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Hydrogeology and Water Quality of the Pepacton Reservoir Watershed in Southeastern New York

Part 3. Responses of Stream Base-Flow Chemistry to Hydrogeologic Factors and Nonpoint-Sources of Contamination

Scientific Investigations Report 2004-5008

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By Paul M. Heisig and Patrick J. Phillips

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U.S. Department of the Interior
Gale A. Norton, Secretary

U.S. Geological Survey
Charles G. Groat, Director

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Conversion Factors, Datum and Abbreviations

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square mile (mi^2)	2.590	square kilometer (km^2)
Volume		
million gallons (Mgal)	3,785	cubic meter (m^3)
cubic foot (ft^3)	0.02832	cubic meter (m^3)
Flow rate		
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8×°C)+32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$°C=(°F-32)/1.8$$

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Altitude, as used in this report, refers to distance above the vertical datum.

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

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Part 3. Responses of Stream Base-Flow Chemistry to Hydrogeologic Factors and Nonpoint-Sources of Contamination

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Abstract

Base-flow samples were collected seasonally from 20 small streams in the 372-square-mile Pepacton Reservoir watershed to evaluate the effects of hydrogeologic factors and nonpoint sources of contamination on the chemical composition of ground-water discharge. The reservoir provides part of New York City's water supply. The subbasins represented one of three general types of land use, each with at least 45 percent forested area (mostly on the hillsides): farmed (dairy) land, formerly farmed land with low-density residential development, or forested land with little or no development. The subbasin areas ranged from 0.38 to 10.23 square miles. All streams were sampled in December 2000 and in May, July, and October 2001. Three of the sites were designated as land-use-index sites and were sampled as many as five additional times during the study. No samples exceeded state or federal drinking-water standards for chloride, sodium, nitrate, orthophosphate, herbicides, or herbicide degradates.

The chemical composition of base-flow samples was classified into major-ion water types, which were broadly defined as naturally occurring and road-salt-affected water types. About one-third of the base-flow samples were road-salt-affected types. Natural water types were differentiated as dilute or evolved. Dilute waters have bicarbonate and sulfate as dominant anions and evolved waters have only bicarbonate as a dominant anion. Dilute water types indicate relatively short ground-water residence times or contact with unreactive aquifer material. Evolved waters have either longer ground-water residence time or contact with more reactive aquifer material than dilute ground waters. The larger subbasins with wider valley-bottom areas were more likely to have evolved water types than small subbasins with little floodplain development.

Positive correlations between selected constituents and the intensity of nonpoint sources emphasize the connection between land use, shallow ground-water quality, and stream base-flow water quality. Chloride and sodium, which are relatively conservative constituents, showed strong linear relations with annual estimates of road-salt application during all four sampling periods. Nonconservative constituents, such as the nutrients nitrate and orthophosphate, showed linear relations with manure production rate among farmed basins, but only at specific times of the year because of losses through biologic activity. Nitrate showed the strongest relation in winter because losses to biological activity were at a minimum. Orthophosphate showed the strongest relation in early summer, when hydrologic and chemical conditions appear to favor release from sediments. Atmospheric nitrogen deposition is an additional source of nitrogen that can be released from mature or stressed forested basins.

Detections of herbicides (atrazine, metolachlor, simazine) and herbicide degradates (Metolachlor ESA, alachlor ESA, deethylatrazine) in base flow were closely correlated with subbasins in which corn was grown during the study. Atrazine was detected at the farmed index site only in early summer, after application and two rain storms. This detection corresponded to the peak orthophosphate concentration. In contrast, metolachlor ESA was detected in nearly all farmed-index-subbasin samples and peaked in late summer, when percent base-flow contributions from farmed valley-bottom areas were likely highest.

The implications of this study are that seasonal and more frequent base-flow surveys of water chemistry from small stream basins can help refine the understanding of local hydrogeologic systems and define the effects of nonpoint-source contamination on base-flow water quality. The concentration of most nonpoint sources in valley-bottom or lower-hillside areas helped indicate the relative contributions of water from hillside and valley-bottom areas at different times of year. The positive correlations between the intensity of nonpoint-source activities and nonpoint-source constituents in base flow underscores the link between land use (nonpoint sources), ground-water quality, and surface-water quality.

Introduction

Nonpoint-source contamination of ground water and surface water is a particular concern within New York City's upstate water-supply watersheds. Contaminant loading in these watersheds affects ground-water, which discharges to streams that flow to the reservoirs. Nutrient loading to New York City water-supply reservoirs can promote excessive algal growth that can impair reservoir water-quality. Definition of natural water chemistry and chemical responses to different types and degrees of nonpoint sources within watershed areas can provide useful information to water-resource managers.

Streamflow during dry periods (base flow) is sustained by ground-water discharge, either from springs or from seepage directly into stream channels. A base-flow sample from a stream draining a small basin thus provides a composite sample of shallow ground water discharge from the stream basin above the sampling point. Such samples provide an overview of the effects of nonpoint sources within a watershed subbasin; similar results based on only ground-water samples would require a much more expensive and extensive well network. Base-flow samples are desirable in that they also indicate the quality of water flowing to the local reservoir.

The Pepacton Reservoir, in the western Catskill Mountains of southeastern New York (fig. 1) is a part of the East Branch Delaware River, impounded by the Downsville Dam. It is the largest reservoir within the Delaware watershed, whose four reservoirs provide about 50 percent of New York City's water supply. Land use within the 372 mi^2 Pepacton watershed is characterized by scattered hamlets and large areas of forested and formerly farmed lands, with smaller areas supporting agriculture (primarily dairy farms). Low-density residential development is most common within the formerly farmed areas.

In 2000, the U.S. Geological Survey (USGS), in cooperation with the New York State Department of Environmental Conservation (NYSDEC), began two parallel studies covering hydrogeology and water quality within the Pepacton watershed. One 2-year study of the quality of ground-water discharge resulted in three reports: two covering small upland basins with different land uses (this report (part 3) and Phillips and Heisig, 2004 (part 1)) and one covering streams in reaches of major valleys (Heisig, 2004 (part 4)). The concurrent study compiled and summarized the surficial geology and presented estimates of recharge for basins with stream-gaging stations within the Pepacton watershed (Reynolds, 2004 (part 2)).

Purpose and Scope

This report documents the results of base-flow water-quality sampling from 20 small basins in the Pepacton watershed over a one-year period. Samples are classified according to major-ion water type and are interpreted as a response to local hydrogeology (ground-water flow paths) and

(or) nonpoint source contamination of shallow ground water. The occurrence of selected nonpoint-source constituents (chloride and sodium, nitrate, orthophosphate, and herbicides) in base flow are compared to their rate of production or application within each subbasin.

The principal objectives of this investigation were to (1) collect and analyze the chemistry of base-flow samples from 20 streams in small (0.38- to 10.23-mi^2) subbasins over a 1-year period, as a surrogate for shallow ground-water chemistry, (2) classify the samples according to major-ion type (dilute or evolved, and whether affected by road salt), (3) identify the probable sources of the constituents of concern, and (4) relate the occurrence and concentrations of those constituents (chloride and sodium, nitrate, orthophosphate, and herbicides) to their annual production or application rate in each subbasin.

The study entailed (1) establishing streamflow-sampling sites in small subbasins, each representing one of three general land-use categories (forested, farmed, or formerly farmed), then designating one site in each category as an "index" site, (2) collecting base-flow samples for chemical analysis from all sites four times a year, and from the three index sites as often as nine times a year, and (3) correlating the application or production rates (or application area) of selected nonpoint-source contaminants (road salt, livestock manure, and herbicides) within each subbasin with the base-flow concentrations in the respective streams. The results of the study provide watershed managers with stream base-flow chemistry responses to different types and intensities of nonpoint sources within the Pepacton watershed. These responses can be used to assess whether water-quality goals for the watershed are being met. The results also approximate average shallow ground-water quality within the sampled areas of the watershed

Previous Investigations

Previous investigations that include parts of the Pepacton watershed have described the geologic framework, glacial deposits and deglaciation, and nitrogen species in stream water. The geologic framework has been discussed by Fluhr (1953) (Pepacton Reservoir area) and by Soren (1963) (all of Delaware County). Glacial geology and deglaciation in the western Catskill mountains was discussed by Kirkland (1973) and Ozvath (1985). A study of nitrogen species in stream water from forested Catskill watersheds (Lovett and others, 2000) included five sites within the Pepacton watershed.

Description of Study Area

The Pepacton watershed covers 372 mi^2 within the western Catskill Mountains of New York, mostly within Delaware County, but also in small sections of Greene and Ulster Counties (fig. 1). The Downsville Dam impounds the East Branch Delaware River (Pepacton Reservoir) at

Figure 1. Hydrography, sampling network sites with associated drainage basins, and location of reference stream-gaging station within the Pepacton watershed, western Catskill Mountains, New York.
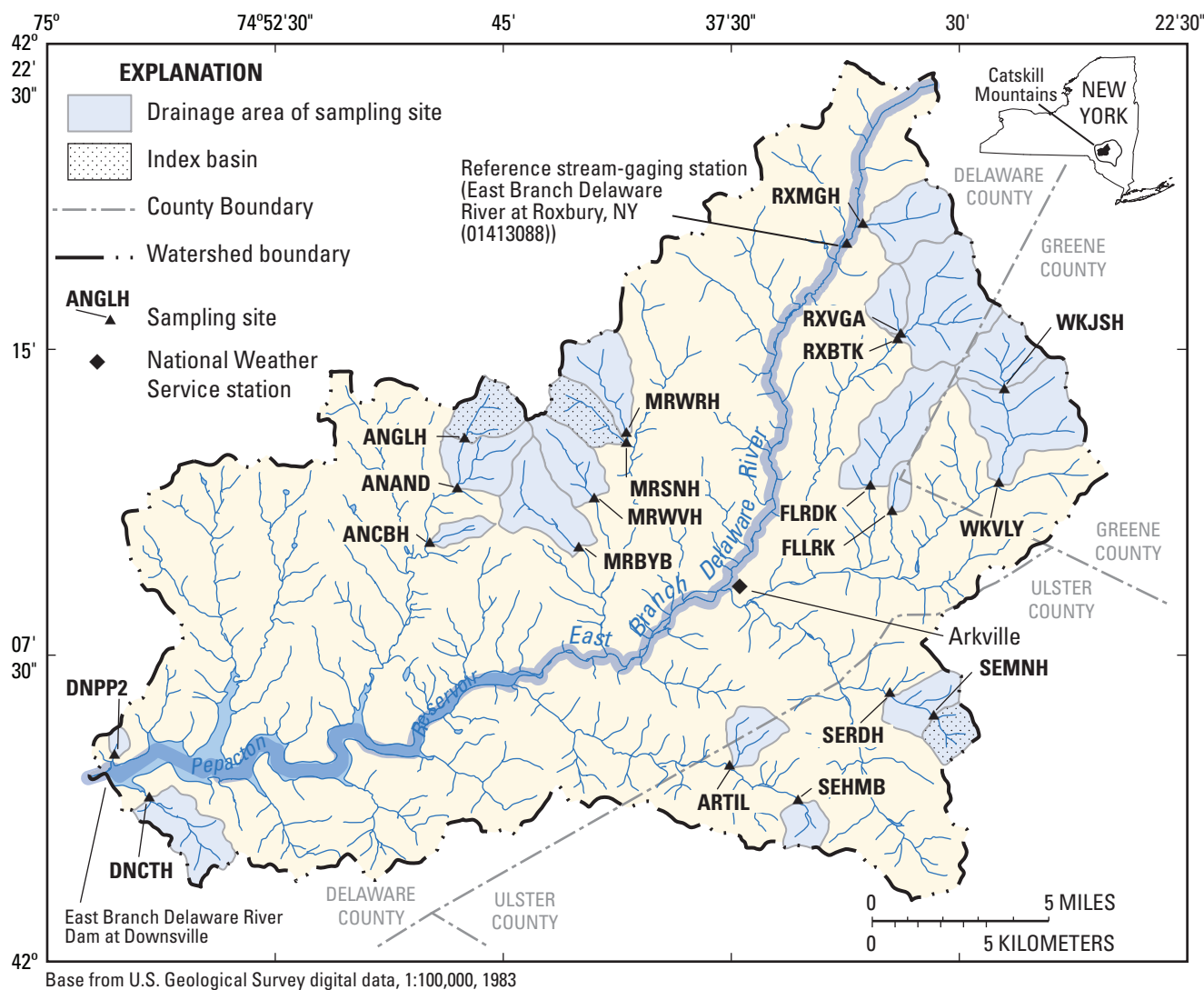
ANAND	Gladstone Hollow Brook near Andes
ANCBH	Campbell Hollow Brook
ANGLH	Gladstone Hollow Brook north of Andes
ARTIL	Mill Brook Tributary
DNCTH	Cat Hollow Brook
DNPP2	Pepacton Reservoir West End Tributary
FLLRK	Little Red Kill
FLRDK	Red Kill
MRBYB	Bryants Brook
MRSNH	Sanford Hollow Brook

MRWRH	Winter Hollow Brook
MRWVH	Weaver Hollow Brook
RXBTK	Batavia Kill
RXMGH	Montgomery Hollow
RXVGA	Tributary to Batavia Kill
SEHMB	Mill Brook
SEMNH	Rider Hollow Brook east of Mapledale
SERDH	Rider Hollow Brook near Mapledale
WKJSH	Vly Creek above Halcott Center
WKVLY	Vly Creek near Halcott Center

the downgradient end of the watershed. Maximum relief in the watershed is about 2,800 ft, with the highest elevations bordering the eastern and southeastern edges. The Pepacton watershed is rural, with scattered small villages and hamlets in the valleys. Upland areas are largely forested, but valley bottoms and lower hillsides are largely open fields. Land use within this watershed has undergone a major change in the

last few decades. Agriculture (primarily dairy farming) was widespread in valley-bottom and hillside areas - only the steepest upland areas remained forested. Dairy farming has decreased sharply over the past thirty years, and presently (2002) is generally limited to the most favorable lands in the larger valleys, and in some upland basins with relatively low average slopes. Former dairy-farmed areas in upland basins

are now either overgrown fields in various stages of forest regrowth, along with some hayfields, or areas of low-density residential development. Many of the dwellings are second homes of New York City and New Jersey residents.

Hydrogeology

The general hydrogeologic framework within the Pepacton watershed is nearly flat-lying clastic sedimentary rock of Devonian age (Fisher and others, 1970) overlain by discontinuous glacial deposits and minor recent alluvium. Most of the upland subbasins are well drained and contain few lakes or wetlands.

Bedrock within this part of the Catskills includes cliff-forming sandstone and conglomerate units alternating with softer shale and siltstone units that result in a stepped pattern that is visible on steep hillslopes. Ground-water flow in the bedrock is chiefly through fracture openings. The ground-water flow system in upper hillslope areas is primarily within bedrock (the water table is within the bedrock, although perched water-table conditions can occur in overlying glacial deposits) and is most active within the upper 150 ft of rock (Heisig, 1999). The water table is within glacial deposits as they become thicker down slope toward the valley bottom. Bedrock underlying the valley bottom is completely saturated.

The glacial deposits typically mantle all but the steepest hillslopes and hilltops. Till is most common on hillslopes and valley bottoms in small upland subbasins. Stratified deposits (ice-contact deposits, outwash, and recent alluvium) generally increase in valley bottoms in the downvalley direction.

Till is the most widespread glacial deposit within the upland subbasins investigated in this study. It is an unsorted mixture of clay to boulder-sized materials, and deposits may reach thicknesses of nearly 100 ft (Fluhr, 1953). These deposits are typically thickest on the lower parts of south-facing hillslopes that were in the lee of advancing ice (Coates, 1966), and in upland valleys (Soren, 1963). Till is thin or absent on hilltops and on steep hillsides, particularly in high-relief uplands along the extreme eastern and southeastern boundaries of the watershed.

Ozvath (1985) reported on (1) textural differences among till deposits and (2) downvalley transitions from till to stratified deposits within small upland valleys of the western Catskill Mountains. Till on upper hillslopes is fine-grained (sandy silt to silty loam), compact, and lacks stratification. These deposits grade into looser colluvium on steep slopes. In contrast, till in the valley bottom and lower hillsides of upland valleys is typically coarser grained (loamy silt to silty sand) and less compact than that on the upper hillslopes, and commonly includes discontinuous lenses of stratified sediments. Ozvath (1985) interpreted the upper hillslope deposits as lodgement till (deposited by ice) and the lower hillslope and valley-bottom deposits as ablation till (deposited during melt-out of stagnant ice). Ablation till in the valley-bottom areas gradually transitions to stratified sediments in the

down-valley direction, as increasing drainage area gave rise to greater amounts of meltwater (and runoff) from stagnant ice.

Ground-water flow paths from bedrock in the hillslopes to glacial deposits and streams in the valley bottoms depend largely on the permeability of the glacial deposits. Deposits of low permeability (lodgement or ablation till) will likely shunt much of shallow ground-water flow from hillsides to land surface as spring discharges that flow to the valley stream (Burns and others, 1998; Heisig, 1999). Most hillside ground-water flow will remain in the subsurface as permeability increases in the valley bottom with the downvalley transition from ablation tills to more permeable stratified deposits. Ground water will discharge directly to the valley stream, rather than as springs on the lower hillsides. Differences in ground-water flow paths can affect ground-water chemistry, as explained further on.

Precipitation and Runoff

High relief (2,800 ft) within the watershed results in a wide range in annual precipitation and runoff among subbasins. Mean annual precipitation (1951-80) ranges from about 40 in/yr in the center of the watershed to about 55 in/yr at the highest elevations in the southeast corner (Randall, 1996). Runoff, the part of precipitation available for ground-water recharge and overland flow, can be as little as 22 in/yr in the center of the watershed and as much as 40 in/yr in the southeast corner (Randall, 1996).

Precipitation measurements at the National Weather Service station at Arkville (fig. 1) indicate that 2001 was a relatively dry year; annual precipitation was about 5 in. below the long-term annual mean (K. Eggleston, Cornell University Northeast Regional Climate Center, written commun., 2002). Monthly precipitation for April, May, October, and November 2001 was 22 to 65 percent lower than the 1948-2000 monthly means. These months are typically favorable for ground-water recharge. April recharge, however, was increased by a mid-month melting of a thick snowpack, especially in the higher elevations, that had persisted from March snowstorms.

Methods and Approach

Use of base-flow samples as a surrogate for ground-water discharge required definition of 'base-flow conditions' as a guide for sampling the small streams (10 mi^2 drainage area) used in this study. Base-flow conditions were defined by at least three consecutive preceding days with less than 0.25 in. total rain and no snowpack. Most late-winter and early-spring sampling was omitted to avoid the meltwater from the snowpack because of extended periods with above-freezing daytime high temperatures. Base flow can be diluted by meltwater under natural conditions, or it can be concentrated by the addition of road-salt leachate.

The East Branch Delaware River at Roxbury, NY stream-gaging station (01413088) was used as a reference site

(fig.1) for assessment of base-flow conditions and seasonal changes in base-flow discharge because none of the network sites were gaged. The Roxbury station was chosen because its small drainage area (13.5 mi^2) was closest in size to the network subbasins.

Sampling-Site Selection

Criteria for selection of sampling sites were based on physical characteristics of the upgradient drainage area. Subbasins were chosen to avoid lakes, wetlands, and point-sources of contaminants, such as wastewater-treatment plants and road-salt storage facilities. Discharges from any of these sources could alter the chemical composition of base flow so that it is not representative of ground-water discharge. The subbasins also were selected to collectively represent (1) the range in degree of till cover, bedrock exposure, and slope, and (2) three general types of land use—forested land with little or no residential development or roads, former farmland with low-density residential housing, and currently (2001) farmed land (primarily dairy farms). The farmed and formerly farmed land uses all had at least 45 percent forested area. 'Formerly farmed' refers to unforested land that was not used for row crops or as pasture for a dairy farm during the study. Information on subbasin characteristics (area, annual runoff, slope), nonpoint sources of contaminants (septic-system density, annual road-salt-application rates, manure production), land use (percentage of subbasin occupied by forest and cornfields), and site-naming conventions are provided in table 1.

Sampling and Analytical Procedures

Each of the 20 sites (table 1) was sampled four times—in December 2000 and in May, July, and October 2001). Three of these sites were used as land-use index sites — SEMNH (forested), ANGLH (dairy farmed), MRSNH (formerly farmed) — and were sampled as many as five times in addition to the four network surveys. The dates of network and index-site sampling are indicated on the streamflow hydrograph in figure 2.

The narrow width and shallowness of most of the streams required grab samples, but equal-width-increment samples (Shelton, 1994) were collected during the December 2000 sample survey at sites representing the two largest subbasins (WKVLY, RXBTK; fig. 1). Specific conductance, temperature, dissolved oxygen, and pH were measured in the field during sample collection. Dissolved oxygen and pH were not measured in about 15 percent of samples because of subfreezing temperatures and equipment failure. Stream discharge was measured at the time of sampling during the December 2000 and July 2001 surveys.

Base-flow samples were analyzed for major ions, dissolved organic carbon (DOC), iron, manganese, selected trace elements, and nutrients (dissolved nitrogen species

and dissolved orthophosphate) by the USGS National Water Quality Laboratory in Denver, Colo. Orthophosphate was included because an analytical technique with a low minimum reporting limit (MRL) of 0.007 mg/L was available.

All samples from the index sites, and a subset of 12 other sites in the December and July sample surveys were analyzed for dissolved agricultural pesticides and their degradates. The 12 sites included nine of the farmed subbasins and the remainder represented formerly farmed land or predominantly forested land.

Two analytical procedures were used for the pesticide analyses—the SH2010 method (for 47 pesticides and selected degradates) at the USGS National Water Quality Laboratory (Zaugg and others, 1995), and the LCAA method (for three degradates of chloroacetanilide herbicides) at the USGS Kansas Organic Geochemistry Research Laboratory (Lee and others, 2001). A list of all pesticides and pesticide degradates for which samples were analyzed is given in Phillips and Heisig (2004). The detection limits of the SH2010 and LCAA methods range from 0.001 to nearly 0.01 µg/L.

Replicate and field blank samples were collected for 13 and 8 percent of the samples, respectively. Results of these analyses met project data-quality objectives. Results of the laboratory analyses are given in Butch and others (2002).

Acknowledgments

Stream Base-Flow Chemistry - Responses to Hydrogeologic Factors and Nonpoint Sources of Contamination

Base-flow chemistry in small streams largely indicates the average chemistry of the discharging ground-water that

Table 1. Physical and land-use characteristics of stream subbasins in which base-flow samples were collected in Pepacton Reservoir watershed in southeastern New York, 2000-01.

[mi², square miles, in/yr, inches per year, ton/mi², tons per square mile per year. Sites in boldface are index sites and were sampled more frequently than other sites. Sampling-site and subbasin locations are shown in fig. 1.]

Site name*	USGS Station Number	Stream Name	Drainage area (mi²)	Runoff (in/yr)	Average basin slope (ft/mi)	Septic-system density (units per mi²)	Annual application or production rate (ton/mi²) Road salt	Livestock manure	Percentage of subbasin area Row crop	Forest
ANAND	1414840	Gladstone Hollow Brook near Andes	5.79	25.5	1,111	13.3	17.6	3.63	1.2	62.2
ANCBH	1414860	Campbell Hollow Brook	0.90	23.3	1,306	2.2	2.5	4.43	0.00	49.6
ANGLH	1414835	Gladstone Hollow Brook north of Andes	2.56	26.0	1,086	6.6	9.7	5.33	0.89	62.2
ARTIL	1414290	Mill Brook Tributary	1.96	27.8	1,301	1.5	0.5	0.00	0.00	93.7
DNCTH	1416870	Cat Hollow Brook	3.75	24.4	1,244	9.3	33.5	0.00	0.00	94.5
DNPP2	1416895	Pepacton Reservoir West End Tributary	0.38	24.0	1,178	5.3	0.0	0.00	0.00	98.1
FLLRK	1413343	Little Red Kill	0.79	25.9	714	29.1	7.5	0.00	0.00	85.5
FLRDK	1413346	Red Kill	5.52	26.0	1,143	11.6	2.7	0.00	0.00	85.5
MRBYB	1413990	Bryants Brook	4.39	24.1	1,238	9.1	26.1	1.92	0.00	77.3
MRSNH	1413930	Sanford Hollow Brook	2.50	25.9	1,207	23.2	3.1	0.03	0.00	77.3
MRWRH	1413920	Winter Hollow Brook	3.46	26.2	1,023	22.5	8.0	1.78	1.50	67.8
MRWVH	1413950	Weaver Hollow Brook	3.13	25.0	1,403	10.2	6.5	1.79	0.00	79.1
RXBTK	141309740	Batavia Kill	9.02	26.5	1,310	13.2	1.9	0.37	0.17	65.7
RXMGH	1413085	Montgomery Hollow	3.67	26.2	1,544	10.1	2.5	0.59	0.00	81.1
RXVGA	141309730	Tributary to Batavia Kill	1.67	26.1	1,098	20.4	3.0	0.00	0.00	46.9
SEHMB	1414280	Mill Brook	1.41	36.3	1,521	0.0	0.0	0.00	0.00	99.8
SEMNH	1413274	Rider Hollow Brook East of Mapledale	1.69	35.6	1,713	0.0	0.0	0.00	0.00	99.8
SERDH	1413276	Rider Hollow Brook near Mapledale	4.07	34.2	1,549	5.7	3.2	0.00	0.00	98.4
WKJSH	1413303	Vly Creek above Halcott Center	3.25	27.5	1,447	4.0	2.1	0.39	0.36	88.9
WKVLY	1413306	Vly Creek near Halcott Center	10.23	28.2	1,276	8.8	2.5	0.62	0.12	82.2

*Site Name - first two letters are an abbreviation of the USGS topographic quadrangle map in which site is located; last three letters are an abbreviation of the stream-valley (hollow) name or that of the nearest hamlet.
Topographic map names and abbreviations are as follows:

Andes (AN)	Fleischmans (FL)	Seager (SE)
Arena (AR)	Margaretville (MR)	West Kill (WK)
Downsville (DN)	Roxbury (RX)	
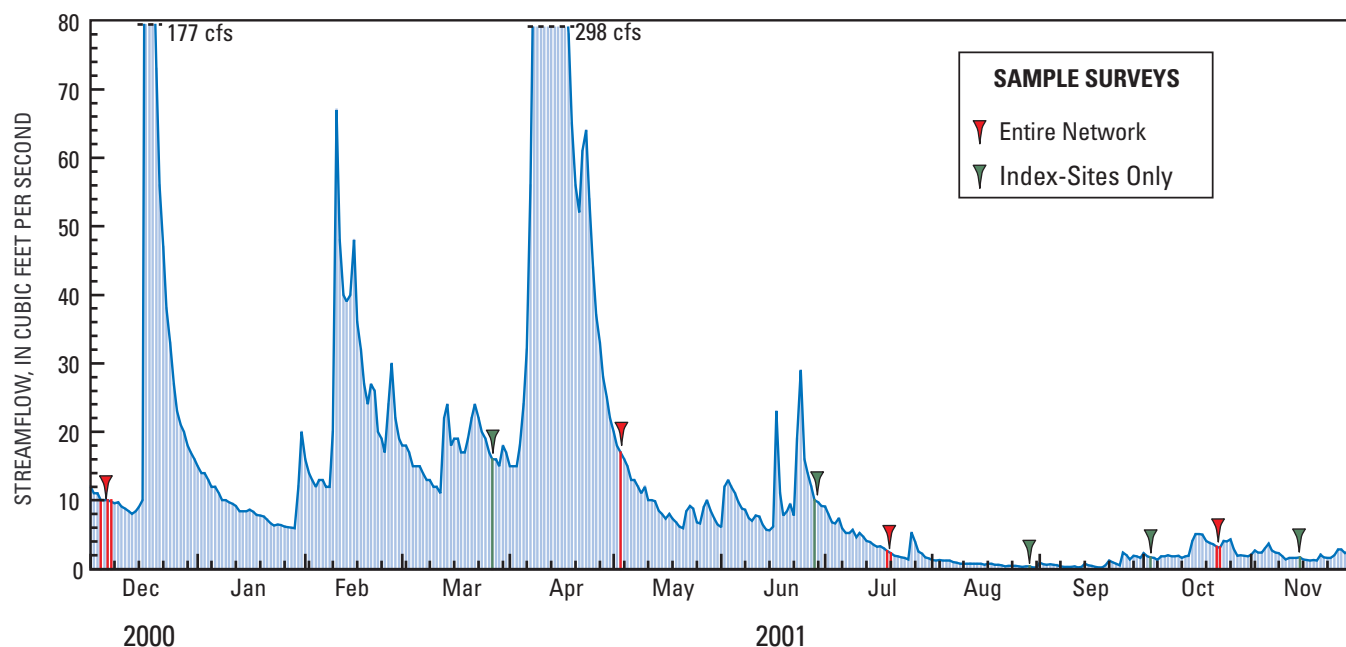
Figure 2. Streamflow at the East Branch Delaware River at Roxbury, N.Y. stream-gaging station (01413088) and sampling dates of network surveys and additional index-site surveys. (Site locations are shown in fig. 1.)

sustains streamflow. Ground-water chemistry, in turn, reflects the chemical changes along flow paths from water-rock interactions and from chemical additions to ground water from human activities (especially nonpoint sources). Water chemistry was evaluated by major-ion water type and by selected constituents associated with nonpoint sources within the study area.

Major-Ion Water Type

Major-ion concentrations of water samples classified as water types provide a useful framework for interpretation of the waters sampled in this study. Differences in relative ion concentrations among basins and within basins over time can indicate differences in relative ground-water residence time and changes in contributions to base flow from hillslope areas. These characteristics reflect the hydrogeologic framework underlying a stream basin. Water types are named for predominant ions (from highest to lowest concentration) that constitute at least 10 percent of the total cations or anions, respectively, in milliequivalents per liter. For example, calcium-magnesium-bicarbonate-sulfate ($Ca-Mg-HCO_3-SO_4$) waters are the most common water type identified in the study area. Water types determined at each stream site during each of the four sampling periods are shown in fig. 3.

Acid neutralizing capacity (ANC) values are herein converted to bicarbonate (HCO_3) concentrations for determination of chemical water-type. The pH range of the

samples indicated that bicarbonate was the primary source of acid-neutralizing capacity.

Hydrogeologic and Human Controls on Water Type

Ground-water chemistry, and by inference, the water chemistry observed in base flow, evolves as water moves through a ground-water flow system (for example, Back, 1966; Wunsch, 1993; Stuyfzand, 1999) (figs. 4A and 4B). This chemistry can be altered (especially in shallow ground-water) by downward leaching of contaminants from human activities, such as application of salt to roads.

Natural factors that control the degree of change in ground-water chemistry include the mineral composition, surface area, and permeability of the rock materials, and the hydraulic gradients and fracture interconnection within these materials. These factors affect the reactivity of the rock material and the residence or contact time of the ground water flowing through it. In general, unreactive materials and short contact times minimize changes in ground-water composition. Streams that maintain the same base-flow water type year-round (fig. 3) indicate short ground-water residence times and (or) unreactive rock material. Reactive materials and long residence times promote changes in ground-water composition.

Fractured bedrock is considered less reactive than unconsolidated deposits in the shallow ground-water flow

A. WATER TYPES AND SELECTED CHEMICAL CONCENTRATIONS

EXPLANATION

Water Types – each ion listed represents 10 percent of total cations or anions, respectively, in milliequivalents per liter. Sites in boldface are index sites.

Naturally occuring waters, or waters minimally affected by road salt

Dilute mixed-ion waters

Calcium - Bicarbonate - Sulfate $(Ca-HCO_3-SO_4)$

Calcium - Magnesium - Bicarbonate - Sulfate $(Ca-Mg-HCO_3-SO_4)$

Evolved bicarbonate waters

Calcium - Bicarbonate $(Ca-HCO_3)$

Calcium - Magnesium - Bicarbonate $(Ca-Mg-HCO_3)$

Road-salt-affected waters

Chloride and (or) sodium are 10 percent total cations or anions, but are not the most abundant ions

Same as above except chloride is the most abundant anion

Selected Chemical Concentrations –

Chloride ≥ 2 mg/L

51 ───Bicarbonate 25 mg/L

Specific conductance, in microsiemens/cm at 25°C

$\geq$ greater than or equal to

B. STREAMFLOW AT REFERENCE STREAM-GAGING STATION (ROXBURY)
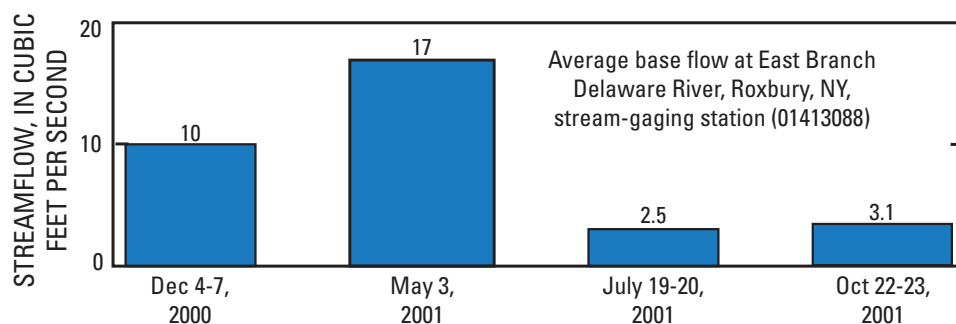
Figure 3. A. Major-ion water types and selected chemical concentrations for samples from four base-flow surveys, December 2000 through October 2001, compared with B. streamflow at the reference stream-gaging station. (Locations are shown in fig. 1.)

A. GROUND-WATER TYPE EVOLUTION

Natural Ground-Water Evolution →

Human-Induced Changes →

Ca-HCO$_3$-SO$_4$
Dilute mixed-ion waters
Ca-Mg-HCO$_3$-SO$_4$

Long ground-water flow path or reactive aquifer material

Ca-HCO$_3$
Evolved bicarbonate waters
Ca-Mg-HCO$_3$

Road salt application

Lime application on agricultural fields

Road salt application

Cl and (or) Na are defining ions

Ca-Mg-HCO$_3$

Cl and (or) Na are defining ions

Cl is most abundant anion

B. GROUND-WATER TYPE DISTRIBUTION AND FLOW

EXPLANATION

Ground-water types – listed ions are 10 percent of total cations or anions, respectively, in milliequivalents per liter.

Naturally Occurring

Dilute mixed-ion waters (Ca-HCO$_3$-SO$_4$)

Evolved bicarbonate waters (Ca-HCO$_3$)

Human Affected

Limed fields in agricultural areas (Ca-Mg-HCO$_3$)

Road-Salt affected (Cl and Na are defining ions)

→ Subsurface flow

⤳ Spring discharge

≥ greater than or equal to

Salted Roadway

Stream

Limed Field

BEDROCK

UNCONSOLIDATED MATERIAL
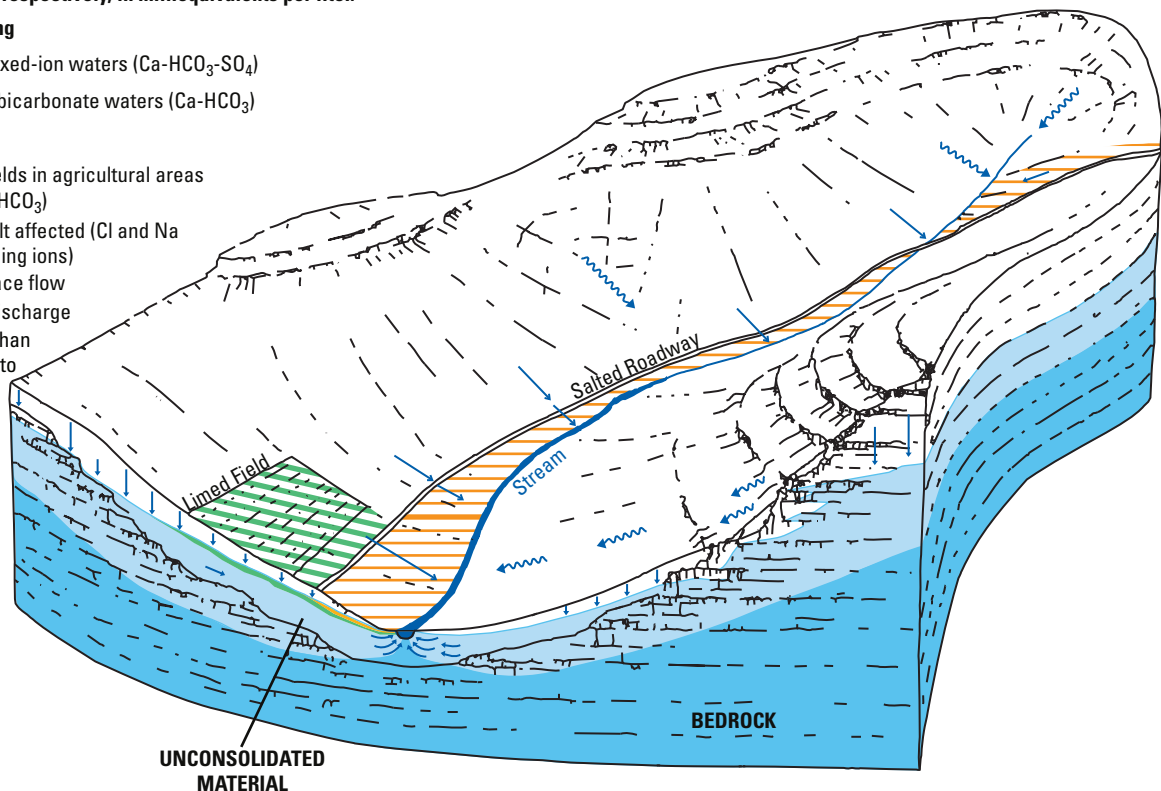
Figure 4. A. Conceptual model of shallow ground-water evolution from base-flow water-type determinations, starting with dilute mixed-ion water types and proceeding through natural and human-induced changes. B. Generalized stream basin depicting the hydrogeologic framework with ground-water flowpaths and the distribution of major-ion water types in ground water that discharges to the stream.

systems within the Pepacton watershed for several reasons. Fractures in bedrock have much less surface area than do pore spaces in unconsolidated materials, so there is less opportunity for water-rock reactions. In addition, minor amounts of (reactive) calcite in the bedrock (Gale and Siever, 1986) have likely been leached from the surfaces of shallow fractures. Till and other glacial deposits, however, may contain reactive materials such as carbonate-rock fragments transported from source areas to the north. Fractured bedrock is the primary pathway for ground-water movement on the upper, and typically steepest, slopes of most stream basins; steep gradients and high numbers of shallow, conductive fractures (Heisig, 1999) imply relatively rapid ground-water flow and short residence (or contact) times with aquifer material in these areas.

Bedrock at high elevations is probably the least reactive of all because large quantities of water flush the system and because soil leaching rates from acid rain are high. Total runoff, the part of precipitation available for ground-water recharge or overland flow within a basin, generally increases with basin elevation. The highest total annual runoff values among basins are nearly 50 percent greater than lowest values. High elevation also correlates with high soil leaching rates (losses of exchangeable base cations on soil exchange sites) in forest soils (Lawrence and others, 1999). Thus, large fluxes of water and high leaching rates in forest soils, coupled with thin till deposits and high hydraulic gradients in underlying fractured bedrock resulted in relatively dilute (and stable) ground-water and base-flow chemistry from the high-elevation subbasins (ARTIL, SEHMB, SEMNH, SERDH; fig. 1).

In contrast, the thickest unconsolidated deposits typically are on lower hillslope or valley-bottom areas, and low gradients in these deposits increase the likelihood of changes in water chemistry. Large subbasins in the network (8-10 mi^2; RXBTK, WKVLY; fig. 1) have the longest ground-water flow paths because the valley bottoms are relatively wide and are permeable enough to conduct most hillslope water to the stream through subsurface flow rather than surface flow. Flow through valley-bottom deposits with high surface area increases contact time with rock fragments, which increases the likelihood of a change to a more evolved water type prior to discharge as base flow.

The primary human control on base-flow water types is the addition of substances to the land surface that can be dissolved by precipitation, infiltrate through the soil, and join the shallow ground-water flow system. These substances include salt applied to roadways, manure applied to farm fields and, to a lesser extent, lime applied to farm fields (fig. 4B).

Naturally Occurring Water Types

Four natural water types were identified in base-flow samples. These water types consist of two water-type pairs, each pair including a dilute and an evolved water type. The difference between the pairs is the presence or absence of magnesium as a dominant cation (figs. 3 and 4). In both

figures, the calcium-only pair is represented by shades of blue and the calcium-magnesium pair is represented by shades of green. The dilute components, calcium-bicarbonate-sulfate (Ca-HCO_3-SO_4) and calcium-magnesium-bicarbonate-sulfate (Ca-Mg-HCO_3-SO_4) waters, are mixed-ion water types with relatively low specific-conductance values (figs. 3, 4A). Mixed-ion waters are typical of an initial water composition in ground-water flow systems (Back, 1966; Wunsch, 1993) and represent relatively short residence times and (or) flow through unreactive soil and aquifer material. The remaining two types, calcium-bicarbonate (Ca-HCO_3) and calcium-magnesium-bicarbonate (Ca-Mg-HCO_3), are evolved ground waters that represent increased residence times or short residence times in contact with more reactive soil or aquifer material. Dissolution of carbonate minerals (calcite or dolomite) in unconsolidated deposits, bedrock, or in the soil (associated with lime application) increase bicarbonate concentrations in these waters (reported as acid-neutralizing capacity (ANC)) to the point where bicarbonate becomes the only dominant anion (figs. 3, 4A).

Stream samples with Ca-HCO_3-SO_4 and Ca-HCO_3 water types drain basins with relatively high average slopes, high total runoff, high elevation, and thin, discontinuous till coverage. These basins border the eastern and southeastern edges of the watershed. The water type in two basins with these characteristics (SEMNH, SERDH; fig. 1) are exceptions; they are both characterized as a Ca-Mg-HCO_3-SO_4 water type (fig. 3). However, magnesium is a dominant cation only because calcium concentrations (3.2 – 4.6 mg/L) are exceedingly low in these subbasins of high total runoff, little till, high forested area, and high leaching rates. Waters from these basins are among the most dilute in this study (see specific-conductance data in fig. 3).

Samples of evolved Ca-HCO_3 water from site RXVGA, collected during high base-flow conditions, are unusual because the drainage basin is small. The basin is no longer farmed and has low-density residential development. Apparently, there is a more reactive natural or human-derived carbonate source in this area compared with other parts of the Pepacton watershed. Streams that drain two other small nearby basins (not part of this network) had similarly high calcium and bicarbonate concentrations, but their land uses were different. One basin had a lower density of residential development than RXVGA and the other was farmed.

Stream samples with Ca-Mg-HCO_3-SO_4 and Ca-Mg-HCO_3 water types drain subbasins in the northern and central areas of the watershed that have relatively low average basin slopes, which generally correspond to a high degree of till cover and, potentially, additional reactive carbonate minerals. In general, bicarbonate, calcium, and magnesium increased with decreasing average basin slope in the Pepacton watershed. Base flows from forested subbasins, however, consistently had lower bicarbonate values than subbasins with low percentages of forest area. Till appears to be a natural source of carbonate minerals, but in agricultural areas, liming of fields is an additional human-derived source. Elevated

magnesium concentrations in base flow from a forested subbasin such as DNPP2 (fig. 1) indicate that the magnesium is likely derived from a natural source.

Lime periodically applied to farm fields in the form of crushed limestone (D. Dewing, Cornell Cooperative Extension, Delaware County, oral commun., 2002) gradually dissolves and can infiltrate to the water table. Most farm fields tend to be in the lower elevations of a given agricultural subbasin (similar to roadways) so that the greatest influence of lime application on base-flow chemistry is during dry summer periods, when the forested-hillside area contributions to base flow are at a minimum. A farmed subbasin (such as ANGLH) shows greater increases in bicarbonate, calcium, and magnesium during these periods than an adjacent, formerly farmed basin (MRSNH; fig. 5). Addition of a reactive carbonate source to a basin can result in the development of a mature Ca-Mg-HCO$_3$ water type within a relatively short residence time (figs. 4A and 4B). Large bicarbonate increases (100+ percent) from high to low base-flow samples from farmed subbasin sites ANGLH and MRWRH suggest that lime is an additional source of carbonate. The May to July increase in bicarbonate at subbasin MRWRH was sufficient to change the water-type definition from a salt-affected type to a Ca-Mg-HCO$_3$ type (fig. 3); a similar shift is evident at site ANGLH in fig. 5.

Chloride- and Sodium-Affected Water Types

The fundamental difference among water types shown in figure 3 is the presence or absence of sodium and chloride as dominant ions (orange and red boxes). Sodium and chloride were not dominant ions in base-flow samples from forested, undeveloped areas; concentrations were typically less than 1 milligram per liter (mg/L). Human activities contribute most of the sodium and chloride detected in stream samples from this area. Application of rock salt (sodium chloride) on roads for deicing purposes is the primary source of these ions. Salt applied to roads dissolves and infiltrates soils with meltwater or rainwater in roadside areas. The water moves through the soil to the water table and joins the shallow ground-water flow system. As the ground water flows downgradient and ultimately discharges to the local stream, sodium and chloride are transported with it (fig. 4B). Chloride and sodium are among the dominant ions in water types from subbasins with state or county roads. The persistence of these water types at some sites throughout the year suggests that sodium and chloride are partly retained in the unsaturated zone and that subsequent recharge continues to transport these ions downward to the shallow ground-water flow system. Toler and Pollock (1974) documented retention of road-salt chloride in the unsaturated zone adjacent to a salted road, and other studies, among them Granato and others (1995) and
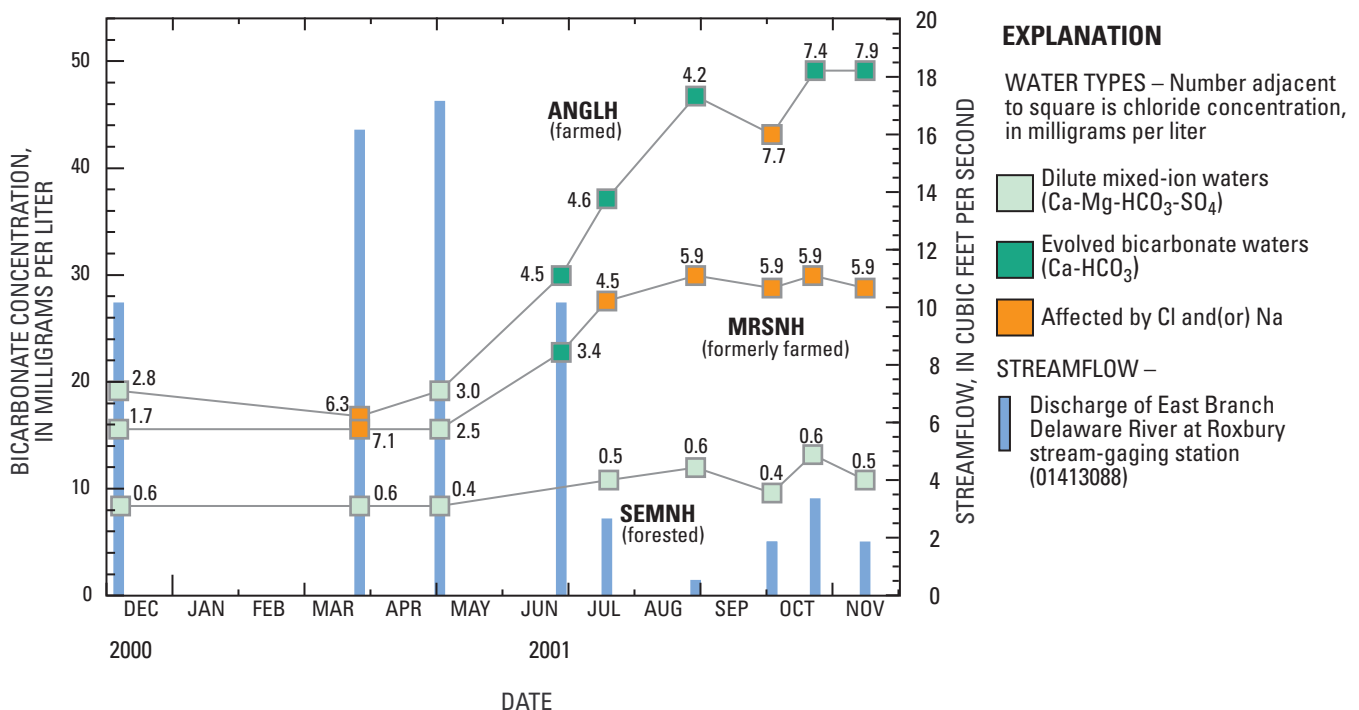

Figure 5. Bicarbonate (HCO$_3$) concentration at the three index sites over time, with the major-ion water type, chloride concentration, and corresponding daily mean streamflow from the reference stream-gaging station keyed to each sample. (Locations are shown in fig. 1.)

Jones and Sroka (1997), have documented the persistence of elevated chloride concentrations throughout the year in shallow ground water downgradient of salted roads. Stream base flows affected by the discharge of road-salt-contaminated ground water are discussed by Howard and Haynes (1997), Rosenberry and others (1999), and Heisig (2000).

Elevated sodium and chloride concentrations are not limited to the sites shown in red and orange on figure 3. All subbasins with salted roads have higher sodium and chloride concentrations in stream base flow than in streams from undeveloped subbasins. Samples that contain chloride concentrations of 2 mg/L or greater, regardless of water type, are likely affected by road-salt contamination and are noted in figure 3. Chloride and sodium concentrations are related to the salt-application rate (see following discussion of chloride and sodium; p. 13).

Chloride and sodium data effectively link land-use activities (source areas) and shallow ground-water quality to stream-base-flow quality, despite low concentrations. For example, the roadway in figure 4B shows the primary location of salt input within a hypothetical basin. Because most roads in the region parallel the local stream, road-salt-affected ground water is typically limited to an area between the road(s) and the local stream. Increases in chloride and sodium during dry periods imply that the percentage of ground-water contribution to streamflow from valley-bottom areas increases relative to that from forested hillside areas.

Implications of Spatial and Temporal Water-Type Variation

Changes in base-flow water type at network sites were common during the course of the study (fig. 3). Most of these changes paralleled a decrease in streamflow from high flows in the winter and spring to low flows in the summer and fall. Average daily discharges at the Roxbury, N.Y. station ranged from 2.5 to 17 cfs (fig. 3) for the four seasonal surveys and from 0.36 to 17 cfs for more frequent samples at the three index sites (fig. 5). Streamflow measurements at sampling sites were limited to the winter and summer surveys. Low discharges from the summer survey were a fraction (5 to 48 percent) of corresponding measurements from the winter survey. Summer-survey streamflow was 25 percent of the winter-survey streamflow at the Roxbury, N.Y. reference station.

Streams usually had mixed-ion water types during the winter and spring surveys; the remainder were moderately affected by road salt (chloride and sodium were among the dominant ions, but were not the most abundant) (fig. 3). As streamflows decreased during an especially dry summer and fall of 2001, about half the streams that started out with dilute, mixed-ion waters shifted to evolved waters or waters moderately affected by road salt; the other half remained the same water type. Streams moderately affected by road salt typically remained the same type or became highly affected (chloride was the most abundant anion).

Variations in base-flow water type resulted from changes in hillside and valley-bottom contributions to base flow and from the presence or absence of human activities. Two source areas of ground-water flow to streams are springs that drain hillside areas and diffuse ground-water seepage from valley-bottom deposits. Valley bottoms are narrow in V-shaped valleys (DNCTH, MRBYB) and are relatively broad in U-shaped valleys (MRWVH, MRWRH; fig. 1). The valley bottoms of larger subbasins (RXBTK, WKVLY) contain stratified deposits. Hillside springs represent ground water derived primarily from high-gradient flow (short residence time) in fractured bedrock. This geochemical environment is relatively unreactive, resulting in a dilute mixed-ion contribution to streamflow. Hillside areas are also generally forested, which minimizes human activities and associated chemical changes. Thus, in small subbasins dominated by hillside sources and with little human activity (SEMNH, for example), base flow consistently was a dilute mixed-ion water type (figs. 3 and 5). Seven of the twenty streams in the network (fig. 3) had a single water type during this study.

Base flow in most larger subbasins became an evolved water type or a water type affected by human sources as the relative contribution from hillside source-areas decreased and valley-bottom source areas increased. Water in hillside (upland) areas, which account for the majority of the land area in all subbasins, is the dominant source of water (mixed ion) to streams during high base-flow periods (late fall, early winter, and spring; fig. 3). Permeable shallow bedrock in hillsides progressively drains as conditions become drier during the growing season, which reduces the hillside source contribution to the local stream. Direct upland-flow contributions to main-valley streams are also diminished by infiltration through streambeds as tributaries enter larger valleys (Randall, 1978). Ground-water contributions to base flow from valley-bottoms therefore increase (as a percentage of base flow) as upland water sources decrease. Base flow from the largest subbasins without major roadways shifts to an evolved water in which bicarbonate is the single dominant anion. This change occurs through either natural ground-water evolution along a flow path or possibly through dissolution of lime on agricultural fields (figs. 4A and 4B). Base flow from other large subbasins with more heavily salted roadways shifts to a salt-affected water type.

Selected Constituents Associated with Nonpoint Sources

Nonpoint-source contributions from four sets of constituents were evaluated with respect to their production or application rates within the subbasins in an effort to define relations between base-flow quality and land-use practices. The constituents included: chloride and sodium, nitrogen species, orthophosphate, and herbicides. Chloride and sodium were chosen because they are widely applied as road salt and because chloride, a conservative ion, provides a basis for comparison with less conservative constituents. Nutrients

(nitrogen species and orthophosphate) are indicators of animal and human wastes and commercial fertilizers and can cause nuisance algal growth in streams and lead to eutrophication of lakes and reservoirs. Nutrient inputs from streams are a water-quality issue for several of New York City's water-supply reservoirs, including the neighboring Cannonsville Reservoir (New York City Department of Environmental Protection, 2002). Herbicides are associated with row-crop cultivation and are of concern because they can adversely affect aquatic life and drinking-water quality. No samples exceeded any state or federal drinking-water standards.

Four nonpoint sources were quantified within each subbasin: 1) deicing salt applied to roadways, 2) domestic wastewater disposed of in septic systems, 3) livestock waste applied to land surface (primarily from dairy farms), and 4) herbicides applied to row-crop fields. Each constituent was plotted in relation to subbasin production or application rates and the results are discussed in the sections that follow.

Chloride and Sodium

Leachate from road salt applied during the winter can infiltrate the unsaturated zone, reach the water table, and flow to nearby streams, resulting in elevated chloride and sodium concentrations in base flow throughout the year (figs. 3, 4A, and 4B). The annual rate of road-salt application in each subbasin was calculated from data provided by the New York State Department of Transportation (NYSDOT), Delaware County, and six town highway departments. The data included road-salting practices, annual salt usage, road types, and road mileage.

Because it is relatively inexpensive, sodium chloride (rock salt) is the primary road-deicing product used by all highway departments in the Pepacton watershed. Some departments use other types of salt as a supplement; for example, NYSDOT and one town use liquid magnesium chloride as a "dressing" on mixtures of sand and salt to prevent it from freezing and to provide immediate deicing action on roads. The Delaware County Department of Public Works uses solid calcium chloride as an additive on county roads (W. Reynolds, Commissioner, Delaware County Department of Public Works, oral commun., 2001). All departments except NYSDOT use sand or cinders mixed with salt on paved roads; NYSDOT uses salt only. The highest annual road-salt-application rates per mile of two-lane paved road were 40 ton/mi by NYSDOT and 32 ton/mi by Delaware County; the lowest rates were between 1 and 12 ton/mi by the towns.

Dirt roads are common in most towns, but salt application varies among highway departments. Some departments use only sand because salted dirt roads can become rutted; others apply the same amount of salt as on paved roads.

Estimation of the total salt tonnage annually applied in each subbasin was limited to sodium chloride because it was the most extensively used deicing material and was the most easily quantified. Annual application rates for each type of road (state highway, county road, or town road (paved and dirt)) were multiplied by the respective road lengths and summed for each subbasin. These totals were then divided by the corresponding subbasin areas to determine the annual salt application (tons) per square mile of each subbasin (table 1) to facilitate comparisons among subbasins. Subbasins SERDH and ARTIL were omitted from the calculations because the reported application practices and amounts of salt usage were uncertain; this, coupled with low road density, would have given unreliable estimates. Also omitted were the subbasins with no roads (SEMNH, DNPP2, SEHMB) because zero values could not be plotted on the natural log scales used in the scatterplots.

Log base-flow concentrations of chloride and sodium are positively correlated with the log of annual salt-application rates per square mile of subbasin in each of the four network base-flow surveys (fig. 6). This not only corroborates the more general water-type results presented earlier—it indicates that road-salt leachate entering a local, shallow ground-water flow system has a predictable effect on stream base-flow chloride (and sodium) concentrations. Sodium concentrations are similar to those of chloride where little or no salt is applied and less than chloride in basins with the highest application rates (fig. 6). Cation exchange of sodium primarily for calcium likely accounts for the relatively low sodium concentrations in basins with the highest salt application rates (Shanley, 1994).

Although sodium and chloride concentrations in all base-flow samples were not of concern from a drinking-water-quality perspective, the correlation between salt-application rates and the concentrations of sodium and chloride in streams (fig. 6) indicates a direct link between human-derived nonpoint-source contaminants applied at land surface and the quality of shallow ground-water discharge and stream water. This link provides a basis for evaluating the potential for transport of other nonpoint-source contaminants to streams.

Base-flow chloride concentrations increased with each sampling survey from December 2000 through October 2001 (fig. 7). In general, the lowest concentrations corresponded to the highest base flows (December and May), and the highest concentrations corresponded to the lowest base flows (July and October). High base flows include a larger component of flow from mostly forested hillside areas than do low base flows, which are primarily derived from valley bottom areas, where road-salt application is typically concentrated.

The May chloride concentrations in subbasins with high salt-application rates equaled or exceeded those of December, even though the May discharges exceeded the December discharges, and thus provided a greater potential for dilution. In contrast, the May concentrations in subbasins with low salt-application rates were similar to the December concentrations (fig. 7). Chloride concentrations from stream basins with high salt-application rates were higher in May than December because recharge of water containing road salt near streams is likely saltier after the winter period of salt application (May) than before it (December). The low (background) December and May concentrations in basins with low salt-application
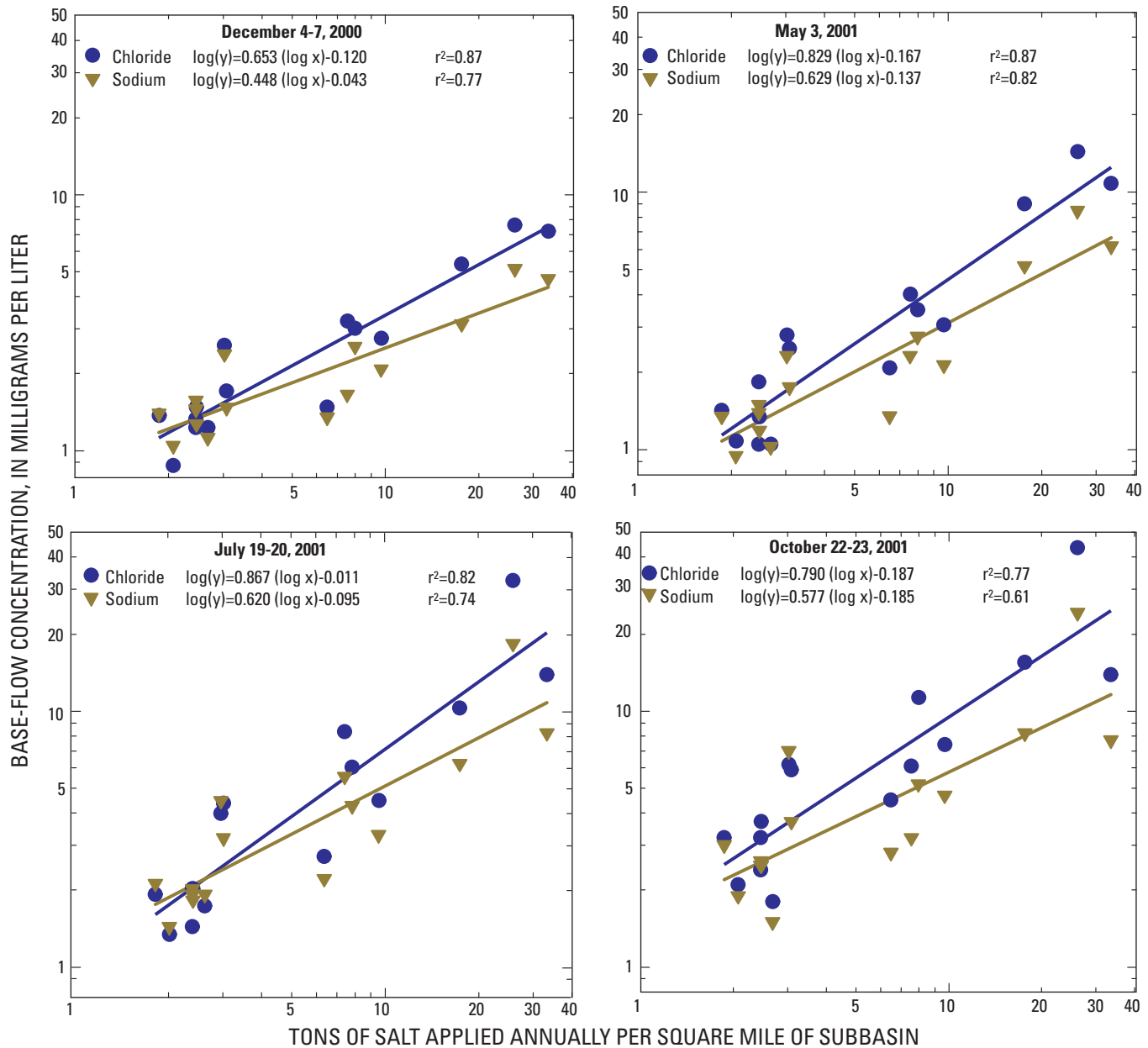
Figure 6. Base-flow concentrations of chloride and sodium as a function of annual road-salt-application rate in each subbasin during the four network sample surveys, Pepacton Reservoir watershed, southeastern New York, December 2000 through October 2001.

rates are consistent with the relatively small amount of salt applied and the large amount of dilution provided by uncontaminated water from forested hillside areas.

In summary, the strong relations between road-salt use and base-flow chloride and sodium concentrations imply that land use, shallow ground-water quality, and stream base-flow quality are intimately connected within the Pepacton watershed. Flow-based variations of base-flow chloride reflect the predominance of roads (and road-salt inputs) in valley-bottom areas and the natural variation of base-flow water contributions from hillside areas.
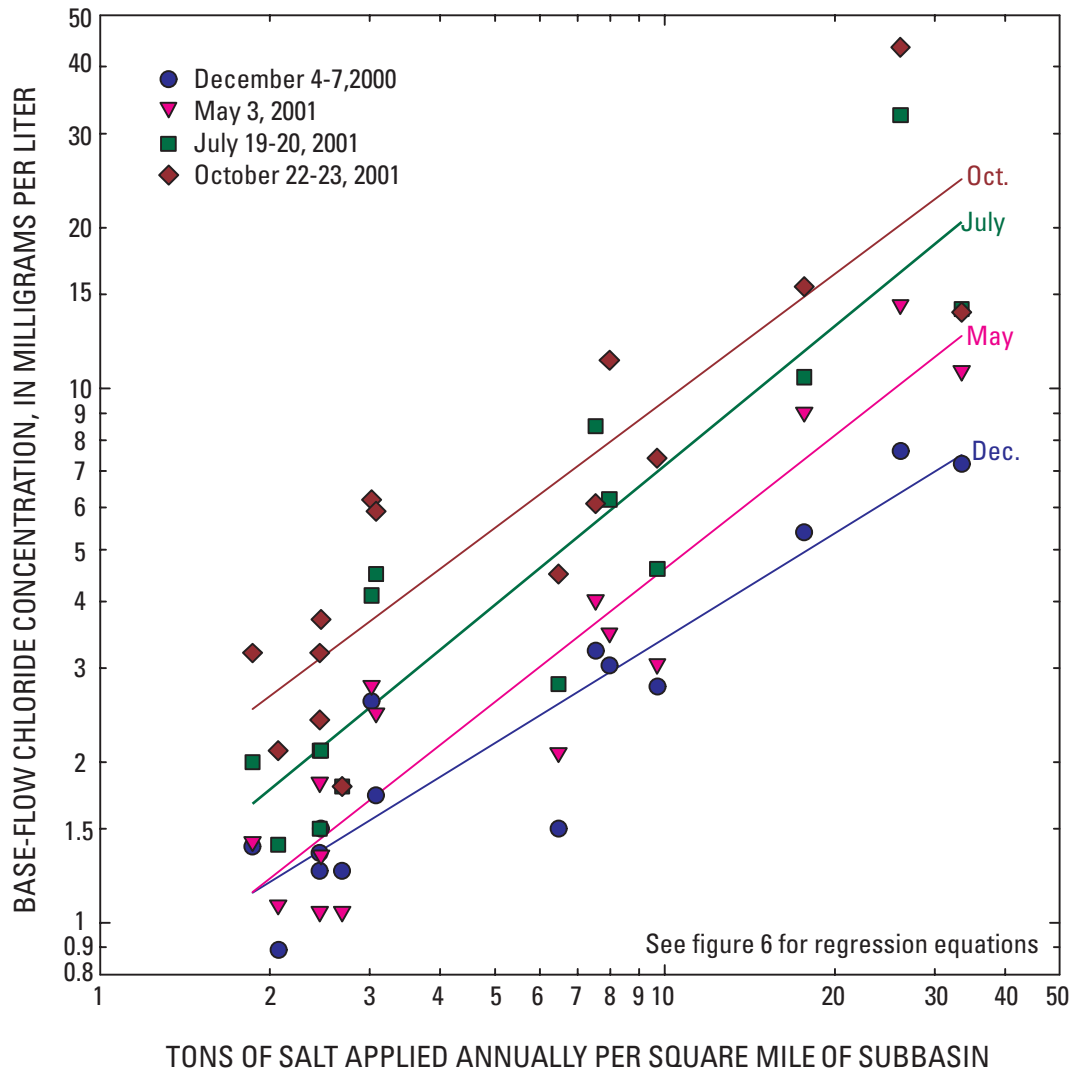
Figure 7. Comparison of base-flow chloride concentration as a function of subbasin annual salt application rate among the four network sample surveys, Pepacton Reservoir watershed in southeastern New York, December 2000 through October 2001.

Nitrogen Species

Nitrogen (N) cycling in the environment is complex, as there are many biologically mediated pathways for uptake and transformation. The nitrogen (as N) analyses of base-flow samples encompassed (1) nitrite and nitrate, (2) nitrite, (3) ammonia and organic nitrogen (organic N), and (4) ammonia. All nitrite and ammonia concentrations were below the minimum reporting levels (0.06 and 0.04 mg/L, respectively) except at the farmed site ANGLH on June 28, 2001, when nitrite was detected. Therefore, the nitrite-and-nitrate analyses

and the ammonia-and-organic-N results are referred to as "nitrate" and "organic N", respectively.

Characterization of Nitrogen Sources

Sources of N to ground water and stream base flow in the Pepacton watershed include: 1) atmospheric deposition, modified by vegetation, 2) leachate from septic systems, and 3) manure and other fertilizers applied to land surface. All are considered nonpoint sources and are described further on in relation to base-flow N concentrations.

Atmospheric Deposition, Nitrogen Saturation, and Nitrogen Depletion

The northeastern United States has high rates of atmospheric N deposition, and the Catskill Mountains have among the highest N-deposition rates in the Northeast (Ollinger and others, 1993). The N is derived from many pollution sources, including powerplant and automobile emissions, and is deposited on the land surface as wetfall and dryfall. A state of N saturation can be reached if the deposition rate exceeds the demand of the forest vegetation (Agren and Bosatta, 1988; Aber and others, 1998). N saturation results in the leaching of excess nitrate to streams.

Forested watersheds with a history of forest cutting or burning can apparently have long-term N deficits (Aber and Driscoll, 1997; Goodale and others, 2000). Lovett and others (2000) suggested that differences in forest tree-species composition, which may be a response to forest history, may also affect nitrogen output to streams in the Catskill Mountain region. They found the lowest nitrate levels in forested watersheds where red oak is a dominant species. These watersheds were probably subject to long-term human disturbance (harvesting, fire) because they were accessible, on the fringes of the Catskill Mountains and at low elevations.

In general, mature or declining forests are more likely to show N saturation and high rates of leaching than growing, immature forests or open fields on former farmland (Aber and others, 1998). Former farmlands, which make up a large part of the watershed, are likely to have N deficits and contribute low N concentrations to streams after many years of crop harvests followed by forest regrowth (Zak and others, 1990). Thus, atmospheric N deposition most likely increases N in streams that drain predominantly forested subbasins within the Pepacton watershed. These increases in base-flow concentrations were likely to be small because most N export occurs under high-flow conditions. The percent forested area of each subbasin is listed in table 1. Base-flow nitrate concentrations in forested subbasins were expected to be lower than in subbasins with agricultural or septic-system N sources.

Septic-System Wastewater

Human waste that enters the unsaturated zone from septic systems is a source of nitrogen to ground water (Robertson and others, 1991). Septic effluent initially contains reduced forms of nitrogen (ammonia and organic N), but these are largely transformed to nitrate through microbial action in the presence of oxygen within the unsaturated zone if allowed sufficient time. Nitrate is relatively stable in oxygenated, shallow ground water and, barring denitrification, particularly in organic-rich near-stream sediments, it is eventually discharged to local streams. A recent study of small streams in New York City's Croton watershed indicated that septic-system density (up to 1,000 systems/mi^2) in stream drainage areas was positively correlated with base-flow nitrate concentration (up to about 3 mg/L as N (Heisig, 2000).

Estimates of septic-system density (number of systems per square mile of drainage basin) within each of the subbasins (table 1) were derived from digital-ortho-quarter-quad imagery (DOQQs) and field verification. All subbasins had low septic-system densities of fewer than 30 systems per square mile. This density (30 systems/mi^2) did not raise nitrate concentration in base flow above the range of background concentrations (for zero or near-zero system densities) in the Croton watershed (Heisig, 2000). Estimates of nitrate concentration in base flow based on septic-system-density within the Pepacton watershed also would exaggerate the nitrate contribution in base flow because many of the homes are second homes that have only periodic use. Despite no measurable basinwide response in base-flow nitrate to low septic-system densities, the quality of shallow ground water immediately downgradient from individual septic systems (acting as point sources) is degraded by septic effluent (Robertson and others, 1991; Ptacek, 1998; Wilhelm and others, 1994; and Morrill and Toler, 1973).

Manure and Commercial Fertilizers

Manure (livestock waste) and commercial fertilizers can be important sources of nutrients to streams draining agricultural watersheds (Gburek and Folmar, 1999; Jordan and others, 1997; and Owens and others, 1992). Nitrate is the dominant form of N exported in stream base flow. The most commonly used fertilizer within the Pepacton watershed is manure from dairy farms; this constitutes about 90 percent of the total amount of fertilizer applied within the watershed (D. Dewing, Cornell Cooperative Extension, Delaware County, oral commun., 2002). Commercial fertilizers account for the remaining 10 percent. Herein, manure refers to livestock waste, in solid and liquid forms. Manure generated in barns during the nongrowing season is spread on row-crop fields or on pastures. Feedlots likely receive manure year-round. Pastures also receive manure directly from grazing cattle during the growing season, as do streams that flow through pastures or between barns and pastures.

The assessment of livestock density within the subbasins entailed sending survey forms to dairy farmers and following up as necessary with phone calls or field visits. Other types of livestock were assessed through field surveys. Estimates of annual manure production for different age and size cows and other livestock were based on, or interpolated from, data presented in Midwest Plan Service (2000). Annual manure-production estimates for all livestock within each subbasin (in tons) were totaled and divided by the number of square miles within the respective subbasin, to obtain the annual rate (table 1). Manure production was highest among subbasins with dairy farms, because dairy cows are the primary source of manure. The highest annual rate was about 5 tons per mi^2.

Biological Uptake and Transformation of Nitrogen in Streams

Nitrogen concentrations in stream base flow represent source concentrations decreased to varying extents by biological processing during: (1) infiltration from source areas to the ground-water table, (2) ground-water transport, and (3) discharge to streams through streambeds (the hyporheic zone, which is immediately beneath or adjacent to the stream channel). Microbially mediated denitrification, with net transformation of nitrate to nitrogen gas (lost to the atmosphere), is possible within aquifer material or the hyporheic zone where sufficient organic material is present. Once in streams, nutrients such as nitrate can be removed through uptake by macrophytes, algae, and microbes. The degree of growth and nutrient uptake by autotrophs, such as diatoms, green algae, and cyanobacteria, is dependent on factors such as: scour, light, nutrients, temperature, current, and substrate (Allen, 1995). Microbial activity increases with increased organic matter (leaf litter) entering streams (Mulholland and others, 1985). Seasonal changes in these factors result in variable N removal from stream water and thus variable N concentration in base flow over an annual cycle. Burns (1998) estimated in-stream nitrate losses, with some seasonal variation, in two reaches of a Catskill Mountain stream.

Base-flow N that is retained in stream biomass is most likely transported by stormflows that induce scour and dislodge algae, leaf litter, and microbes.

Base-flow concentrations of nitrate in streams of the Northeast show a seasonal pattern that appears to be generally consistent, regardless of local land use. Base-flow nitrate concentrations tend to be highest from December through April, when low temperatures and minimal daylight suppress biological activity. Nitrate concentrations from May to early October are generally lower than in the winter period and may progressively decrease as temperatures warm and biological activity increases (denitrification, uptake of nutrients). The lowest concentrations of the year typically occur during the few weeks immediately after leaf fall (Murdoch and Stoddard, 1992; Allen, 1995), when the addition of leaf organic matter spurs microbial activity in streams. This seasonal pattern has been observed in a variety of settings in the Northeast—in forested watersheds (Murdoch and Stoddard (1992) and Goodale and others (2000)), in agricultural watersheds (Owens and others (1991), Owens and others (1992), Wall and others (1998), and Pionke and others (1999)), and in suburban watersheds (D. Borchert, New York City Department of Environmental Protection, written commun., 2000).

Dissolved Organic Nitrogen and Nitrate in Base Flow

Different seasonal variations in organic-N and nitrate concentrations are evident in the base-flow samples. Nitrate concentrations show the seasonal pattern described above and show the strongest correlation with manure production

in the December 2000 stream survey. Organic-N and nitrate concentrations were relatively low; the highest organic-N concentration was 0.29 mg/L as N. The highest nitrate concentration was 1.1 mg/L as N. This nitrate concentration is much lower than the maximum base-flow nitrate (about 3 mg/L) measured in suburban subbasins with high densities of septic systems in the Croton Watershed (Westchester and Putnam Counties, New York (Heisig, 2000)). A base-flow nitrate concentration of 1.1 mg/L (as N) would correspond to a suburban subbasin with a low to moderate septic density (about 300 septic systems/mi^2).

Nitrate, organic-N, and stream-temperature base-flow data for the three index subbasins are shown in figure 8 along with corresponding flow data from the East Branch Delaware River station at Roxbury, N.Y. The subbasins represent the best examples of three distinct land-use associations within the Pepacton watershed: 1) SEMNH represents forested, with no development, 2) ANGLH represents farmed (dairy farms), with some forest and residential development, and 3) MRSNH represents former farmland, with low-density residential development, forested areas, and minor (non-dairy) livestock.

Organic Nitrogen

Elevated organic-N concentrations in surface water or ground water are generally considered an indicator of organic waste (Hem, 1985) or a wetland source. Organic N was detected only in samples from the farmed index subbasin (ANGLH), except for one winter sample from the formerly farmed index subbasin (MRSNH). No organic-N was detected in the samples from the forested index subbasin (SEMNH). The primary source of organic N in the ANGLH samples is probably manure because this subbasin contains no wetlands. Seasonal concentrations in this subbasin varied by as much as 100 percent. The highest concentrations were in winter and summer samples, and the lowest were in the spring and fall samples (fig. 8).

The seasonal changes in organic-N concentration at the ANGLH site (fig. 8) reflect the seasonal changes in contributions to base flow and in microbial activity. The high winter concentrations presumably resulted from the suppression of microbial decomposition by low temperatures, and the spring decrease probably resulted from dilution by the large, dilute upland base-flow component, which would have contained no manure. In addition, the rising stream-water temperature in May (fig. 8) would have spurred microbial activity and thereby lowered the organic-N concentrations. The summer organic-N concentrations were highest in late June and July, then decreased until early October, when they reached a secondary peak. The lowest concentrations of organic N were reached during late October and early November, when microbial activity increased in response to leaf litter in the stream (Murdoch and Stoddard, 1992; Allen, 1995).

Warm-weather increases in organic-N concentration coincided with (1) the proportionate increase in the ground-
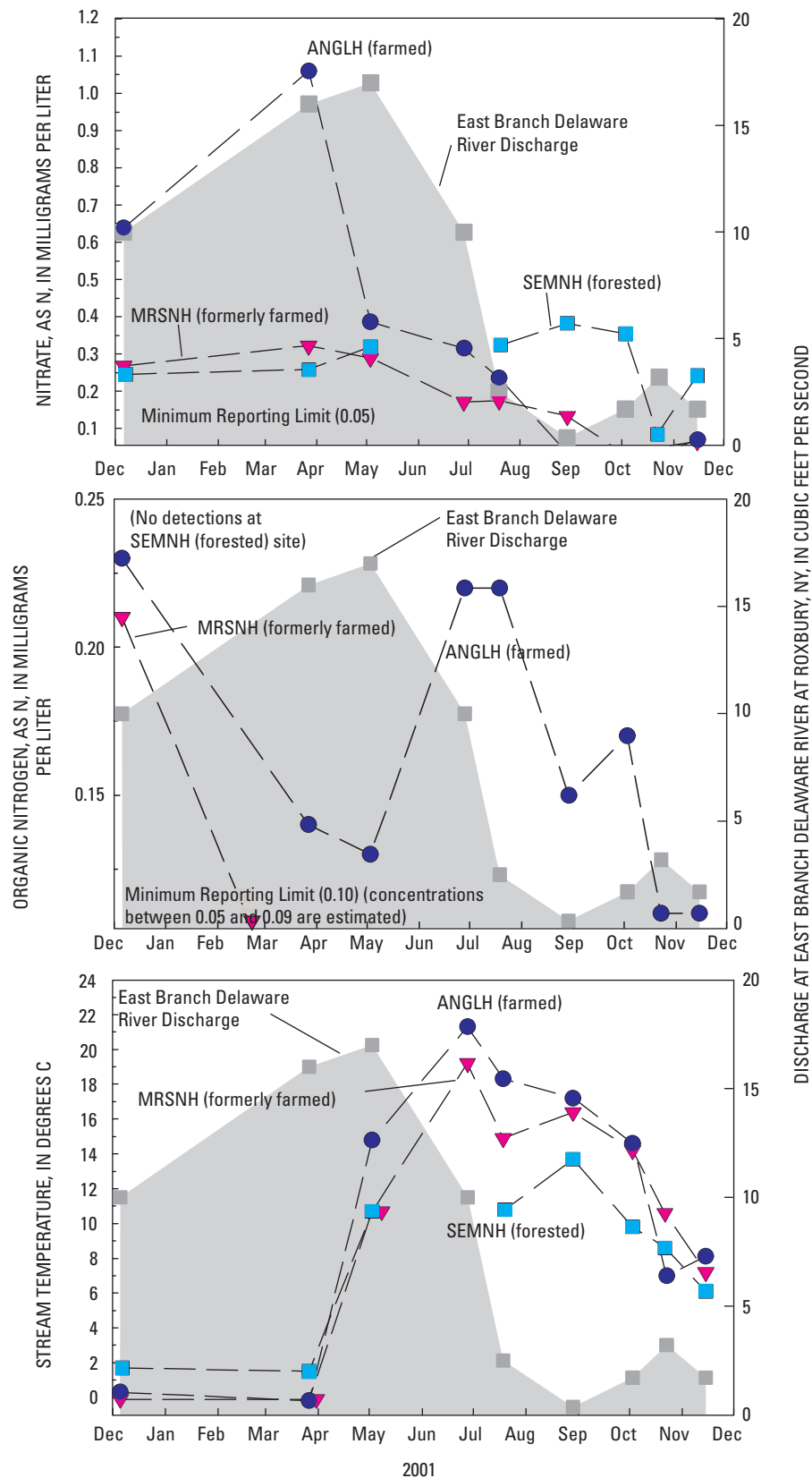
Figure 8. Nitrate concentration, organic nitrogen concentration, and stream-water temperature at the three index sites (ANGLH, MRSNH, and SEMNH) during base-flow conditions, and discharge of the East Branch Delaware River at the reference stream-gaging station at Roxbury, N.Y., December 2000 through November 2001. (Locations are shown in fig. 1.)

water contribution to base flow from valley-bottom areas as the hillside contributions decreased, and (2) increased livestock defecation close to or directly into the stream during grazing or while moving to pasture. Increases in dissolved manganese, iron, and DOC (dissolved organic carbon, possibly from manure) at ANGLH during late June and July indicated the discharge of anoxic ground water from at least part of the valley bottom area to the stream. The organic-N concentration was positively correlated with DOC concentration.

The data from this study indicate a direct association between organic-N concentrations in streams and farmed subbasins. The maximum organic-N concentrations were in December 2001, but elevated concentrations were most widespread in July. Organic N constituted the smallest percentage of total dissolved N (nitrate plus organic N) in May, when nitrate concentrations were decreasing, and drainage from uncontaminated hillside sources was greatest, and constituted the largest percentage of total N in October, when nitrate concentration was at a minimum. The month in which the largest number of nonfarmed subbasins (three) had measurable organic-N concentrations was December. One of these subbasins (FLLRK, table 1) contains a small wetland that could be the source of organic N (and DOC). Organic N was detected most frequently at the six farmed subbasins in which annual manure production was greater than 1.75 ton/mi^2. Measurable concentrations of organic N were detected in samples collected from three or four (50 or 66 percent) of these six sites in December, May, and October, and in the samples collected from all (100 percent) of these sites in July.

Nitrate

Nitrate concentrations varied among the three index sites (fig. 8). The highest concentrations occurred at the farmed index site (ANGLH) during the relatively high flows of winter and early spring, when biological activity was at a minimum. The highest concentration, in March, may have been partly due to prior snowmelt from farmed areas of the subbasin. Nitrate concentrations at the formerly farmed and forested index sites were similar to one another through the winter, and these concentrations were among the highest measured at the formerly farmed site.

Nitrate concentrations in the high early-May base flows that followed snowmelt were similar among the three index sites; therefore, the dominant streamflow component in all three subbasins at that time probably was drainage from the forested hillside areas. Increases in stream-water temperature and growth of algae before leaf-out may partly account for the subsequent early-spring decrease in nitrate concentrations at the farmed subbasin.

The farmed and formerly farmed index sites (ANGLH and MRSNH) showed a progressive decrease in nitrate concentrations from summer to early fall, but the forested index site (SEMNH) showed a gradual increase (fig. 8). The decrease at the farmed and formerly farmed index sites may

be due to the open fields and minimal shade, which would allow sunlight to increase the water temperature and in turn enhance algal growth and promote other biological activity, both of which decrease nitrate concentrations (fig. 8). Algal growth at the farmed index site would be further favored by a greater supply of nutrients than at the other sites; biological uptake at this site lowered the nitrate concentrations to below the reporting limit from late August through early October. In contrast, the base-flow nitrate concentration at the formerly farmed index site was below the minimum reporting limit only in early October.

The forested index site, which receives minimum light and had the lowest water temperature and the poorest nutrient availability, showed a slight increase in nitrate concentrations during the summer and early fall. This observation may reflect a relative increase in headwater spring contributions during dry periods. Late fall or spring recharge that has flushed excess soil nitrate to shallow, fractured bedrock (Murdoch and Stoddard, 1992) results in relatively stable summer headwater spring discharges (Burns and others, 1998) with somewhat elevated nitrate concentration. Stable or increasing nitrate during the summer at the forested index site (SEMNH), whose subbasin has high relief and headwater springs, suggests little net uptake of nitrate by algal growth in the stream.

The seasonal patterns in base-flow nitrate concentrations at the index sites were also observed at the other streams in the network—a general decrease from December 2000 through October 2001. The largest decline was after leaf fall during late October, when nitrate concentrations were at or below the minimum reporting limit of 0.1 mg/L as N in 60 percent of the samples.

Nitrate Concentrations in Relation to Nonpoint Sources

Base-flow nitrate concentrations for each of the four sampling surveys were plotted in relation to annual manure-production rates (fig. 9), and all sites were grouped by amount of forested subbasin area (table 1)—greater than 90 percent, 75 to 90 percent, or less than 75 percent. Subbasins with the highest percentages of forest area are most likely to be N-saturated and export excess nitrate. Base-flow nitrate concentrations are affected by manure production, although the effects are masked by biological activity during the warm weather months and following leaf off in the fall. The regression lines shown for December 2000 and May 2001 in figure 9 are based on only farmed-subbasin data (basins with manure production) and are included for comparison with the forested- and formerly farmed-subbasin nitrate data. The results from each of the four sample surveys are discussed in chronological order below.

December 4-7, 2000. These samples provided the closest representation of nitrate concentrations in shallow ground water because biological activity was minimal in the streams at this time (fig. 9). The predominant source of nitrogen was manure, and the base-flow nitrate concentration showed a positive linear correlation with annual manure-production
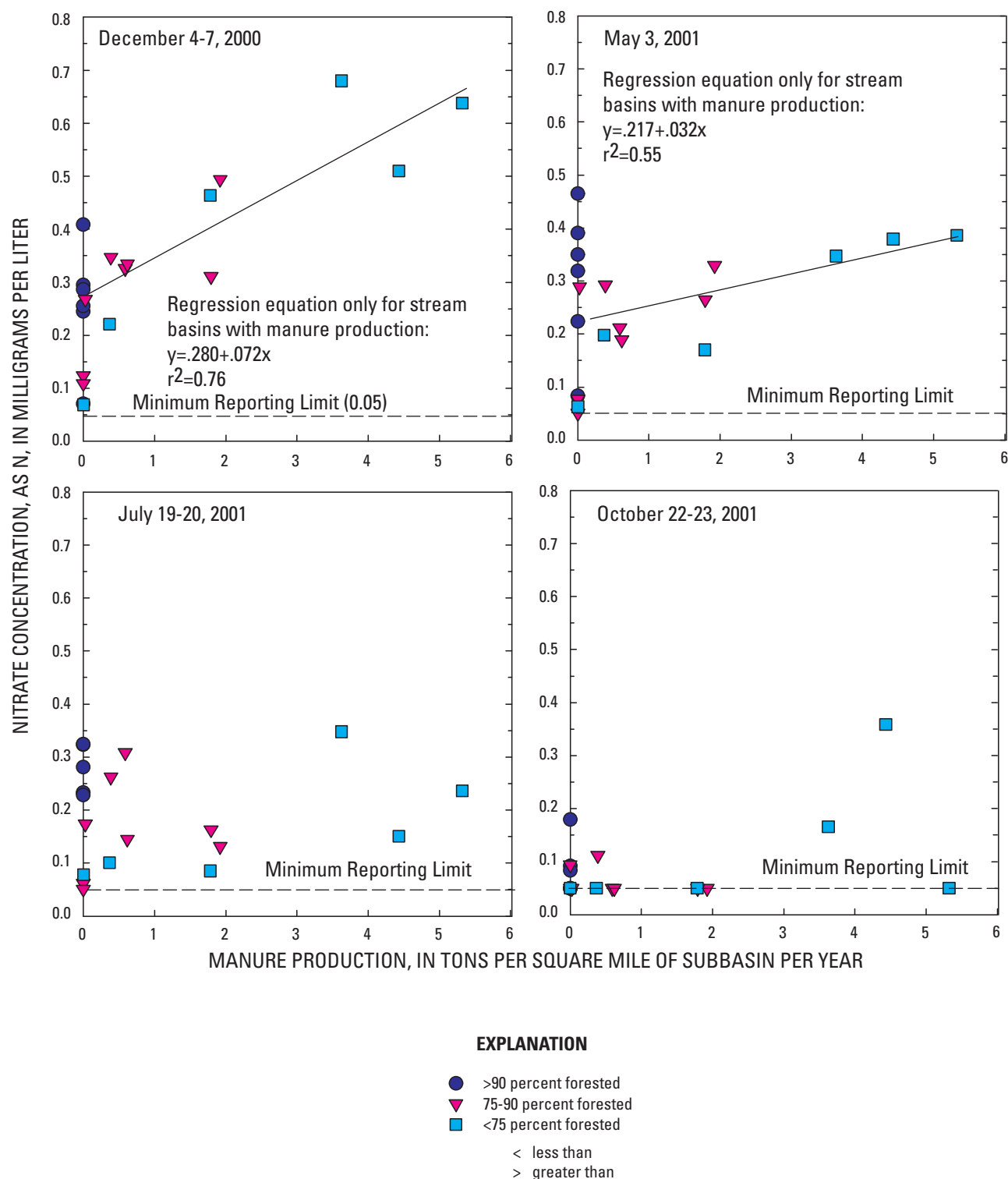
Figure 9. Base-flow nitrate concentration as a function of annual manure-production rate in sampled subbasins of the Pepacton Reservoir watershed in southeastern New York during four sample surveys, December 2000 through October 2001.

rate. Nitrate concentrations in most of the forested subbasins were lower than in farmed subbasins but showed an equally wide concentration range that probably reflects differences in forest history. For example, streams in high-relief, poorly accessible subbasins with mature forests (SEHMB, fig. 1) had the highest nitrate concentrations among forested subbasins. Those in subbasins with low relief and greater accessibility (DNPP2, fig. 1) and a probable history of tree harvesting, possibly followed by regrowth of different tree species (Lovett and others, 2000), had low nitrate concentrations. The lowest base-flow nitrate concentrations were generally in formerly farmed basins; this is consistent with the low nitrification rates found in abandoned farm fields by Zak and others (1990) and histories of long-term nutrient loss from cultivated fields and nitrogen uptake during forest regrowth.

May 3, 2001. May 2001 samples were collected during the highest base-flow conditions of the study—10 days after a peak flow caused by the final spring snowmelt. Base-flow nitrate concentrations at farmed subbasins continued to be positively correlated with manure-production rates, but the maximum concentrations were only about half of those measured in December 2000. This decrease is attributed to a combination of nitrate uptake or nitrate removal through algal growth and denitrification in the streams, and dilution of near-stream nutrient sources by discharge from springs that drain unfarmed hillside areas. The May nitrate concentrations in forested subbasins were generally about 0.1 mg/L greater than in the December sample survey and equaled or exceeded those at the farmed-subbasin sites. Base-flow nitrate concentrations were below 0.1 mg/L at most formerly farmed subbasins and in the low-relief forested basin (DNPP2).

July 19-20, 2001. This sampling survey occurred during the lowest base flows and the highest water temperatures of the four sampling periods. The July nitrate concentrations in nearly all streams had decreased since May, presumably in response to increased uptake by algae and plants, and to denitrification. Little correlation was discernible between manure-production rate and the July base-flow nitrate concentrations in the farmed subbasins as the nitrate values approached the minimum reporting limit (fig. 9). Base-flow nitrate concentrations at forested subbasins exceeded those at most of the farmed subbasins because nitrate concentrations in forested subbasins remained stable during the summer, while all others decreased, as described earlier. Baseflow nitrate concentrations at two farmed subbasins that were more than 80 percent forested with low manure-production rates were similar to those of the forested subbasins (fig. 9).

October 22-23, 2001. The October nitrate concentrations were the lowest of the four sampling surveys. The concentrations at half of the sites were at or below the minimum reporting limit. The October samples were collected during the leaf-off period, when microbial activity (nutrient uptake, nitrification) was spurred by leaf litter in the streams. No correlation was evident between manure-production rate and base-flow nitrate concentrations. Two of the farmed subbasins had nitrate concentrations that were among the highest in this survey, but the forested-subbasin samples had a greater number of nitrate detections.

Effects of Seasonal Changes on Nitrogen Concentrations

The seasonal changes in nitrate concentrations in general, and in the relation between nitrate concentration and manure-production rate, appear to reflect the strong effect of biological processes in streams or within streambeds (the hyporheic zone). Therefore, identification and evaluation of the ground-water sources of base-flow nitrate is best done with winter data, which represent the period when biological activity is minimal. In other seasons, nitrate retention by algae and plants and nitrate loss through denitrification reduce the nitrate-source contributions to a greater degree in farmed subbasins than in forested subbasins (figs. 8 and 9). High N retention in farmed subbasins is the result of greater nutrient availability, less forest area, and thus, more light reaching streams and warmer stream-water temperatures than in forested watersheds. Increased organic-carbon loading from animal waste in farmed subbasins may also facilitate loss of nitrogen through denitrification. Nitrogen from ground-water discharge that is retained in biomass is most likely transported in stormflows (as dissolved and particulate forms) rather than in base flow, because scour can remove algae, leaf litter, and microbes. Thus, use of base-flow nitrate during the growing season for comparison of nitrogen sources among basins with different land uses gives a false impression of nitrogen-source contributions. Greater retention of nitrogen in biomass in productive streams (farmed subbasins) than in less productive streams (forested subbasins) can make forested subbasins (by default) a greater source of base-flow nitrate during the growing season (figs. 8 and 9). However, total nitrogen (all dissolved and particulate species) exported during all streamflow conditions is almost certainly greatest from farmed subbasins with manure production.

Phosphorus

Phosphorus (P) is a nutrient of concern in New York City reservoir watersheds because it can spur algal growth, which in turn can lead to eutrophic conditions in reservoirs (Correll, 1998). Phosphorus is one of the principal nutrients in manure (Midwest Plan Service, 2000) and is the primary source of P (initially organic P) in streams that drain farmed areas in the Pepacton watershed. Another source of P is chemical-fertilizer supplements; these are a much smaller source than manure, however, and their application rates were not quantified in this study. A third P source is septic wastewater (Robertson, 1995; Robertson and others, 1998), but its contribution to base-flow concentrations was not considered important because of low septic-system densities within the subbasins selected for the study (table 1). Therefore, nonpoint-source P contributions were estimated only from manure-production data in each subbasin, as shown earlier for nitrate (fig. 9 and table 1).

Orthophosphate was the form of P selected for this analysis because it typically is the dominant dissolved form in streams. It also is the primary P species that is sorbed onto sediments and that is directly available for uptake by aquatic biota (Ryden and others, 1973; Correll, 1998). Organic-P is probably the predominant form of P in manure, but subsequently can be chemically or biologically transformed to orthophosphate.

Mobility of Orthophosphate and Organic Phosphorus

Orthophosphate transport in sediments is limited by sorption-desorption processes. Materials that have a strong affinity for P include: iron (Fe), aluminum (Al), and manganese (Mn) oxide or hydroxide precipitates, clays, carbonates, and organic matter (Sims and others, 1998; Fox, 1993). Desorption of P from sediments can occur where P concentrations in the surrounding waters are low. Phosphorus release from metal oxides and hydroxides can occur under anaerobic conditions (Allen, 1995; Hendricks and White, 2000; Sallade and Sims, 1997b) when the metal ions (particularly Fe) are reduced through bacterial decomposition of organic matter. This process is a potential means of P release from three sources—P-rich (manured) seasonally saturated soils (Vadas and Sims, 1998), sediment that is washed into drainage ditches from cultivated fields during storms (Sallade and Sims, 1997a, b), and hyporheic zones along streams (Hendricks and White, 2000).

Organic forms of P may have greater mobility than orthophosphate. The leaching and loss of P from agricultural areas are most commonly reported where many years of manure applications have increased the P content of the soil beyond the amount required by crops (Sims and others, 1998). Decreases in the P-sorption capacity of soils have been linked to manure application by Bache and Williams (1971) and Mozaffari and Sims (1996). P that is derived from manure has been reported to have greater downward mobility than P derived from chemical fertilizer through a soil layer with a high P-sorption capacity (calcium carbonate; Eghball and others, 1996); organic forms of P were surmised to have greater mobility than inorganic forms. Organic P that reaches streams can be converted to orthophosphate by streambed microbial communities that produce exoenzymes (Hendricks and White, 2000). Phosphorus transport to streams can be a serious issue at dairy farms, where the need to dispose of manure is constant, regardless of soil conditions (Sims and others, 1998).

Transport of P through soils and from local ground-water systems to streams is facilitated by high soil permeability and by artificial drainage in the soils and underlying saturated deposits. In general, transport is also favored in coarse-grained sediments with low metal-oxide and clay content, although some fine-grained soils contain macropores that can facilitate rapid downward movement. Artificial drainage, such as subsurface drains, represents a short circuiting of local hydrologic systems, which enhances P export (both dissolved and particulate-P) by accelerating drainage from the farm fields to surface waters (Ryden and others, 1973; Gaynor and Findlay, 1995).

Orthophosphate concentrations in streamflow are affected by stream biota. Increased uptake is likely during periods of algal growth that typically peak under optimal light conditions—before leaf-out in the spring—and possibly again, although to a lesser degree, in the fall (Allen, 1995). Stream biota can release dissolved organic or inorganic P through excretion from cells or during cell lysis (Allen, 1995).

Orthophosphate in Base Flow

Orthophosphate detection in stream base flow was closely associated with manure production in farmed basins (fig. 10). Orthophosphate concentrations at the farmed index site (ANGLH) were equal to or greater than the minimum reporting level (0.007 mg/L as P) in all samples except those from the leaf-off period in late October and mid-November 2001. The maximum concentration was 0.077 mg/L as P. In contrast, all samples from the formerly farmed index site (MRSNH) were at or below the MRL. Concentrations at the forested subbasin index site (SEMNH) exceeded the MRL only from mid-July through early October (maximum concentration 0.011 mg/L as P).

The fluctuations of orthophosphate concentration in samples from the farmed index site (ANGLH) indicated a nonconservative behavior unlike that of nitrate (and unlike the conservative behavior of chloride). Relatively low concentrations occurred during higher base flows in December, March, and early May—that is, high base flows with large upland flow contributions had low orthophosphate concentrations. The most striking feature of orthophosphate occurrence was a period of maximum concentrations from at least late June through mid-July (fig. 10). Nearly all farmed subbasin samples exhibited a similar pattern. Summertime elevated concentrations of soluble P in a small, farmed watershed in Pennsylvania also have been reported by Gburek and Heald (1974) and Pionke and others (1999). Orthophosphate concentrations from late August through early October (lowest flows) were similar to those from the spring period (highest flows). Samples from late October through early November were below the MRL, and this, like nitrate, is attributed to uptake by microbial activity in the presence of leaf litter.

The early to mid-summer 2001 peak in orthophosphate concentrations may have resulted from a combination of hydrologic, biological, and chemical factors:

1. First, the peak spring concentrations coincided with a period of transition from elevated spring base flows with a strong hillside component to relatively stable, low summer base flows (mid-August) in which valley-bottom or near-stream ground-water contributions to base flow are enhanced (fig. 10). Springtime recharge in valley-bottom areas of subbasins in which manure has been applied would probably provide a downward flush of organic carbon,
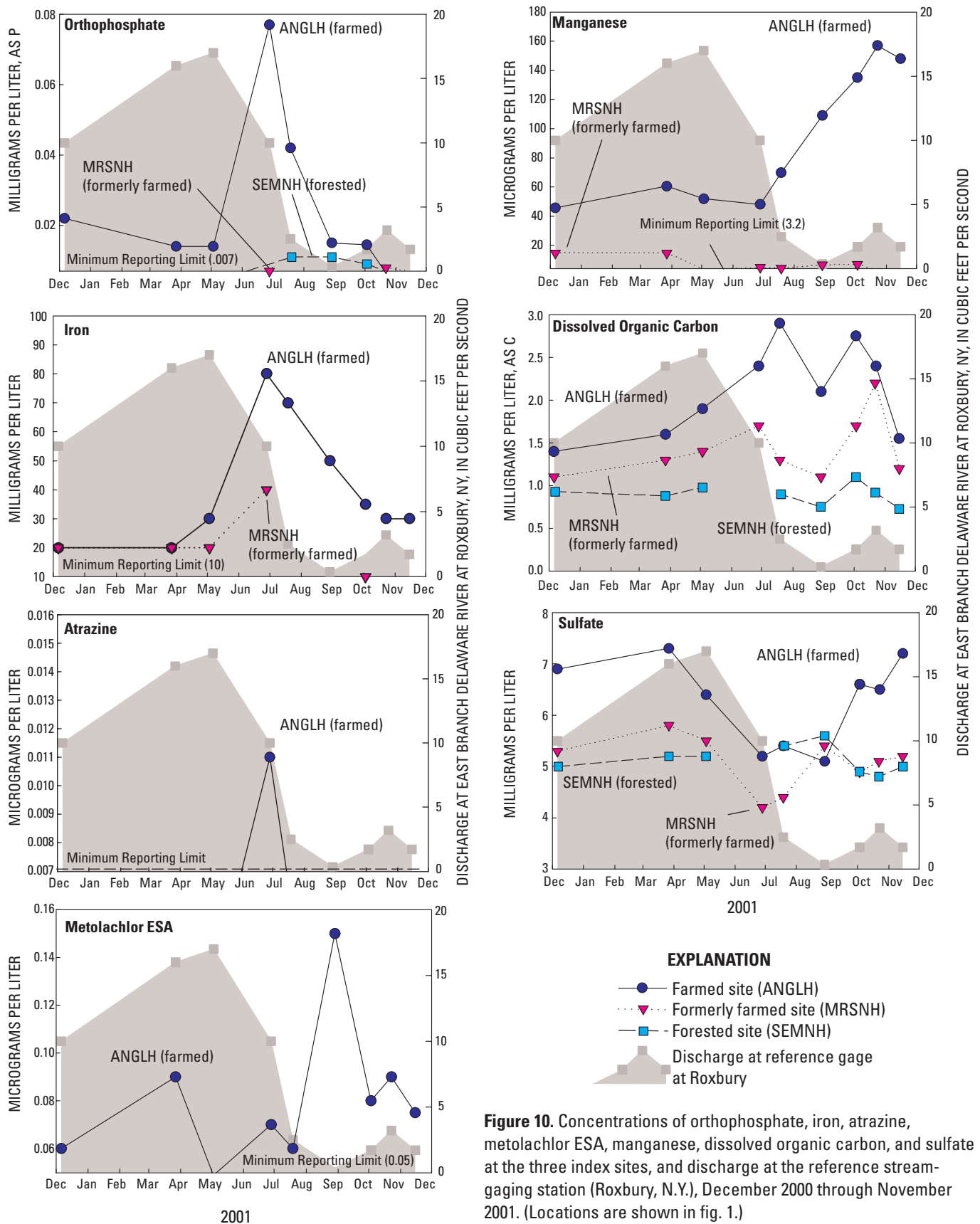
Figure 10. Concentrations of orthophosphate, iron, atrazine, metolachlor ESA, manganese, dissolved organic carbon, and sulfate at the three index sites, and discharge at the reference stream-gaging station (Roxbury, N.Y.), December 2000 through November 2001. (Locations are shown in fig. 1.)

nutrients (including organic forms of P), and herbicides to a rising water table. Organic P may be more readily transported than orthophosphate (Eghball and others, 1996).

2. Periodic springtime rises of the water table into orthophosphate-bearing soil horizons would provide at least an intermittent potential source of phosphorus to the ground water flowing to the stream. Two large storms (greater than 1 in. of precipitation) occurred in June 2001, one of which was 4 days before the June index-site sample survey. The peak concentration of the herbicide atrazine, which is applied in late spring, in the June samples indicated that recent ground-water recharge to valley-bottom deposits was entering the stream.

The movement of organic carbon to ground water, and its subsequent decomposition by bacteria, could create local anoxic conditions in the shallow ground water, which is at its highest water level in the spring. The spring peak in orthophosphate concentration also coincided with a peak in dissolved iron (Fe) concentration, which decreased thereafter much more slowly than the orthophosphate concentrations (fig. 10). Iron in solution in ground-water discharge suggests at least local anoxic conditions. The simultaneous occurrence of Fe and orthophosphate peaks may indicate the dissolution of P-bearing metal oxides or hydroxide precipitates. Periodic submergence and dissolution of P-bearing metal oxides and hydroxides in soils by high ground-water levels might explain the relatively brief orthophosphate peak. The ground-water transport of dissolved orthophosphate by sorption-desorption processes is typically slow, but phosphorus-saturated soils near streams or linked to subsurface drainage systems may enhance orthophosphate transport (fig. 10).

3. Streambed sediments with sorbed P, washed from farm fields and deposited within streams, could be a potential source of P in stream water (Sallade and Sims, 1997a,b). P sorbed to soil particles could be brought into solution through (1) dissolution of metal oxides and hydroxides under anoxic conditions, such as in stagnant, organic-rich waters or in streambeds where anoxic ground water is discharging, (2) desorption from clay or organic material, or (3) microbial transformation of organic P to orthophosphate.

Trends in the concentrations of other chemical species affected by redox conditions at the ANGLH site also indicated the discharge of anoxic ground water during the summer; they included organic N, dissolved organic carbon (DOC), sulfate, and manganese (Mn). For example, the peak in organic-N concentrations coincided with the orthophosphate and Fe peaks (figs. 8, 10), but the concentrations decreased more gradually over the summer and fall. DOC concentrations increased, and sulfate concentrations decreased, during this flow-transition period, and then remained relatively stable during the low flows of late summer and early fall (fig. 10). In contrast, Mn concentrations increased steadily from midsummer to midfall. The observed manganese-oxide coatings on streambed rocks indicated the discharge of anoxic ground waters containing dissolved Mn and the

subsequent precipitation of Mn as it became oxidized within the stream. The brevity of the P peak relative to those of other chemical species associated with anoxic conditions may indicate temporary sources of P (such as the unsaturated zone during periods of high ground-water levels) or depletion of available P in near-stream areas or in streambed sediments. P concentrations in streams can be decreased by nutrient uptake by algae and bacteria.

The trends in orthophosphate concentrations at the ANGLH subbasin were generally consistent with those at the other farmed-subbasins, especially those with extensive dairy farming. An increase in orthophosphate concentrations at site ANCBH throughout the study period was anomalous, however, and the reasons for it are unknown.

The orthophosphate concentrations obtained during each of the four sampling periods were compared with the manure-production estimates (fig. 11) in the same manner as for nitrate. The highest orthophosphate concentrations of each sampling period were at farmed-subbasin sites with high manure-production rates. The farmed-subbasin samples showed positive linear correlations with manure production in July and, to a lesser extent, in May, but little correlation in October or December. The orthophosphate concentrations at predominantly forested sites and formerly farmed sites were at or only slightly above the MRL (.007 mg/L) from July to October. All concentrations from forested and formerly farmed sites were at or below the MRL during the other sampling periods. Thus, a general seasonal pattern was observed in which orthophosphate was elevated in all subbasins from July through October, with farmed subbasins peaking in concentration in July and showing the best correlation of orthophosphate with annual rates of manure production.

Herbicides

Corn is grown in the Pepacton watershed to support dairy farming and cultivated fields are typically treated with herbicides during late spring. Studies in several agricultural areas of New York (Phillips and others, 1999, 2000a, 2000b; Eckhardt and others, 2000; Phillips and Heisig, 2004) have detected herbicides, generally at low concentrations, in ground water and surface waters, including the Pepacton Reservoir. Herbicide concentrations were determined for all index-subbasin samples and for the December 2000 and July 2001 sample surveys.

Herbicide concentrations in base-flow samples showed a strong association with corn cultivation within the respective subbasins (fig. 12). A relatively weak relation between the intensity of corn cultivation and total herbicide base-flow concentration probably was the result of several factors, including the generally low herbicide concentrations in all samples, and the small percentages of subbasin area under cultivation (0 to 1.2 percent, table 1).

Three herbicides (atrazine, metolachlor, and simazine) and three herbicide degradates (alachlor ESA (ethanesulfonic
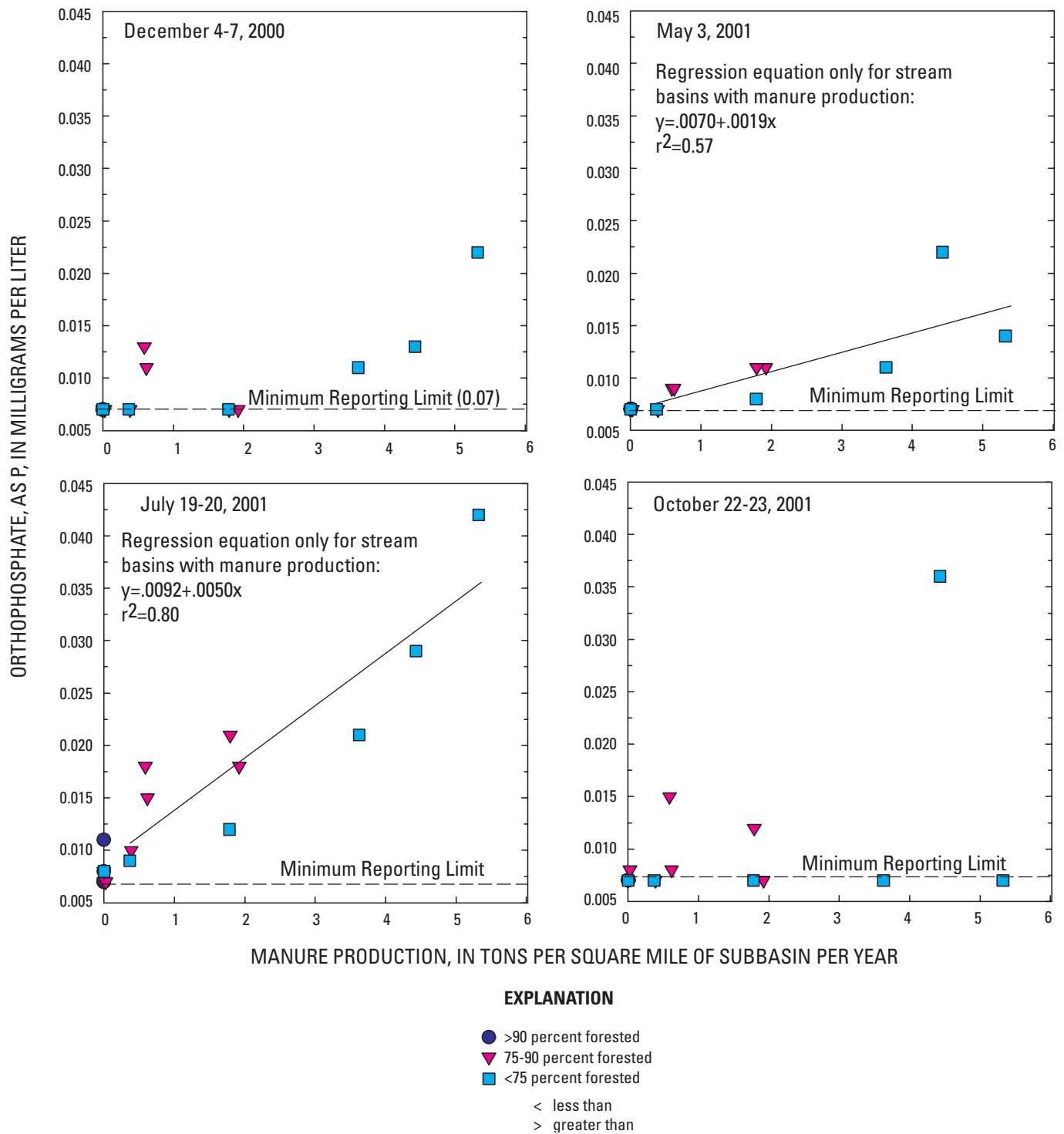
Figure 11. Orthophosphate concentrations as a function of annual manure-production rate in sampled subbasins of the Pepacton Reservoir watershed in southeastern New York during four sampling surveys, December 2000 through October 2001.

acid), deethylatrazine, and metolachlor ESA) were detected in base-flow samples during this study. Atrazine and metolachlor are used on cornfields, and simazine (detected only once) has a variety of uses, including corn crops. Metolachlor ESA was detected the most often and at the highest concentrations; the maximum concentration was 0.42 mg/L. The concentrations of the other five compounds were less than 0.10 mg/L.

The ratio of metolachlor ESA to its parent compound (metolachlor) was calculated for all Pepacton watershed subbasins; results are given in Phillips and Heisig (2004). All base-flow samples had high ratios that were within the range typical of ground water rather than surface runoff (Phillips and others, 1999); this is consistent with the assumption that the samples collected in this study were derived solely from ground-water discharge.

The frequency of herbicide and herbicide-degradate detection was strongly associated with row-crop (corn) production at the three index sites. All nine samples from the farmed-subbasin index site (ANGLH) from December 2000 through November 2001 contained at least one herbicide (including the values estimated for concentrations below the MRL; Childress and others, 1999). No samples from the forested-subbasin index site contained any herbicide or herbicide degradate. Only two samples from the formerly farmed-subbasin index site contained an herbicide or herbicide degradate (Phillips and Heisig, 2004); one contained deethylatrazine (a degradate), and one contained simazine, an herbicide that has other applications in addition to corn crops.

The pattern of atrazine occurrence at the farmed index subbasin (ANGLH) paralleled that of orthophosphate. Only the late-June concentration was above the MRL (fig. 10). The winter, spring, and late-summer concentrations were estimated values (below the MRL), and no atrazine was detected in the fall samples (Phillips and Heisig, 2004). The similarity between the patterns of atrazine and orthophosphate occurrence may indicate similar hydrologic pathways—both constituents are applied to row-crop fields, and both reached their peak concentrations in base flow just after a post-application storm. Subsurface drains are not widespread in this subbasin but, where present, may provide local short circuits from the soil to the stream. Soil-water herbicide and orthophosphate contributions to ground water and base flow presumably decrease through the summer as the water table declines and the soils drain.

Metolachlor ESA occurrence at the farmed index subbasin stream was nearly the opposite of atrazine (fig. 10). It was detected in all samples but the May 2001 sample and was highest during the lowest base-flow conditions. This pattern suggests a strong association with ground water from the valley bottom, where most farm fields are located. Non-detection in the May sample is consistent with dilution of valley-bottom ground-water concentrations by high base-flow contributions from forested upland areas.

All basins with any degree of corn row-crop area (table 1) and two basins formerly under corn cultivation had the only detections of herbicides or herbicide-degradates in the December 2000 and July 2001 surveys. Herbicide occurrence in streams was related to agricultural land use in the stream basins by comparing total herbicide concentrations with the percent of basin area used for corn cultivation (fig. 12). Total herbicide concentrations were used rather than individual concentrations because 1) the three herbicides detected are nonconservative, 2) use of any one herbicide may not be uniform among the farmed basins, and 3) concentrations of
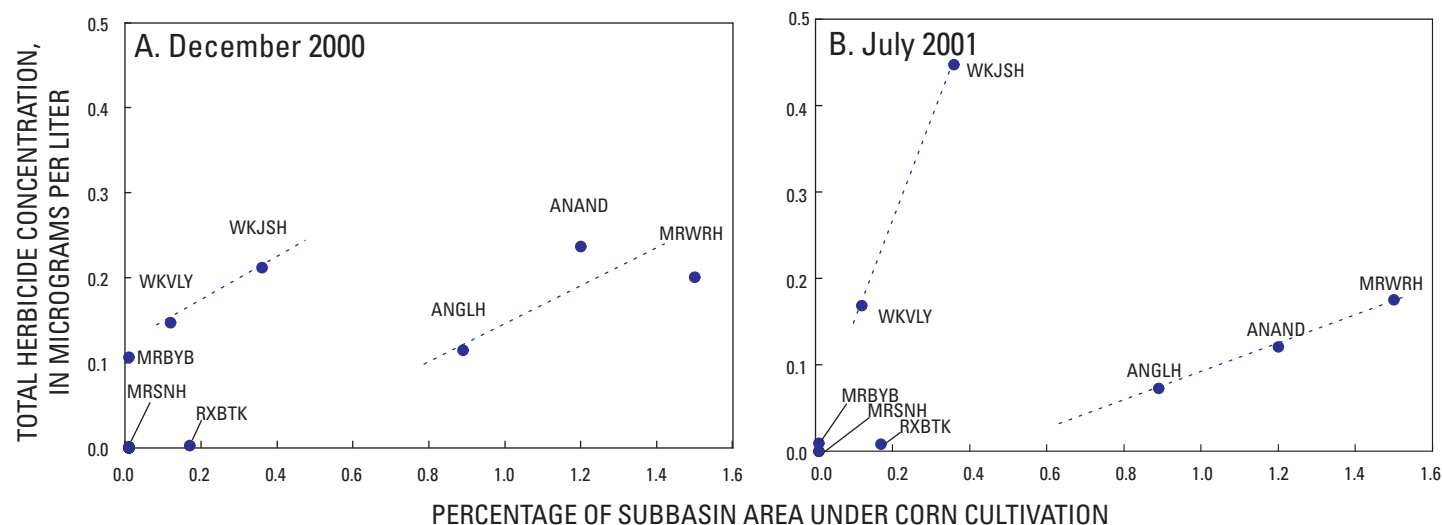

Figure 12. Total herbicide concentration (sum of atrazine, metolachlor, simazine, and associated degradates) in base flow as a function of basin area under cultivation. Trend lines are drawn among nested or adjacent subbasins. (Site locations are shown in fig. 1.)

individual compounds were low. Estimates of percent subbasin area in corn cultivation were derived from a 2001 field survey. Phillips and Heisig (2004) found significant positive Spearman nonparametric correlations between total herbicides in base flow and percent subbasin area in corn cultivation for the December 2000 and July 2001 surveys.

The relation between total herbicide concentration in base flow and the percentage of subbasin area used for corn cultivation differs among subbasins (fig. 12), probably as a result of differences in (1) herbicide-application history, types of herbicides used, and application rate; (2) soil properties such as permeability, organic carbon content, and clay content; (3) annual runoff, slope, proximity to a stream, ground-water flow paths, and residence time; and (4) uncertainties associated with measurement of extremely low herbicide concentrations (near the detection limits). The herbicide-application history may be a major factor, in that land use has shifted away from agriculture over the past few decades. For example, the relation of total-herbicide concentration to percentage of subbasin used for row crops differs sharply between the eastern part of the watershed and the north-central part; subbasins WKJSH and WKVLY in the eastern part (fig. 1) have much smaller percentages of cropland than subbasins in the north-central part (ANGLH, ANAND, MRWRH), yet subbasins WKJSH and WKVLY have similar total herbicide concentrations in base flow (fig. 12).

Summary and Conclusions

In 2000-01, the USGS, in cooperation with NYSDEC, investigated the effects of hydrogeologic factors and land use on the quality of ground-water that discharges to local streams in the Pepacton watershed in southeastern New York. Base-flow samples were collected from 20 subbasins throughout the watershed from December 2000 through November 2001 and were analyzed for major ions and selected nonpoint-source constituents (nutrients, herbicides) that reflect local land use. Samples were collected seasonally (December, May, July, and October) at all sites, and as many as five additional times at three index sites that were selected to represent three end-member land-use categories—farmed land (mostly dairy farms), formerly farmed land with low-density residential development, and forested land with little or no residential development. Temporal changes in base-flow composition at the index sites were plotted, as were the relations between concentrations of selected constituents and corresponding measures of nonpoint-source intensity.

Base flow (dry-weather streamflow) in the Pepacton watershed consists of ground water that discharges from seeps, springs, and directly to streams from the valley-bottom deposits. Base-flow chemistry, therefore, reflects subbasin lithology, hydraulic flow paths, and land use. Base flow was categorized by major-ion water type as either naturally occurring or affected by road salt. Road-salt-affected waters

were widespread. The naturally occurring waters (unaffected by salt) were designated as dilute or evolved on the basis of the predominant ions. Dilute waters are mixed-ion types with low specific conductance and short residence times and (or) short flow paths within the ground-water system, generally along high-gradient upland flow paths through fractured bedrock. Evolved waters have bicarbonate as the single dominant anion and higher specific conductance than most dilute waters. Evolved water composition indicates longer flow paths and (or) greater contact with reactive material in the valley-floor material than dilute waters. Seasonal changes in water type at a given sampling site over the study period are attributed to seasonal decreases or increases in the dilute ground-water contribution from uplands in relation to the more highly evolved contributions from valley-bottom areas.

Base-flow concentrations of chloride and sodium from road salt, and of nitrate, orthophosphate, and herbicides from agricultural practices, showed a positive correlation with their application rate, production, or areal occurrence within the respective subbasins. This correlation indicates a strong link between contaminants from nonpoint sources in valley bottoms or lower hillside areas, the local ground-water flow system, and base-flow water quality.

The concentrations of chloride and sodium (conservative ions) were correlated with the rate of road-salt-application rates in all four sampling periods. The highest concentrations occurred during the summer and fall, when the ground-water contributions from valley-bottom areas (with most of the roadways) were the greatest of the year.

Nitrate concentrations in base flow decreased seasonally through processes of denitrification or biological uptake near or within the stream. These processes are minimized by low temperatures; therefore, winter nitrate concentrations are the highest of the year and give the closest approximation of the concentrations in ground-water discharge. Two identified sources of nitrate in base flow of the study area are livestock manure and nitrogen from atmospheric deposition. Base-flow nitrate concentration showed a positive linear correlation with annual rates of manure application in the December 2000 samples, but not in the samples collected during warm weather or after leaf-off in the fall, when biological uptake or chemical transformation in and near the stream lowered the concentrations. Nitrate uptake in streams within farmed subbasins was enhanced by the greater amounts of sunlight reaching the streams, and by warmer water temperatures and higher phosphorus concentrations than in the forested subbasins. The relatively low retention of atmospheric nitrogen by vegetation in forested subbasins, and the low nitrate uptake in shaded forest streams, resulted in relatively stable nitrate concentrations through the summer in those subbasins.

The primary source of phosphorus in base-flow samples from farmed subbasins was manure. Orthophosphate was detected in all but one sample from the farmed-subbasin index site; the latter sample was collected during the fall leaf-off period, when biological activity is spurred by leaf

organic carbon in the streams. Maximum orthophosphate concentrations at that site occurred in the early summer and midsummer, when the nitrate concentrations were minimal. Orthophosphate concentrations at the forested and formerly farmed subbasin index sites were low and were detected only in samples collected from July through October.

The peak orthophosphate concentration at the farmed index subbasin occurred at the end of June 2001, shortly after two storms, and coincided with the atrazine peak and with broader peak concentrations of dissolved iron, organic nitrogen, and DOC. The simultaneous occurrence of peak concentrations suggested association with recent recharge from the storms. The occurrence of recent recharge (high ground-water levels) with the DOC peak and with reducing conditions in base flow (as indicated by the dissolved iron) at the farmed index subbasin suggested that the orthophosphate could have been released from the nearby soils or streambed sediments as the metal oxides were reduced. The July 2001 samples from farmed subbasins indicated a positive linear relation between base-flow orthophosphate concentration and manure-production rate.

The pattern of herbicide and herbicide-degradate occurrence was positively correlated with corn cultivation in subbasins, but the relations with area under cultivation were inconsistent among the subbasins. Atrazine concentration was highest during high early-summer base flows, but metolachlor ESA concentrations peaked during low base flows in the summer and fall, when valley-bottom ground-water contributions were greatest. Differences in the timing of concentration peaks, and the concentrations themselves, in base flow suggest seasonal factors that affect the movement of these constituents, or their release to streams.

The results of this study indicate that base-flow chemistry from small, well-drained stream basins reflects local hydrogeologic factors and the intensity of nonpoint sources within the basins. Shifts in relative water contributions from hillside and valley-bottom areas are evident from major-ion water type and from selected constituents associated with nonpoint sources in the valley bottoms. Seasonal or consistent correlations among chloride, sodium, nitrate, orthophosphate, and herbicides and the measures of the intensity of nonpoint sources provide information on the interaction of these constituents with soil or aquifer material, biota, and hydrologic conditions.

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