked for compliance with the specified control limits.

8. Non-blank corrected data and blank corrected data were checked for proper calculations.

The data verification procedures also included an evaluation of the database with respect to data precision, accuracy (interlaboratory differences), representativeness, completeness, and comparability. Results of these evaluations were detailed by Byers et al. (1989) and Schmoyer et al. (1989) for the NE, and by Van Remortel et al. (1988) for the SBRP.

5.5.5.2.2.3 Validation of laboratory data --

Validation of the DDRP laboratory data checked relationships among the routine samples in the context of sampling classes, pedons, and horizons. These checks were made subsequent to the verification activities that evaluated batch-level laboratory QA/QC data and a limited number of internal consistency checks on routine data. Because the internal consistency checks conducted as part of the verification process were limited by time, more of these were added to the validation activity.

Numerous values of a given variable that appeared reasonable when correlated or regressed against all of the values in the database for that variable could appear as distinct outliers when compared with other values for that variable within a sampling class, pedon, or horizon. To check for these outliers, the data for each variable were grouped by sampling class and master horizon and evaluated using a custom SAS program that performed a box-and-whisker outlier test (Velleman and Hoaglin, 1981). Values that fell outside the interquartile range (IQR) ± three times the IQR, as well as values with QA/QC or verification flags that fell outside the IQR ± 1.5 times the IQR, were flagged as outliers.

All of the data flagged as outliers were evaluated individually by DDRP soil scientists. Outliers were evaluated with respect to (1) data for the same variable in the horizons above and below, (2) variability within the sampling class for that variable, (3) values for related parameters (such as CEC in acetate and chloride extraction solutions), (4) pedon horizon descriptions, (5) notes accompanying the pedon description data, (6) QA/QC data such as field and preparation laboratory duplicates, and (7) verification flags that had been assigned to the data. A validation flag (V1 to V9 or DH) was assigned to each outlier (see Chapter 7, Turner et al., in review).

A number of additional internal consistency checks also were run for the individual routine sample data as part of the validation activity. These were primarily checks of expected relationships that were requested by DDRP scientists prior to establishing confidence levels for the data.

The final step of data validation was to assign confidence levels of zero (good or high confidence) to four (bad or low confidence) to all data values, based on the assigned number and type of laboratory, QA, QC, verification, and validation flags. In assigning levels of confidence, values with DH flags were automatically given level V4; these are most certainly bad data. Values with V5 flags are those that appeared as outliers on the box-and-whisker test, but are probably valid data based on all the available information; they are the expected outliers in the dataset. Values with V3 flags are probably also good data; they probably appeared as outliers due to the way the data were grouped, or aggregated. For example, Bs and Cg horizons are very different from other B and C subhorizons, but were included with other B and C horizons in the evaluations. V3 and V5 flags were defined as informational only. Several pedons with samples that received V7 flags were later deleted from further use in the DDRP. The data for these samples are probably valid, but the pedons were probably contaminated, making them not representative of the established DDRP sampling classes.

Only data with levels of confidence of zero, one, and two have been used in most DDRP analyses. Data with levels of confidence of three or four have been discarded from most analyses, including all data aggregation schemes.

5.5.6 <u>Data Summary</u>

5.5.6.1 Summary of Sampling Class Data

The percentage area of each sampling class in the target population was calculated using the procedure shown in Figure 5-20. First, the area of each sampling class on each watershed was estimated from the area and composition of each map unit. The regional or subregional area of a sampling class was estimated as a weighted sum over watersheds, using the inverse of the watershed inclusion probability as a watershed weight. Total area was calculated by summing over all sampling classes.

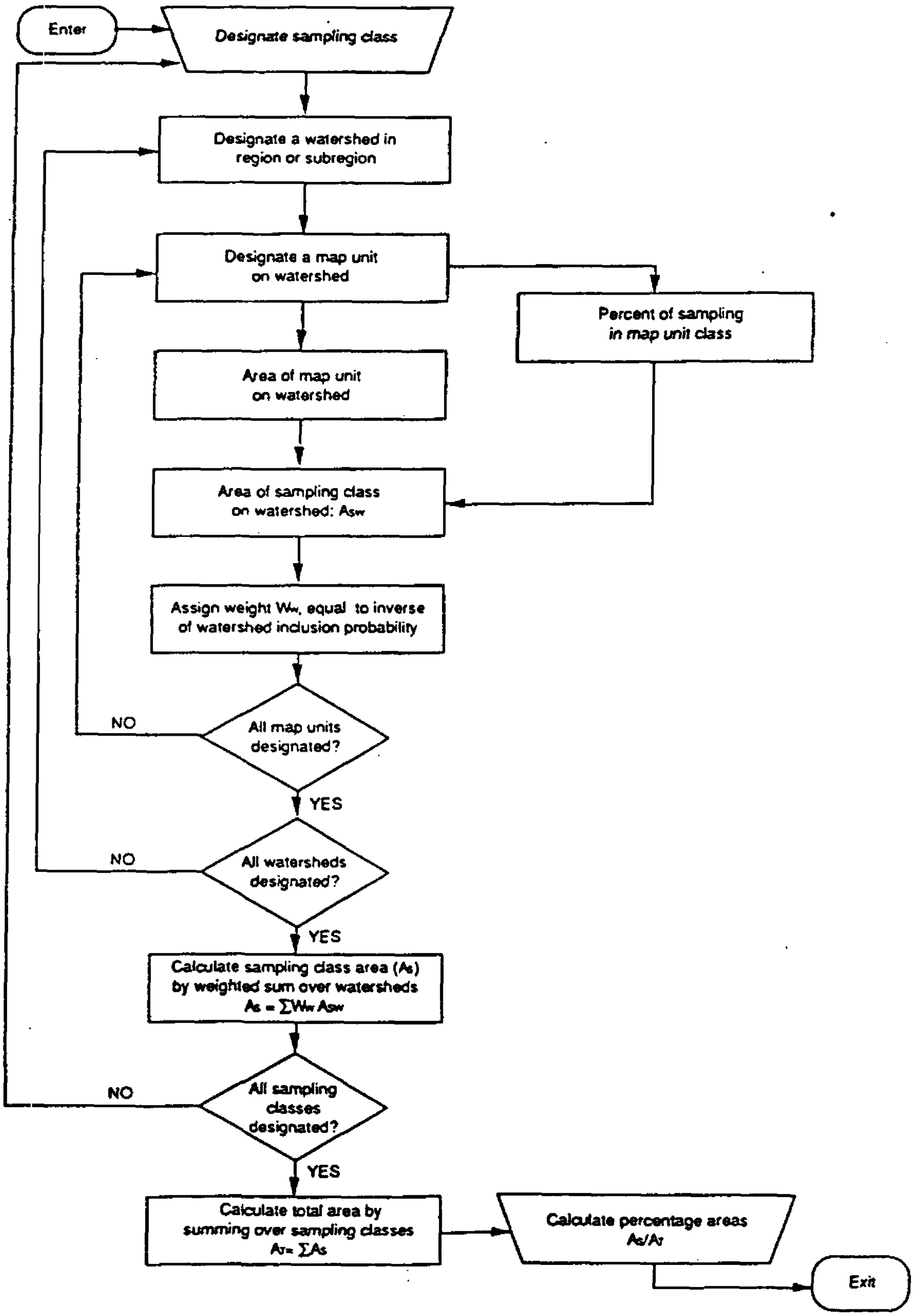


Figure 5-20. Calculation of percentage of regional or subregional area in each soil sampling.

Percentages were calculated by dividing the area of each sampling class by the total area. This procedure yielded unbiased estimates (Figures 5-21, 5-22) of the relative areas of sampling classes in the target population; that is, all watersheds in the regions that meet the conditions stated in Section 5.2.4.

Depending on the intended use, data from individual soil samples were aggregated to horizons, pedons, sampling classes and watersheds (Sections 8.8.8, 9.2.2.3). For every routine pedon included in the DDRP database for the NE, Figure 5-23 shows the pedon-aggregated values of pH (water, 0.01 M $CaCl_2$), CEC (NH_4Cl), base saturation, clay content, extractable sulfate (water, PO_4), and the slope and x-intercept of the sulfate isotherms. The corresponding data for the SBRP are shown in Figure 5-24.

5.5.6.2 Cumulative Distribution Functions

Cumulative distribution functions (CDFs) of the variables included in Figures 5-23 and 5-24 were calculated for the target population using the procedure shown in Figure 5-25. Sampling class means were given weights equal to the percentage of the area of the target population occupied by the corresponding class. CDFs for the NE and SBRP (Figure 5-26) were obtained by ordering the sampling class means and summing the weights. Table 5-30 shows medians of these variables by region and also by subregion.

5.6 DEPOSITION DATA

The regional nature of the Project required estimates of precipitation and atmospheric deposition (wet and dry) developed in a standardized manner across the eastern United States. Study sites for the DDRP were selected statistically and had no direct information for deposition. Furthermore, time and budgetary constraints precluded the instrumentation of sites and, thus, the direct acquisition of any deposition data. As discussed in Sections 2.1, 3.1, and 4.3.1, the DDRP was designed to focus on the long-term effects on surface water chemistry of deposition of sulfur. Although sulfur is the primary deposition variable of interest, complete deposition chemistry is required for the Level I statistical analyses (Section 8), the Level II base cation analyses (Section 9.3), and the Level III watershed modelling (Section 10).

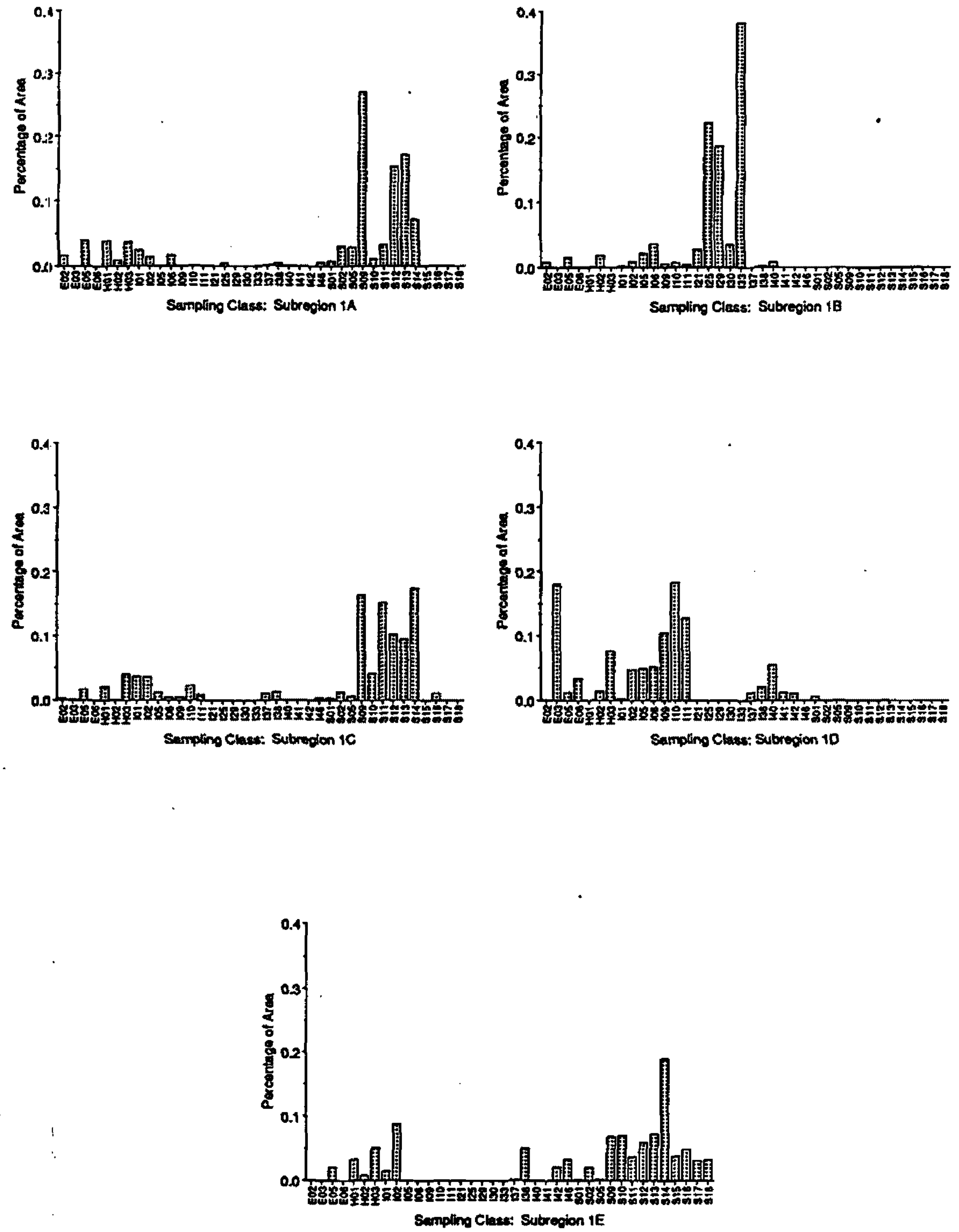


Figure 5-21. Relative areas of sampling classes in the northeastern subregions.

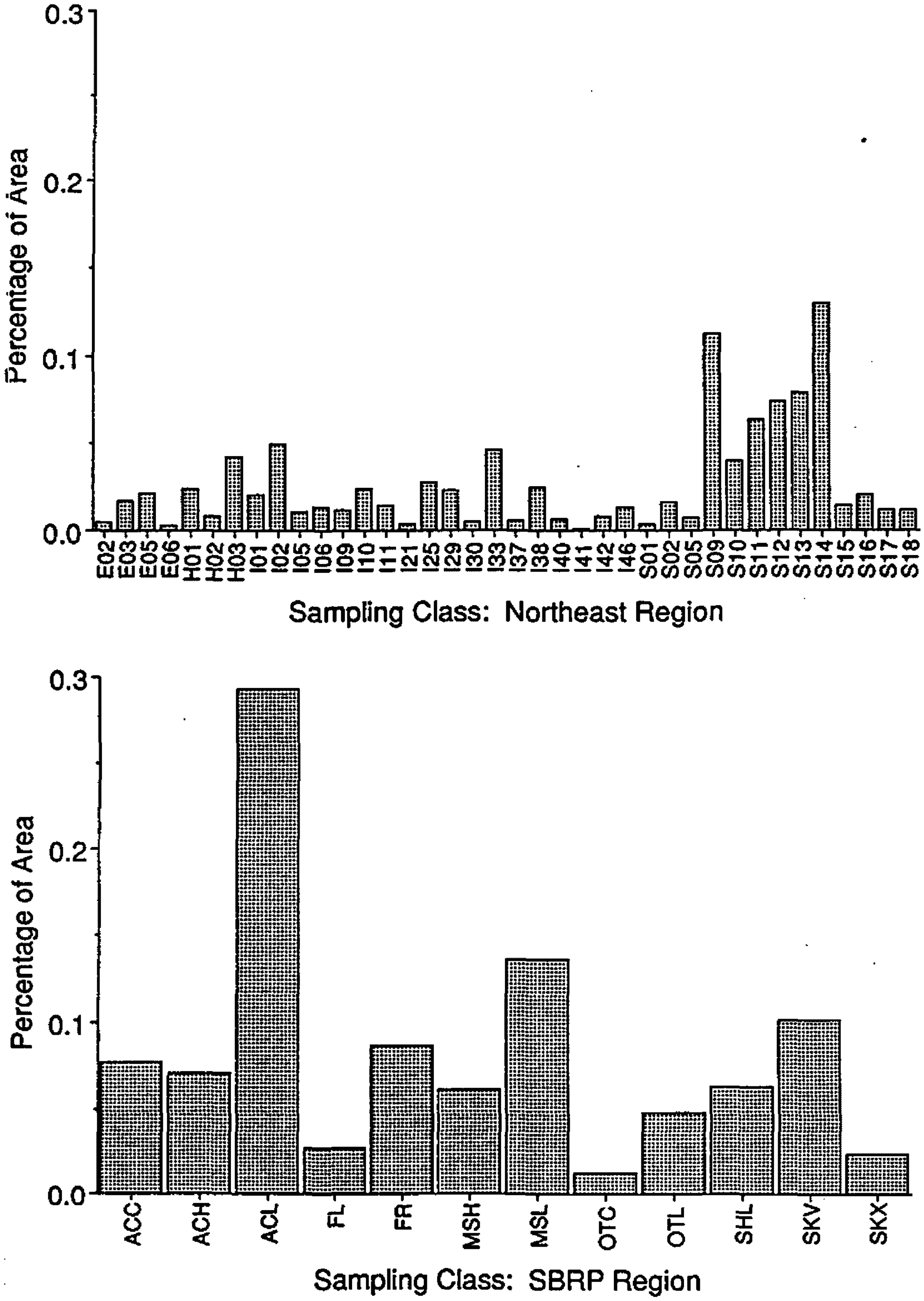


Figure 5-22. Relative areas of sampling classes in the entire Northeast and Southern Blue Region Province.

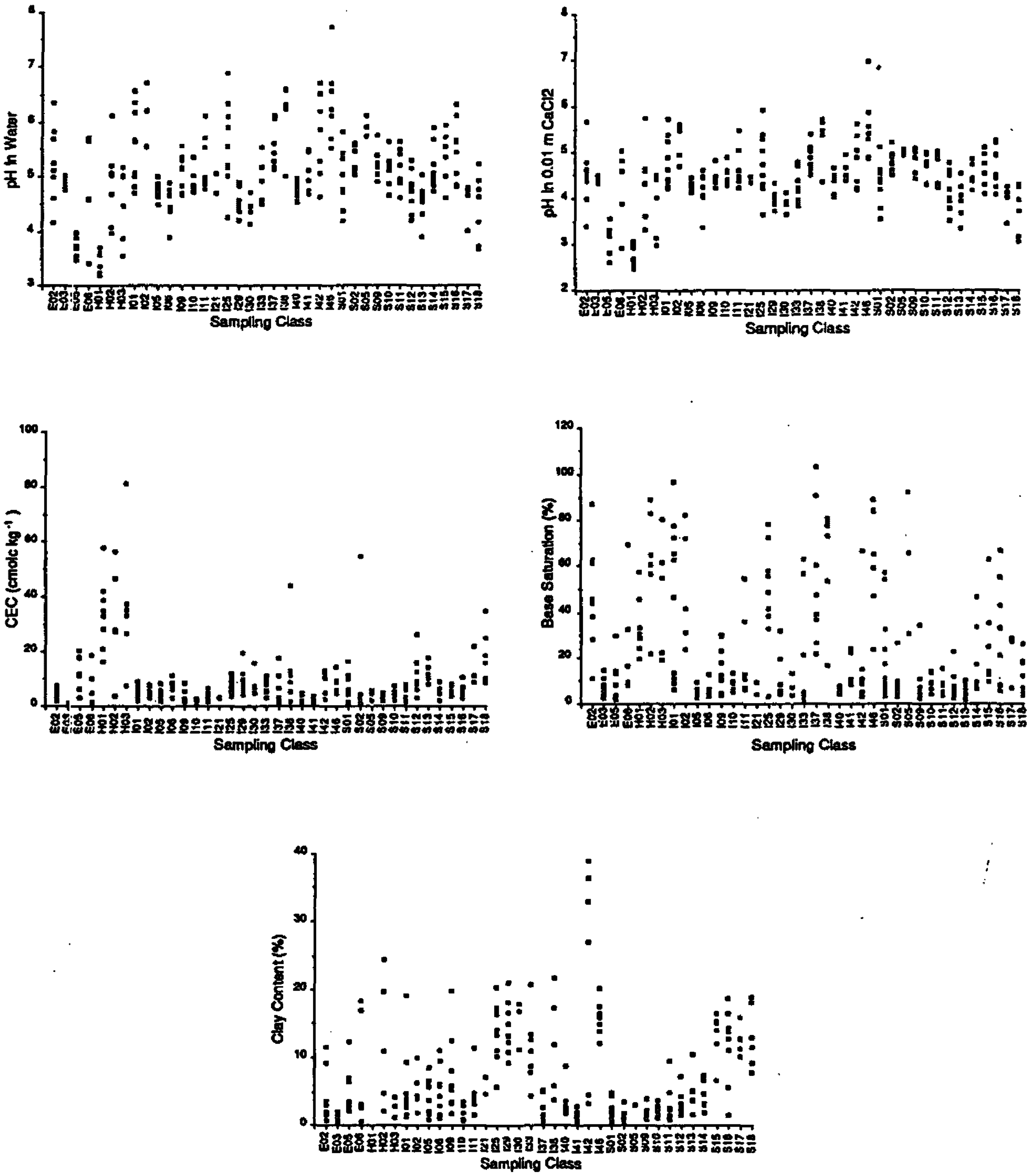


Figure 5-23. Aggregated soil variables for individual pedons in the Northeast (continued).

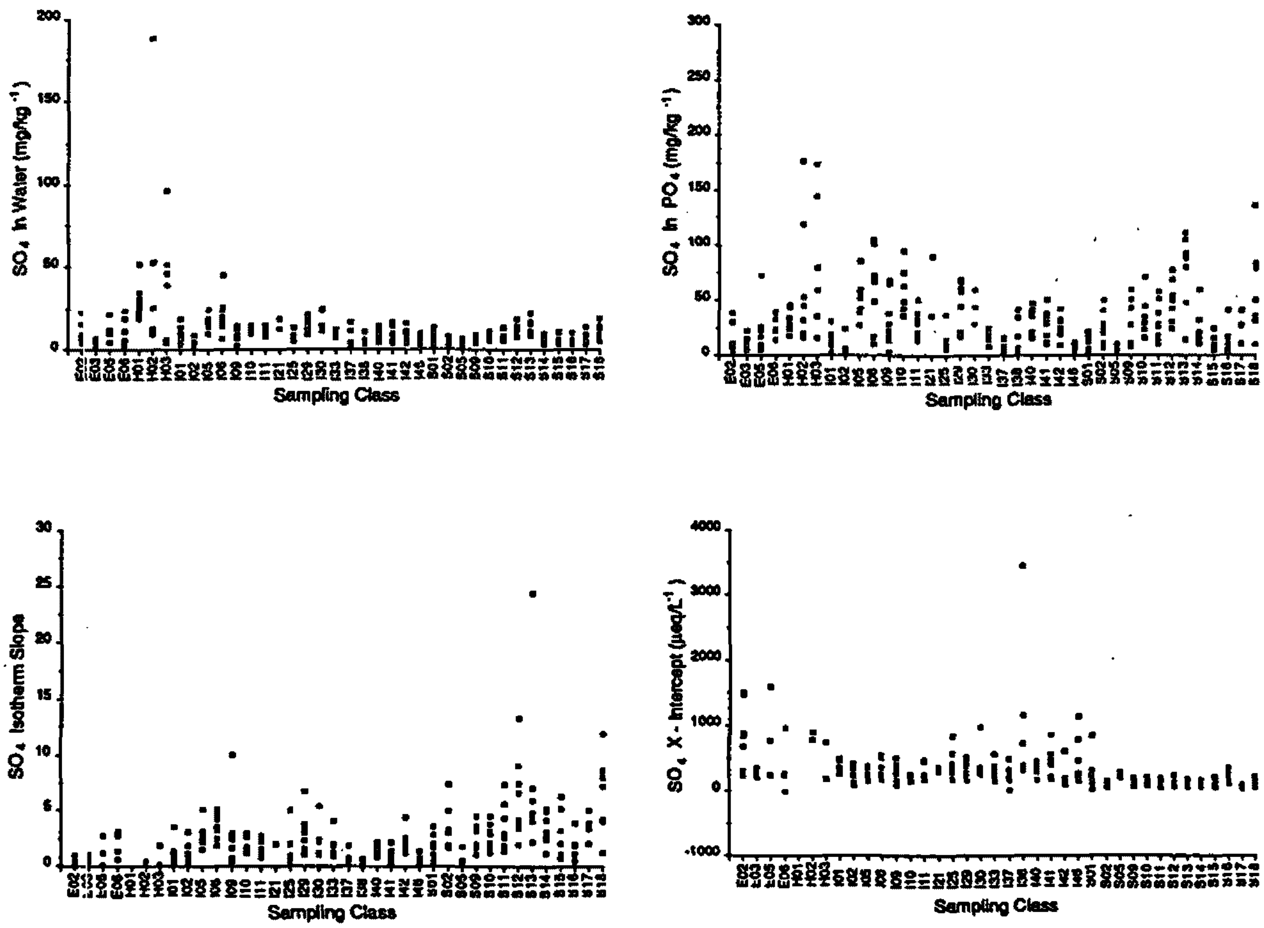


Figure 5-23. (Continued).

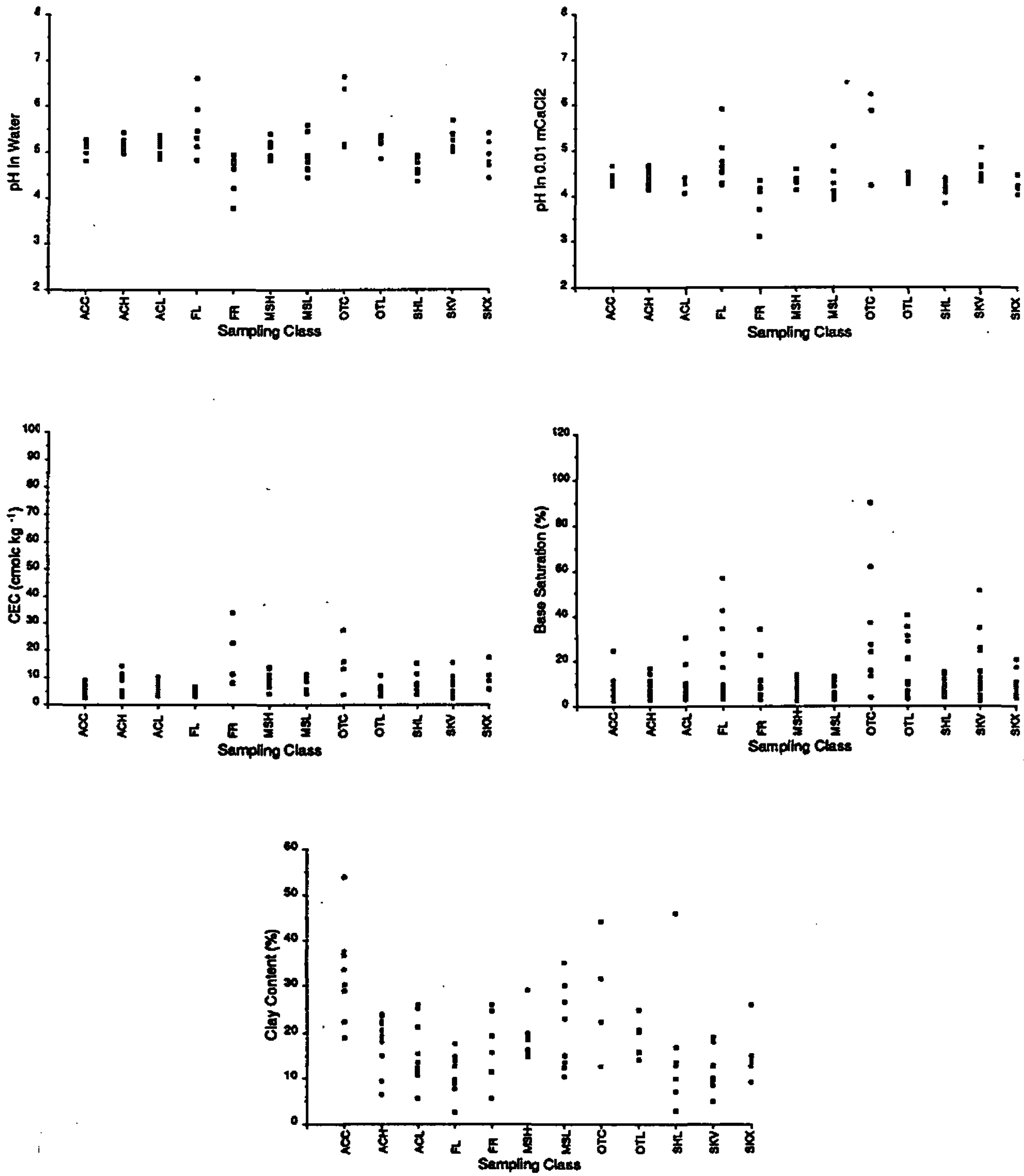


Figure 5-24. Aggregated soil variables for individual pedons in the Southern Blue Ridge Province (continued).

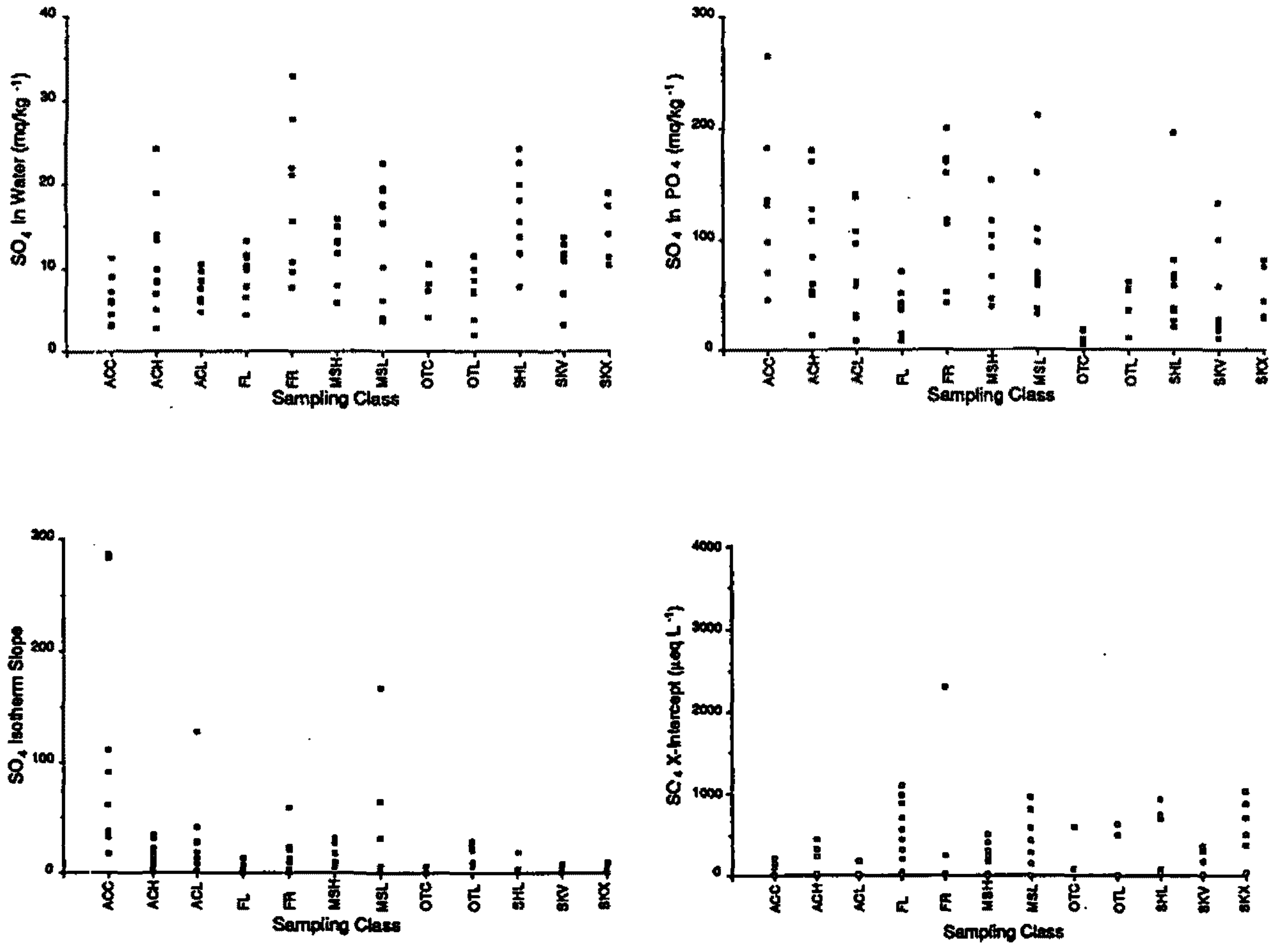


Figure 5-24. (Continued).

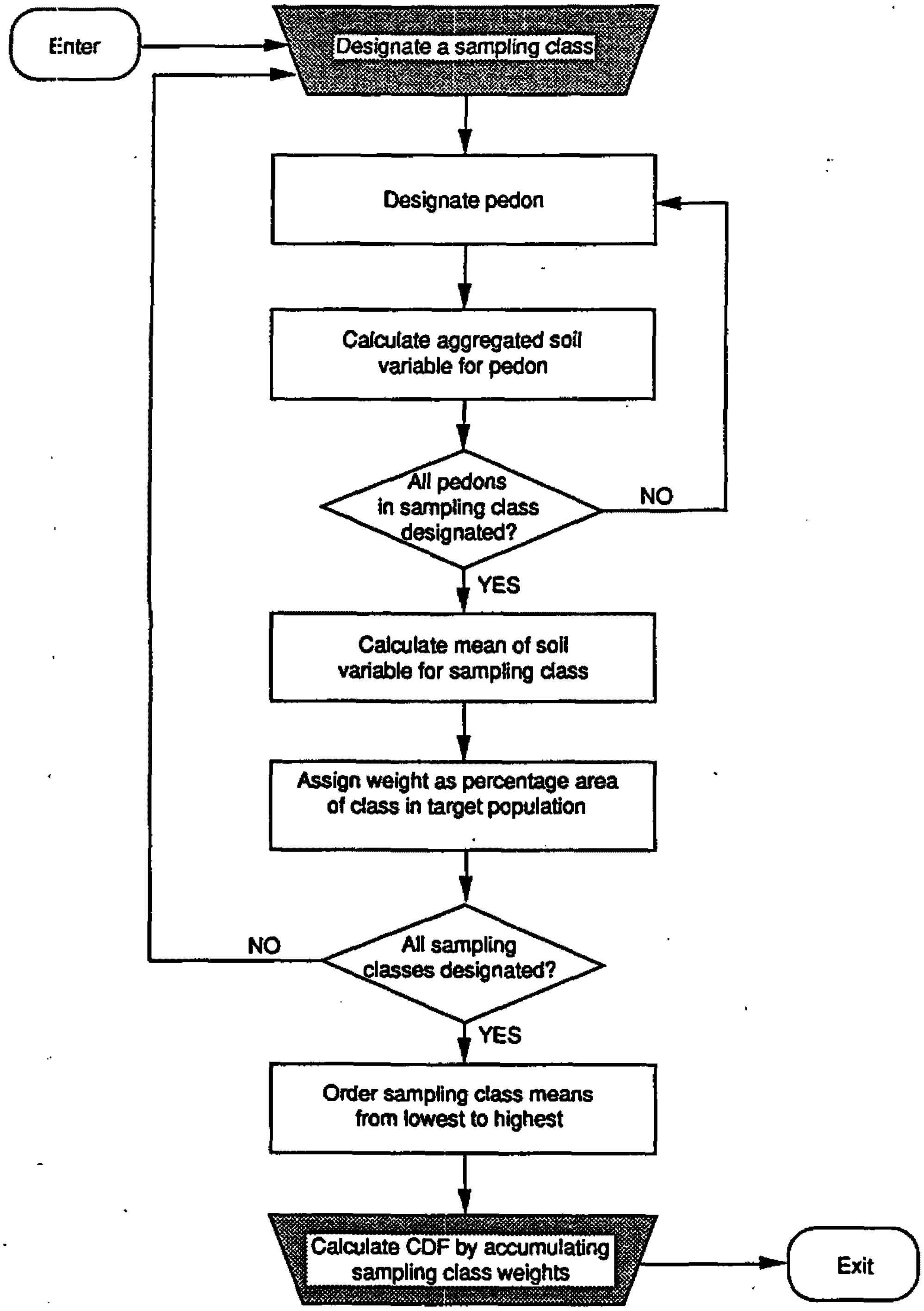


Figure 5-25. Calculation of cumulative distribution function for a soil variable in a region or subregion.

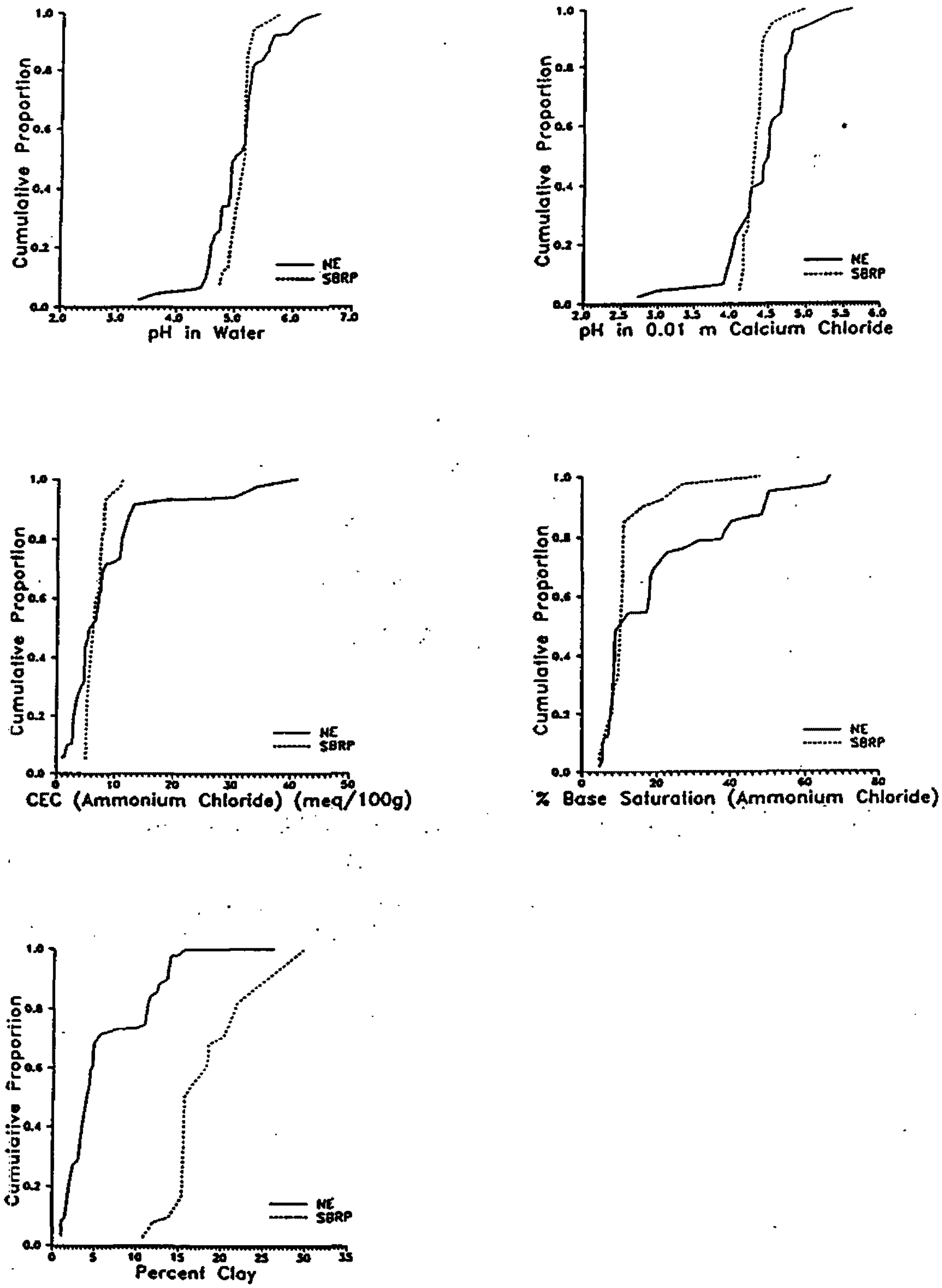


Figure 5-26. Cumulative distribution functions for pedon aggregated soil variables for the Northeast and the Southern Blue Ridge Province (continued).

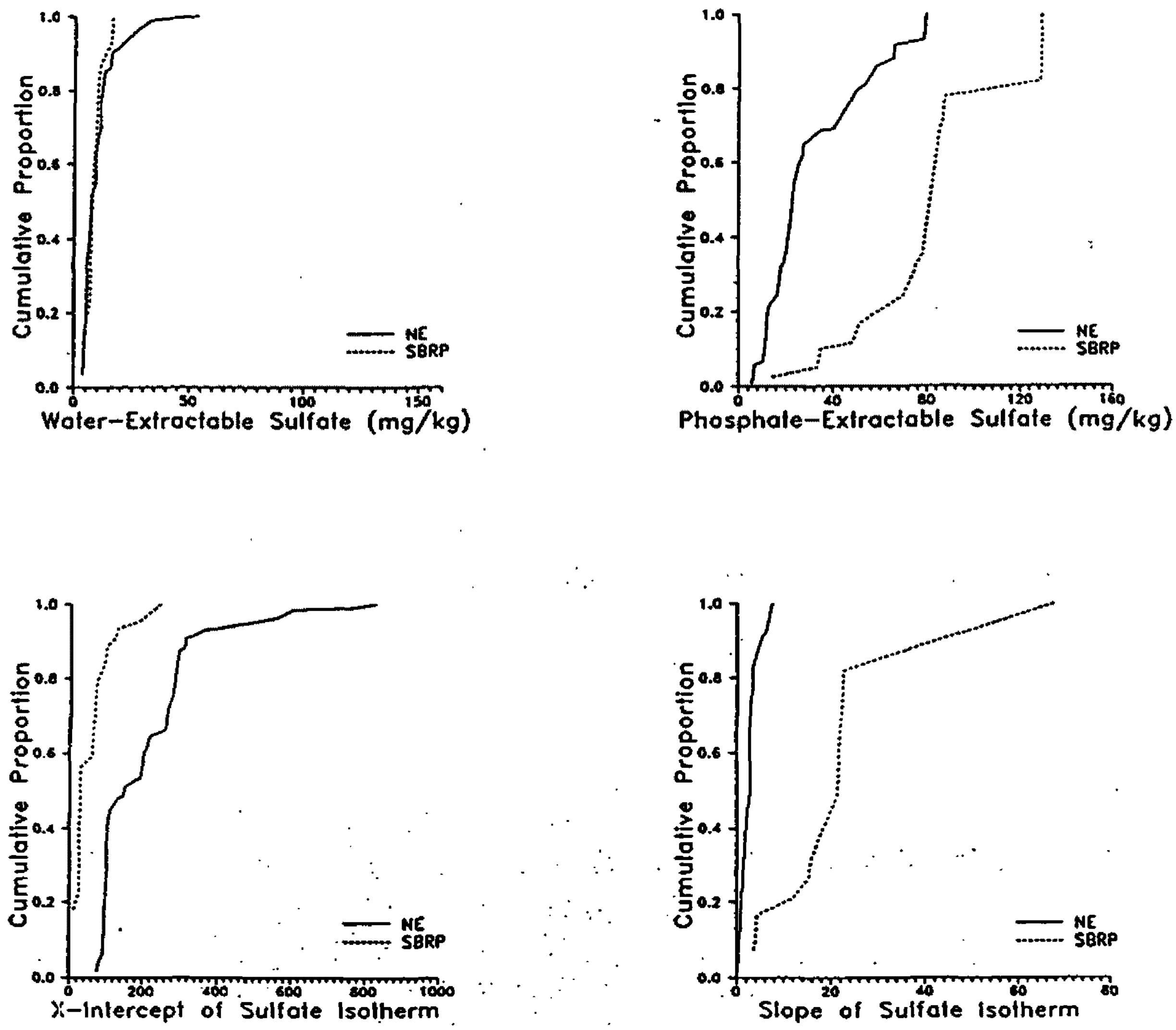


Figure 5-26. (Continued)

Table 5-30 Medians of Pedon-Aggregated Values of Soil Variables for the DDRP Regions and Subregions.

Variable	Units	Median for (Sub)Region						
		1A	1B	1C	1D	1E	NE	SBRP
pH (water)	-----	5.0	4.9	5.2	4.9	5.2	4.9	5.1
pH ($CaCl_2$)	-----	4.5	4.5	4.3	4.4	4.5	4.5	4.3
CEC	meq 100g	7.0	7.0	5.0	2.0	6.0	6.0	7.0
BS	%	9.0	20	9.0	7.0	18	10	10
Clay	%	3.0	11.5	3.5	2.0	4.5	4.0	16.0
SO_4 (water)	mg kg^{-1}	9.5	9.5	7.0	9.5	6.5	7.0	8.0
SO_4 (PO_4)	mg kg^{-1}	24	18	23	27	22	23	82
Isotherm slope	-----	2.9	1.7	2.8	1.2	2.8	2.8	21.4
Isotherm intercept	mg l^{-1}	101	285	103	262	106	148	30

5.6.1 Time Horizons of Interest

5.6.1.1 Current Deposition

Current deposition is of interest within the DDRP because of the Level I Analyses to determine (1) the current status of sulfur retention within watersheds (Section 7) and (2) the current relationship among atmospheric deposition, watershed and soil factors, and surface water chemistry (Section 8). This interest/requirement led to the development of a deposition dataset that represents atmospheric deposition as of the early to mid 1980s. This deposition dataset, the "long-term annual average" (LTA) dataset, is described more fully in Section 5.6.3.2.

5.6.1.2 Future Deposition

The major question driving the DDRP concerns the response of surface water chemistry to atmospheric deposition in the future. Within the DDRP we were requested by the U.S. EPA's Office of Air to evaluate two sulfur deposition scenarios for each study region. The first deposition scenario was constant deposition at current levels. For the NE, the second scenario was for sulfur deposition to remain constant at current levels for 10 years, then to ramp down for 15 years to a level 30 percent below current, and to remain at that level for the duration of all Level II and III simulations. For the SBRP, the second scenario was for sulfur deposition to remain constant at current levels for 10 years, then to ramp up for 15 years to a level 20 percent above current, and to remain at that level for the duration of the Level II and III simulations. These scenarios are illustrated in Figure 5-27.

5.6.2 Temporal Resolution

5.6.2.1 Level I Analyses

The Level I Analyses were performed as static analyses of current relationships and thus required data at only an annual resolution. The LTA dataset fulfilled this requirement.

5.6.2.2 Level II Analyses

The simulations of the Level II Analyses were performed using annual time steps and thus required deposition at the same resolution. The LTA dataset was used in a repetitive fashion for this work, i.e.,

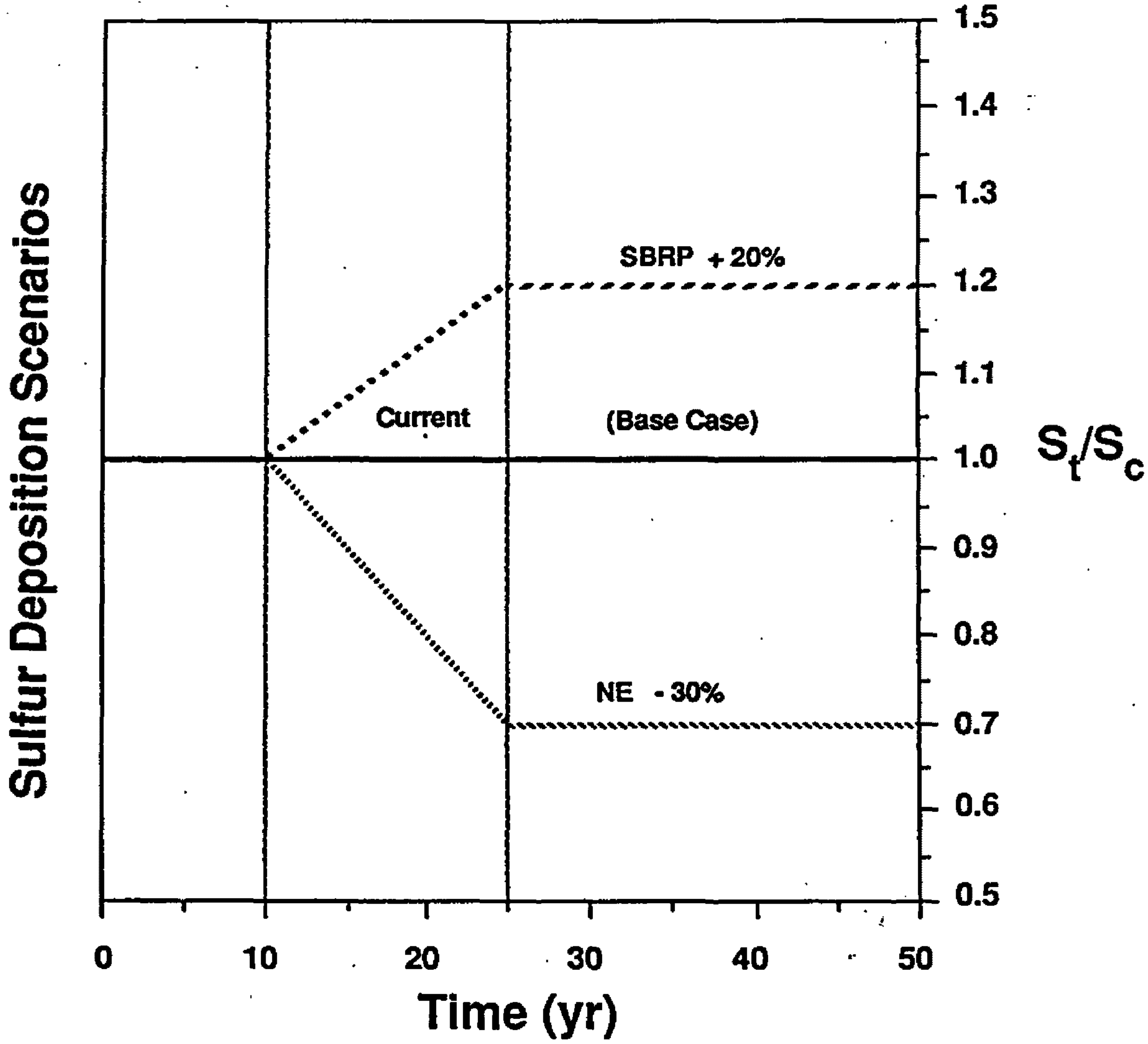


Figure 5-27. Sulfur deposition scenarios for the NE and SBRP for Level II and III Analyses. Ration of total sulfur deposition at time t (S_t) to current total sulfur deposition (S_c).

the year was repeated for each year of the simulation and was adjusted appropriately for the increase and decrease scenarios (see Section 5.6.3.2). The LTA dataset matched the resolution of the watershed runoff dataset (Section 5.7).

5.6.2.3 Level III Analyses

The watershed models used in the Level III Analyses required a fine time resolution of precipitation data for the calibration of the hydrologic portions of those models (see Sections 10.5.1 and 10.5.2). This requirement necessitated the development of a finer resolution deposition dataset for the Level III Analyses. This dataset, termed the "typical year" (TY) dataset, has a daily resolution of precipitation and a monthly resolution of deposition and was used exclusively in the Level III Analyses. It was also used as a comparative check against the LTA dataset in (1) the Level I Analyses for sulfur retention (Section 7) and (2) the Level II Analyses for sulfate adsorption (Section 9.2) and base cation depletion (Section 9.3).

5.6.3 Data Acquisition/Generation

Where possible we attempted to use deposition data (wet and dry) as available from specialized deposition projects within the National Acid Precipitation Assessment Program (NAPAP). A very difficult constraint of the DDRP analyses, however, was that the datasets used had to be complete in terms of chemical composition (i.e., all major ions), regional coverage, and internal consistency (e.g., charge balance). Such datasets were not available within NAPAP. Thus, as explained below, we had to generate such data ourselves as best possible. In the course of this data generation, we consulted at length with available authorities (both within and external to NAPAP) regarding the reasonableness of our assumptions, methods, and data generated. Because the deposition datasets for the Level III Analyses were the most complex and in some cases were the basis for construction of other datasets, we begin with a description of the Level III typical year dataset.

5.6.3.1 Level III Analyses - Typical Year Deposition Dataset

As noted in Section 5.6.2.3, the TY dataset was designed to provide a daily resolution of precipitation and a monthly resolution of deposition in order to be consistent with the hydrologic and model time step requirements of the Level III models (see Section 10.5). The TY dataset was designed to represent a yearly precipitation regime that was, indeed, "typical" of current climatological conditions for the study regions. The dataset was used repetitively (i.e., for each year) for the Level III simulations with appropriate adjustments during the increase or decrease scenarios (Figure 5-27).

5.6.3.1.1 Wet deposition -

An approach for determining wet deposition data was developed through close consultation with A. Olsen and his staff who manage the Acid Deposition System database (ADS) at Battelle-Pacific Northwest Laboratories (PNL). The ADS database is comprised of data from all of the major wet deposition monitoring networks in the United States. After the approach was developed, the actual component datasets were developed by A. Olsen and his staff.

Initially we investigated the use of wet deposition data derived by spatial interpolation (kriging) of deposition monitored at ADS sites. Several factors immediately acted to dissuade us from this approach. First was the relatively poor spatial coverage by the ADS sites, which are widely scattered geographically. As a test of interpolation, we kriged wet sulfate deposition, in and about the area of the Adirondack State Park (NY) and visually compared the spatial patterns of wet deposition to these sites with the patterns of sulfate flux from watersheds in the Adirondacks (see Section 7 for a thorough discussion of computation of sulfur input/output budgets). Previous work has indicated that sulfur inputs probably are in balance with sulfur outputs in the Adirondacks (Rochelle et al., 1987; Rochelle and Church, 1987). Visual comparison indicated that the wet input patterns poorly coincided with the output patterns. As a comparison, we computed wet sulfate inputs by multiplying together wet sulfate concentration kriged from ADS sites with precipitation kriged from the much denser network of sites of the National Oceanographic and Atmospheric Administration (NOAA) National Climatic Data Center (NCDC). Patterns produced by this procedure were much closer in agreement to observed patterns of sulfate outflux from the Adirondack watersheds.

A second important consideration was the efficacy of interpolating monthly values of deposition or wet concentration from ADS sites. The geographic sparseness of the ADS network and the occasional paucity of monthly data (e.g., during extremely dry months or months during which samples were not acceptable due to contamination) argued strongly against this approach (A. Olsen, personal communication).

A third consideration was that daily precipitation data, needed as inputs to the hydrologic models of the Level III Analyses were not available from the ADS sites.

As a result, we decided to develop for each individual DDRP study site (1) an appropriate typical year of wet concentration chemistry obtained from a nearby linked ADS site and (2) a daily precipitation dataset for a nearby linked NCDC site for the same year as selected for the typical year deposition chemistry for the linked ADS site. Wet deposition at the DDRP site is then the product of the wet chemistry and precipitation datasets. This type of multiplicative approach (in general) has been discussed and endorsed by Vong et al. (1989).

Sites for wet deposition chemistry (ADS) and daily precipitation (NCDC) were carefully selected for each DDRP study site based on geographic location, elevation, and terrain. This selection was made by DDRP staff in close coordination with A. Olsen and project cooperators involved in the Level III modelling who were familiar with the requirements of the models and the need for appropriate linkages between the precipitation inputs and hydrologic outputs from the study watersheds. The ADS and NCDC sites selected for pairing with the DDRP study sites are shown in Plates 5-14 through 5-19.

Plate 5-14. ADS and NCDC sites linked with DDRP study sites for NE Subregion 1A. The "concentration zone" indicates to which DDRP sites the appropriate typical year of wet concentration chemistry from the linked ADS site was applied. The "precipitation zone" indicates to which DDRP sites the appropriate precipitation (i.e., same year as selected for the linked ADS site and intersecting concentration zone) from the linked NCDC site was applied. See text for further description.

SUBREGION 1A
DDRP SITE LOCATIONS

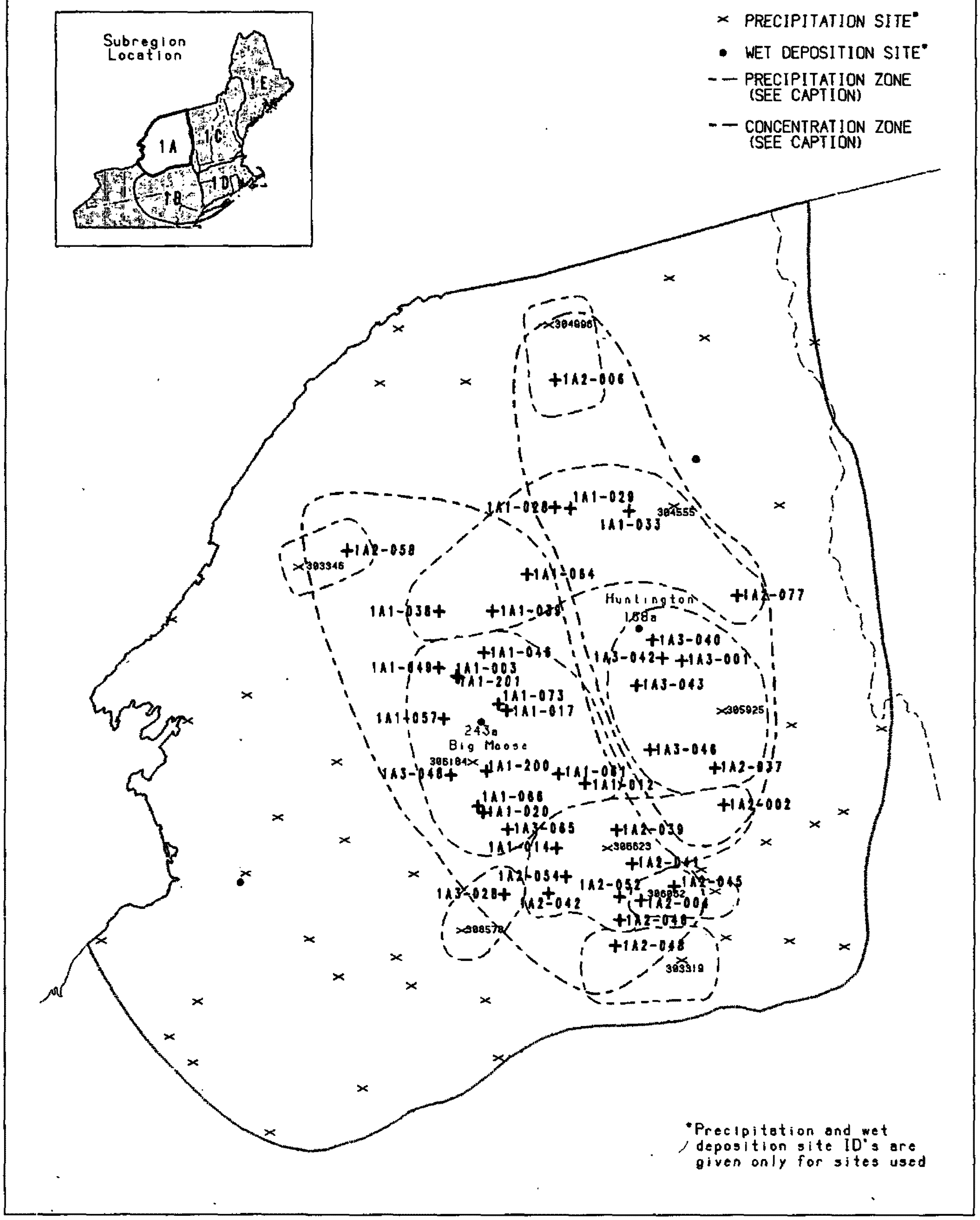
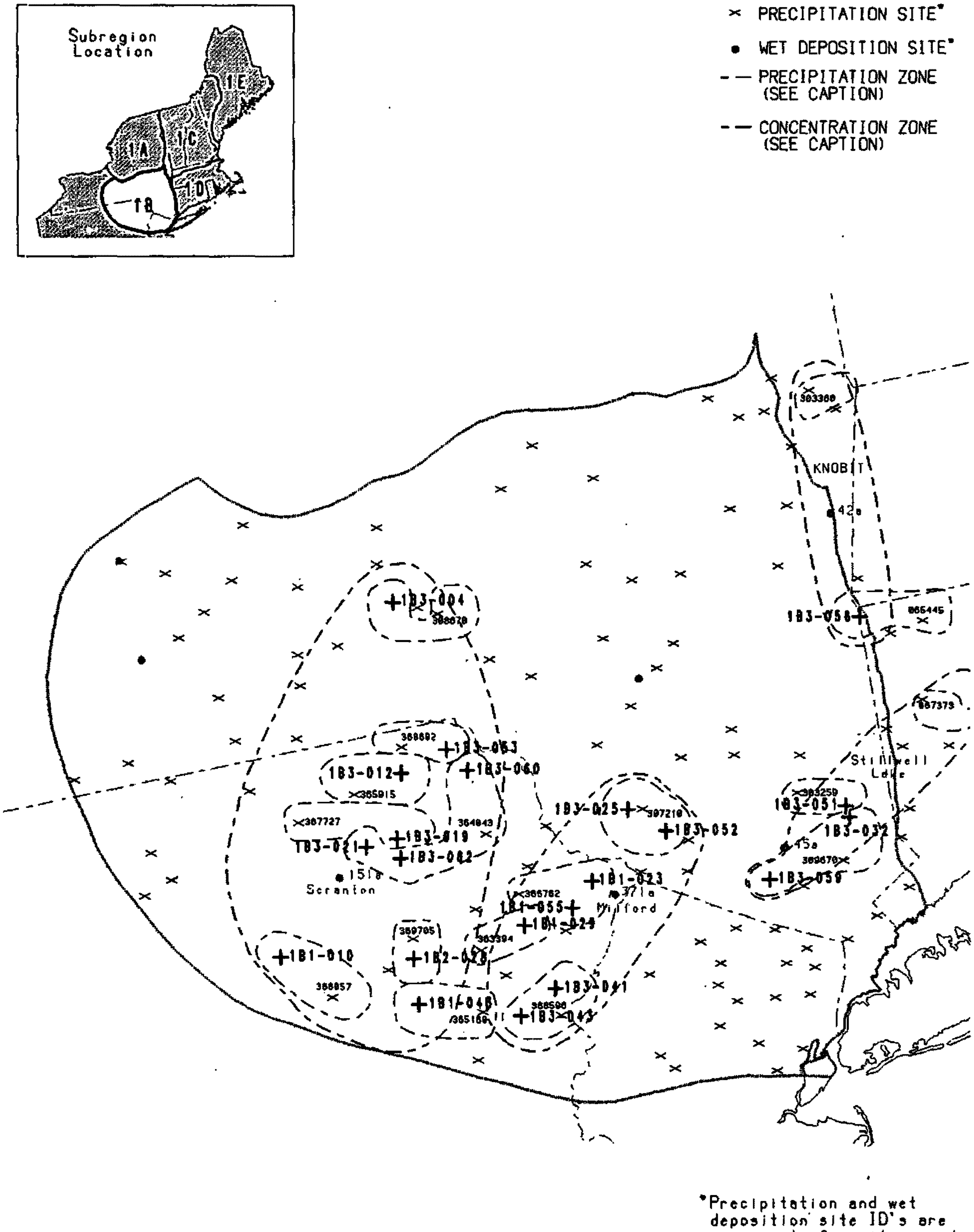


Plate 5-15. ADS and NCDC sites linked with DDRP study sites for NE Subregion 1B. The "concentration zone" indicates to which DDRP sites the appropriate typical year of wet concentration chemistry from the linked ADS site was applied. The "precipitation zone" indicates to which DDRP sites the appropriate precipitation (i.e., same year as selected for the linked ADS site and intersecting concentration zone) from the linked NCDC site was applied. See text for further description.

SUBREGION 1B
DDRP SITE LOCATIONS



*Precipitation and wet deposition site ID's are given only for sites used

Plate 5-16. ADS and NCDC sites linked with DDRP study sites for NE Subregion 1C. The "concentration zone" indicates to which DDRP sites the appropriate typical year of wet concentration chemistry from the linked ADS site was applied. The "precipitation zone" indicates to which DDRP sites the appropriate precipitation (i.e., same year as selected for the linked ADS site and intersecting concentration zone) from the linked NCDC site was applied. See text for further description.

SUBREGION 1C
DDRP SITE LOCATIONS

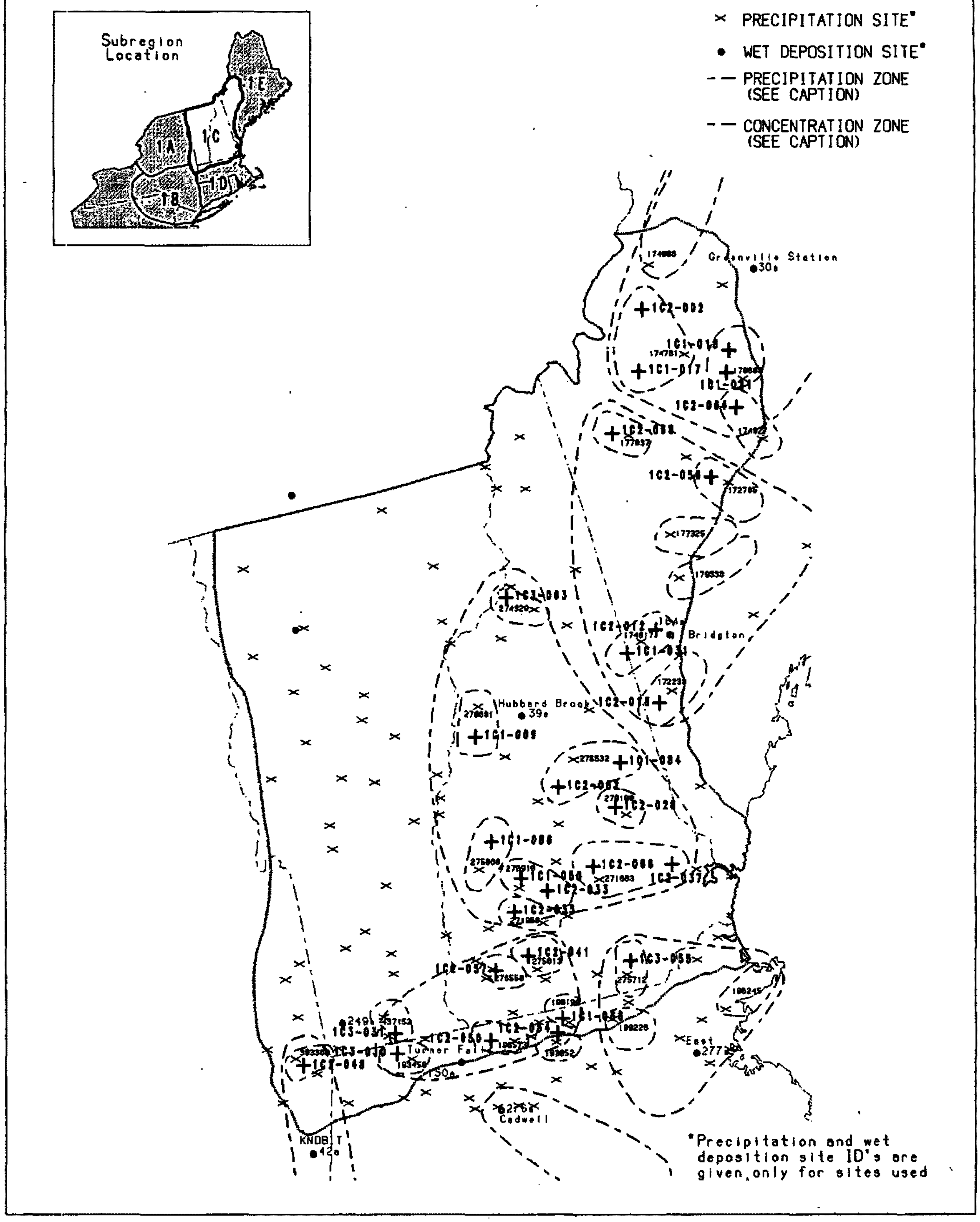
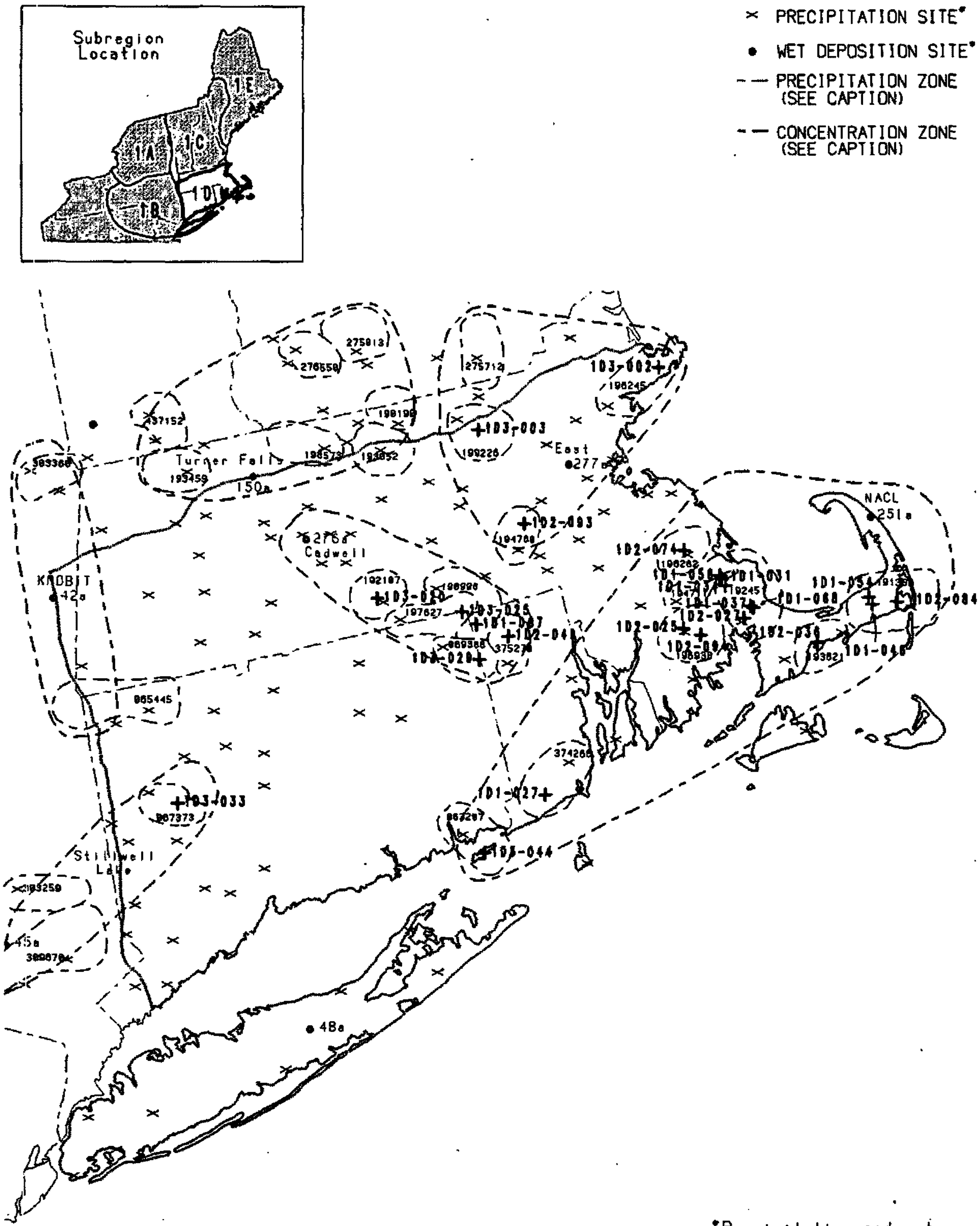


Plate 5-17. ADS and NCDC sites linked with DDRP study sites for NE Subregion 1D. The "concentration zone" indicates to which DDRP sites the appropriate typical year of wet concentration chemistry from the linked ADS site was applied. The "precipitation zone" indicates to which DDRP sites the appropriate precipitation (i.e., same year as selected for the linked ADS site and intersecting concentration zone) from the linked NCDC site was applied. See text for further description.

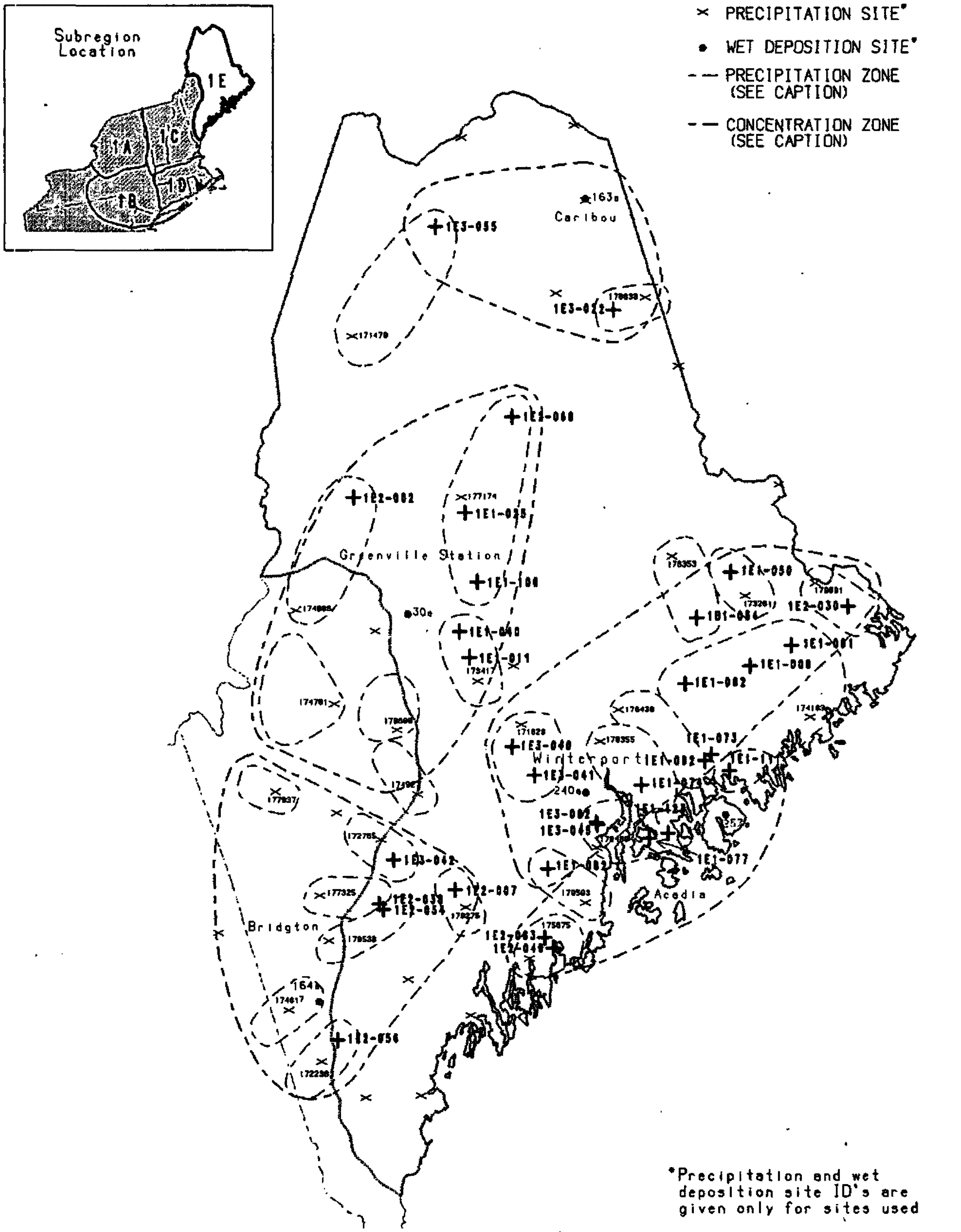
SUBREGION 1D
DDRP SITE LOCATIONS



*Precipitation and wet deposition site ID's are given only for sites used

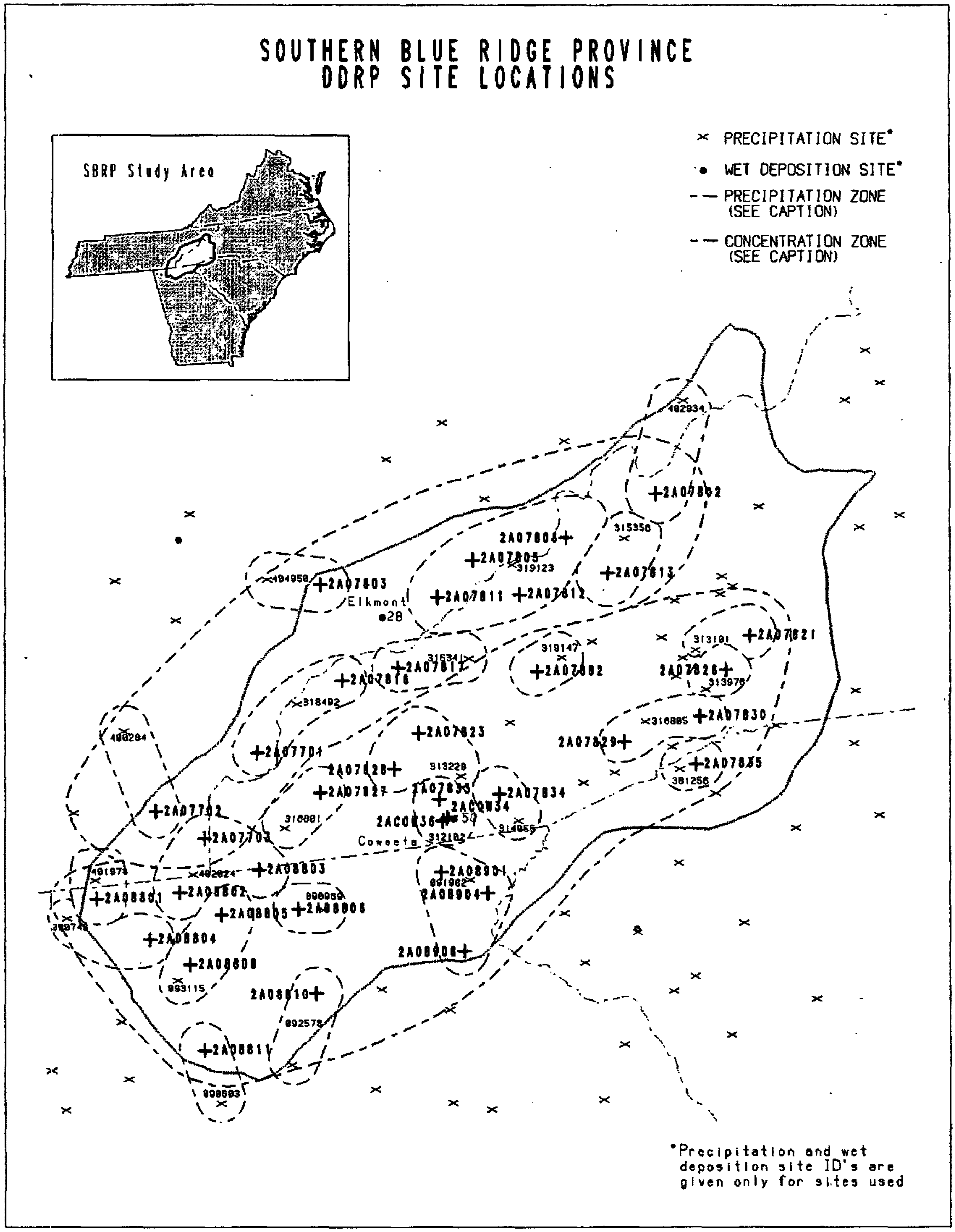
Plate 5-18. ADS and NCDC sites linked with DDRP study sites for NE Subregion 1E. The "concentration zone" indicates to which DDRP sites the appropriate typical year of wet concentration chemistry from the linked ADS site was applied. The "precipitation zone" indicates to which DDRP sites the appropriate precipitation (i.e., same year as selected for the linked ADS site and intersecting concentration zone) from the linked NCDC site was applied. See text for further description.

SUBREGION 1E
DDRP SITE LOCATIONS



*Precipitation and wet deposition site ID's are given only for sites used

Plate 5-19. ADS and NCDC sites linked with DDRP study sites for the SBRP. The "concentration zone" indicates to which DDRP sites the appropriate typical year of wet concentration chemistry from the linked ADS site was applied. The "precipitation zone" indicates to which DDRP sites the appropriate precipitation (i.e., same year as selected for the linked ADS site and intersecting concentration zone) from the linked NCDC site was applied. See text for further description.


SOUTHERN BLUE RIDGE PROVINCE
DDRP SITE LOCATIONS
SBRP Study Area
PRECIPITATION SITE*
WET DEPOSITION SITE*
PRECIPITATION ZONE (SEE CAPTION)
CONCENTRATION ZONE (SEE CAPTION)
Elkmont
Coweeta
*Precipitation and wet deposition site ID's are given only for sites used

5.6.3.1.1.1 Wet deposition chemistry --

Precipitation chemistry data were obtained from the ADS database. For each ADS site the entire history (usually less than five years) of daily or weekly data was obtained. The annual cumulative distribution functions (CDFs) for each individual year were compared with the summary CDFs of data for all years. The typical year was selected as the year that compared best to all years for sulfate concentration, nitrate concentration, and precipitation. After the typical year was selected, monthly wet deposition chemistry was computed using the procedures recommended by the Unified Database Committee (Olsen et al., 1989). Their quarterly criteria were applied to each month. When monthly data for the typical year selected did not meet the criteria, an alternate typical year was used.

5.6.3.1.1.2 Daily precipitation --

The same year chosen as the typical year for deposition chemistry was used as the typical year for precipitation at the linked NCDC site.

In a few cases precipitation data were not available for the ADS typical year. In this event the closest years with respect to sulfate concentration, nitrate concentration, and precipitation were used for which precipitation data were available. An additional advantage of using the NCDC sites was that long-term data are available for these sites allowing adjustments of individual years and days of data to a long-term norm for the location. In this case daily precipitation at each NCDC site was adjusted using a nearby site with 30-year normal monthly and annual data. Sites and data were obtained from the NCDC tape TD9641: Monthly Normals of Temperature, Precipitation, and Heating and Cooling Degree Days 1951-80.

Daily precipitation during a month was adjusted to match the 30-year normal for the month. Each daily value was multiplied by the ratio of the 30-year normal for the month and the monthly total for the typical year selected. This procedure also ensured that the typical year annual total matched the annual 30-year normal.

(Information on data completeness and quality for the ADS sites is available from A. Olsen, PNL.)

5.6.3.1.2 Dry deposition –

The determination of representative typical year estimates of dry deposition at the DDRP study sites was a very difficult task. The accurate measurement of dry deposition to watersheds is a developing art and for the purposes of the DDRP, no network of sites existed that was able to provide the regionally consistent information that our analyses required. Instead, we had to rely on estimates from a variety of modelling and inferential techniques. (Note that we used the term "estimates" (as opposed to "data") to describe derived values for dry deposition for all variables. To describe the grouping of these estimates, however, we use the term "database".) Information on estimates of dry sulfur deposition from the Regional Acid Deposition Model (RADM) (Chang et al., 1987) was obtained from R. Dennis (AREAL-RTP) and S. Seilkop (Analytical Sciences, Inc.) as was information on possible annual-scale relationships among fine particle dry deposition of base cations and chloride and wet deposition of those same ions. We combined this information with other information on (1) dry deposition to surfaces, (2) canopy scavenging, (3) throughfall, and (4) pertinent information on interactions among atmospheric deposition and watershed ion budgets to construct complete (major ions) suites of dry deposition to represent a typical year for each of the DDRP study sites.

5.6.3.1.2.1 Sulfur –

Interim or first-stage dry sulfur deposition estimates for DDRP study sites were provided based upon output available from RADM (R. Dennis and S. Seilkop, personal communication and unpublished internal report, 1987a; Clark et al., 1989). Previous site estimates made by the Regional Lagrangian Model of Air Pollution (RELMAP) (Eder et al., 1986) appeared to suffer from an over-smoothing problem and were judged inadequate for our work. (R. Dennis and S. seilkop, personal communication). Because this over-smoothing problem could not be corrected in time to provide estimates for the DDRP, RADM was used.

The first-stage estimates were based on the simulation of six three-day episodes and the results averaged to establish regional dry deposition. "Ground-truth" data on dry sulfur deposition from a sparse number of measurement sites (Hicks et al., 1986; Hosker and Womack, 1986) were used to geographically adjust (spatially calibrate) the RADM output. Output from RADM is to points on an 80 x 80 km grid. Estimates at those points were then kriged to individual DDRP study sites.

We performed an evaluation of the first-stage dry sulfur deposition estimates by combining them with the wet deposition data and constructing sulfur input/output budgets for sites in the NE. Use of the first-stage dry sulfur estimates resulted in computed inputs that were slightly lower than outputs (for a Subregion 1A). In the NE, and especially in this Subregion there is good reason to believe that watersheds are in a steady-state situation with regard to sulfur (i.e., inputs = outputs) (see Section 7 and Galloway et al., 1983a; Rochelle et al., 1987; Rochelle and Church, 1987). An increase in the first-stage dry sulfur deposition estimates of 20 percent slightly increased the estimated total sulfur inputs and brought the input/output budgets for Subregion 1A more closely to the steady-state point. [Note, however, that this slight adjustment had no effect on conclusions on regional patterns of sulfur retention in eastern watersheds (see Section 7).] The uncertainty associated with the RADM outputs could conceivably have bias of 20 percent. Indeed, ground-truth data from the only two northeastern sites available (West Point, NY, and Whiteface Mountain, NY) indicated an underestimate by RADM at these sites by 40 and 20 percent, respectively, even after geographic spatial calibration (R. Dennis and S. Seilkop, personal communication and unpublished internal report, 1987). Consideration of these factors by the DDRP staff in close coordination with the Level III modellers (J. Cosby, J. Schnoor, S. Gherini; see Section 10) led to the joint decision that the first-stage dry sulfur deposition estimates from RADM should be adjusted upward by 20 percent annually in the NE. This adjustment was made to the annual estimates for the DDRP NE study sites, and all subsequent manipulations (as described in this section) to the estimates of dry sulfur deposition were performed on this adjusted or second-stage dataset. No comparable watershed data were available in the SBRP to check the deposition estimates because the SBRP is a region where atmospherically deposited sulfur generally is strongly retained (Galloway et al., 1983a; Rochelle et al., 1987; Rochelle and Church, 1987). Thus, no such comparable adjustments were made to the annual dry sulfur deposition estimates provided for the SBRP.

The next step was to apportion the dry sulfur deposition on a monthly basis. Because scavenging of dry sulfur deposition should be a function of canopy development, we used the watershed vegetation information from the DDRP mapping (Section 5.4.1.3) to adjust for monthly partitioning. This was a two-step process. First, we assigned a leaf area index (LAI) (Table 5-31) to each vegetation type (coniferous, deciduous, and open), based, in part, on values used by Gherini and Goldstein (1984) (see Table 5-31). We used two variations on this approach: (1) we assigned an LAI of 0.25 to deciduous vegetation during the months of November through March and (2) we partitioned our "mixed" vegetation class as half deciduous and half coniferous. Second we applied an iterative predictor-corrector technique to apportion the monthly deposition so that its sum closely approximated the second-stage annual dry sulfur deposition totals. Application of these procedures provided a third-stage (final) dry sulfur deposition dataset for which the annual sum of the monthly dry deposition was within two percent of the second stage annual value on the average for any watershed.

5.6.3.1.2.2 Base cations and chloride –

Computation of individual watershed values for dry deposition of base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and chloride (Cl^{-}) involved quite a number of considerations and computational steps. At the heart of the computation was the development of a technique (Eder and Dennis, in revision) that used regression analysis between measured annual wet deposition and the annual geometric means of ambient air concentration (used with deposition velocities to compute dry deposition). Data used in the development of the technique and relationships were obtained from the Ontario Ministry of the Environments Acid Precipitation in Ontario Study (APIOS) (For a description of the network and its data collection and analysis techniques see Chan et al., 1982 and Tang et al., 1986.) Because of the manner in which the ambient concentrations were measured, these relationships probably apply only to fine particle (< 2 μm) dry deposition. For the purpose of computing annual fine particle dry deposition, it

Table 5-31. Monthly Values of Leaf Area Index (LAI) Used to Apportion Annual Dry Deposition to Monthly Values

Month	LAI d	LAI c	LAI o
Jan	0.25	12	1
Feb	0.25	12	1
Mar	0.25	12	1
Apr	0.5	12	1
May	1.0	13	1.5
Jun	2.5	14	1.5
Jul	4.0	15	1.5
Aug	4.5	15	1.5
Sep	4.5	15	1.5
Oct	1.0	15	1
Nov	0.25	14	1
Dec	0.25	13	1

LAI d = leaf area index for deciduous vegetation
LAI c = leaf area index for coniferous vegetation
LAI o = leaf area index for open areas

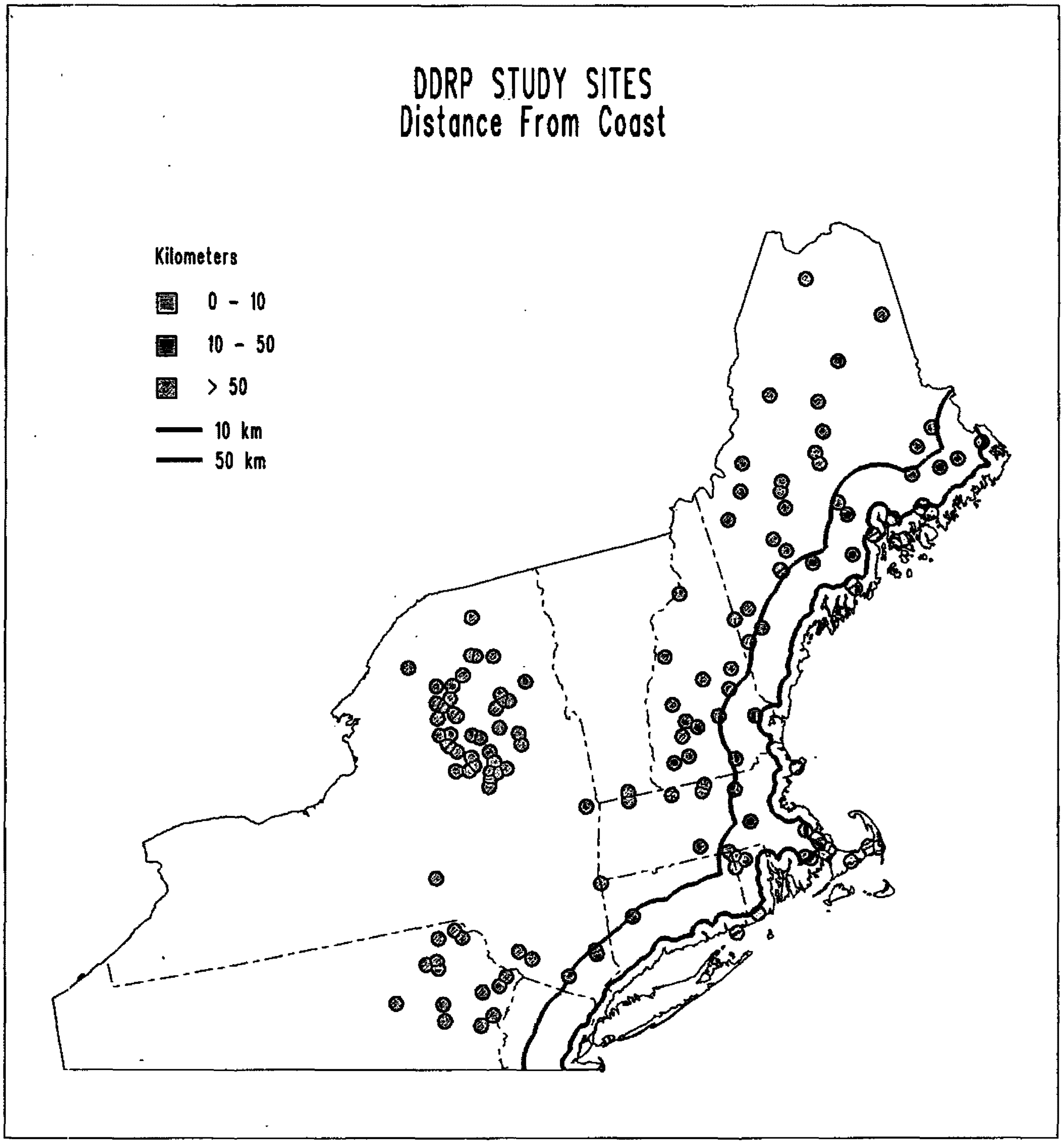
was assumed that deposition velocities were roughly equivalent among the base cations at 0.8 cm sec^{-1} for heavily forested vegetative situations (Eder and Dennis, in revision) (this is the condition for the DDRP watersheds, inasmuch as most have vegetative coverage of at least 80 percent).

This approach was developed from data at inland stations and probably is inappropriate for use in near-coastal situations. Watersheds close to the coast can be strongly influenced by sea salt inputs of wet deposition (considered in the selection of ADS sites for computation of typical year wet deposition), but development of fine particle dry deposition using the approach outlined above would probably lead to overestimates. The relative proximity of DDRP study sites to the coast is shown in Plate 5-20. Sites located within 10 km of the coast are probably strongly influenced by sea salts but sites greater than 50 km from the coast are probably negligibly influenced (Sullivan et al., 1988a). Because of this likely effect, we substituted annual wet deposition data from adjacent but more inland ADS sites for this computation for 20 near-coastal DDRP sites.

The annual fine particle dry deposition had to be partitioned into monthly components. The annual values first were partitioned based upon 13 28-day months (Eder and Dennis, in revision), and then they were repartitioned by DDRP staff into the 12 months comprising the TY dataset.

Coarse particle (> 2 m) dry deposition also can be an important contributor to vegetative canopies and, thus, to watersheds (Lindberg et al., 1986; Stensland, personal communication). A major debate currently exists as to whether "inputs" of dry base cations and chloride originate within or external to watersheds (of the size studied by DDRP) (Hicks, personal communication). We feel that a majority of such inputs arise externally and thus we applied a ratio of coarse-to-fine particle dry deposition to account for this influence. We estimated these rations based on a number sources of information (1) information presented by Lindberg et al. (1986), (R. Munson, personal communication), and (3) consideration in input/output budget calculations. To a large degree, these values were derived iteratively in concert with the other computations we for estimating dry deposition of these ions. The ratios used

Plate 5-20. DDRP study sites relative to distance from Atlantic Coast (<10 km, 10-50 km, >50 km).


DDRP STUDY SITES
Distance From Coast
Kilometers
0 - 10
10 - 50
> 50
10 km
50 km

are shown in Table 5-32. Computed coarse-particle dry deposition values were added to the values of fine-particle dry deposition.

We next applied an adjustment for scavenging using the monthly LAIs indicated in Table 5-31. We again assumed that the "mixed" vegetation class was half coniferous and half deciduous. Application of these LAIs, however, resulted in values of total dry deposition that appeared much too large in relation to output fluxes of the ions from the study watersheds, i.e., inputs of base cations appeared to nearly equal outputs and inputs of chloride greatly exceeded outputs. Assuming that outputs of base cations from watersheds usually significantly exceed outputs and that inputs of chloride should roughly equal outputs (in undisturbed locations, see Section 10.5.7), then the values obtained using the above procedure were unrealistically high.

Scavenging of dry deposition by vegetative canopies (especially coniferous canopies) is subject to a pronounced "edge effect" whereby lower windspeeds and ambient concentrations within interior canopies result in markedly lower effective dry deposition to those interior regions (Dasch, 1987; Grennfelt, 1987). We reasoned that this process could be represented by a function of the form of the well-known Michaelis-Menten equation and used to adjust the "effective" coniferous canopy scavenging. In this way, scavenging of base cations and chloride within our watersheds would not be computed using total coniferous LAIs, but rather the coniferous LAIs would be adjusted (in effect) so that as the areal coniferous coverage of a watershed increased, its effect on scavenging reached an effective plateau rather than increasing linearly. We used this approach to adjust total dry deposition until the chloride budgets approximately balanced in undisturbed NE sites. The final equation used in the adjustment was

$$\%\ CON_e = (30 * \%\ CON)/(15 + \%\ CON) \qquad \text{(Equation 5-1)}$$

where $\%\ CON$ = mapped percent coniferous coverage
$\%\ CON_e$ = effective percent coniferous coverage

Table 5-32. Ratios of Coarse-to-Fine Particle Dry Deposition

Ion	Ratio
Calcium	1.5
Magnesium	1.0
Sodium	1.0
Potassium	1.0
Chloride	0.2

These computations of dry base cation deposition leave a great deal to be desired. The final values, however, relate well to (1) estimates of dry deposition-to-wet deposition ratios observed by Lindberg et al. (1986) for a southeastern forested catchment, and (2) previously modelled estimates at Woods and Panther Lakes in the Adirondack Mountains (R. Munson, personal communication).

5.6.3.1.2.3 Nitrate and ammonium –

We had no objective or mechanistic approach to use for estimating dry deposition of nitrate and ammonium. Instead, we assumed that total dry deposition of nitrate was equal to wet deposition and that total dry deposition of ammonium was equal to one-half wet deposition. These ratios approximate values measured by Lindberg et al. (1986) in an eastern forested watershed.

5.6.3.1.2.4 H^+ –

We computed dry H^+ deposition as the difference between dry anions and other dry cations. When the sum of other dry cations was greater than the sum of dry anions, we set dry H^+ to zero.

5.6.3.1.2.5 Ion ratios –

The ratios of dry deposition to wet deposition for all ions for the NE and SBRP study sites for the TY dataset are shown in Table 5-33

5.6.3.1.2.6 Comparisons with Direct Measurements

Although extensive data do not exist with which to compare the DDRP estimates, there is some limited information) obtained as a personal communication from Dr. Bruce Hicks, Atmospheric Turbulence and Diffusion Division, Environmental Research Laboratories, NOAA) that can be used for this purpose.

For example, preliminary NOAA estimates of wet and dry sulfur deposition for the NE (sites in central Pennsylvania, Whiteface Mountain and Howland, Maine) and the SBRP (Oak Ridge) are highly comparable to regional averages of the DDRP estimates. The regional average of DDRP estimates of wet

Table 5-33. Ratios of Dry Deposition to Wet Deposition for DDRP Study Sites for the Typical Year (TY) Deposition Dataset

NE	Median	Mean	Standard Deviation
SO_4^{2-}	0.44	0.48	0.12
Ca^{2+}	1.13	1.12	0.42
Mg^{2+}	1.92	1.82	0.72
Na^+	1.29	1.29	0.61
K^+	1.56	1.66	0.71
Cl^-	0.38	0.33	0.12
$*NO_3^-$	1.0	1.0	-
$*NH_4^+$	0.5	0.5	-
H^+	0.47	0.46	0.23

SBRP	Median	Mean	Standard Deviation
SO_4^{2-}	0.62	0.60	0.12
Ca^{2+}	1.72	1.54	0.39
Mg^{2+}	1.83	1.69	0.45
Na^+	1.14	1.06	0.35
K^+	1.48	1.36	0.36
Cl^-	0.40	0.36	0.10
$*NO_3^-$	1.0	1.0	-
$*NH_4^+$	0.5	0.5	-
H^+	0.50	0.52	0.16

* nitrate set to 1.0, ammonium set to 0.5

sulfur deposition in the NE is roughly 15 percent greater than the NOAA estimate for the sites examined and the DDRP estimate of dry sulfur deposition is about 25 percent less than the NOAA estimate. The estimates of total sulfur deposition in the NE are virtually identical; the total and even the individual component estimates (i.e., wet and dry) in the SBRP are within 4 percent (B. Hicks, personal communication).

A comparison of regional (i.e., NE and SBRP) dry/total deposition ratios as obtained from the DDRP estimates and "as quantified by NOAA for the same region" shows remarkable agreement for both regions for sulfate, nitrate and ammonium. No NOAA values are available for chloride so no comparison can be made for that ion. The DDRP estimates of the dry/total ratio for base cations is generally just over twice as high as the NOAA values for the NE and ranges from 4 to 10 times as great in the SBRP. This difference is due at least partly to the fact that DDRP estimates for base cation deposition include an estimate for large particle dry deposition, whereas the NOAA values do not. For example, a comparison of the average DDRP estimates of small particle base cation deposition for five watershed sites in proximity to the NOAA West Point station show good agreement (i.e., within 20 percent for calcium sodium and magnesium; within 50 percent for potassium) with the measured NOAA values at that site (B. Hicks, personal communication). To account in part for the uncertainties associated with the DDRP estimates of base cation dry deposition, we performed sensitivity analyses (see Section 9) with datasets having much reduced base cation values (Section 5.6.3.2.4). More formal uncertainty analyses were performed with the integrated watershed models (Section 10). In general, DDRP analyses and the conclusions drawn from them were not sensitive to these uncertainties (see Sections 9 and 10).

5.6.3.1.3 Sulfur deposition scenarios -

Typical year total sulfur deposition (as sulfate) is shown in Plates 5-21 through 5-27. As described in Section 5.6.1 (see Figure 5-27), the DDRP was requested to examine the effects of scenarios of both current and altered sulfur deposition in the NE and SBRP. The sulfur increases and decreases were performed as sulfate with both dry and wet deposition altered at equal and constant percentages (of the total) each year. It seemed appropriate that only wet and dry H^+ should be adjusted to coincide with

Plate 5-21. Pattern of typical year sulfate deposition for the DDRP NE study sites.

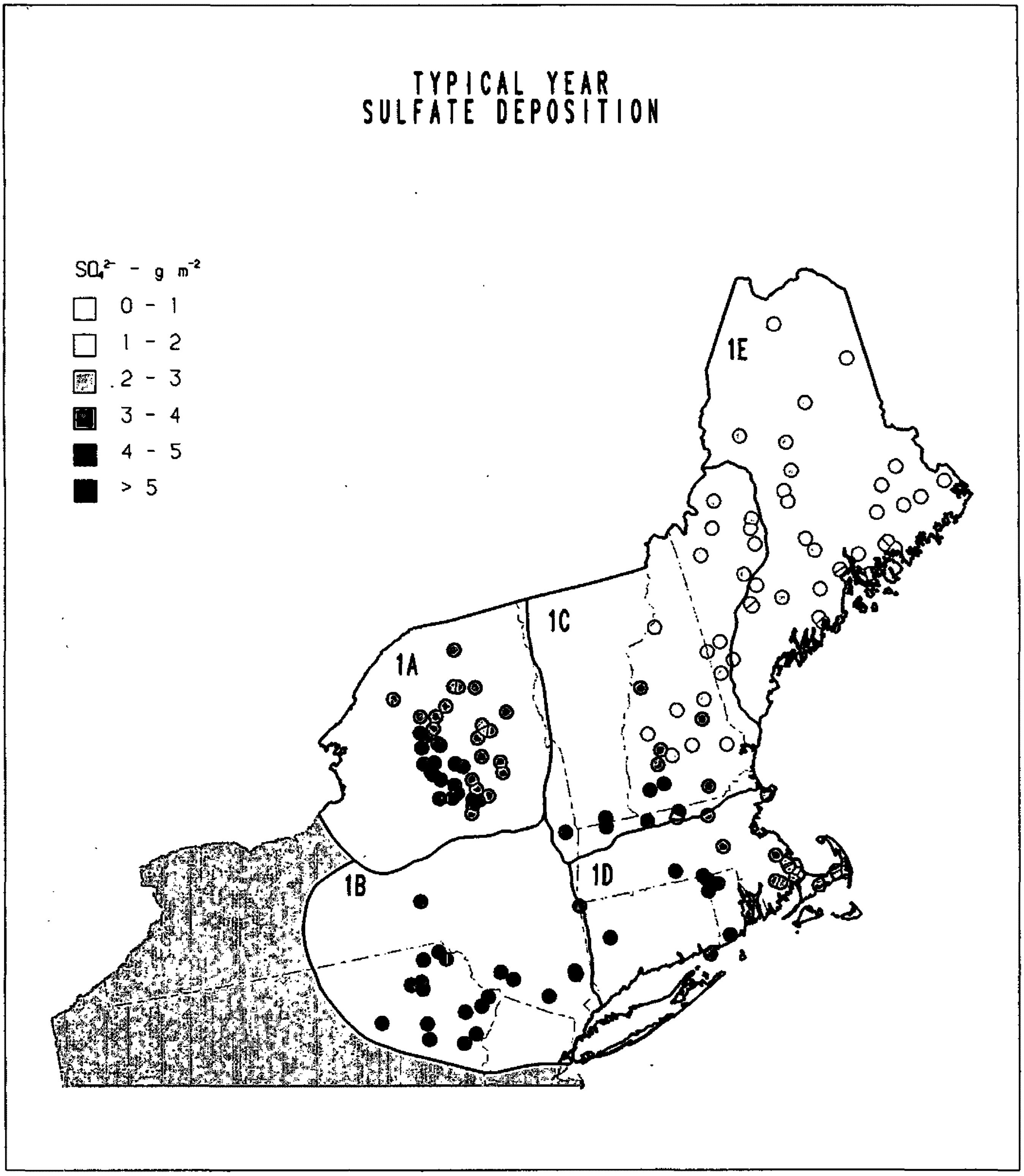

TYPICAL YEAR
SULFATE DEPOSITION
SO_4^{2-} - g m^{-2}
0 - 1
1 - 2
2 - 3
3 - 4
4 - 5
> 5
1A
1B
1C
1D
1E

Plate 5-22. Pattern of typical year sulfate deposition for the DDRP study sites in Subregion 1A.

SUBREGION 1A
TYPICAL YEAR
SULFATE DEPOSITION

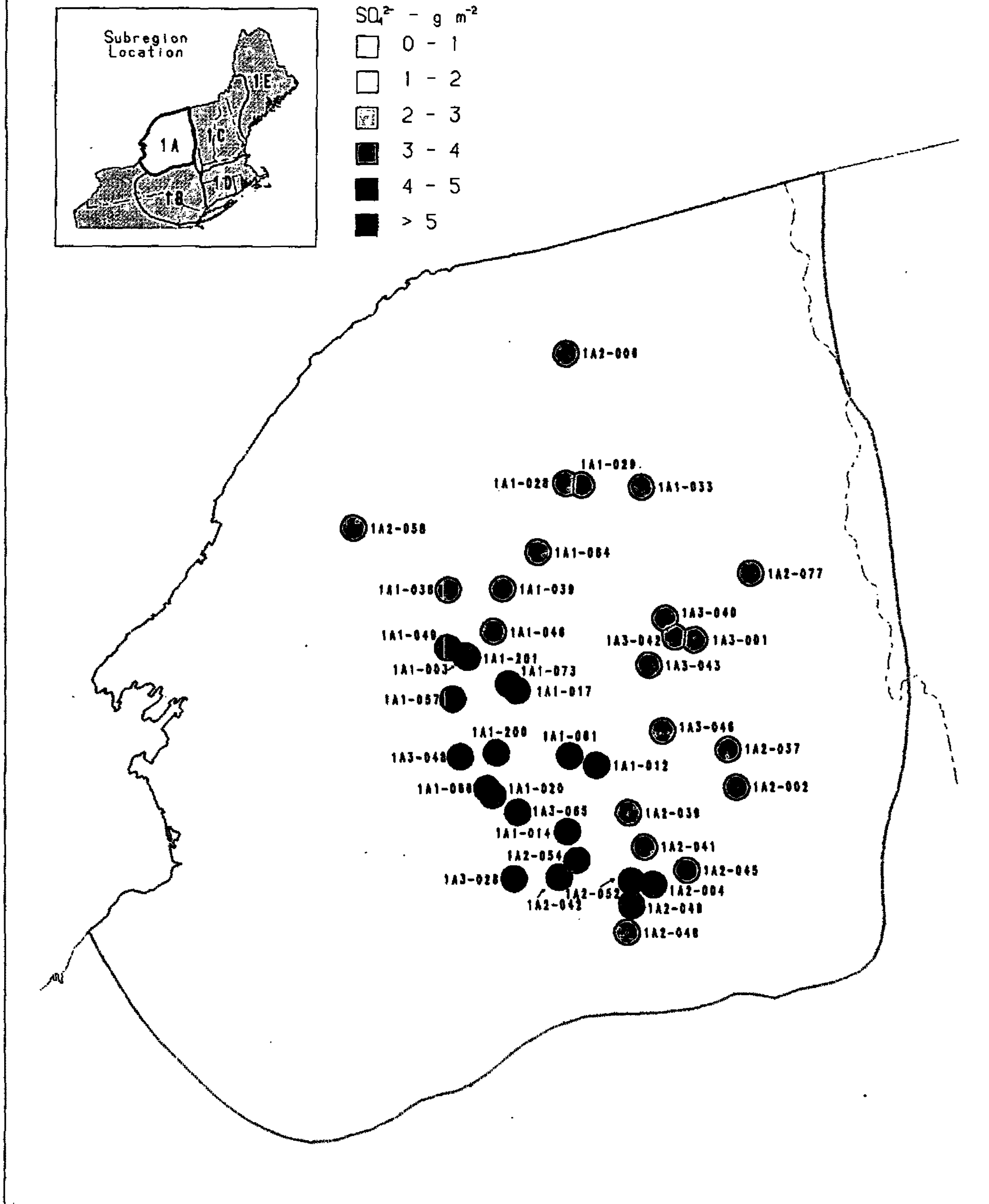


Plate 5-23. Pattern of typical year sulfate deposition for the DDRP study sites in Subregion 1B.

SUBREGION 1B
TYPICAL YEAR
SULFATE DEPOSITION

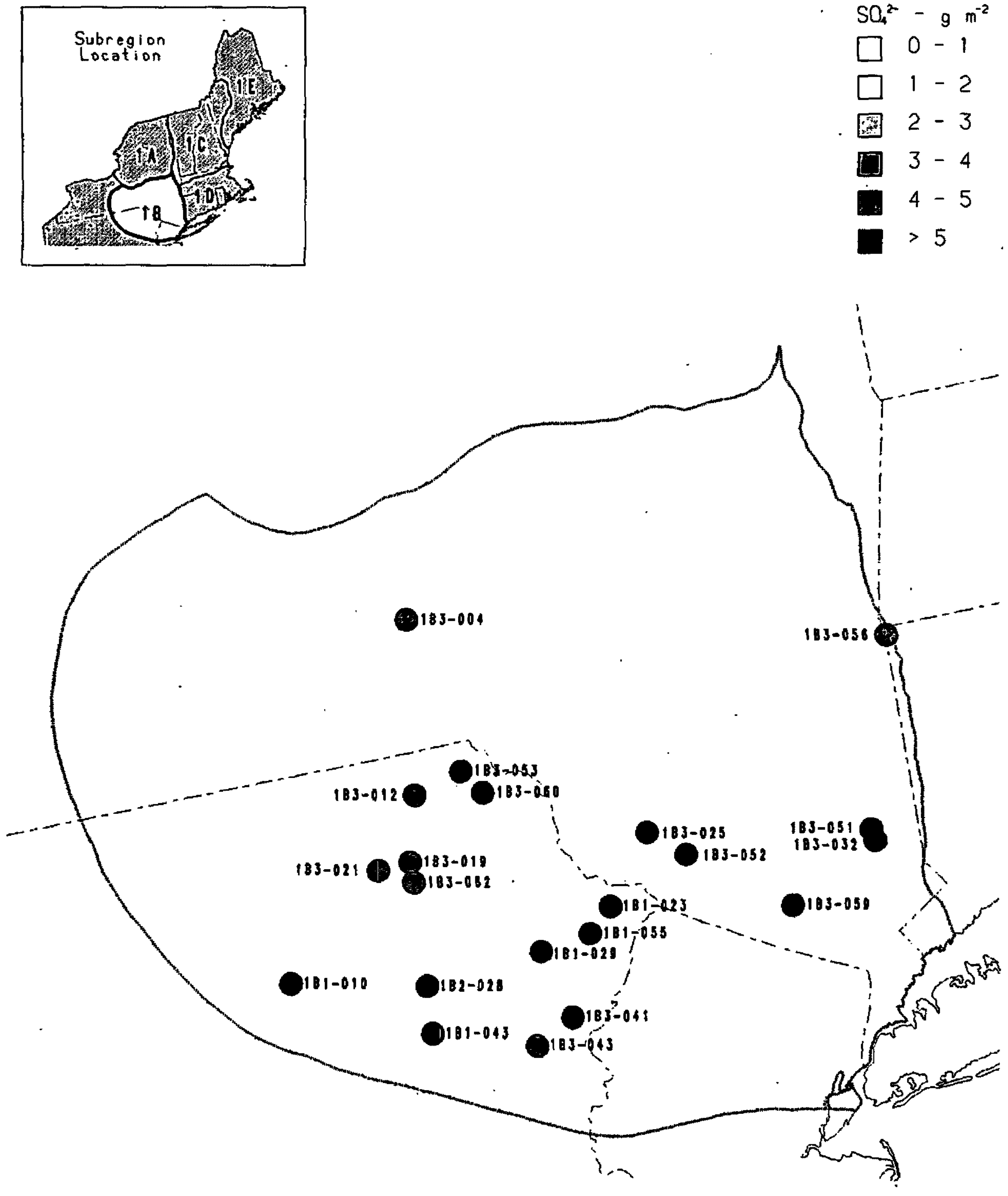


Plate 5-24. Pattern of typical year sulfate deposition for the DDRP study sites in Subregion 1C.

SUBREGION 1C
TYPICAL YEAR
SULFATE DEPOSITION

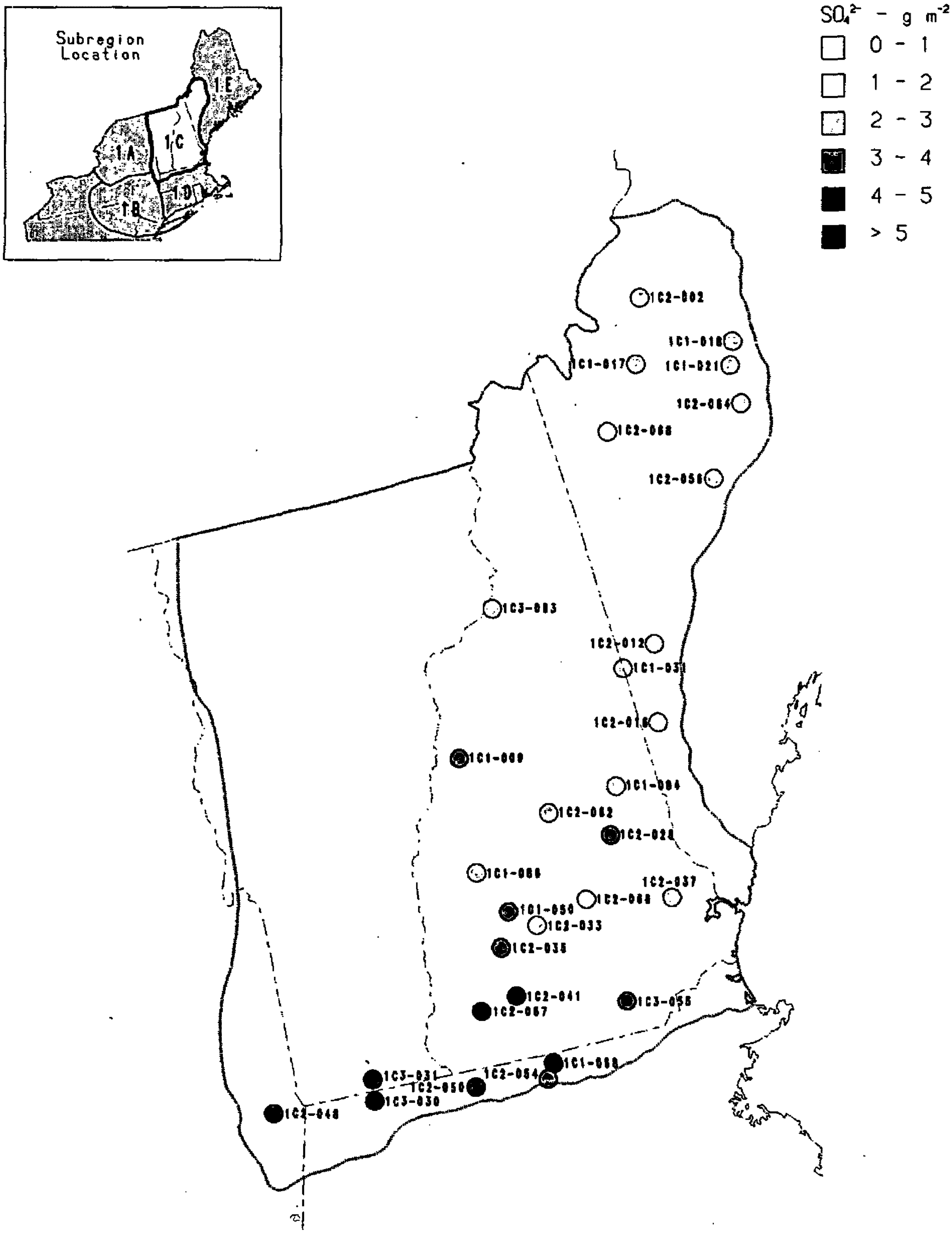


Plate 5-25. Pattern of typical year sulfate deposition for the DDRP study sites in Subregion 1D.

SUBREGION 1D
TYPICAL YEAR
SULFATE DEPOSITION

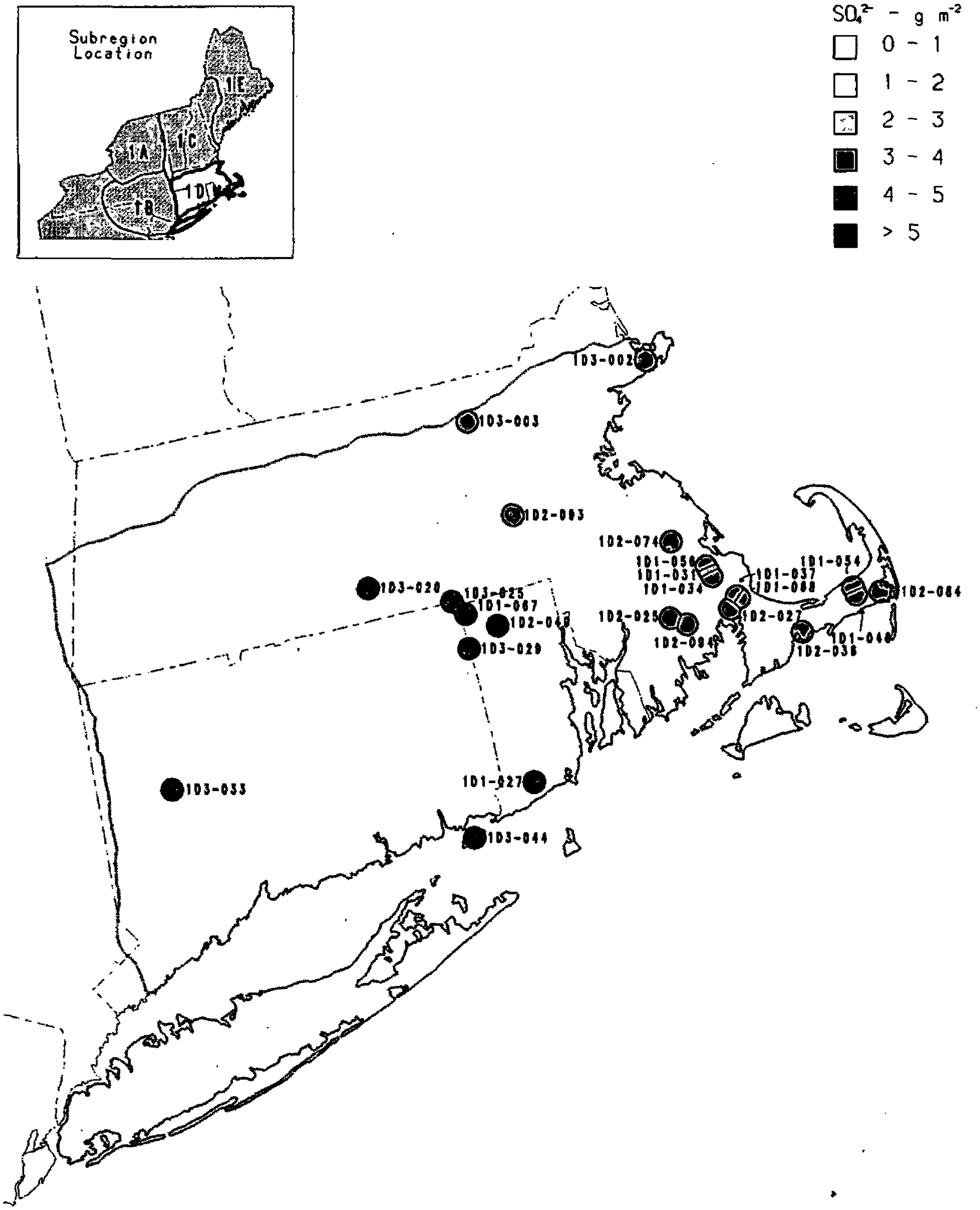


Plate 5-26. Pattern of typical year sulfate deposition for the DDRP study sites in Subregion 1E.

SUBREGION 1E
TYPICAL YEAR
SULFATE DEPOSITION

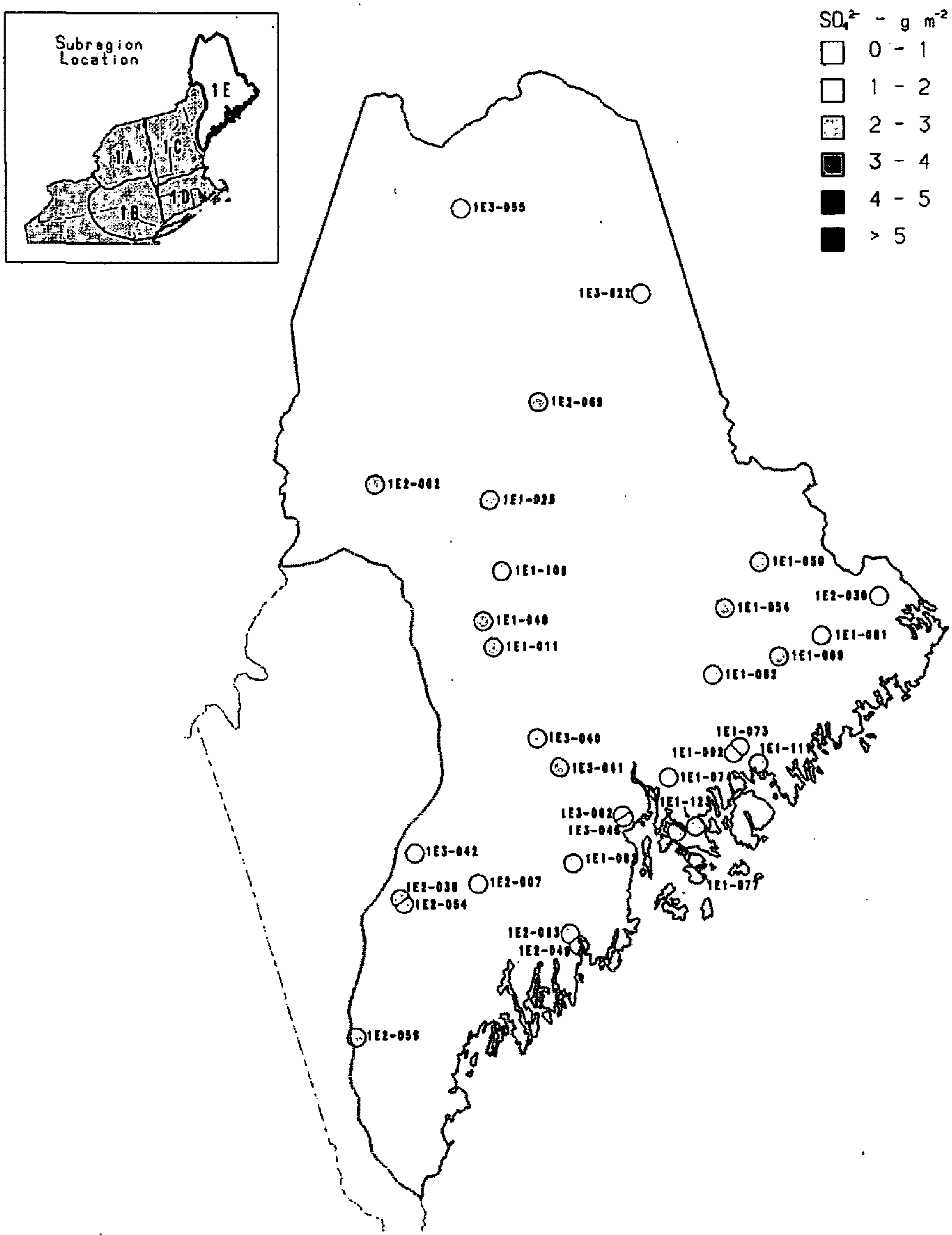
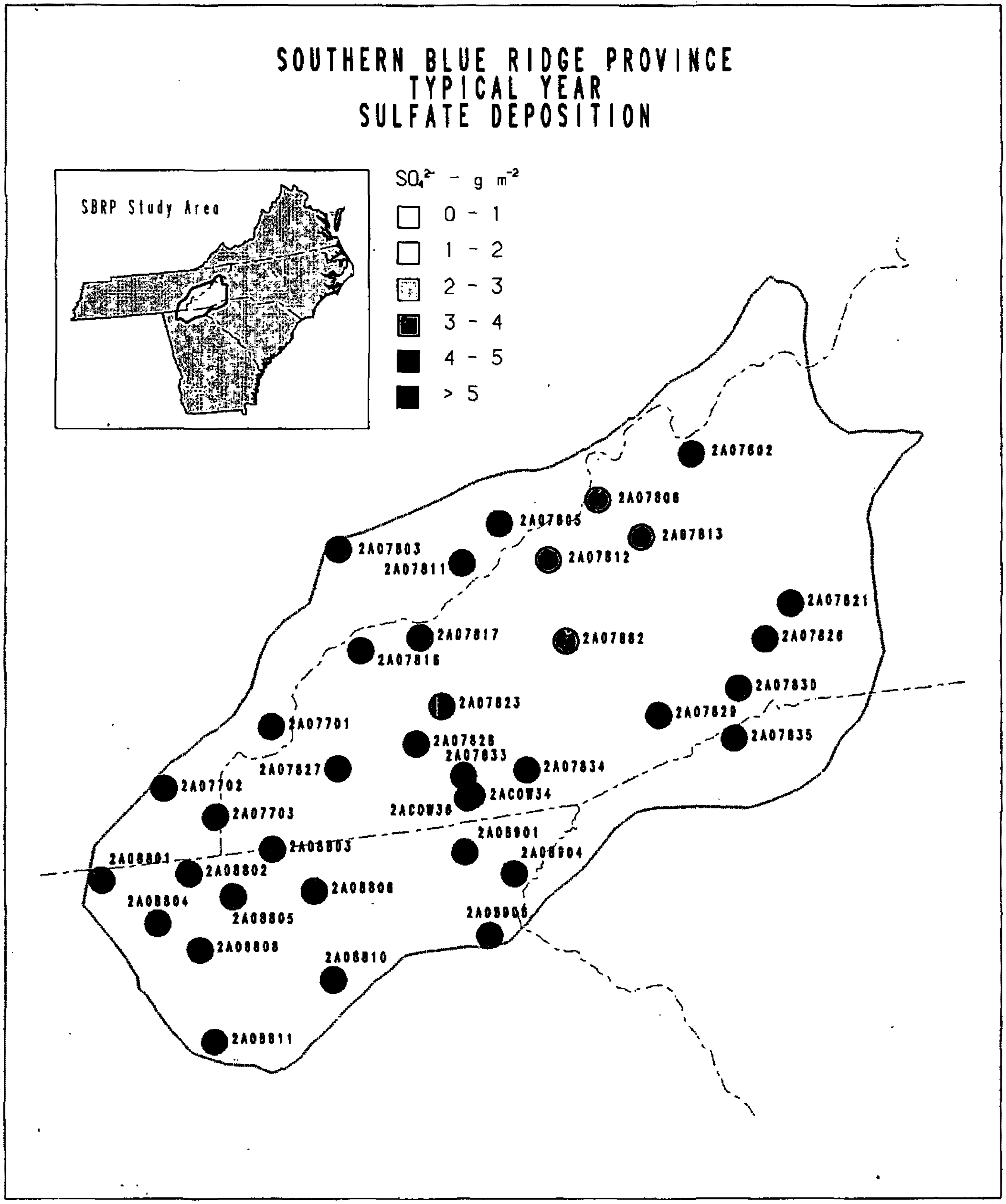


Plate 5-27. Pattern of typical year sulfate deposition for the DDRP SBRP study sites.


SOUTHERN BLUE RIDGE PROVINCE
TYPICAL YEAR
SULFATE DEPOSITION
SBRP Study Area
SO_4^{2-} - g m^{-2}
0 - 1
1 - 2
2 - 3
3 - 4
4 - 5
> 5
2A07802
2A07806
2A07805
2A07813
2A07803
2A07811
2A07812
2A07821
2A07817
2A07882
2A07826
2A07816
2A07830
2A07823
2A07829
2A07701
2A07835
2A07828
2A07833
2A07827
2A07834
2A07702
2ACOW34
2ACOW36
2A07703
2A08901
2A08803
2A08904
2A08801
2A08802
2A08806
2A08804
2A08805
2A08906
2A08808
2A08810
2A08811

these changes (A. Olsen, R. Dennis, personal communication) and that was the procedure followed. Wet H^+ was adjusted equal to the wet sulfate adjustment and dry H^+ was recomputed so that the sum of dry cation inputs was not less than the sum of dry anion inputs (on an equivalent basis) in any month.

5.6.3.2 Level I and II Analyses - Long-Term Annual Average Deposition Dataset

As discussed in Section 5.6.1.1, it was appropriate to develop a dataset of atmospheric deposition at an annual resolution to represent "current" deposition as of the early-to-mid 1980s. This dataset was called the long-term annual average (LTA) dataset and was used in the Level I and II Analyses (Section 5.6.2).

5.6.3.2.1 Wet deposition -

The objectives for developing LTA wet deposition estimates were to produce at each DDRP site annual wet deposition representative of (1) current (early to mid 1980s) atmospheric chemistry conditions and (2) average regional spatial deposition patterns. Our approach is to use 5-year average precipitation chemistry available from six regional and national wet deposition networks in conjunction with 30-year normal (1951-1980) annual precipitation available at a much greater spatial density. Annual wet deposition is computed as the product of annual precipitation amount and annual precipitation chemistry. This approach was discussed in detail in Section 5.6.3.1.1. We considered the estimation of annual wet deposition at a site to be computed by developing an annual estimate of precipitation at the site, an estimate of annual wet deposition chemistry (precipitation-weighted concentration) at the site, and taking their product.

5.6.3.2.1.1 Wet deposition chemistry --

Wet deposition chemistry data were provided by A. Olsen (PNL) from the ADS database of regional and national wet deposition monitoring networks. Annual precipitation-weighted concentration was estimated for each watershed based on 1982-1986 data from the monitoring networks. The process for developing the estimates is similar to those discussed by Wampler and Olsen (1987) and described further by Vong et al. (1989). Briefly, the procedure used the following steps. For each wet deposition monitoring site, annual summaries for each ion species were computed using the procedures described by the Unified Deposition Database Committee (UDDC) (Olsen et al., 1989). An average over 1982-1986 was completed for all sites that had three or more years that met the UDDC data quality rating. Simple kriging (applied to moving areas to minimize trend effects) provided wet deposition chemistry estimates at each DDRP site.

5.6.3.2.1.2 Annual precipitation –

Annual precipitation estimates were provided by A. Olsen. The estimates are derived from 30-year (1951-1980) normal precipitation data obtained from the National Climatic Data Center. Simple kriging applied to subregions of the United States was used to estimate annual precipitation at each DDRP site. The subregions were developed to maximize the homogeneity of precipitation spatial patterns and improve the model used within the kriging estimation procedure.

5.6.3.2.2 Dry deposition -

Dry deposition for all ions for the LTA dataset was computed from LTA wet deposition using the dry/wet ion ratios developed in the TY dataset for each ion for each DDRP watershed.

5.6.3.2.3 Sulfur deposition scenarios -

The annual sulfur deposition (as sulfate) for the LTA dataset is shown in Plates 5-28 through 5-34. The altered sulfur deposition scenarios were computed by decreasing or increasing (as appropriate) the sulfate values in the original LTA dataset in the same manner as described in Section 5.6.3.1.1 for the TY dataset and then adjusting dry H^+ as described in Section 5.6.3.1.2.4.

5.6.3.2.4 Decreased base cation LTA datasets -

Because the dry deposition of base cations in the TY and LTA datasets appeared higher than might be expected from sparse measured data (B. Hicks, personal communication), we produced additional LTA datasets having base cation dry deposition set at 50 percent and 0 percent of the original LTA values. This was done to test the sensitivity of the Level II watershed base cation modelling analyses presented

Plate 5-28. Pattern of LTA sulfate deposition for the DDRP NE study sites.

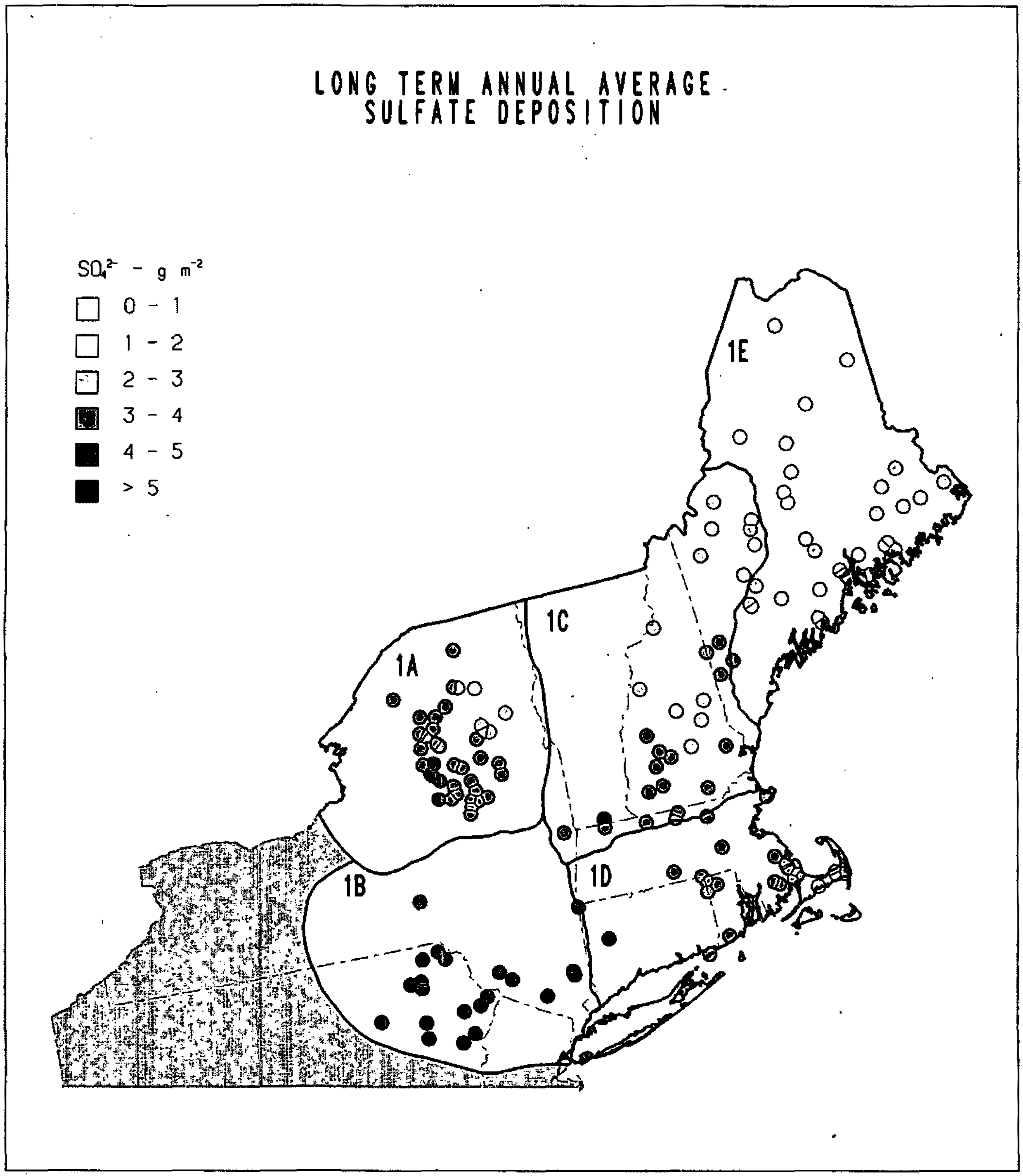

LONG TERM ANNUAL AVERAGE
SULFATE DEPOSITION
SO4 2- - g m-2
0 - 1
1 - 2
2 - 3
3 - 4
4 - 5
> 5
1A
1B
1C
1D
1E

Plate 5-29. Pattern of LTA sulfate deposition for the DDRP study sites in Subregion 1A.

SUBREGION 1A
LONG TERM ANNUAL AVERAGE
SULFATE DEPOSITION

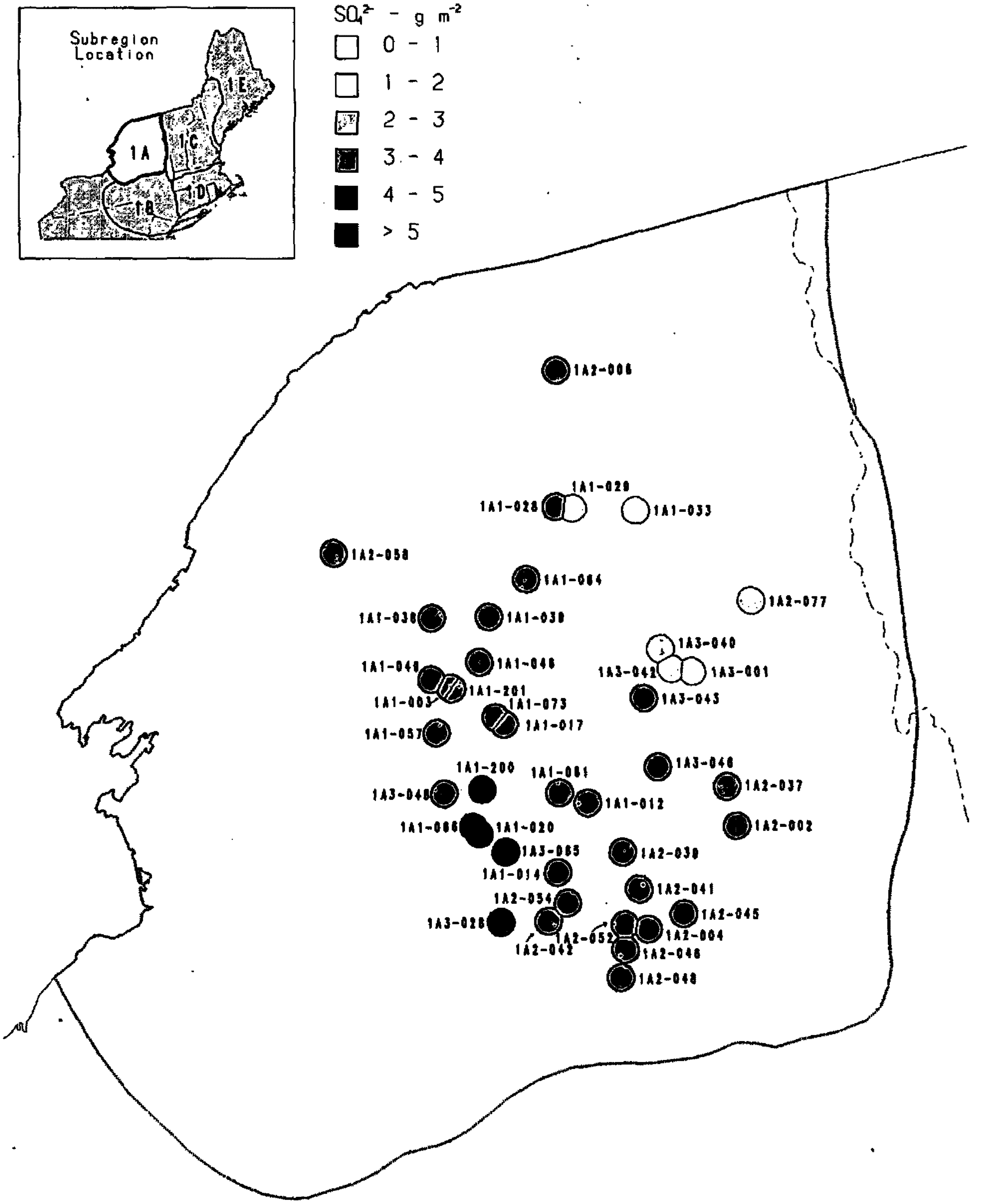


Plate 5-30. Pattern of LTA sulfate deposition for the DDRP study sites in Subregion 1B.

SUBREGION 1B
LONG TERM ANNUAL AVERAGE
SULFATE DEPOSITION

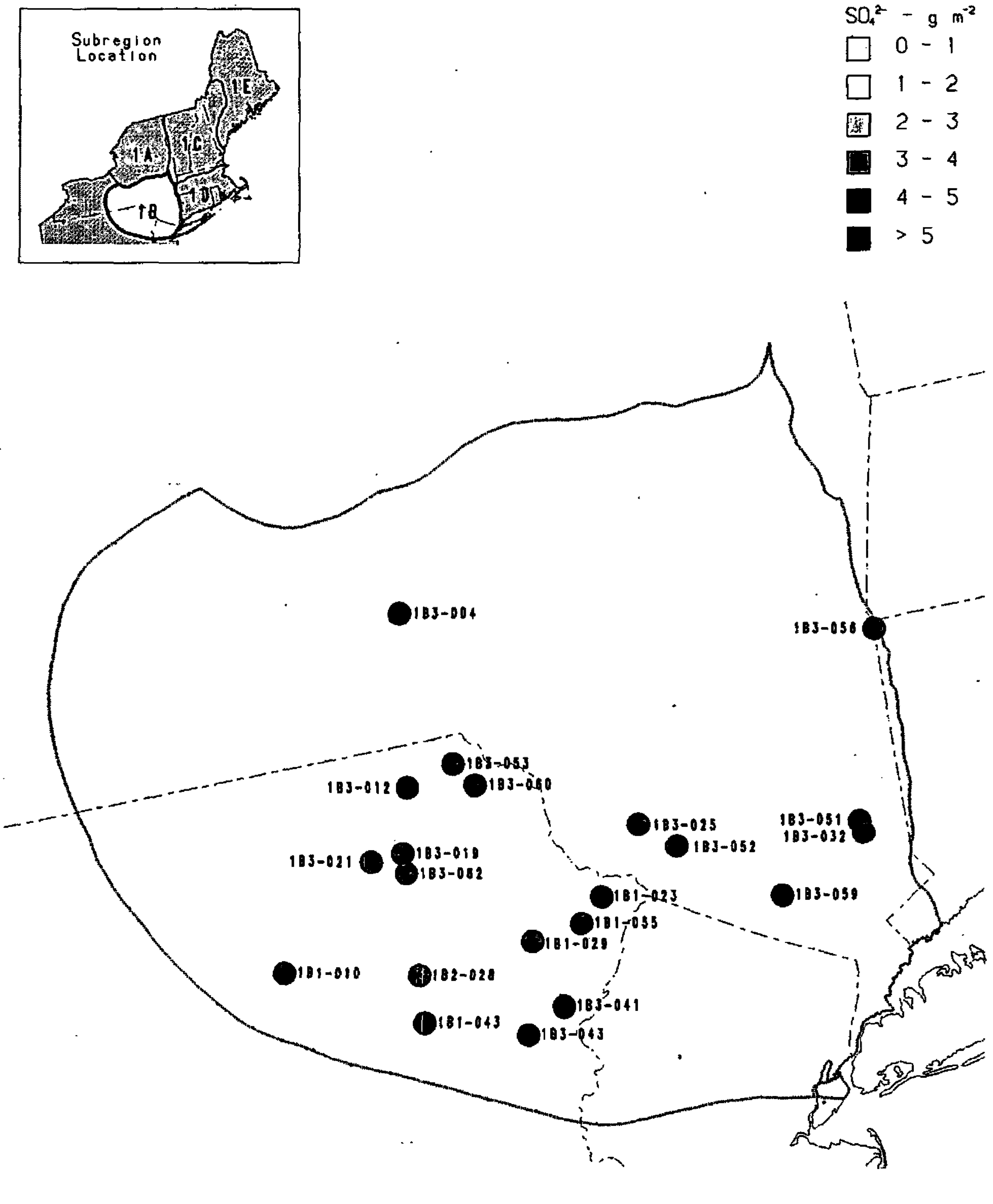


Plate 5-31. Pattern of LTA sulfate deposition for the DDRP study sites in Subregion 1C.

SUBREGION 1C
LONG TERM ANNUAL AVERAGE
SULFATE DEPOSITION

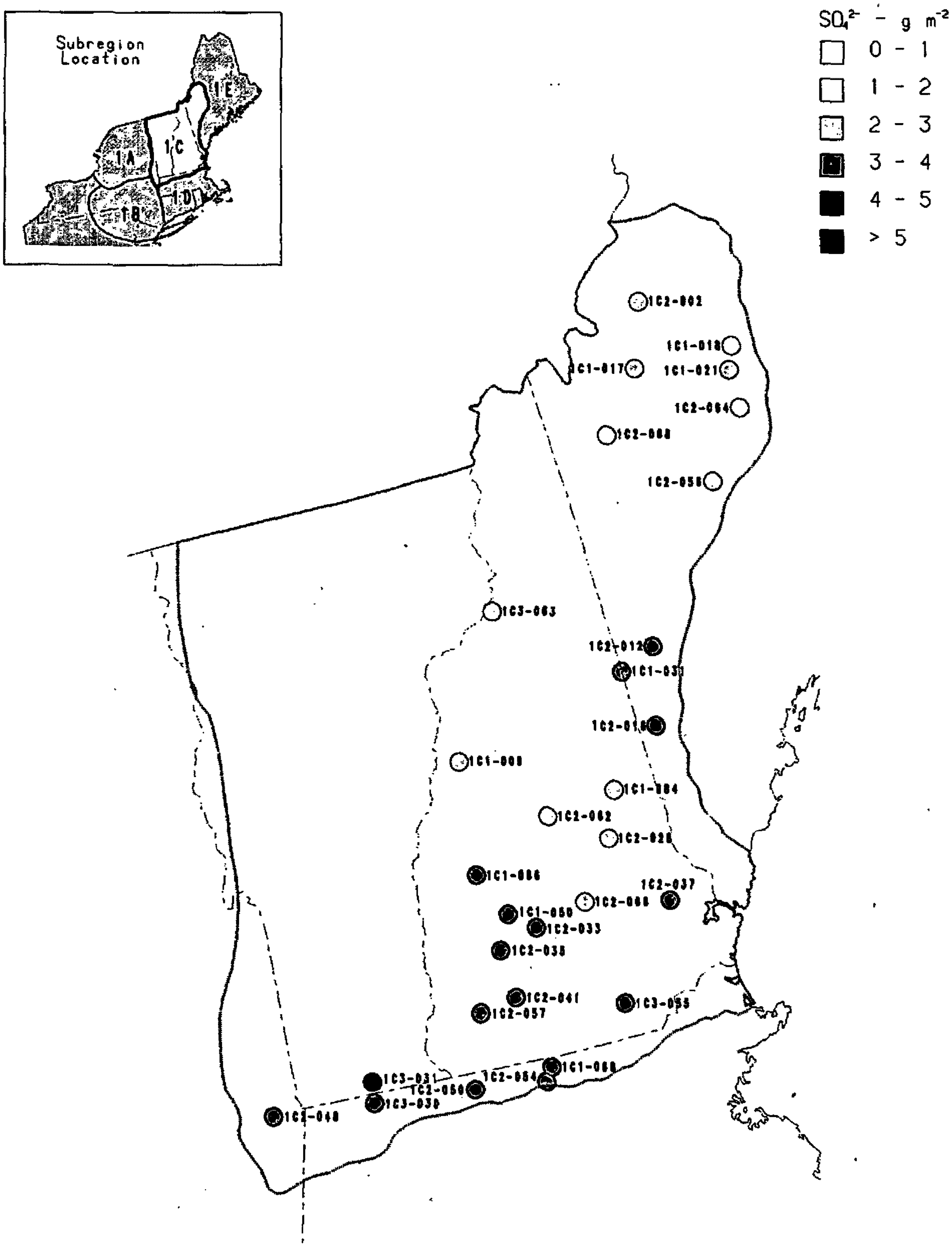


Plate 5-32. Pattern of LTA sulfate deposition for the DDRP study sites in Subregion 1D.

SUBREGION 1D
LONG TERM ANNUAL AVERAGE
SULFATE DEPOSITION

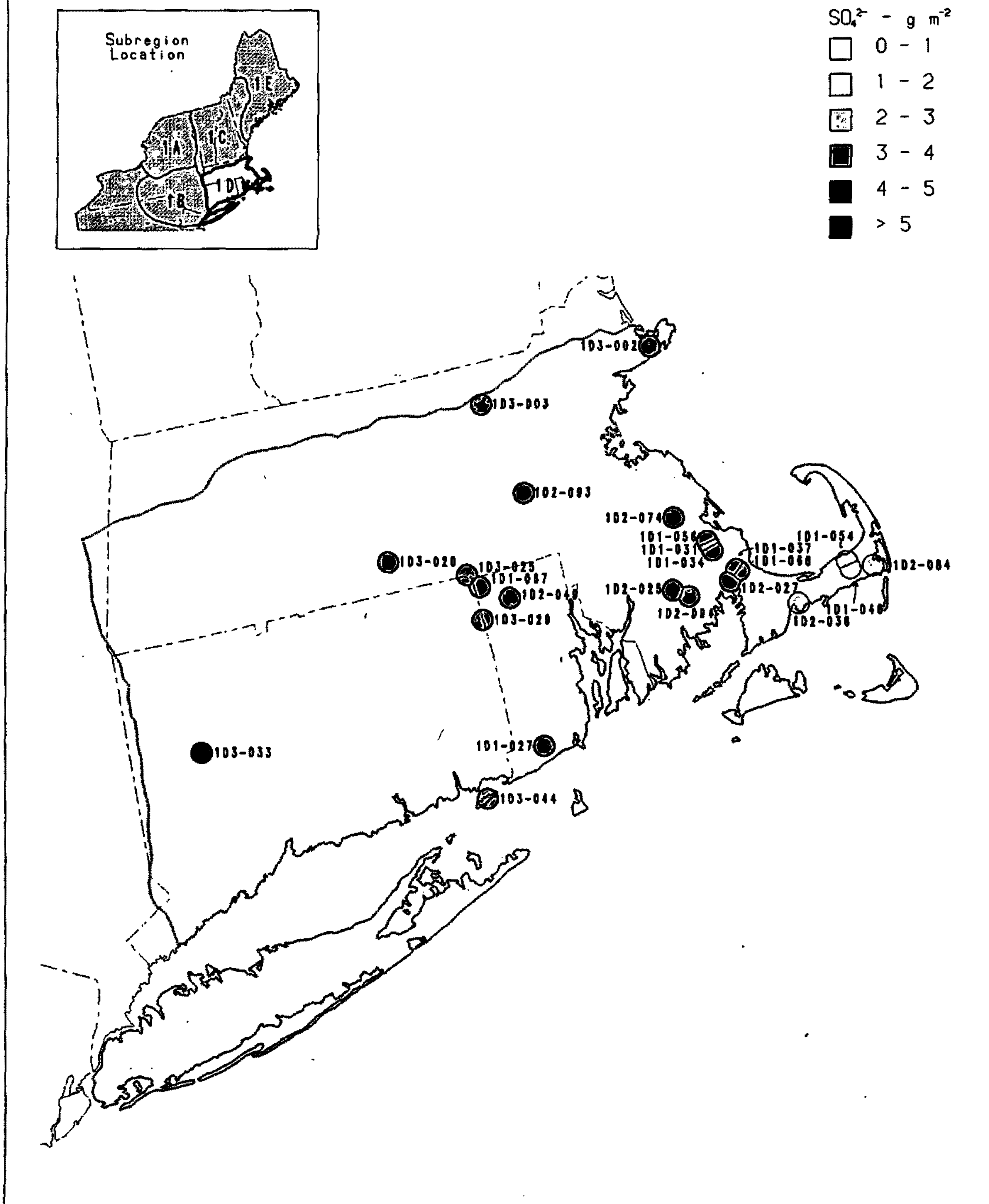


Plate 5-33. Pattern of LTA sulfate deposition for the DDRP study sites in Subregion 1E.

SUBREGION 1E
LONG TERM ANNUAL AVERAGE
SULFATE DEPOSITION

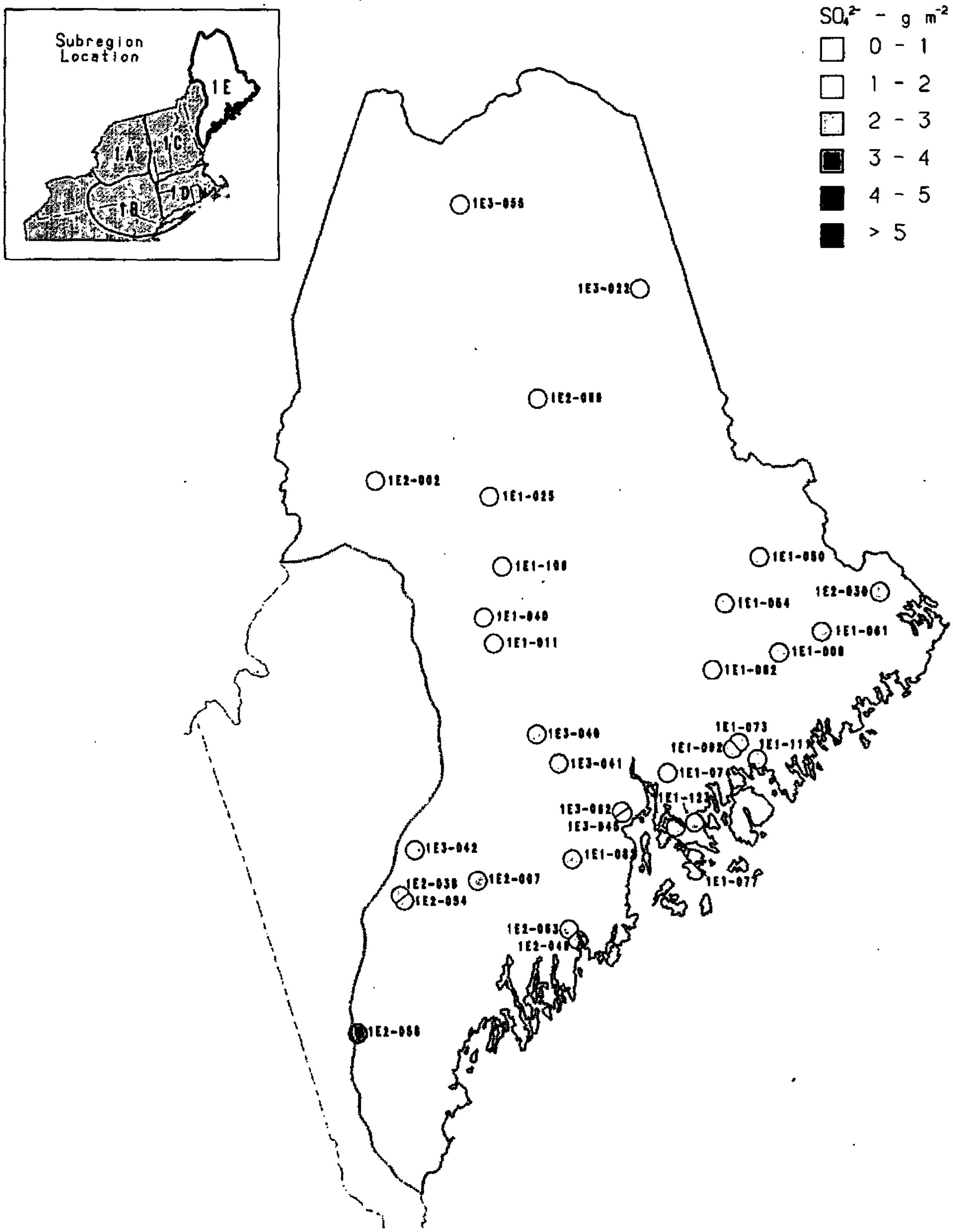
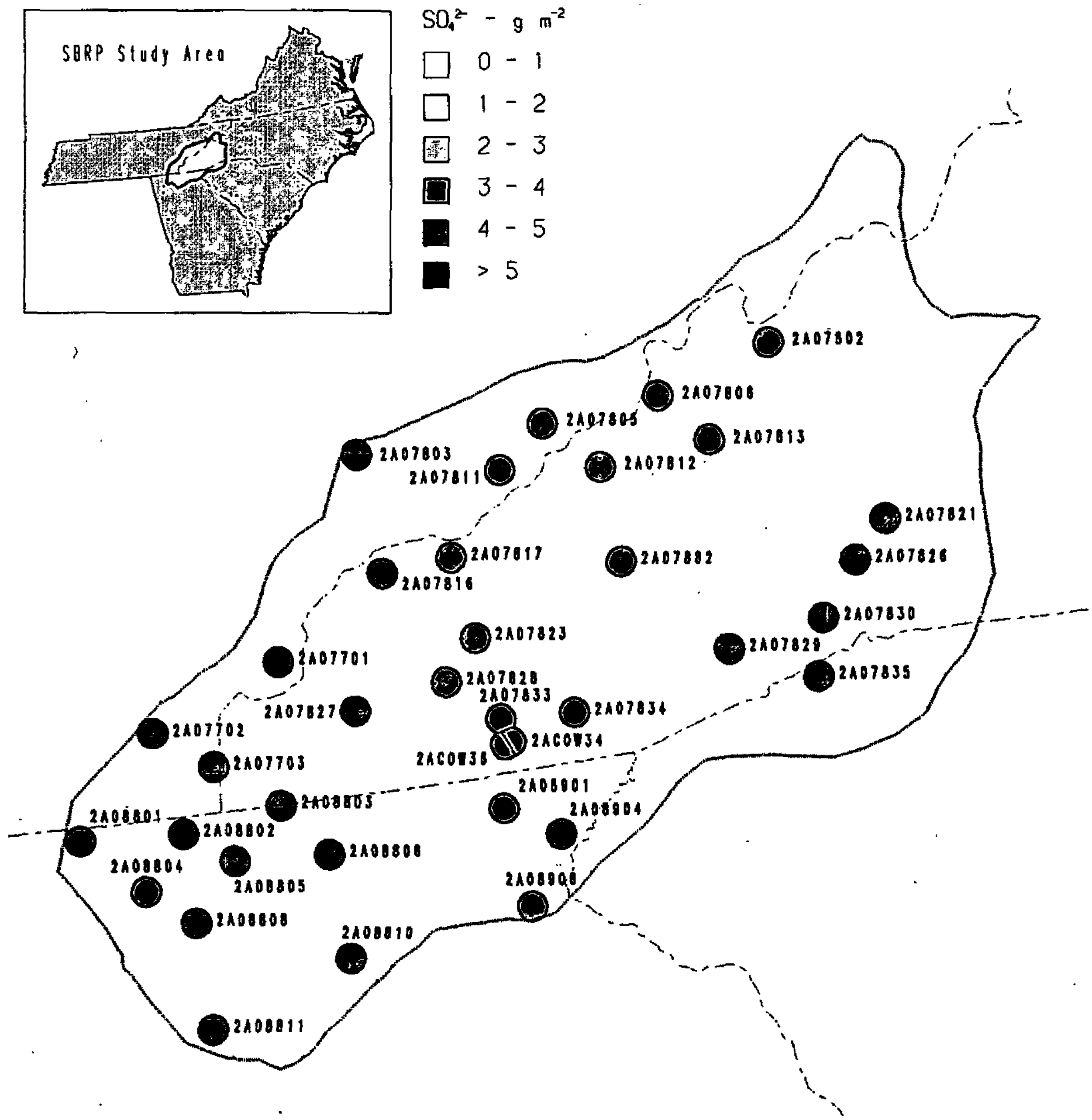


Plate 5-34. Pattern of LTA sulfate deposition for the DDRP SBRP study sites.

SOUTHERN BLUE RIDGE PROVINCE
LONG TERM ANNUAL AVERAGE
SULFATE DEPOSITION



in Section 9.3. In these datasets dry H^+ again makes up the difference between the sum of dry anions and the sum of other dry cations. These datasets are referred to here as LTA-reduced base cations (LTA-rbc) and LTA-zero base cations (LTA-zbc), respectively. Analysis using these datasets might be of special interest relative to recent hypotheses presented by Driscoll et al. (1989b) concerning the potential role of base cation deposition in controlling the chemistry of dilute surface waters in the NE (for further discussion see Section 3).

5.6.4 Deposition Datasets Used in DDRP Analyses

Table 5-34 presents a summary of the analyses to which the deposition datasets described above were applied in the DDRP. For a discussion of quantitative uncertainties associated with the use of these data see Section 10.10.

5.7 HYDROLOGIC DATA

5.7.1 Runoff

An estimate of average annual runoff for the DDRP study sites is necessary for all three levels of analysis. Given the site selection procedures used in the DDRP, it is not surprising that the DDRP study sites are ungaged and measured values of annual runoff are not available. Three options existed for obtaining estimates of runoff. The first, gaging the systems, would not have been practical to obtain the estimates of runoff needed, given the relatively short time frame of the DDRP and the large number of sites. The second option was to use an interpolation method, such as kriging, to estimate runoff at each site. Large variability in topography across the regions, and in other features that influence runoff, limited the applicability of this method. The third option was selected for estimating runoff to each DDRP site: (1) interpolations were made based runoff contour maps developed with existing runoff data and (2) expert judgment of hydrologists experienced in runoff mapping.

5.7.1.1 Data Sources

Working in cooperation with the USGS, a runoff contour map of average annual runoff for 1951-80 (Figure 5-28, Krug et al., in press) was developed to use for interpolating runoff at the DDRP sites.

Table. 5-34. Deposition Datasets Used in DDRP Analyses

Dataset	Sulfur Retention (Section 7)	Level I Statistics (Section 8)	Level II Base Cation (Section 9.2)	Sulfate Adsorption (Section 9.3)	Level III Modelling (Section 10)
TY	X	-	X	X	X
LTA	X	X	X	X	-
LTA-rbc	-	-	X	-	-
LTA-zbc	-	-	X	-	-

TY = Typical Year
LTA = Long-Term Annual Average
LTA-rbc = Long-Term Annual Average - Reduced Dry Base Cations (dry base cations = 50% of LTA)
LTA-zbc = Long-Term Annual Average - Zero Dry Base Cations (dry base cations set to 0)

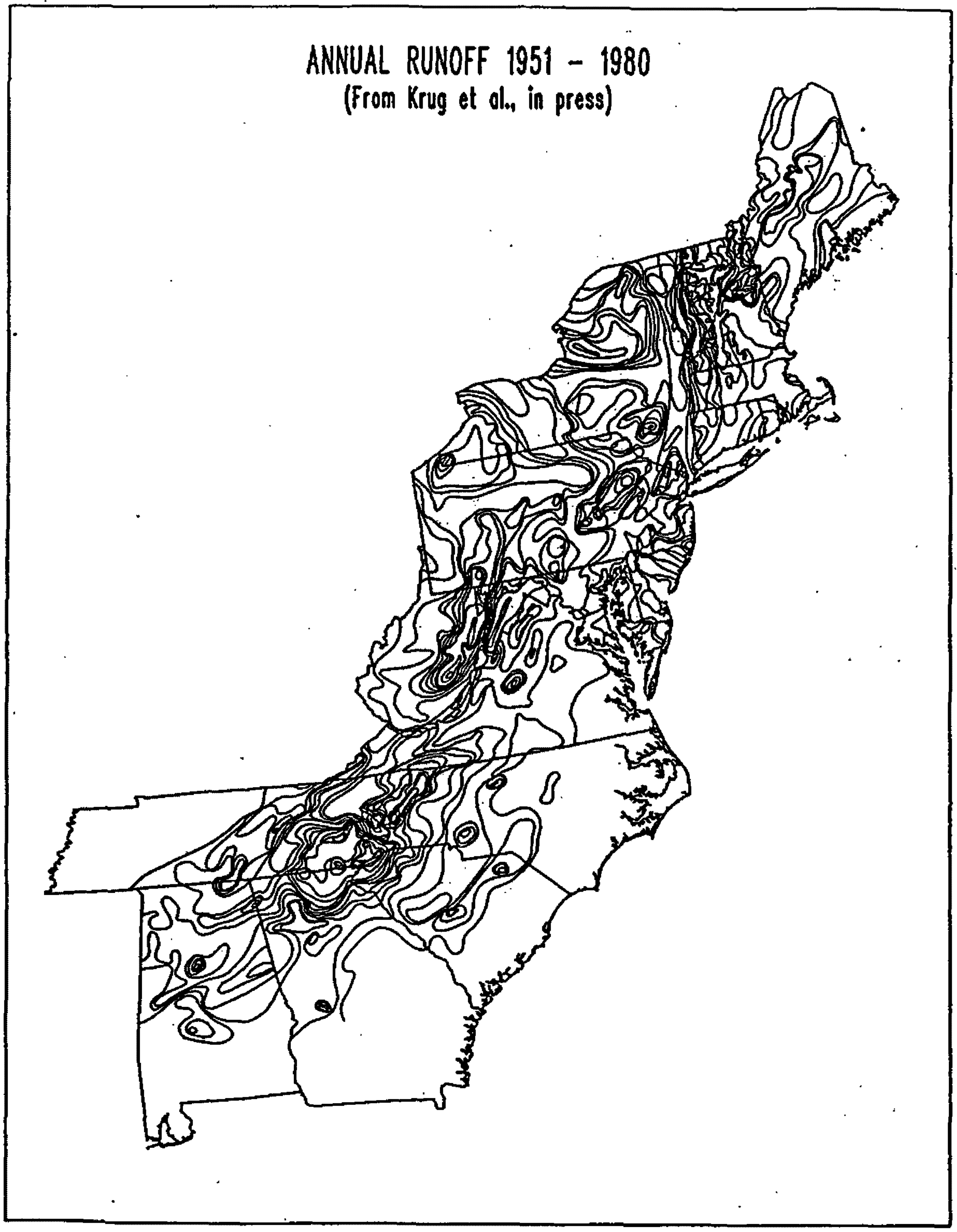


Figure 5-28. Example of average annual runoff map for 1951-80 (Krug et al., in press).

The map was developed to encompass the NE, Mid-Appalachian, and SBRP Regions of the eastern United States (Figure 5-28). Average annual runoff data for the 30-year period was taken primarily from watersheds of less than 2,590 km^2 having no diversions or regulations. If a gaging station did not have a complete set of records for the 30-year period, then Krug et al. (in press) calculated a 30-year estimate using standard correlation methods described by Matalas and Jacobs (1964). Runoff contours were plotted at a 1:500,000 scale at 5.1-cm (2-in.) intervals up to 76.2 cm (30 in.) and at 12.7-cm (5-in.) contour intervals for runoff greater than 76.2 cm (30 in.). (Krug et al. (in press) have provided more specific information on map development and quality assurance.)

5.7.1.2 Runoff Interpolation Methods

A simple nearest-contour linear interpolation method was used to estimate runoff for each DDRP site. The Krug et al. (in press) map was digitized into a GIS system by the USGS. Using the GIS (Campbell et al., in press), we the DDRP study sites were overlaid onto the runoff contour maps and runoff was interpolated at each DDRP site to the nearest one inch based on the nearest contour to a site. The nearest contour was determined using an engineer's scale to measure a line from the station location perpendicular to the contour (Rochelle et al., in press).

5.7.1.3 Uncertainty Estimates

Determining a quantifiable estimate of the uncertainty associated with the runoff interpolations is important to the effective use of the runoff data in the Levels I, II, and III Analyses. Working with the USGS, we conducted an analysis to estimate the uncertainties in using a runoff contour map to determine runoff at a specific site. This analysis was incorporated into the development of the 1951-80 runoff map (Rochelle et al., in press; Krug et al., 1988). We randomly selected a subset of the total USGS sites available for map development and withheld these sites from use in map development. Then we used the runoff contour map to interpolate runoff at these sites and compared the interpolated values to the actual long-term measured values. We determined that runoff could be estimated, on the average, within approximately 8.9 cm (3.5 in. or 14.9 percent) of the actual measured runoff. [See Rochelle et al. (in press b) for a complete discussion of the uncertainty analysis.]

A second analysis was conducted to test the consistency of interpolating runoff using the hand-linear interpolation method described above. For the NE region, 883 NSWS watersheds were plotted on the 1951-80 runoff contour map, and runoff was interpolated to each site. A 146-watershed subset of the 883 NSWS sites was plotted onto the runoff contour maps, and runoff was interpolated at the test sites a second time. We compared the two independent estimates to check for consistency in using the hand-linear interpolation method. We found that 11 percent of the sites had a 2.5-cm (1-in.) difference between the two interpolations (5 percent runoff difference) and 1 percent had a 5.1-cm (2-in.) difference between the two runoff interpolations. The results of a paired t-test indicate that the hand interpolation method is reasonably consistent with no significant differences in runoff between the two iterations ($t=0.65$, $p=0.51$). Rochelle et al. (in press b) provide a full description of all uncertainty analyses.

5.7.2 Derived Hydrologic Parameters

The hydrologic pathway followed by precipitation in reaching surface waters is an important factor affecting the processes that control the response of surface water chemistry to acidic deposition. Determining the hydrologic pathways in a watershed is difficult without extensive hydrologic information. Often collecting such data is expensive and requires long periods of data collection to yield hydrologically meaningful information. We have attempted to use other indirect methods to describe the hydrology of the DDRP study watersheds and to, in turn, relate these characteristics to surface water chemistry. We have included hydrologic/geomorphic parameters from three sources for use in the DDRP: (1) parameters calculated by the hydrologic model TOPMODEL (Beven and Kirkby, 1979; Beven, 1986), (2) empirical index of soil contact calculated using Darcy's Law, and (3) mapped hydrologic/geomorphic parameters collected from topographic maps and aerial photography.

5.7.2.1 TOPMODEL

5.7.2.1.1 Northeast -

5.7.2.1.1.1 Model description --

TOPMODEL (Beven and Kirkby, 1979; Beven, 1986; Wolock et al., in press) was chosen to estimate an index of flowpath partitioning because the model requires readily available topographic and soils information, and it predicts internal hydrologic states that can be used to partition streamflow. TOPMODEL characterizes flowpath partitioning by characterizing the spatial distribution of ln(a/KbTanB) where "a" is the area drained per unit contour, "TanB" is the local slope, "K" is the hydraulic conductivity, and "b" is the depth to bedrock. The critical topographic/soils information for a watershed as a whole is the spatially aggregated distribution function of ln(a/KbTanB). The first three moments can be routinely used to characterize the distribution (Wolock et al., 1989).

High values of ln(a/KbTanB) indicate areas in the catchment that are likely to produce surface runoff. These would typically be characterized as topographically convergent, low transmissivity areas. Conversely, low ln(a/KbTanB) values represent areas that have low potential for surface runoff generation (e.g., well-drained soils draining little upslope area). The mean of ln(a/KbTanB) is the critical parameter for characterizing an individual watershed.

5.7.2.1.1.2 Data sources --

5.7.2.1.1.2.1 Soil Conservation Service mapping

To characterize the distribution function of ln(a/KbTanB), TOPMODEL requires information on depth to bedrock ("b") and hydraulic conductivity ("K"). Values of "b" and "K" were estimated based on mapped information obtained from the DDRP Soil Survey (Lammers et al., 1987b; Lee et al., 1989a). To obtain estimates of "K", soil texture classes were associated with the soil types based on SCS texture classifications (Soil Survey Staff, 1981). Next, saturated hydraulic conductivity values ("K") were assigned to the texture classes based on data available in Rawls et al. (1982) (Table 5-35). Values of "b" were assigned by using a mid-point for each depth-to-bedrock class except the highest class (greater than or equal to 30 m), in which case a value of 30 m was assigned (see Table 5-10).

5.7.2.1.1.2.2 Digital elevation models

Local slope ("TanB") and the area drained per unit contour ("a") were computed using USGS 1:250,000-scale digital elevation models (DEM) (Elassal and Caruso, 1983). 1:250,000 DEM data comprise

Table 5-35. DDRP texture classes and saturated hydraulic conductivity (K) for the NE study systems. Estimates of (K) are based on data available from Rawls et al. (1982).

Soil Texture Class	Hydraulic Conductivity (cm/hr)
Sand	21.00
Loamy sand	6.11
Sandy loam	2.59
Loam	1.32
Silt loam	.68
Muck	15.00
Fine sandy loam	3.00
Mucky peat	14.00
Gravelly loam	3.00
Gravelly loamy sand	7.00
Channery silt loam	1.00
Variable	1.00
Mucky loamy fine sand	17.00
Channery loam	1.50
Complex	1.00
Very gravelly sandy loam	3.50
Peat	12.00
Channery very fine sandy loam	3.00
Coarse sand	21.00
Fibric	10.00
Gravelly sandy loam	3.50
Sandy clay loam	0.43
Clay loam	0.23
Silty clay loam	0.15
Sandy clay	0.12
Silt clay	0.09
Clay	0.06
Mucky loam	5.00

a three arc-second elevation grid interpolated from USGS 1:250,000-scale topographic maps. Three arc-seconds represented approximately 60 x 90 m in the NE.

5.7.2.1.1.3 Model calculations --

5.7.2.1.1.3.1 ln(a/KbTanB)

The spatial distribution of ln(a/KbTanB) was derived by combining estimates of "b" and "K" with the topographic values of "a" and "TanB" (Wolock et al., 1989). First, the appropriate DEM was overlaid with DDRP Soil Survey soil and depth-to-bedrock maps for the individual watershed using the ERL-C ARC/INFO GIS. Files containing the soils and topographic information were then output for subsequent analysis. The elevational data were used to calculate the total area draining into each grid cell ("A"), as well as the contour length ("C") and slope ("TanB") along which this area drained out of the cell (a=A/C). Given DX and DY (the X and dimensions of the cell), an initial value for "A" of DX*DY was assigned to each point. To perform the calculations for a given cell, the elevation of the cell was compared to that of its four diagonal and four cardinal neighboring points. Values of ln(a/KbTanB) were then computed as follows: (1) "TanB" was calculated as the weighted average of all downhill direction slopes, (2) "C" was determined as the cell boundary length with neighboring downhill cells, (3) estimates of "K" and "b" were combined with a/TanB, and (4) ln(a/KbTanB) was calculated. The area that drained into the cell was then partitioned to all its downslope neighbors in quantities proportional to "TanB"and "C", and added to the previous values of "A" for those downhill points. All calculations of ln(a/KbTanB) and subsequent partitioning of area were performed in order of decreasing elevation. The estimated values of ln(a/KbTanB) were then aggregated throughout the watershed; a shifted gamma distribution was fit; and the first three moments of the distribution were estimated.

5.7.2.1.1.4 Model output --

The index ln(a/KbTanB) is used to characterize flowpath partitioning of the DDRP watersheds (see Section 8.2.1.2.2.4.2). The index is a measure of the importance of quick flow mechanisms within a watershed. Watersheds with high mean values of ln(a/KbTanB) tend to have a higher percentage of storm runoff in quick flow (e.g., return flow). Conversely, watersheds that have low mean values of ln(a/KbTanB) tend to be dominated by slower hydrologic mechanisms (e.g., sub-surface storm flow). Personnel and time constraints limited the SBRP analyses to ln(a/TanB) rather than ln(a/KbTanB).

5.7.2.1.2 Southern Blue Ridge Province -

5.7.2.1.2.1 Model description --

For the SBRP, we used TOPMODEL to estimate an index of flowpath partitioning by characterizing the spatial distribution of ln(a/TanB), where "a" is the area drained per unit contour and "TanB" is the local slope. This is similar to analyses in the NE (see Section 5.7.2.1.1.1) except that only topographic factors are used to partition streamflow. Personnel and time constraints limited the SBRP analyses to ln(a/TanB) rather than ln(a/Kb TanB).

5.7.2.1.2.2 Data sources --

Local slope ("TanB") and area drained per unit contour ("a") were computed using DEM data as described in Section 5.7.2.1.1.2.2. Three arc-seconds represented approximately 75 x 90 m in the SBRP.

5.7.2.1.2.3 Model calculations ln(a/TanB) --

The spatial distribution of ln(a/TanB) was derived similarly to ln(a/KbTanB) (see Section 5.7.2.1.1.3.1) except that soils information ("K" and "b") was not included. The calculation of ln(a/TanB) was completed as follows. First, a DEM was overlaid with the appropriate DDRP Soil Survey watershed map using the ERL-C ARC/INFO GIS. Files containing the elevation for grid points within the watershed were output for subsequent analysis. The elevational data were used to calculate the total area draining into each grid cell ("A"), as well as the contour length ("C") and slope ("TanB") along which this area drained out of the cell (a=A/C). Given DX and DY (the X and Y dimensions of the cell), an initial value for "A" of DX*DY was assigned to each point. To perform the calculations for a given cell, the elevation of the cell was compared to that of its four diagonal and four cardinal neighboring points. Values of ln(a/TanB) were then computed as follows: (1) "TanB" was calculated as the weighted average of all downhill direction slopes, (2) "C" was determined as the cell boundary length with neighboring downhill cells, and (3) ln(a/TanB) was calculated. The area that drained into the cell was then partitioned to all its downslope neighbors in quantities proportional to "TanB" and "C", and added to the previous values of "A" for those downhill points. All calculations of ln(a/TanB) and subsequent partitioning of area were performed in order of decreasing elevation. The estimated values of ln(a/TanB) were then aggregated throughout the watershed, a shifted gamma distribution was fit, and the first three moments of the distribution were estimated.

5.7.2.1.2.4 Model output –

The index ln(a/TanB) was used for SBRP analyses (see Section 5.7.2.1.2.3) rather than ln(a/KbTan-B). Model interpretation is similar, however, and is more fully described in Section 5.7.2.1.1.4.

5.7.2.2 Soil Contact (Darcy's Law)

The amount of contact precipitation has with the soils component of a watershed is one factor determining the chemistry of the resultant runoff. The potential for contact is a function of soil depth, permeability, and slope. One approach to estimating a potential for soil contact is to use Darcy's Law to calculate a theoretical maximum soil contact time and an index of potential contact. Darcy's Law can be defined as:

$$Q = KAS \qquad \text{(Equation 5-2)}$$

where Q equals lateral soil flow, K is an estimate of the saturate hydraulic conductivity, A is the cross-sectional area of flow and S is the hydraulic gradient. Q is then normalized by watershed area and related to annual runoff to estimate an index of potential soil contact (Peters and Murdoch, 1985).

Peters and Murdoch (1985) working with the ILWAS study systems (Murdoch et al., 1984) used Darcy's Law to develop an index of potential soil contact for Woods Lake and Panther Lake watersheds. They found the high pH lake system (Panther Lake) had a high potential for soil contact based on Darcy's Law and the low pH system (Woods Lake) had a low potential for contact. They found that the high contact system characteristically had deeper soils than the low potential contact system. We have applied the Darcy's Law technique described by Peters and Murdoch (1985) to the DDRP study sites to calculate (1) an estimate of potential lateral flow and (2) an index of the maximum potential for soil contact (see Section 8.2.1.2.2.4.1).

5.7.2.2.1 Data used and sources -

5.7.2.2.1.1 Soil mapping data –

5.7.2.2.1.1.1 Hydraulic conductivity (K)

A weighted-average hydraulic conductivity (K) for each watershed was determined by estimating K using soil mapping texture delineations for each of the soil components mapped in the DDRP Soil Survey as described earlier (Section 5.7.2.1.1.2.1). Estimates of K based on soil texture were obtained using values presented in Rawls et al. (1982). The DDRP Soil Survey provides an estimate of the percentage of watershed occupied by each soil component (see Section 5.2). We used these percentages to calculate a weighted-average K per watershed.

5.7.2.2.1.1.2 Cross-sectional area (A)

The cross-sectional area "A" was determined by multiplying the perimeter of the lake by the average depth of permeable material. By using lake perimeter we were able to determine the average area at the point of contact between the soil matrix and the surface water system. Lake perimeter was measured from watershed maps prepared by the DDRP Soil Survey and digitized into the ERL-C ARC/INFO GIS (Campbell et al., in press). As part of the DDRP Soil Survey, depth-to-bedrock classes were mapped for each of the watersheds (see Table 5-10). We determined an average depth for each watershed by calculating a weighted-average depth to bedrock based on the proportion of the watershed occupied by each class. For the calculation we used the mid-point of each Class (see Table 5-10) except for Classes I and VI; we used 0.5 m for Class I and 30 m for Class VI.

5.7.2.2.1.1.3 Slope (S)

An average slope for each watershed was calculated based on the slope estimates associated with the DDRP Soil Survey map units (Lee et al., 1989a). Each map unit has a slope class designation indicating associated slope. Table 5-36 shows the SCS slope classifications associated with the map units. We calculated an area weighted-average slope based on the area of each map unit within a watershed proportional to the total watershed area using the mid-point of each class presented in Table 5-36.

5.7.2.2.1.2 Runoff --

An estimate of the average annual runoff for each site was determined from the Krug et al. (in press) runoff contour map described in Section 5.7.1. Runoff interpolation methods are discussed in Section 5.7.1.3.

5.7.2.2.2 Model calculations --

We applied the Darcy's Law calculation to non-seepage lakes in DDRP NE watersheds. Figure 5-29 diagrams the algorithm used to apply the Darcy's Law equation to the watersheds. The final outputs from these calculations are an estimate of the potential lateral flow and an index of soil contact.

5.7.2.3 Mapped Hydrologic Indices

Previous investigators (Hewlett and Hibbert, 1967; Dingman, 1981; Woodruff and Hewlett, 1970; Carlston, 1963; Lull and Sopper, 1966; Vorst and Bell, 1977) have attempted to relate hydrologic characteristics to mapped watershed geomorphic/hydrologic parameters for forested watersheds. In general, most of the previously reported research is at the event level or covers short time periods (i.e., days or weeks). The DDRP is primarily interested in longer time frames (e.g., annual time steps). For use in the Level I Analyses, we have developed a hydrologic indices database for the NE and SBRP study systems. The primary goal is to be able to link these geomorphic/hydrologic parameters to the current surface water chemistry of the study systems (NSWS chemistry).

5.7.2.3.1 Data sources -

The geomorphic/hydrologic parameters (hydrologic indices) were determined from three data sources. First, all area measurements came from maps prepared as part of the DDRP Soil Survey (Section 5.2). The second major source of information is 7.5' and 15' topographic maps. Topographic

Table 5-36. SCS slope classifications.

Class	Slope(%)	midpoint
A	0 - 3	1.5
B	3 - 8	5.5
C	8 - 15	11.5
D	15 - 25	20
E	25 - 45	35
F	45 - 70	57.5

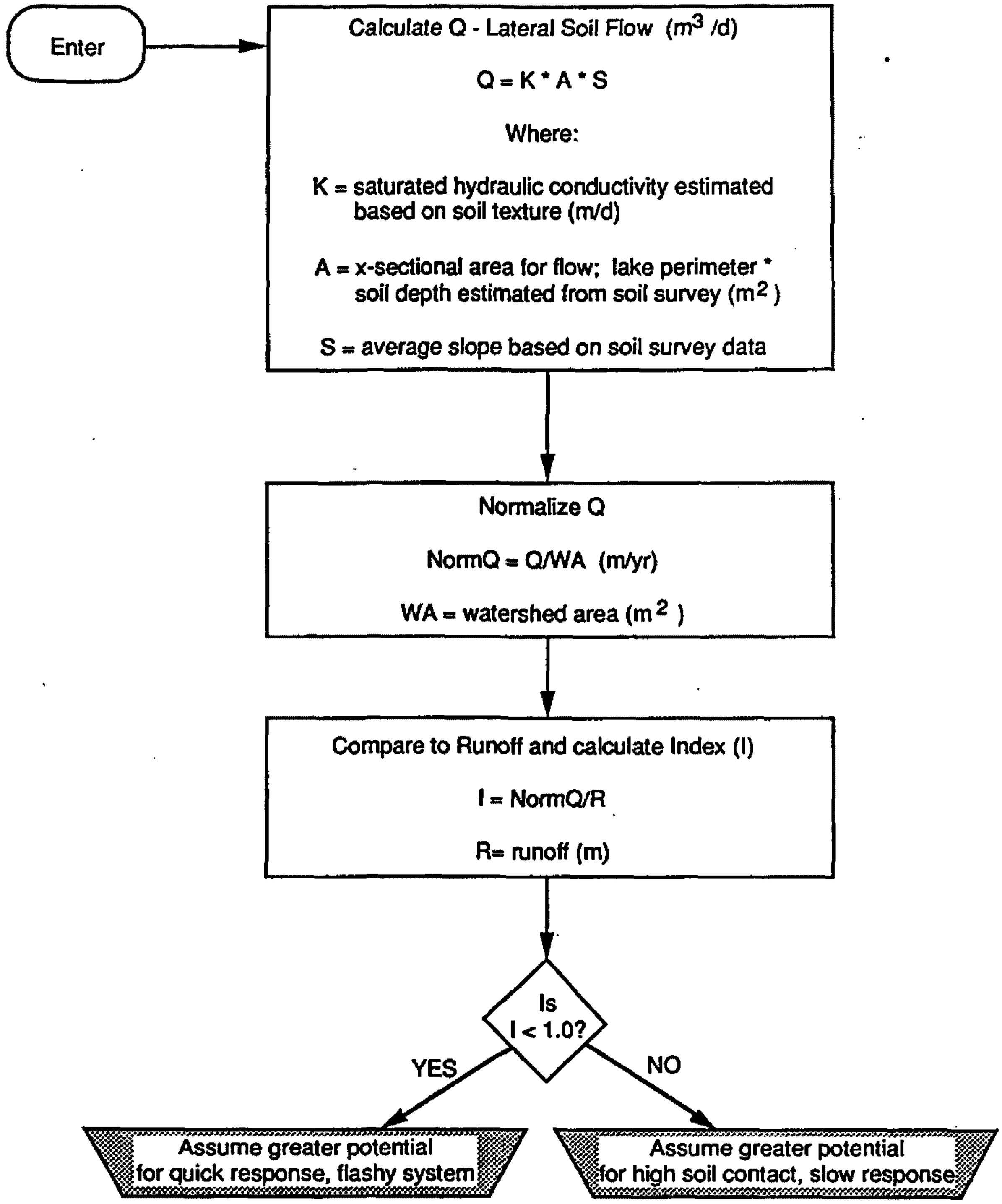


Figure 5-29. Flow chart of Darcy's Law soil contact calculation as applied to the DDRP study sites.

maps were used for elevational and length measurements, for stream delineations and for sub-basin determination. Whenever possible, 7.5' maps were used. For 70 of the DDRP sites, however, only 15' maps were available. The last source of mapped information was obtained from aerial photography taken as part of the DDRP land use survey (see Sections 5.4.1.6 and 5.4.2.7; Liegel et al., in review). The aerial photos were used to check stream delineations and other specific information obtained from the topographic maps.

5.7.2.3.2 Data collection procedures (Northeast) -

Geomorphic parameters were defined from map measurements taken from 7.5' topographic maps (when available) or from 15' topographic maps from the USGS topographic map series. All map information was digitized and entered directly into a computer database via an interactive program (K. Nash, personal communication). Table 5-37 describes all measured or computed parameters. The majority of the measures identified in Table 5-37 were selected from geomorphic/hydrologic parameters listed by the U.S. Department of Interior (1977). Additionally, we have included parameters that are specifically descriptive of lake watersheds. These are watershed area-to-lake area ratio (WS_LA), watershed perimeter-to-lake perimeter ratio (PERIMRAT), and percent area in open water bodies, including the primary lake of the watershed (H2O_WS).

Three additional measures included in the geomorphic/hydrologic database are average annual runoff (R), retention time (T_R) for the primary lake, and lake volume (V). "R" was interpolated (Rochelle et al., in pressb) from a runoff contour map (Krug et al., in press) of average annual runoff for 1951-80. T_R and V were estimated by the NSWS (see Kanciruk et al., 1986a).

To ensure consistency, all map measurements were made by the same individual according to pre-established methods. Also, we conducted a quality check to ensure that the data were accurate and measurements were consistent. First, a 10 percent subset of 144 watersheds was re-digitized and compared against the original measurements. The differences were compared to published interpretation errors (USDI, 1977).

Table 5-37. Mapped and calculated geomorphic parameters collected for the NE study sites.

Parameter	Description	Units
Measured		
B_CENT	Drainage basin centroid expressed as an X,Y coordinate	
B_LEN	Length of drainage basin; air-line distance from basin outlet to farest upper point in basin	km
B_PERIM	The length of the line which defines the surface divide of the drainage basin	km
A_H	Area of all open water bodies in drainage basin	km^2
INT	Total length of intermittent streams as defined from USGS topographic maps of aerial photos	km
A_L	Area of the primary lake	km^2
L_CENT	Primary lake centroid expressed as X,Y *coordinates*	
L_PERIM	Perimeter of primary basin lake	km
MAX_EL	Elevation at approx. highest point	m
MIN_EL	Elevation of primary lake	m
PERIN	Total perennial stream length as defined from USGS topographic maps and aerial photos	km
SUB_BAS(n)	Area of each sub-catchments in the drainage basin	km^2
STRMORDER	Maximum stream Order (Horton) of streams in the watershed (aerial photos used to aid in reducing cooling problems between 7.5 and 15 minute maps)	
TOTSTRM	Total stream length; combination of perennial and intermittent	km
A_W	Total watershed area	km^2

continued

Table 5-37 (continued)

Parameter	Description	Units
Calculated		
B_SHAPE	Basin Shape ratio; B_LEN ^{2}/WS_AREA	
B_WIDTH	Average basin width; WS_AREA/B_LEN	km
COMPACT	Compactness Ratio; ratio of perimeter of basin to the perimeter of a circle with equal area; $(PERIM)/(2*(\ * A_W)^{.5})$	
DDENSITY	Drainage Density; TOTSTRM/WS_AREA	
ELONG	Elongation Ratio; (4 * WS_AREA)/L_BEN	
H20_WS	Ratio of open water bodies area to total watershed area H2O_AREA/WS_AREA	
MAX_REL	Maximum relief; MAX_ELEV - MIN_ELEV	m
M_PATH	Estimate of mean flow path;	m
PER_DD	Drainage density calculated from perennial streams only PERIN/WS_AREA	
PERIMRAT	Ratio of the lake perimeter to the watershed perimeter; Lake Perimeter/B_PERIM	
REL_RAT	Relief Ratio; (MAX_ELEV-MIN_ELEV)/B_LEN	
ROTUND	Rotundity Ratio; $(B\_LEN)^2/(4 * WS\_AREA)$	
WM_PATH	Estimate of weighted mean flow path;	m
WS_LA	Ratio of the total watershed area to the area of the primary lake	

continued

Table 5-37 (continued)

Parameter	Description	Units
Additional		
T_{Ra}	Lake retention time	yr
V^a	Volume of the primary lake	$10^6 m^3$
R	Average annual runoff; interpolated to each site from Krug et al. (1988) runoff map	cm

Second, we conducted internal database checks to determine gross data entry errors and to identify obvious errant values. The internal data verification checks were (1) all areas and lengths were greater than zero, (2) maximum elevation was greater than minimum elevation, (3) sub-basin areas were less than watershed area, (4) open water areas were less than watershed area, and (5) the lake perimeter was less than the basin perimeter.

Third, watershed elevations and areas were also checked against data in a separate database constructed as part of the DDRP Soil Survey (Lee et al., 1989a). The elevation data in the databases differed by less than 10 percent. Total areas in both databases were within 10 percent for 136 watersheds. We checked the 8 watersheds individually to determine and resolve remaining discrepancies.

5.7.2.3.3 Data collection procedures (Southern Blue Ridge Province) -

Data collection procedures were the same as those used for the NE study watersheds except that some parameters not appropriate for stream systems were not derived for the SBRP dataset. Table 5-38 lists parameters included in the SBRP hydrologic indices database.

As with the NE, data collection was mainly from 7.5' and 15' topographic maps. All map measurements for the SBRP were made in-house at ERL-C, and area measurement data were obtained using the GIS. Stream channels were estimated based on USGS perennial stream delineations and field checks by SCS soils mappers (see Section 5.4.2.8.3.2).

To ensure consistency, all SBRP measurements were made by the same individual. We conducted an independent check on all map measurements and digitized information. Any measurement or data entry discrepancies were checked and corrected as appropriate.

Table 5-38. Mapped and calculated geomorphic parameters collected for the SBRP study sites.

Parameter	Description	Units
Measured		
B_CENT	Drainage basin centroid expressed as an X,Y coordinate	
B_LEN	Length of drainage basin; air-line distance from basin outlet to farest upper point in basin	km
B_PERIM	The length of the line which defines the surface divide of the drainage basin	km
MAX_EL	Elevation at approx. highest point	m
MIN_EL	Elevation at watershed outlet	m
SUB_BAS(n)	Area of each sub-catchments in the drainage basin	km^2
STRMORDER	Maximum stream Order (Horton) of streams in the watershed (aerial photos used to aid in reducing cooling problems between 7.5 and 15 minute maps)	
TOTSTRM	Total stream length; perennial	km
WS_AREA	Total watershed area	km^2
Calculated		
AVG_EL	Average elevation; (MAX_ELEV + MIN_ELEV)/2	m
B_SHAPE	Basin Shape ratio; B_LEN ^{2}/WS_AREA	
B_WIDTH	Average basin width; WS_AREA/B_LEN	km
COMPACT	Compactness Ratio; ratio of perimeter of basin to the perimeter of a circle with equal area; (PERIM)/(2*(* A_W)$^{.5}$)	
DDENSITY	Drainage Density; TOTSTRM/WS_AREA	

continued

Table 5-38. Mapped and calculated geomorphic parameters collected for the SBRP study sites. (cont)

Parameter	Description	Units
ELONG	Elongation Ratio; (4 * WS_AREA)/L_BEN	
MAX_REL	Maximum relief; MAX_ELEV - MIN_ELEV	m
M_PATH	Estimate of mean flow path;	m
REL_RAT	Relief Ratio; (MAX_ELEV-MIN_ELEV)/B_LEN	
ROTUND	Rotundity Ratio; $(B\_LEN)^2/(4 * WS\_AREA)$	
TOT_DD	Estimated drainage density based on crenulations identified on topo map	
WM_PATH	Estimate of weighted mean flow path;	m
Additional		
R	Average annual runoff; interpolated to each site from Krug et al. (1988) runoff map	cm

SECTION 6

REGIONAL POPULATION ESTIMATION

6.1 INTRODUCTION

The purpose of this section is to describe the procedures used to extrapolate analyses on individual watersheds to the target populations in the study regions. This process of extrapolation is called population estimation.

6.2 PROCEDURE

6.2.1 Use of Variable Probability Samples

Probability samples were selected for lake watersheds in the Northeast and stream watersheds in the Southern Blue Ridge Province (SBRP). Any quantity that can be defined for a sample unit (i.e., for each watershed) can be extended to a corresponding population quantity through the probabilistic structure of the sample. The quantity can be a measured variable or a model-based estimate. It can be a number, a vector, or a function. In the Eastern Lake Survey (ELS), most quantities were measured values, and the measurement error tended to be small relative to the sampling variation. In contrast to the ELS, many of the quantities produced in the DDRP are model outputs believed to have significant uncertainty associated with them. The population estimation techniques provided below apply to any probability sample with defined inclusion probabilities. Thus, they are applicable to any identifiable subset of the DDRP sample. Explicit provision is made for including uncertainty associated with the quantity that is extended to the regional population.

In the ELS and, hence, the DDRP, the size of the target population is not precisely known. The sampling frame for the ELS consisted of designated lakes on USGS maps. In some cases during field sampling in the ELS, a field visit to the sample lakes selected from this frame indicated that some water bodies designated as lakes on the map actually were not lakes, but rather marshes or old beaver ponds, for example. When these "non-lakes" were subsequently excluded from the sample, a similar proportion of lakes also had to be excluded from the target population, effectively reducing its size. Thus, the size of the target population is estimated from the sample size. This presents no particular difficulty as long as each unit in the sample has a known inclusion probability.

The design of the surface water surveys and the DDRP also permits arbitrary subsetting of the sample. In some cases, the subsetting would correspond to a redefinition of the target population (e.g., the exclusion of seepage lakes). In such cases, the inclusion probabilities for the remaining sample units do not change, which, as can be seen from Equation 6-1 below, implies a smaller target population. In other cases, the subset should be viewed as a subsample. In these cases, a smaller sample is being used to make an inference about the same target population, and the inclusion probabilities do change. This might occur if a selected lake could not be sampled or simulated for some reason. Inferences can still be made about the same target populations, but the inclusion probabilities would change.

6.2.2 Estimation Procedures for Population Means

The structure of the DDRP sample is almost identical to the structure of the ELS Phase II sample. The differences are primarily in the conditional probability of inclusion in the second phase of the sample: the DDRP sample was reduced by exclusion of lakes with large watersheds and the Phase II sample was reduced at random. The estimation procedures are parallel to those detailed in the ELS Phase II Data Analysis Plan (Overton,1987). Let n be the size of the sample selected from the target population, let p_i be the probability that sample unit i was included in the sample, and let p_{ij} be the joint inclusion probability of units i and j. For sample unit i, let y_i be the "true" quantity, and let z_i be the observed quantity, i.e., the unknown true value with an associated error e_i. The error may be an observation error or a measurement error; it could also be a prediction error. In each case we assume that the characteristics of the error distribution are known, and that the uncertainty in the observed values is characterized by that error distribution. The basic estimation procedures will follow the Horvitz-Thompson estimator (Cochran, 1977) for variable probability samples; some details, however, will depend on assumptions made about the observation error. Several distinct error models are treated below.

In one case, the uncertainty is due to an additive error term, so that the magnitude of the uncertainty is constant over the range of the response. The observation is related to the true value through the equation $z_i = y_i + e_i$. Two distributions were available to handle this case: the error term was assumed to have either a normal distribution with mean 0 and variance σ^2 or a uniform distribution over the interval (-a,a). For this uniform distribution, the mean is 0 and $\sigma^2 = a^2/3$.

In a second case, the magnitude of the uncertainty depends on the magnitude of the response. This can be modelled with a multiplicative error term, where the uncertainty is proportional to the response, so that $z_i = y_i e_i$. We assumed that the uncertainty followed a log-normal distribution with a mean value of 1 and a variance $\sigma^2 = RSD^2$, where RSD was the relative standard deviation.

An implication of the above multiplicative model is that the uncertainty goes to 0 along with the response. In some instances, however, there was appreciable uncertainty even when the response was 0. For these cases, we assumed that the uncertainty was proportional to the sum of the response plus an offset (h), so that the observation equation was $z_i = y_i + (y_i + h)e_i = y_i(e_i + 1) + he_i$. The mean value of the error term was 0, and the $\sigma^2 = RSD^2$. As above, a log-normal distribution was used for this case.

The error structure affects only the variance of the population total, the variance of the population mean, and the estimator of the cumulative distribution function and its associated variance. The estimator of the target population size and population total take the same form under all of the above error structures.

Estimator of population total, $\hat{T}$:

$$\hat{T} = \sum_{1}^{n} z_i/p_i \qquad \text{(Equation 6-1)}$$

Estimator of the size of the target population, N:

$$\hat{N} = \sum_{1}^{n} 1/p_i \qquad \text{(Equation 6-2)}$$

Estimator of population average, $\hat{Y}$:

$$\hat{Y} = \hat{T}/\hat{N} \qquad \text{(Equation 6-3)}$$

Both $\hat{T}$ and $\hat{N}$ are random variables, and both are unbiased estimators of the respective population quantities. However, $\hat{Y}$, similar to most ratio estimators, is a slightly biased estimator of the population average.

6.2.3 Estimators of Variance

For all three error models, the estimator of the variance of $\hat{T}$ has the form

$$\mathrm{Var}(\hat{T}) = \sum_{i}^{n} \frac{(1 - p_i)z_i^2}{p_i^2} + \sum_{i}\sum_{j>i}^{n}\left(\frac{(p_{ij} - p_i p_j)z_i z_j}{p_i p_j p_{ij}}\right) + g(e,z) \qquad \text{(Equation 6-4)}$$

where g(e,z) is a function that depends on the error model and the sample data. For the additive model, $g(e,z) = \sigma^2 \hat{N}$; for the multiplicative model, $g(e,z) = \sigma^2 \Sigma z_i^2/p_i$, and for the multiplicative model with offset, $g(e,z) = \sigma^2 \Sigma(z_i + h)^2/p_i$, where h is the offset.

The variance of $\hat{N}$ is estimated by

$$\mathrm{Var}(\hat{N}) = \sum_{i}^{n} \frac{(1 - p_i)}{p_i^2} + \sum_{i}\sum_{j>i}^{n}\left(\frac{(p_{ij} - p_i p_j)}{p_i p_j p_{ij}}\right) + g(e,z) \qquad \text{(Equation 6-5)}$$

The joint inclusion probabilities p_{ij} are determined by the structure of the DDRP sample. They are computed according to the algorithm in the ELS Phase II Analysis Plan (Overton, 1987).

Finally, the variance of the estimator of the population average was obtained from a first-order variance propagation using Equations 6-4 and 6-5:

$$\mathrm{Var}(\hat{\bar{Y}}) = \mathrm{Var}(\hat{T})/\hat{N}^2 + \hat{T}^2\mathrm{Var}(\hat{N})/\hat{N}^4 - \hat{T}\mathrm{Cov}(\hat{T},\hat{N})/\hat{N}^2, \qquad \text{(Equation 6-6)}$$

where

$$\mathrm{Cov}(\hat{T},\hat{N}) = \sum_{i}^{n}\sum_{j>i}^{n}(p_i p_j - p_{ij})(1/p_i - 1/p_j)(z_i/p_i^2 - z_j/p_j^2)$$

Confidence intervals will be derived from the usual normal theory, e.g., a 95 percent CI on the population average is given by

$$\bar{Y} \pm 1.96\sqrt{\mathrm{Var}(\bar{Y})}.$$

6.2.4 Estimator of Cumulative Distribution Function

Let N(y) be the total number in the population with the value of Y less than or equal to y, so that the cumulative distribution function of Y is $F_Y(y) = N(y)/N$. An estimator of N(y) is

$$\hat{N}_z(y) = \sum_{z_i \leq y}^{n} 1/p_i = \sum_{i=1}^{n} v_i(y)/p_i,$$

where

$$v_i(y) = \begin{cases} 1, & z_i \leq y \\ 0, & z_i > y \end{cases}$$

An estimator of the cumulative distribution function of Y is

$$\hat{F}_Y(y) = \hat{N}(y)/\hat{N}$$

The variance of $\hat{F}_Y$ has both a sampling component and a component due to measurement uncertainty. The variance of the $\hat{N}(y)$ and covariance of $\hat{N}(y)$ and $\hat{N}$ are needed to calculate the sampling variance of $\hat{F}_Y$. These are given by

$$Var(\hat{N}(y)) = \hat{F}_Y(y)(1-\hat{F}_Y(y))\Sigma\ 1/p_i^2 + \hat{F}_Y^2(y)Var(\hat{N})$$

and

$$Cov(\hat{N},\hat{N}(y)) = \hat{F}_Y(y)Var(\hat{N}).$$

Then a first order variance propagation formula gives

$$Var(\hat{F}_Y) = Var(\hat{N}(y))/\hat{N}^2 + \hat{N}^2(y)Var(\hat{N})/\hat{N}^4 - \hat{N}(y)Cov(\hat{N}(y),\hat{N})/\hat{N}^2$$

for the sampling variance. A Monte Carlo procedure was used to calculate the measurement variance. The sampling variance and the measurement variance were added to obtain total variance.
The median and quintiles of the distribution of Y were estimated by the linear interpolation of $\hat{F}_Y$.

6.3 UNCERTAINTY ESTIMATES

The quantities displayed in this report are the end result of a sequence of operations, beginning with collection of a physical sample in the field and ending with the production of a table or graph. A variety of steps were conducted, including chemical analyses, data aggregation, data reduction, and processing of the data through various mathematical models. The final result contains an element of uncertainty that has its origin in the design, in the implementation of the field protocol, and in the precision of the basic measurement process (e.g., the chemical analytic precision). The uncertainty on the final result can be quantified by propagating the uncertainty (or its mathematical analog) through the same sequence of operations as were the data.

In the DDRP, several techniques have been used to propagate uncertainty through a functional relationship (which could be a complex simulation model as well as an explicit function). Let $f(x_1, x_2, ..., x_n)$ be a function of the variables $x_1, x_2, ..., x_n$ with uncertainties $e_1, e_2, ..., e_n$, respectively. The probability distributions (or at the least the variances) of the uncertainties are presumed known. If the functional relationship is such that partial derivatives can be easily obtained, then the variance of functional values can be estimated using a first-order linear approximation to the functional relationship:

$$Var(f) = \Sigma(\partial f/\partial x_i)^2 \sigma_i^2$$

In the case of a simulation model, the function is the model itself, and the partial derivatives cannot be calculated explicitly. An approximation to the partials can be obtained by perturbing the x_i's in turn. If a suitably small perturbation is chosen, then the ratio of the change in output to the perturbation is an estimate of the partial derivative. These estimates can then be used in a first-order propagation as above.

A disadvantage of both of the above techniques is that they ignore possible correlations among the uncertainties. One way to account for such correlations is to propagate not only variances but also covariance terms. The "first-order, second-moment" technique used in the Enhanced Trickle Down uncertainty analysis is a means of doing exactly that. A first-order approximation is made to the model, and Kalman filtering techniques are used to build up an estimate of the state variable variance-covariance matrix. A final method that was used in uncertainty assessment was Monte Carlo. The Monte Carlo method is applied by repeatedly calculating the value of f, each time perturbing the value of each x_i by a random quantity drawn from the respective uncertainty distribution. Monte Carlo is most easily applied when uncertainties are statistically independent, but can also be applied when correlations exist. A variant of Monte Carlo, called "fuzzy optimization", was used in the uncertainty analyses for the Model of Acidification of Groundwater in Catchments.

6.4 APPLICABILITY

This section discusses the procedures for the Level I, II, and III population estimation approaches for DDRP, including the statistical formulas that will be used to estimate population means, variances, and cumulative frequency distributions. The population estimation procedures are generic and do not depend on the level of analysis. The specific target populations for inference, however, do depend on the analyses performed. Not all DDRP watersheds were used at each level of analysis so the target population will vary. The explicit target populations being considered in the analysis are discussed in Sections 8, 9, and 10. The generic uncertainty estimation procedures introduced in this section also are more explicitly discussed for each of the individual analyses in Sections 8, 9, and 10.