

# Work Plan of the Neversink Watershed Study in the Catskill Mountains of Southeastern New York

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# CONTENTS

Abstract .....	1
Introduction .....	1
Purpose and Scope .....	1
Effects of Acidic Deposition .....	2
Effects of Climate Change .....	3
Current State of Watershed Science .....	3
Project Objectives .....	4
Basin Description .....	4
Physiography and Geology .....	4
Soils .....	5
History of Vegetation and Land Use .....	5
Climate .....	6
Catskill Data Bases .....	6
Precipitation .....	6
Long-Term Stream Monitoring .....	6
Short-Term Stream Monitoring .....	8
Research Approach .....	8
Topic A. Small (First-Order) Watersheds .....	8
Work Element 1. Subsurface-Water Residence Time .....	9
Work Element 2. Hillslope Gradients of Soil Chemistry .....	10
Work Element 3. Extrapolation of Relations to Other First-Order Watersheds .....	11
Topic B. Intermediate and Large Watersheds .....	11
Work Element 1. Spatial Controls in Intermediate and Large Watersheds .....	12
Work Element 2. Effect of Watershed Size on Temporal Variations in Stream Chemistry .....	12
Topic C. Landscape Controls of Stream Chemistry .....	13
Work Element 1. Identifying the Effect of Landscapes on Neversink River-Water Quality ..	14
Work Element 2. Modeling the Sources of Landscape Effects on Stream-Water Quality ....	15
Topic D. Nonconservative Transport of Nitrate and Aluminum in Stream Water .....	15
Work Element 1. Nitrate .....	15
Work Element 2. Aluminum .....	17
Topic E. Nitrogen Cycling .....	18
Work Element 1. Quantifying Nitrogen Budgets .....	19
Topic F. Water Quality and its Effects on Aquatic Biological Communities .....	20
Effects of Acidification on Fish and Invertebrate Populations .....	21
Mechanisms of Fish Stress and Mortality .....	21
Use of Biological Indices in Characterizing Water Quality .....	21
Work Element 1. Aquatic Toxicity .....	22
Work Element 2. Integrity of Biological Communities .....	23
Geographic Information Systems (GIS) Support Activities .....	24
Deliverables .....	25
References Cited .....	26
Appendixes .....	31
1. Field Implementation Schedule .....	32
2. Analytical Methods .....	36
3. Quality-Assurance Plan for Streamflow Measurements .....	40
4. Data management .....	41

## FIGURES

1. Map of Neversink watershed showing locations of streamflow-gaging stations . . . . . 2
2. Map of Wildcat and Winnisook watersheds showing locations of measurement sites . . . . . 9

## TABLE

1. Location, drainage area, and period of record at historical and long-term monitoring sites in the Catskill Mountain region. . . . . 7

## CONVERSION FACTORS

<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
millimeter (mm)	0.03937	inch
meter (m)	3.281	foot
kilometer (km)	0.6214	mile
square kilometers (km <sup>2</sup> )	0.3861	square mile
hectare (ha)	2.471	acre
square meter (m <sup>2</sup> )	10.76	square foot
liter (L)	0.2642	gallon
cubic meter (m <sup>3</sup> )	35.31	cubic foot
cubic meter per day (m <sup>3</sup> /d)	264.2	gallon per day
liters per second (L/s)	0.0353	cubic feet per second
liters per minute (L/m)	2.118	cubic feet per minute

## ABBREVIATIONS

micromoles per liter (μmol/L)

Temperature can be converted from degrees Celsius (°C) to degrees Fahrenheit (°F) by the following equation:

$$^{\circ}\text{F} = 9/5\ ^{\circ}\text{C} + 32$$

**Sea level:** In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level datum of 1929.

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## Abstract

The Neversink River drains into the Neversink Reservoir, which is part of the New York City water-supply system in the Catskill Mountains of southeastern New York State. The U.S. Geological Survey (USGS) is conducting a 5-year (1990-95) water-quality assessment of the Neversink River basin to evaluate watershed factors that control stream-water quality over spatial scales ranging from a few hectares to 240 square kilometers. Because the basin contains minimal development, the focus of the assessment is on natural processes and effects of acidic deposition, the factors that most strongly affect surface-water chemistry. The final product is to be a conceptual model of the spatial distribution of the major controls of stream-water quality in the Neversink basin.

The assessment contains six topics of investigation: (1) small watersheds, (2) intermediate and large watersheds, (3) effects of landscape on stream chemistry, (4) effects of nonconservative transport of nitrate and aluminum in stream water, (5) nitrogen cycle, and (6) water quality and its effects on aquatic biological communities. Approaches include streamflow monitoring and chemical analysis of stream water throughout the basin; computerized modeling of flow and stream chemistry through TOPMODEL; spatial analysis of soil chemistry; use of stable isotopes to identify subsurface flowpaths; monitoring wet and dry atmospheric deposition; in-stream nutrient-cycling studies with added tracers; fish shocking and aquatic invertebrate sampling; and onsite fish-bioassay studies. The information collected in this study will be related through a Geographic Information System (GIS) to develop the conceptual model. Because the Neversink basin is minimally affected by human activity, the conceptual model will provide a basis for comparison with other watersheds and provide a foundation for development of a management model that incorporates development scenarios.

## INTRODUCTION

The City of New York relies on five reservoirs in the Catskill Mountains to supply drinking water to 8 million residents. Historically this water has been of high quality, but it could be adversely affected in the future by changes in land use, continued deposition of atmospheric pollutants, and (or) changes in climate. The need for development of effective watershed-management strategies to address these issues prompted the New York City Department of Environmental Protection (NYCDEP) in 1990 to begin a research investigation, in cooperation with the U.S. Geological Survey (USGS), to evaluate factors that affect water quality in Catskill watersheds. This investigation is being done in the Neversink River basin, in the southeastern part of the Catskill Mountain region of New York State (fig. 1). The USGS is evaluating the watershed and stream-channel processes that control stream-water chemistry, and the New York State Department of Environmental Protection is concurrently evaluating processes within the Neversink Reservoir, to which the Neversink River is tributary.

## Purpose and Scope

This report describes in detail the goals, approaches, and expected deliverables of the Neversink Watershed study. Because this report is a work-plan, its scope is limited to a presentation of background information and planned methods, without data collected in the project or conclusions based on interpretive activities of the project.

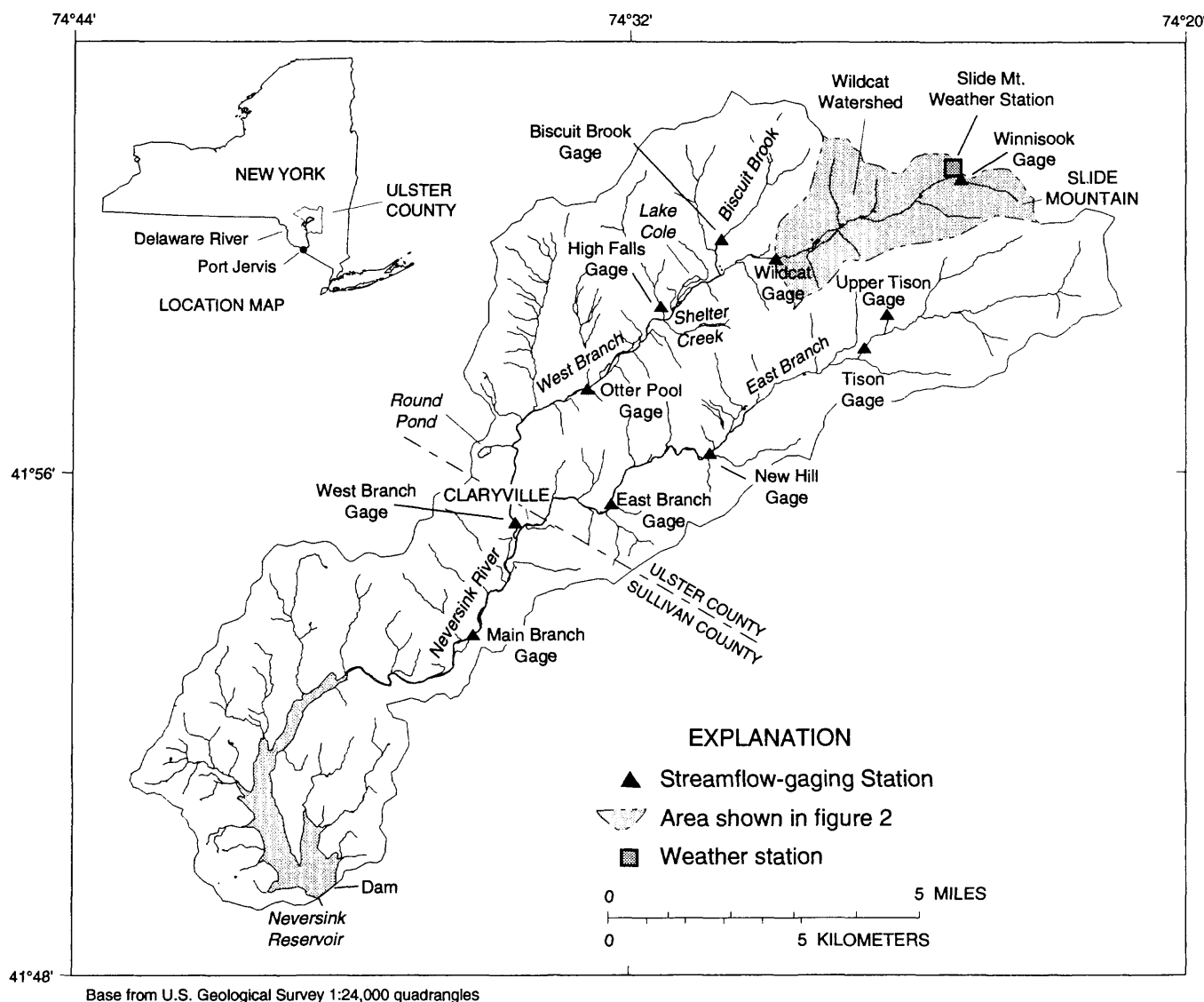
The report (1) describes the physical characteristics of the Neversink basin and the monitoring system, (2) presents the work elements of each of the six research topics, (3) describes the eight watershed components to be defined through GIS, and (4) lists the final products (deliverables). Appendix 1 lists the beginning and completion dates for each research

topic, Appendix 2 describes the analytical methods used for water and soil analysis, Appendix 3 describes the quality-assurance plan for streamflow measurement, and Appendix 4 describes the computerized data-management approaches to be used.

## Effects of Acidic Deposition

The Catskill region has one of the highest rates of acidic deposition in the Northeast (Stoddard and Murdoch, 1991). Both chronic and episodic acidification of surface waters in the Catskill region have been documented, and streams in the Neversink River basin are the most severely affected. Thus, atmospheric

deposition is probably the primary cause of acidification of Catskill surface waters (Stoddard and Murdoch, 1991). Fish-population densities and biological diversity in the Neversink River are lower than in other Catskill rivers that are less acidic, and episodic acidification has been correlated with fish mortality (U.S. Geological Survey, unpublished data, on file in the New York District office of the U.S. Geological Survey). Nitrate ( $\text{NO}_3^-$ ) concentrations as high as 128  $\mu\text{mol/L}$  have been measured in pristine headwater streams of the Neversink basin during periods of high rainfall and snowmelt (Murdoch and Stoddard, 1992), and, during April 1987, a plume of acidic river water

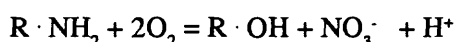


**Figure 1.** Locations of streamflow-gaging stations in the Neversink River watershed.

with  $\text{NO}_3^-$  concentrations greater than 100  $\mu\text{mol/L}$  entered the Neversink Reservoir. Stream acidification has been detected throughout the Neversink basin.

Recent passage of the revised Clean Air Act is likely to result in a reduction of emissions of airborne acidic sulfur compounds in the Northeast, but how this will affect water quality in the Catskills is uncertain. Long-term monitoring at the Hubbard Brook Experimental Forest in New Hampshire has shown a decline in deposition of sulfate ( $\text{SO}_4^{2-}$ ) over the last 2 decades without a corresponding increase in stream-water pH (Driscoll and others, 1989) because the stream-water concentrations of base cations also are decreasing. This decrease in base-cation concentrations in stream water could be due to a decrease in atmospheric emissions of basic particulates through improved particulate-removal technology and decreased fossil-fuel burning (Driscoll and others, 1989).

The revised Clean Air Act also is expected to decrease the atmospheric deposition of nitrogen, but the effect of such decreases on Catskill water quality is unknown. Increasing evidence suggests that forests in which nitrogen has traditionally been considered to be the growth-limiting nutrient could be approaching "nitrogen saturation" (Aber and others, 1989), a condition in which nitrogen is available in excess of plant and microbial demand (Agren and Bosatta, 1988; Skeffington and Wilson, 1988; Aber and others, 1989). Excess nitrogen in forest ecosystems can lead to increased soil nitrification and associated soil acidification according to the following stoichiometry (van Breemen and others, 1982):



Because  $\text{NO}_3^-$  has a low capacity for physical adsorption, it is mobile in soils and therefore can leach cations that can cause surface-water acidification. Accelerated rates of nitrification, induced by forest harvesting, have caused surface-water acidification in Northeastern hardwood forests that are similar to Catskill forests (Lawrence and others, 1987). Aber and others (1989) hypothesized that excess nitrogen could potentially lead to forest decline, and the decreases in forest productivity would in turn increase the pool of excess nitrogen and worsen the leaching of  $\text{NO}_3^-$ , which would increase surface-water acidification.

The higher growing-season concentrations of  $\text{NO}_3^-$  in Catskill streams than in other pristine streams in the

Northeast suggest that Catskill forests could be approaching nitrogen saturation. If so, surface-water quality could decline further as forests become decreasingly productive, despite anticipated decreases in atmospheric nitrogen deposition. The degree to which  $\text{NO}_3^-$  will be leached will depend on the rates of processes such as mineralization, nitrification, plant uptake, and immobilization through microbial reactions. Other factors include the size of nitrogen pools in the current forest ecosystem, as well as stand-age structure; old trees tend to be less productive than young ones and therefore require less nitrogen for growth. Large areas of Catskill forestland have remained uncut for more than 75 years.

## Effects of Climate Change

Several climate models have predicted a detectable increase in global temperature in the next century. One possible result would be an increased frequency of extreme hydrologic conditions, such as droughts and floods, that would affect mineralization and nitrification rates and thereby alter the nitrogen cycle. The effects on water quality in the Catskills could be an increased frequency and severity of surface-water acidification.

Under conditions of nitrogen saturation, extended dry periods could cause a buildup of  $\text{NO}_3^-$  in the soil and subsequent leaching in the first storm after the dry period. Surface-water acidification during this storm would be more severe than during a storm that followed shorter wetting and drying cycles. An increase in the magnitude of storms could also increase the degree of acidification that occurs during high flows by increasing the contributions from acidic source areas and decreasing soil-water residence time (Lawrence and Driscoll, 1990).

## Current State of Watershed Science

Past concern over the effects of atmospheric deposition has resulted in the development of several process-based models that predict effects of various deposition scenarios on water quality (Christophersen and Wright, 1981; Cosby and others, 1985; Gherini and others, 1985). The structure of these models is typically derived from mechanisms studied in plot experiments and extrapolated to the small-watershed scale through "lumping" or statistical averaging, but the

effects of acid precipitation in many small watersheds, including those sampled in the Catskills, show a spatial variation that is not random, but rather is systematically related to stream position on a hillslope (Johnson and others, 1981; Lawrence and others, 1986; U.S. Geological Survey, unpublished data); this variation makes spatial averaging inappropriate. Research is needed to determine how landscape features and patterns affect surface-water quality at the small-watershed scale.

Watershed-acidification models have not been extrapolated beyond the small-watershed scale, mainly because their physical basis is exceedingly complex, although some preliminary efforts to evaluate the relation between watershed scale and streamflow response have been made (Wood and others, 1988). Water-quality investigations downstream from headwater systems have focused primarily on point and nonpoint sources of pollution but have given little consideration to the role of natural watershed controls at this scale. Similarly, studies relating headwaters to higher order streams have focused primarily on how in-stream processes respond to some specific form of pollutant, rather than on natural watershed processes (Bencala and others, 1990; Lawrence and Driscoll, 1988).

## **Project Objectives**

This project is designed to evaluate watershed factors that control stream-water quality over spatial scales ranging from a few hectares to 240 km<sup>2</sup> in the Neversink basin. The focus of the investigation will be on the effects of natural processes and acidic deposition, the two factors believed to most strongly affect surface-water chemistry. The project goal is the development of a conceptual model of spatial variations in stream-water quality and aquatic communities in the Neversink River basin. Because no quantitative spatial model of stream chemistry has been developed at even the small-watershed scale, construction of such a model for the entire Neversink basin is beyond the scope of this project. Quantitative relations will be established, however, that will be directly applicable to the future development of a landscape-based model that mathematically describes spatial relations of surface-water chemistry over a wide range of watershed scales.

The purpose of the conceptual model of this project is to describe spatial patterns of water chemistry and aquatic communities through a combination of survey

information and quantitative relations developed in closely studied, representative types of landscape within the basin. Information obtained from these areas will be extrapolated through a detailed, basin-wide Geographic Information System (GIS) data base. The model will be designed to maximize the potential for transfer of information to Catskill watersheds outside the Neversink basin. The methods used to develop the model should also be transferable to modeling efforts for other upland watersheds in the Northeast.

## **BASIN DESCRIPTION**

The Neversink River basin is part of the Delaware River drainage. It flows generally southwestward through the Neversink Reservoir, then south to its confluence with the Delaware River near Port Jervis, N.Y. (fig. 1). The study area includes only the part of the basin above the Neversink Reservoir, an area of 240 km<sup>2</sup>.

## **Physiography and Geology**

The Neversink River is a clear, energetic mountain river whose valley bottom nowhere exceeds a width of 0.75 km. Upstream from the town of Claryville, 9 km above the reservoir (fig. 1), the river divides into an east and a west branch with watersheds of nearly equal in area. Both branches originate near the summit of Slide Mountain (1,274 m), the highest point in the Catskill Mountains. Hillslopes in the headwaters, and slopes and tributary valleys further downvalley, are steep. The West Branch valley widens just upstream from the junction with Biscuit Brook, and the East Branch valley widens similarly just downstream from the Tison gage. Both branches have discontinuous flood plains from where they widen until they join in Claryville.

Underlying the Neversink basin are flat-lying sedimentary bedrock of Devonian age, overlain by till deposits and alluvium (Rich, 1934; Way, 1972). The Devonian rocks were formed from sediment eroded from former mountains to the east and were deposited as part of a massive delta several thousand meters thick. The Catskill delta has since been uplifted and now stands at a higher elevation than the surrounding land. The bedrock of the Catskill Mountains in the region of the Neversink basin is about 60 percent



sandstone and conglomerate and 40 percent shale and siltstone. Quartz is the dominant bedrock mineral, and muscovite and amphibole are common accessory minerals (Ethridge, 1977). Calcite and hematite are the principal interstitial cement materials in the bedrock but are generally present in only minor amounts.

The bedrock of the Neversink basin is overlain by a veneer of till derived primarily from the most recent glaciation, which ended about 14,000 years ago. The till is thicker in stream valleys than on the steep, upper slopes. Some of the till has been reworked and deposited as alluvium adjacent to stream channels on the valley floors. In the lower East Branch Neversink valley, Rich (1934) mapped till that predates the most recent glaciation.

## Soils

Most of the soils within the Neversink basin are classified as inceptisols in the Arnot-Oquaga-Lackawanna association (Tomes, 1979). Some spodosols underlie coniferous stands. These soils vary in thickness and are excessively to moderately well drained, predominantly steep, and medium textured on uplands. A distinguishing characteristic of these soils is the presence of a dense, cementlike fragipan beginning at a depth of 1/2 m to 1 m below the surface. Fragipans are found only where the till is at least 1 m thick. A fragipan slows the infiltration of water and can result in perched water during and after rainstorms. Rich (1934) believed the fragipan formed beneath the glacier as it deposited and compacted its load, but Kudish (1979) dismissed this idea because fragipans have been found outside glaciated regions and attributed their formation to the presence of adequate silt and clay to cement large soil fragments together.

The soils are generally acidic; Kudish (1979) obtained a mean pH of 5.0 from 150 Catskill mineral-soil samples. The pH distribution of the soils has no systematic spatial or elevational variability. Soil-humus pH is related to the type of vegetation present; Kudish (1979) found the mean pH of coniferous-stand humus from the same 150 sampling locations to be 4.3, and that of deciduous-stand humus to be 4.6. The acidity of soils is a reflection of the base-poor local bedrock. Although some of the till was transported from the north, Parker and others (1964) estimated that at least 90 percent of the till in the Catskills is derived from local rock and sediment.

## History of Vegetation and Land Use

Vegetation in the Neversink basin is primarily northern hardwood forest in which three tree species dominate: American Beech (*Fagus grandifolia*), Sugar Maple (*Acer saccharum*), and Yellow Birch (*Betula alleghaniensis*). Red Spruce (*Picea rubens*) and Balsam Fir (*Abies balsamea*) are the dominant species at elevations above 1,000 m (Kudish, 1979). Stands of hemlock (*Tsuga canadensis*) grow on poorly drained soils. Various herbs, ferns, club mosses, grasses, and wildflowers grow as ground cover beneath the forest canopy; the distribution of these plants is primarily dependent on the pH of the humus layer. (A complete listing of Catskill ground-cover species is given in Kudish, 1979.)

After glaciation ended, the Catskills were first invaded by alpine vegetation, followed by boreal forest (Kudish, 1979). Later, northern hardwoods and hemlock propagated northward into the region and ascended mountain slopes to as high as the minimum till-thickness tolerance of each species would allow. Evidence from pollen in peat bogs indicates that northern hardwoods have been established at high elevations in the Catskills for at least several thousand years (Kudish, 1979).

Man has had a significant effect on the forests of the Catskill Mountains since the mid-1700's, when logs were cut for ship masts and floated downstream. In the early 1800's, an attempt to make the Neversink River navigable for log rafts ended in failure. Leather tanning became the principal Catskill industry in the 1800's; as a result, hemlock trees were felled, stripped of their bark, and left to rot while the bark was transported to nearby streamside tanneries. Many sawmills cut pine and, later, hardwoods into lumber throughout the Catskills during this time.

By the late 19th century, most of the hemlock and pine had been cut, but the forests above 850 m remained mostly undisturbed and remain uncut to date. The upper watersheds of the Catskills were designated a State preserve in 1870.

The Neversink basin is predominantly forested (CLEAR, 1988), although limited cutting continues. A small amount of the open meadow in the river valley is used for horse grazing. The basin contains only a few farms and has a population of less than 1,300.

The greatest physical change in the Neversink basin during the 20th century was the completion of the

Neversink Dam (fig. 1) in 1950; the reservoir flooded about 10 km of the river valley. The only other significant land-use disturbance in the basin is the application of salt to roads that parallel the river. The effect of road salt on water quality in the Neversink River is unknown.

A few small manmade ponds, the largest of which are Round Pond and Lake Cole (fig. 1), are used for recreation in the summer. Wetlands identified by the U.S. Fish and Wildlife Service wetland inventory mapping constitute less than 5 percent of the total basin area.

## Climate

The climate of the Neversink basin is classified as humid continental, with cold winters and moderately warm summers. The range in elevation within the watershed results in distinct spatial variation in temperature and precipitation. The mean annual temperature at the Slide Mountain weather station (808 m) is 4.3°C, and at the summit (1,274 m) has been estimated to be 3.3°C (Kudish, 1979). At Liberty, just west of the basin at an elevation similar to that of the reservoir (472 m), mean annual temperature is 7.2°C (National Oceanic and Atmospheric Administration, 1990). This temperature difference within the watershed is fairly constant through the year.

Mean annual precipitation in the Neversink River basin is among the highest in the Northeast. The summit of Slide Mountain (fig. 1) receives more than 175 cm/yr, 22.7 percent of which falls as snow (Iorio, 1972). During 1950-85, the National Weather Service station at Slide Mountain received a mean of 157 cm/yr, and the weather station at Claryville received 140 cm/yr (National Oceanic and Atmospheric Administration, 1990). The large amounts of precipitation are caused by a combination of Atlantic coastal storms and an orographic effect from storms approaching from the southwest. Precipitation amounts are fairly uniformly distributed throughout the year.

Annual precipitation is closely correlated with annual runoff; the Neversink River averages more than 75 cm/yr, one of the highest runoff rates in the Northeast (Gebert and others, 1985). Cyclic accumulation and melting of the snowpack occurs throughout the winter, and snow depth ranges from 0 to 100 cm. Upper soil layers freeze during periods of little or no snow cover.

## CATSKILL DATA BASES

The data bases that have been developed for streams and precipitation in the central Catskill region provide a basis for comparison with and interpretation of data collected during the project. These data bases can be categorized as (1) long-term precipitation, streamflow, and stream-chemistry data, which will be used primarily for trend analysis, and (2) short-term streamflow and chemistry data, which will be used for specific research objectives.

### Precipitation

The National Weather Service has collected precipitation-volume and air-temperature data since 1948 at Slide Mountain and for shorter periods at the confluence of the West and East branches of the Neversink River and the south end of the Neversink Reservoir as part of their national monitoring program. These data are published in the National Weather Service's annual summaries for New York State. In addition, the NYCDEP has been measuring rainfall at several stations in the watersheds of each reservoir since the reservoirs were built. The USGS has been collecting rainfall-volume data and weekly wet-deposition data at Biscuit Brook (fig. 1) as part of the National Trends Network (NTN) since 1983 (U.S. Geological Survey, unpublished data) and, during 1985-87, the USGS operated an 18-station precipitation-data network for volume and selected stormwater constituents at elevations ranging from 1,274 to 183 m (U.S. Geological Survey, data available in the New York District Office). Preliminary analyses of data from these networks indicate that precipitation increases as elevation increases, and that precipitation chemistry has no clearly defined relation to elevation.

### Long-Term Stream Monitoring

Several data bases have been compiled from long-term monitoring of stream discharge and water quality in the Catskill region. The longest of these data bases was collected by the NYCDEP to monitor waters entering the city reservoir system (table 1). Three of these sites (Neversink River at Claryville, Esopus Creek at Coldbrook, and Rondout Creek at Lowes Corners) also have USGS streamflow-gaging stations at which data have been collected since the NYCDEP program began (in 1951, 1931, and 1937, respectively). The USGS has collected water-quality data seasonally on the

Esopus Creek at Shandaken since 1967 as part of its Hydrologic Benchmark Program and maintains several other stream gages throughout the Catskill region. These data are published in the USGS annual water-data reports.

The USGS has been monitoring stream-water quality at Biscuit Brook, a tributary to the West Branch Neversink River (fig. 1), since 1983 (Stoddard and Murdoch, 1991) as part of its Small Watershed Program, which includes continuous monitoring of discharge and weekly sampling of water quality. Seven other streams have been sampled and their discharge measured 10 to 12 times per year since 1983 as part of the U.S. Environmental Protection Agency

Long-Term Monitoring (LTM) project.

Analyses of these long-term records are reported in Murdoch and Stoddard (1992, 1993), Stoddard and Murdoch (1991), and Stoddard (1991). The data indicate trends of decreasing sulfate concentration and increasing nitrate concentrations in several streams, but the effects on pH and acid-neutralizing capacity (ANC) are unknown (Murdoch and Stoddard, 1993; Stoddard, 1991). Streams in the southern Catskills generally have low ANC (less than 200  $\mu\text{eq/L}$ ), whereas streams in the northern Catskills have moderate ANC (less than 300  $\mu\text{eq/L}$ ). The Neversink River basin contains the most acidic headwater streams of those sampled in the Catskill region.

**Table 1.**—Location, drainage area, and period of record at the long-term monitoring sites in the Catskill Mountain region, N.Y.

[ $\text{km}^2$  = square kilometers]

Site	Latitude	Longitude	Drainage Area ( $\text{km}^2$ )	Period of record
Batavia Kill below Red Falls	42°18'30"N	74°24'30"E	182.8	1921-1944, 1977-1983
Bear Kill above Grand Gorge	42°22'30"N	74°30'30"E	47.2	1968-1989
Bear Kill above Hardenburgh Falls	42°20'00"N	74°28'00"E	70.8	1922-1945
Beaver Kill above Esopus Creek	42°02'45"N	74°16'30"E	57.0	1917-1944, 1977-1979
Birch Creek above Pine Hill	42°08'30"N	74°28'45"E	11.3	1966-1989
Birch Creek at Pine Hill	42°08'00"N	74°28'45"E	19.3	1915-1944, 1966-1983
Bush Kill at West Shokan	41°58'15"N	74°16'45"E	38.0	1917-1944, 1966-1983
Bushnellville Creek at Shandaken	42°07'30"N	74°24'00"E	28.0	1917-1944, 1977-1979
Esopus Creek above Big Indian	42°06'00"N	74°27'00"E	76.9	1917-1944
Esopus Creek below Big Indian	42°06'15"N	74°26'15"E	111.3	1916-1945, 1966-1983
Esopus Creek at Coldbrook	42°01'00"N	74°16'15"E	497.3	1915-1989
Little Beaver Kill at Beechford	42°01'15"N	74°16'15"E	43.3	1917-1944, 1977-1979
Manor Kill above Schoharie Reservoir	42°22'45"N	74°26'00"E	85.6	1921-1945, 1966-1983
Neversink River at Claryville	41°53'30"N	74°35'30"E	172.5	1952-1972, 1984-1989
Rondout Creek at Lowes Corners	41°46'30"N	74°24'00"E	99.7	1965-1972, 1984-1989
Schoharie Creek at Prattsville	42°19'10"N	74°26'45"E	613.8	1922-1989
Stony Clove Creek above Esopus Creek	42°05'00"N	74°19'00"E	90.3	1917-1944, 1977-1979
West Kill above Schoharie Creek	42°15'45"N	74°22'30"E	129.6	1921-1944
Woodland Creek above Esopus Creek	42°04'45"N	74°20'00"E	55.8	1917-1943, 1977-1979
Beaverkill above Black Brook	42°01'02"N	74°34'55"E	20.7	1983 - present
Biscuit Brook above Pigeon Brook	41°59'13"N	74°30'11"E	10.3	1983 - present
East Branch Neversink River at Denning	41°57'48"N	74°27'19"E	34.6	1983 - present
East Brook Neversink River above Tray Mill Brook	41°57'51"N	74°27'02"E	23.7	1983 - present
High Falls Brook at Frost Valley	41°58'33"N	74°31'19"E	7.1	1983 - present
Hollow Tree Brook at Lanesville	42°08'32"N	74°15'01"E	5.0	1983 - present
Rondout Creek above Red Brook	41°56'12"N	74°22'35"E	14.2	1983 - present
Woodland Creek above campground	42°02'22"N	74°20'01"E	9.6	1983 - present

## Short-Term Stream Monitoring

Several short-term data bases of stream-water quality in the Catskill region have also been developed. The USGS conducted a seasonal water-quality-sampling program during 1973-75 on the Neversink River in Claryville in which samples were analyzed for pH, alkalinity, and major cation and anion concentrations. These data are included in the annual USGS data reports for the period (U.S. Geological Survey, 1974, 1975, 1976).

Regional sampling of stream-water quality was done seasonally during 1985-87 at 66 stream stations as part of a cooperative research program with the NYCDEP (U.S. Geological Survey, unpublished data, 1985-87). The seven LTM streams and Biscuit Brook were part of this network, which included the main river entering each of the 5 New York City reservoirs and 6 to 11 tributaries to each of those rivers. In all, 23 stations were established on the Neversink River upstream from the USGS gage near Claryville and were sampled during high discharge in the spring of 1987 (U.S. Geological Survey, unpublished data). Data from this network indicate that stream ANC concentrations decrease from north to south across the Catskills, paralleling decreases in calcium concentrations, whereas concentrations of other constituents were relatively similar across the region. The Neversink River had the lowest recorded ANC and calcium concentrations in the region (Murdoch and Stoddard, 1993).

A major focus of the research projects from 1983 to the present has been episodic acidification—the rapid increases in acidity that occur in streams during rainstorms and snowmelt. Frequent sampling of stream water during rainstorms was done at Biscuit Brook during 1984-85 as part of a USEPA-funded program to study episodic acidification in several regions of the eastern United States (Murdoch and others, 1990). Synoptic surveys of stream chemistry during peak discharge in the spring and fall were done during 1986 and 1987 along the length of the Neversink River above the reservoir as part of the cooperative research program with the NYCDEP (U.S. Geological Survey, unpublished data). During 1988-89, the USEPA again funded episodic acidification research through the Episodic Response Project (ERP), which was designed to define (1) the magnitude and frequency of episodic acidification in headwater streams, (2) the processes that control acidification,

and (3) the effect of episodes on fish and invertebrate populations. Results of these studies have shown that episodic acidification in Catskill Mountain streams can cause mortality and decreased population densities of fish and invertebrates (Murdoch and others, 1991).

## RESEARCH APPROACH

This project contains six topics related to terrestrial and aquatic controls of stream chemistry. The data-collection program for the six topics is projected to last 5 years (1991-95). Project completion is anticipated at the end of the 5th year (1995), and additional support will be sought to continue flow measurements and water sampling at selected sites and to extend nitrogen-budget monitoring.

Work elements have been designed to address specific questions relevant to each of the six topics (designated A through F). Because many of the activities of this project will be original research, the specific approaches to be used in each work element are designed to test particular hypotheses, and the information obtained through hypothesis testing will be used to build the conceptual spatial model. All of the spatial interpretation will use a detailed GIS data base that will represent the entire Neversink basin. (Development of the GIS data base is described in a later section, "Geographic Information System [GIS] Support Activities.") Unanticipated results could require some modification of the approaches described herein, but all modifications will be made in keeping with the overall project goal of developing the conceptual spatial model of Neversink stream-water quality.

### Topic A. Small (First-Order) Watersheds

Many first-order (headwater) streams in the Neversink basin have elevation-related gradients in stream chemistry (hereafter referred to as elevational gradients). In these streams, pH tends to be lowest in the uppermost reaches and to increase steadily downstream. This pattern is typical of North American upland watersheds that overlie noncalcareous bedrock and till (Powers, 1929; Johnson and others, 1981; Lawrence and others, 1986; Driscoll and others, 1988). Increases in stream-water pH with decreasing elevation have been attributed to (1) downstream increases in soil-water residence time (Johnson and others, 1981) and (2) hillslope gradients in soil chemistry, known as soil catenas (Lawrence and others, 1986). Specific

data relating elevational gradients in stream chemistry to spatial patterns of biogeochemical or hydrologic processes within watersheds have not been collected, however.

To quantify the spatial effects of hillslope processes on first-order-stream chemistry, three work elements are designed to evaluate the relative importance of subsurface-water residence time and soil catenas. This information will be used to develop a spatial model for first-order watersheds in the Neversink basin. Winnisook watershed (fig. 2) will be used for most of the small-watershed investigations because its topography and stream chemistry are typical of high-elevation first-order watersheds within the Neversink basin and because this basin is more accessible than most of the other first-order watersheds.

### Work Element 1. Subsurface-Water Residence Time

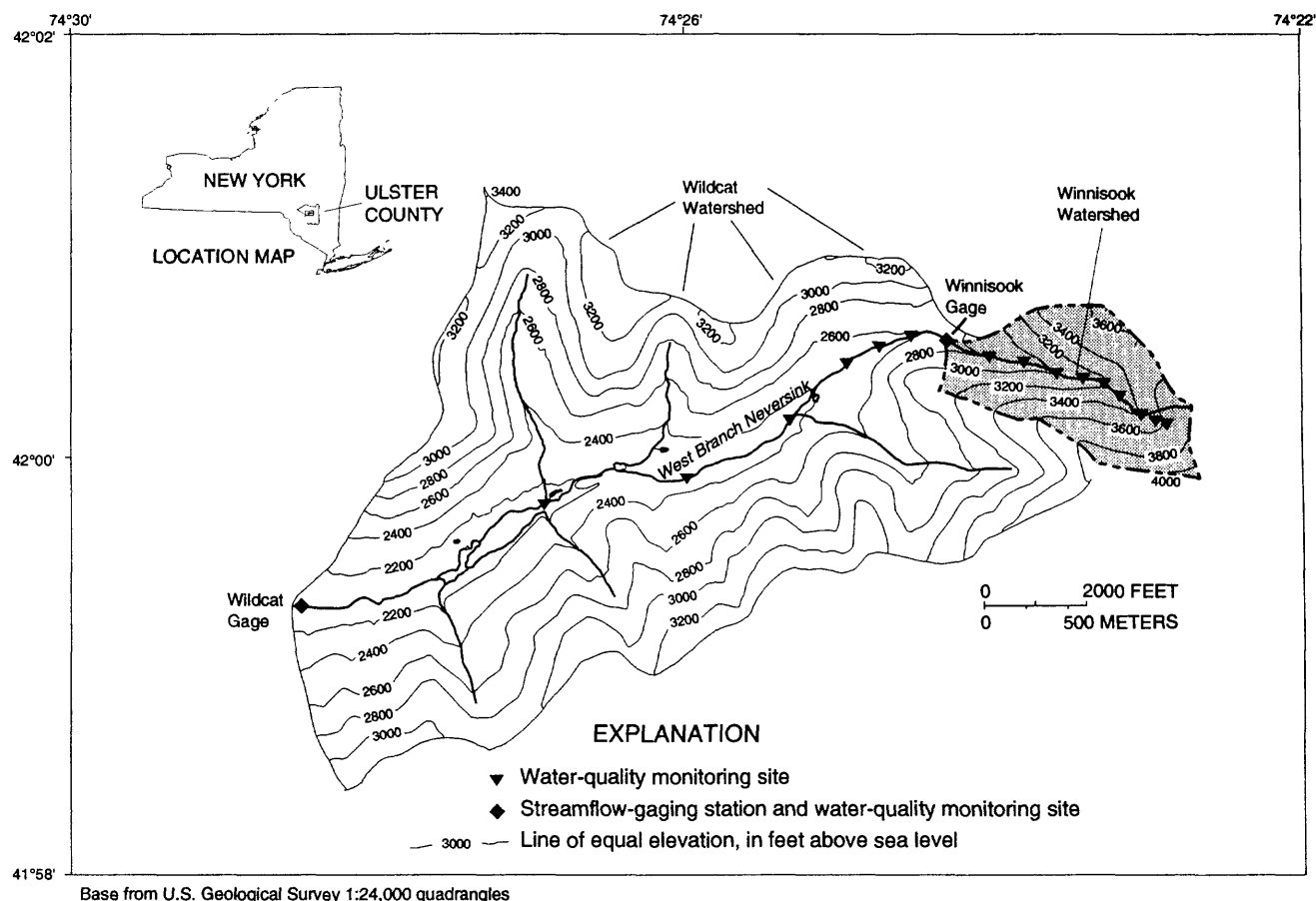
*Hypothesis 1.*—Elevational gradients in stream-water chemistry among headwater streams are a function of subsurface-water residence time.

*Hypothesis 2.*—Subsurface-water residence time in first-order watersheds can be inferred from hillslope position, topography, and hydraulic properties of the soil.

*Objective.*—To develop an empirical relation between spatial variations in stream-water chemistry and indices of subsurface-water residence time that can be computed from a GIS data base.

*Approach.*—Stream-water-sampling sites will be selected such that they divide Winnisook Watershed into eight drainage areas of about equal size (fig. 2). This watershed will be instrumented with a permanent stream gage and throughfall collectors along an elevational gradient. All major seeps along the stream reach from the base of the watershed to the highest sampling site will be identified.

Seepage samples will be collected monthly during nonwinter seasons for 2 years at eight of the seepage sites. Water temperatures will be measured biweekly at all seeps to infer subsurface-water residence time from the temperature fluctuations. Flow at each seep at the time of collection will also be measured. Seep-water



**Figure 2.** Locations of streamflow-gaging stations in Wildcat and Winnisook Watersheds. (Location is shown in fig. 1.)

and stream-water samples will be analyzed for all major solutes. Selected precipitation, seepage, and stream-water samples will also be analyzed for  $^{18}\text{O}$  concentrations to provide additional information on subsurface-water residence time.

Estimates of subsurface-water residence time will also be computed from topographic data and soil hydraulic data through components of the hydrologic model TOPMODEL (Wolock and others, 1990). Topographic contour data will be interpolated onto a regular 30-m grid through ARC/INFO and processed with FORTRAN programs to derive the spatial distribution of the topographic index  $\ln(a/\tan B)$ , where  $a$  is the area upslope from a point that drains down to that point, and  $\tan B$  is the slope. Soil hydraulic data, specifically the saturated hydraulic conductivity ( $K$ ), depth to bedrock ( $b$ ), and porosity ( $n$ ) will be derived from the soil-survey ARC/INFO data. An index of subsurface-water residence time (Wolock and others, 1989) will be computed as  $(bn)^L$ , where  $L$  is the mean of the  $\ln(a/Kb\tan B)$  spatial distribution for the area upslope from a point of interest. The residence-time index will be computed for selected locations in the stream at which water-quality data are being collected to determine whether the index of residence time is a reliable predictor of stream chemistry.

The resulting information will be used to evaluate subsurface-water residence time as a possible control of stream-water chemistry. Temperature fluctuations of seepage, the slope of flow-duration curves, and timing of seepage-flow and seepage-chemistry responses to storms will provide indications of subsurface-water residence time. Digital elevation data available in the GIS data base also will be used to evaluate hillslope position and topography as possible indices of subsurface-water residence time. These indices will be developed as polygon coverages. Empirical relations will then be developed that describe the elevational gradient of stream-water chemistry in this watershed from indices of subsurface-water residence time.

Stream-water samples will be collected biweekly for 2 years and monthly in the 3rd year, and analyzed for all major solutes. Flow will be measured periodically at each of the stream-water-sampling sites to establish a predictive relation between flow at the gage and flow at each of these sites. Sampling over a 3-year period will provide a sufficiently large data base to evaluate relations between concentration and discharge. This information will be used to develop algorithms that describe spatial variations of stream

chemistry for specified ranges of flow if one algorithm is not applicable to all flows.

## Work Element 2. Hillslope Gradients of Soil Chemistry

*Hypothesis 1.*—Consistent elevational gradients in stream-water chemistry in first-order streams are a function of elevational gradients of soil chemistry, known as soil catenas.

*Hypothesis 2.*—Spatial patterns of soil chemistry in first-order watersheds can be inferred from hillslope position, topography, and soils information available from Soil Conservation Service maps.

*Objective.*—To develop an empirical relation between stream-water chemistry and hillslope-soil-chemistry indices available in the GIS data base.

*Approach.*—Comprehensive soil sampling will be done in Winnisook Watershed to investigate the role of hillslope gradients in soil chemistry in determining low-order-stream chemistry. Soil-sampling locations will be selected to encompass the range of slope, aspect, and hillslope positions within the watershed. Samples will be collected from the Oa and Bs horizons along a series of transects perpendicular to the stream; this series will extend from the base of the watershed to the highest elevations. All sampling locations will be recorded by field surveying. Soil chemistry will then be evaluated in relation to hillslope position, slope, and aspect through GIS software. Soil samples will be analyzed for pH, exchangeable bases, exchangeable acidity, total carbon, total nitrogen, KCl-exchangeable Al, and water- and  $\text{NaH}_2\text{PO}_4$ -extractable  $\text{SO}_4^{2-}$ .

Spatial patterns of soil chemistry in forest soils are often difficult to detect because the chemistry typically varies widely over a scale of a few meters or less (Huntington and others, 1988); therefore, a second approach will be used in which nylon-mesh bags filled with mineral soil of uniform composition will be buried in association with the soil pits excavated for the soil sampling. The soil to be used for this experiment will have an initial base saturation greater than 15 percent. The soil will be homogenized, then placed in the bags and inserted in the soil profile. Initial chemistry of the soil will be determined, then, after 1 year, the bags will be excavated and the soil reanalyzed to evaluate the effect of hillslope position. This approach has been used successfully in plot-manipulation studies (David and others, 1990).

The two approaches for identifying spatial patterns in soil chemistry will be evaluated to determine whether stream-water chemistry can be viewed as a function of hillslope variations in soil chemistry. Information available in the GIS data base, including hillslope position, topography, vegetation, and data from Soil Conservation Service soil survey maps, will then be evaluated as possible indices of the spatial patterns of stream chemistry. As in Work Element 1, empirical relations for Winnisook Watershed will be developed to relate spatial variations of stream-water chemistry to soil-chemistry indices available in the GIS data base.

### **Work Element 3. Extrapolation of Relations to Other First-Order Watersheds**

*Hypothesis.*—Empirical relations between stream-water chemistry and indices of (1) subsurface-water residence time, and (2) hillslope patterns of soil chemistry defined in Winnisook Watershed, are applicable to other first-order watersheds in the Neversink basin.

*Objective.*—To test the generality of spatial relations that were developed to describe stream-water chemistry in Winnisook Watershed.

*Approach.*—Stream-water samples will be collected along elevational gradients of about 15 first-order streams and analyzed for all major solutes. From this survey, four streams will be selected that collectively include the range of watershed characteristics that are representative of first-order watersheds within the Neversink basin. A continuous streamflow gage will be installed in one of these streams, which will be in an area of the Neversink basin remote from Winnisook Watershed.

Stream-water-sampling sites within the four watersheds will be positioned to divide the watersheds into about eight subbasins of about equal drainage area. The subbasin streams will be sampled on the same day at low, medium, and high flows, and each sample will be analyzed for all major solutes.

Empirical relations developed for Winnisook Watershed will then be applied to the data from the additional four watersheds, through indices computed from the GIS data base, to test their applicability. These relations will be evaluated over a range of flows in each of the watersheds. Empirical relations to predict spatial patterns of stream chemistry will be

refined through additional information obtained from the four watersheds. This procedure will include an assessment of error propagation to account for unexplained variation in the developed relations. The refined empirical relations will then be used in conjunction with the GIS data base to predict the stream-water chemistry of 20 first-order streams at a point just upstream from the confluence with another stream. These 20 locations will be sampled three times over a wide range of flows to evaluate the accuracy of the predictions.

### **Topic B. Intermediate and Large Watersheds**

The elevational gradients in stream-water chemistry that have been identified in headwater streams within the Neversink basin extend downstream; water entering the Neversink Reservoir tends to have higher pH and ionic strength (with a few isolated exceptions) than water at all upstream sites within the basin. Episodic depressions in pH associated with large streamflows also extend downstream to the reservoir.

Little research has been done on natural watershed processes that affect stream-water chemistry in medium and large watersheds; therefore, the applicability of information from small-watershed research to larger watersheds is unknown. Expanding the scale at which watershed research is conducted lies within the newly evolving discipline of landscape ecology, which has been integrated into land-use planning in Europe for the past decade (Turner and Gardner, 1990). Traditionally, watershed science has relied on either mechanistic investigations in plots, or the “black box” approach, which assumes an entire watershed to be a discrete, homogeneous ecosystem. Neither approach allows extrapolation of small-watershed data to larger areas, whereas landscape ecology emphasizes patterns and processes within areas of differing sizes.

Longitudinal (downstream) gradients of stream chemistry will be evaluated in intermediate and large watersheds to determine whether the spatial variations from headwaters to the reservoir can be interpreted as part of a continuum of the same landscape or reflect a series of discrete landscapes with processes that vary according to local internal patterns. The relation between watershed size and temporal variations in the chemistry of dissolved and suspended solids in intermediate and large watersheds will also be evaluated.

## Work Element 1. Spatial Controls in Intermediate and Large Watersheds

*Hypothesis 1.*—The chemistry of stream water at any point in the basin is a function of the distance from this point to the start of flow in the tributary that is farthest upstream.

*Hypothesis 2.*—The chemistry of stream water at any point in the basin can be viewed as a function of drainage area.

*Hypothesis 3.*—The chemistry of stream water at any point in the basin is a function of subsurface-water residence time, which in turn is a function of topography and hydraulic characteristics of the soil.

*Objective.*—To evaluate the relative importance of landscape positions and drainage area in defining spatial patterns of stream chemistry in watersheds drained by streams that are second order or larger.

*Approach.*—To evaluate controls of stream chemistry in medium-sized watersheds, a streamflow-gaging station will be installed about 5 km downstream from the Winnisook gaging station (Wildcat gage, fig. 2), and 10 sampling sites will be installed between the two gaging stations. Samples will be collected at these sites biweekly for the first 2 years of the project and monthly for the 3rd year, and analyzed for all major solutes. Empirical spatial relations developed for first-order watersheds will then be extrapolated over the reach of 10 sites to determine whether the scale of processes that control spatial patterns of stream chemistry in the headwaters are of equal importance in larger systems.

Water samples and flow measurements will be taken at the five major tributaries to this reach on three separate dates to determine their effect on stream-chemistry gradients. The effect of the tributaries will be quantified through mass-balance calculations and chemical equilibrium modeling through ALCHEMI (Schecher and Driscoll, 1987). The streams of two other intermediate-sized watersheds (Biscuit Brook and Tison Brook, fig. 1, fig. 2) will be longitudinally sampled above the present gages at high, intermediate, and low flows to determine whether longitudinal trends of stream chemistry are consistent among the three watersheds. The GIS data base will be used to help evaluate these trends in relation to watershed characteristics, which include stream order, position on the hill-slope, topography, aspect, drainage area, vegetation, and soils.

Four additional streamflow-gaging stations (Otter pool, West Branch Claryville, East Branch Claryville, and New Hill Bridge, fig. 1) will be installed at locations lower in the drainage than Wildcat gage to evaluate longitudinal gradients of stream chemistry at an increased scale on the East and West Branches of the Neversink River. The present gages on the East Branch and below the confluence of the East and West Branches of the Neversink River (Main Branch; fig. 1) will be included in this analysis. In addition to continuous flow monitoring at these gages, water samples will be collected biweekly for complete chemical analysis. On three occasions, flow at all major tributaries to the East and West Branches and below the confluence of the East and West Branches of the Neversink River will be measured or estimated from a hydraulic model. Stream-water samples will be collected concurrently with flow measurements at these locations for analysis for major solutes. This information will be used for analysis of longitudinal gradients and effects of tributaries in the same manner as for the intermediate-scale watersheds.

## Work Element 2. Effect of Watershed Size on Temporal Variations in Stream Chemistry

*Hypothesis 1.*—Temporal variations in stream chemistry are attenuated as drainage area increases.

*Hypothesis 2.*—Temporal variations in stream chemistry are directly related to the surface-runoff component of streamflow during high flows.

*Objective.*—To determine the magnitude of temporal variations in water quality for the small, medium, and large watersheds within the Neversink basin.

*Approach.*—High-frequency stage-activated stream-water sampling will be done at five gaging stations on the West Branch Neversink River for 1 month during one spring and one fall. Each sample will be analyzed for major solutes. The response of stream chemistry to changes in flow at each sampling site will be compared with the response at the other site to establish a relation between temporal variations in streamflow and watershed size. The model of Johnson and others (1969) will be used to quantify concentration-to-discharge relations. Continuous pH monitors will be installed at the Winnisook and Main Branch gaging stations (fig. 1) to provide additional information on short-term changes in stream chemistry that might not be directly related to changes in flow.



A transfer function (time series) model will be fitted to the flow and concentration data to quantify the strength of the relation between flow and concentration. An index of the surface-runoff component in streamflow will be derived from the GIS topography and soil data bases. The observed strength of the flow-to-concentration relation will be compared with a flow-path index to determine whether spatial patterns in the temporal variation in stream chemistry can be attributed to spatial patterns in flow paths.

In addition to the chemical analysis of solutes, samples collected at the Main Branch site by automatic water sampler will be analyzed for total nitrogen, total phosphorus, and total suspended-solids concentrations. Automatic stage-activated water sampling will be done at this site throughout the study, as will periodic sampling for suspended solids during base flow.

Results of stream-water sampling will be maintained in files directly related to the GIS data base. This information will be used in conjunction with flow data to define the relation between seasonal variations in stream chemistry and watershed size. The GIS data base will be used to integrate the magnitude of the chemical changes over time with their geographic distribution.

### **Topic C. Landscape Controls of Stream Chemistry**

The null hypothesis of the work elements of topics A and B (described above) is that subbasin position along a stream is not the major determinant of soil and stream-water characteristics. In watersheds with significant human activity, for example, point-source chemical contributions can significantly alter any natural downstream pattern of water-quality evolution. Similarly, in relatively undisturbed systems such as the Neversink, certain local soil or surface-water characteristics can cause irregular patterns in water quality along an elevation gradient. Studies have shown, for example, that changes in vegetation can significantly affect water quality along the length of a stream, regardless of elevation (Lawrence and others, 1986). An assessment of the relation between water quality in headwater streams and that in the larger rivers downstream therefore requires information on how nonsystematic changes in landscape can affect stream-water quality.

Chemical changes in water as it moves through the soil have been studied extensively, but the effect of these changes on stream chemistry remains difficult to quantify (Lawrence and Fernandez, 1991; Bishop and others, 1990; David and Driscoll, 1984). Measurement networks with the instrumentation necessary to monitor water flux through a particular zone of a watershed would be prohibitively expensive, and the disturbance inherent in the installation of such numerous instruments would probably disrupt the natural flow of water. Models that mathematically link hydrologic characteristics of basins with chemical characteristics of stream waters have had some success in predicting both the discharges and the concentrations of selected constituents at the outlet of small watersheds (Hooper and others, 1990; Gherini and others, 1985; Christophersen and Wright, 1981). Many of these models include parameters that cannot be uniquely identified by the calibration data, however, and therefore have limited utility outside the range of conditions under which they were calibrated (Hooper and others, 1990).

The "End-Member Mixing Analysis," or EMMA model designed by Christophersen and others (1990), relates "end member" concentrations (observed chemical concentrations in water from specified sources) to stream-water chemistry without use of soil-water flux rates. When plotted on a graph, end-member concentrations delineate the range of stream chemistry that can result from the conservative mixing of end members. End members that affect stream-water quality might include water from the organic horizon of the soil, the mineral horizon of the soil, or deep aquifers. Stream concentrations that plot outside this area indicate either that not all end members have been accounted for, or that mixing is not conservative. Through this approach, the relative contribution of each end member to stream-water concentrations can be estimated, and this information can, in turn, be used to indicate which landscape processes control stream-water chemistry.

This approach can typically be applied to only a few locations, however, because installation of collection equipment is costly, and the question of whether the results are representative of the specific type of landscape would still be unanswered. To relate such "site-specific" information to chemical processes in the Neversink watershed as a whole will require a regional survey of the chemical conditions in several areas for each type of landscape. The survey will include

stream-discharge measurement and water-quality sampling at the upstream and downstream end of stream reaches within selected types of landscape (such as several hemlock groves, wet-soil zones near streams, etc.). The results will be used to compute the chemical inputs to and outputs from each type of landscape, and the average values will be compared with stream-chemistry data from other types of landscapes and from selected stream-monitoring stations on the Neversink River to predict stream chemistry from the landscape chemistry.

The approach to this part of the research program will have two elements. The first will entail (1) reconnaissance of surface waters entering and leaving areas of specific types of landscape to identify which types of landscape have the greatest effect on stream chemistry; (2) mapping of three to five different types of landscape within the watershed to obtain estimates of the spatial distribution, number of areas of each type, and percentage of watershed area occupied each type; and (3) regional surveys of landscape effect on water quality. The EMMA approach, which treats each type of landscape as an end member, will then be used to determine the relative effect of each type of landscape on stream chemistry and predict water quality at selected gaging stations in the Neversink River. The second element will include sampling of surface water, soil water, seep water, and atmospheric deposition at stations representing each type of landscape to identify key hydrologic factors as end members for predicting changes in stream-water quality within those landscapes.

### **Work Element 1. Identifying the Effect of Landscapes on Neversink River Water Quality**

*Hypothesis.*—Specific types of landscape that cause local, nonsystematic changes in stream-water chemistry within a watershed can be identified, and the distribution of these areas (subcatchments) can be used to predict longitudinal changes in stream chemistry in the Neversink River.

*Objective.*—To (1) evaluate relations between specific types of landscape and general spatial variations in stream-water chemistry, and (2) map the spatial distribution and locations of these types of landscape for the spatial model.

*Approach.*—To identify the major types of landscape in the basin through (1) a field reconnaissance,

(2) a sampling program to define flow and (or) chemistry of stream water entering and leaving representative landscapes, and (3) a mapping program to delineate these landscape areas so that information can be incorporated into the GIS data base. The data from each type of landscape will then be averaged for use as end members for predicting stream chemistry.

In the reconnaissance phase of the study, stream water will be sampled throughout the Neversink basin to identify areas in which stream chemistry changes over short distances. These areas could represent (1) major changes in slope or type of soil relative to upstream areas, (2) standing water in lakes, ponds, or wetlands, or changes in the number or productivity of seeps, and (3) changes in forest vegetation. Detailed sampling of stream and seep water will then be conducted in areas where chemical transitions occur. The resulting data will be used to select specific types of landscape for study of their effect on stream-water quality. Detailed sampling of chemical-transition zones will result in longitudinal profiles of stream-water chemistry, temperature, and, in some cases, discharge. Topography of the subcatchments will be characterized, and types of forest stands will be identified.

Once the key types of landscape that affect surface-water chemistry in the Neversink watershed have been identified, a stream-sampling program will be established for each, and stream chemistry and discharge will be measured four times over a wide range at the upper and lower boundaries of each area. Several locations above and below each landscape area will be sampled during each survey. Samples will be a composite of depth-integrated samples collected across the channel to ensure sampling of all water entering that stream segment from each landscape area. From this data set, instantaneous-load calculations (concentration  $\times$  discharge) will be made for each sampling point in the stream, and a net chemical flux for each subcatchment will be calculated as the difference between flux at the upper and lower sampling points of each stream segment. A similar computation will be done for discharge to obtain a net water flux for the subcatchment. The net chemical flux will then be divided by the net water flux to determine a "net concentration" for the subcatchment (Lawrence and Driscoll, 1990). These net concentration values will then be applied through the EMMA approach to determine the relative contribution of each subcatchment to downstream water quality.

The percentage of each type of landscape in each subcatchment (such as hardwood hillslope, hemlock hillslope, wet-soil zone, and so forth) will then be calculated from spatial data available in the GIS data base and used to relate landscape type to spatial patterns of stream chemistry throughout the basin.

## **Work Element 2. Modeling the Sources of Landscape Effects on Stream-Water Quality**

*Hypothesis.*—The chemistry of stream water draining a particular type of landscape is the result of mixing of definable end-member solutions originating from specific positions along the hydrologic flow path of the watershed.

*Objective.*—To identify the watershed characteristics in each landscape area that affect the quality of water transported through that watershed, and to use end-member-mixing analysis to discern how key landscape types can affect stream chemistry.

*Approach.*—The EMMA model requires data on chemical concentrations of solutions in the hydrologic cycle, such as shallow soil water, ground water, and deposition. Solution samples from selected end-member sites in each of the catchments will be collected from four to six times. The soil plots for end-member sampling will be distributed evenly throughout the watershed, with particular focus on the Biscuit Brook, Winnisook, and Shelter Creek watersheds (fig. 1), where other data that support this study are being collected. Measurement techniques will depend on the chosen end member—for example, solutions from poorly drained soils will be sampled with piezometers or basters, whereas solutions from well-drained soils will be sampled with lysimeters. The most likely end members to be monitored during this study include the unsaturated-soil zone, the saturated-soil zone, the ground-water-discharge zone (seeps), stream water, precipitation, and ponded water. Soil water will be collected from soils beneath hardwood and hemlock forest stands. Sampling locations will be recorded in the GIS data base as a point coverage; unique identifying values will be directly related to the chemical data collected at these sites.

Soil water from well-drained soils will be collected by zero-tension lysimeters placed below each of the Oa and Bs soil horizons, and soil water in saturated soils will be sampled through shallow piezometers or skimmed from surface water with a baster. Seep-water

quality will be monitored in all landscape areas used in the study.

The several wetlands, two clusters of small fish ponds, and one lake in the Neversink watershed could have a significant effect on stream-water quality downstream from their outlets. Initially, water quality and discharge at the inflow and outflow points of representative ponded waters, and in the Neversink River above and below the confluence with the ponded-water outlet, will be monitored. If these measurements indicate a significant effect on stream-water quality, additional monitoring will be done.

## **Topic D. Nonconservative Transport of Nitrate and Aluminum in Stream Water**

Historically, many studies of stream and watershed hydrology and geochemistry have assumed that the stream channel acts as an inert pipeline that conservatively transports dissolved solutes downstream (Johnson and others, 1969; Pinder and Jones, 1969). Since the 1970's, however, the effects of stream-channel and near-channel processes on the chemical evolution of stream water have gained increased attention (Robinson and others, 1979; Hill, 1981; Henriksen and others, 1988), although none of the recently developed small watershed models explicitly consider stream-channel processes (Cosby and others, 1985; DeWalle and others, 1988; Christophersen and others, 1990).

Nonconservative transport of many dissolved chemical constituents in rivers and streams in a wide variety of geographic locations has been documented (Hill, 1981; Christensen and others, 1990; Triska and others, 1990b). Within the Neversink River basin, nitrate is of particular concern because it plays a major role in acidification and could stimulate algal growth. The major processes that affect nitrate transport include: physical storage and release (Triska and others, 1990b), reduction (including denitrification and ammonification) in the near-stream zone (Christensen and others, 1990), uptake by aquatic macrophytes (Casey, 1977), immobilization by the autotrophic and heterotrophic epilithic community (Kaushik and others, 1975), and oxidation (nitrification) in stream sediments (Triska and others, 1990a). Because nitrification can be coupled with denitrification in stream sediments, the channel can serve as a nitrate source or sink, depending on which process is dominant. Several studies have found that denitrification is the dominant

process in stream nitrate transport (Kaushik and others, 1975; Van Kessel, 1977; Hill, 1981; Christensen and others, 1990), but at least one study found a stream reach to be a net source of nitrate (Triska and others, 1990b).

In watersheds that are sensitive to acidic precipitation (have a limited capacity to neutralize strong-acid inputs), such as the Neversink, decreases in pH are accompanied by increases in aluminum concentration during high flows (Burns, 1989; McAvoy, 1989). These increases could result from the release of aluminum from the stream-channel substrate (Norton and Henriksen, 1983; Henriksen and others, 1984). In experiments in which acid was added directly to a stream, aluminum concentrations increased downstream, indicating the source of readily mobilized aluminum in the stream substrate (Hall and others, 1980; Henriksen and others, 1988). Most reports of aluminum precipitation in stream channels have been from areas affected by sulfide mineral oxidation (Theobald and others, 1963; Nordstrom and Ball, 1986), but at least one study has reported removal of dissolved aluminum by the substrate in a stream whose watershed does not have abundant sulfide minerals (Lawrence and Driscoll, 1990).

The Neversink Watershed Study will address the effects of stream-channel processes on the chemical evolution of aluminum and nitrate in stream water. Stream reaches that collectively represent the range of water chemistry and substrate conditions found within the watershed will be identified and mapped as polygon coverages in the GIS data base. After detailed study of selected stream reaches, results will be extrapolated to the entire Neversink River watershed on the basis of stream-channel information stored in the GIS data base.

### Work Element 1. Nitrate

*Hypothesis.*—Stream-channel processes have a significant effect on the downstream transport of nitrate in the Neversink River.

*Objectives.*—(1) To determine whether representative stream reaches are sources or sinks of nitrate and estimate the annual variability of stream-reach uptake or release; (2) To quantify the relative roles of physical and biotic storage and release in the downstream transport of nitrate in representative stream reaches; (3) To quantify the relative importance of denitrification and immobilization by substrate materials as within-

channel sinks of nitrate in representative stream reaches. (This objective will be pursued only if the selected stream reaches show significant nitrate losses); (4) To extrapolate results from the above objectives to the entire Neversink watershed.

*Approach.*—A reconnaissance of the Neversink River will be done to select two or three representative stream reaches (200 to 800 m long) for study. Stream-channel characteristics will be incorporated into a GIS coverage of stream data. Maps and aerial photographs will be examined to locate representative stream reaches. Two of the reaches will represent contrasting substrates; the first will be quiescent with abundant sunlight and an organic-rich substrate, and the second will be energetic, with abundant pools and riffles, beneath a closed forest canopy. If necessary, a third reach will be selected for detailed study to represent the diversity of stream-channel types.

Two to four shallow wells will be driven into the stream channel or just adjacent to the stream in each reach during the first year, after selection of stream reaches. These wells will be made of stainless steel and have a 31-cm-long screen and a drive point at the end.

One- to 2-day mass balances of nitrate, ammonium, and chloride will be calculated for each stream reach during four seasonal conditions—early spring with high base flow; late May, just after canopy development; mid- to late summer, during maximum nitrogen uptake; and early October, during leaf fall. These conditions were selected to represent a range of light, temperature, flow, and organic-matter input that are thought to affect nitrate transport.

To estimate the mass balances, flow will be measured with a current meter at the upstream and downstream ends of each reach near the beginning and end of each 24-hour period. Measurements will be made when rain is not expected. If significant rainfall occurs during the measurement period, the experiment will be discontinued until flow conditions stabilize. A reference point will be established near the upstream and downstream ends of each reach, and the water-surface elevation (stage) will be measured frequently during the 24-hour period to record the variations in flow. Samples will be collected at the upstream and downstream ends of each reach every 2 hours. Additionally, at least two samples will be collected daily during the 24-hour period from each well and tributary along the reach.

Mass balances of nitrate, ammonium, and chloride will be calculated for each reach to determine whether the channel is a net source or sink for nitrate and ammonium. Chloride will be assumed to be transported conservatively and will be used to check the uncertainty of each mass-balance calculation. Data from well and tributary samples will be used to calculate additions to or losses from the stream reach if flow measurements indicate that the reach is gaining or losing water. The mass balances will reveal the extent of nitrate gain or loss through a given stream reach and the degree to which downstream changes in concentration vary with substrate type and season and with light, temperature, flow, and organic-matter input. Concentration changes between day and night will indicate the extent of autotrophic uptake relative to denitrification if the stream is a net nitrate sink.

Mass balances over short periods of time will reveal whether a given stream reach is a source or sink for nitrate, but they will not indicate how much of the change in downstream load is the result of abiotic processes rather than biotic processes. To address this question, a series of tracer experiments will be performed during the second year. A tracer containing a nitrate-bearing salt and a conservatively transported salt (chloride or bromide) will be pumped into each stream reach at a location far enough upstream from the top of the reach to allow complete mixing. The tracer will be pumped into the reach for several days at a known rate and at a concentration high enough to raise stream concentrations of each constituent to 20 to 50 percent above background concentrations. Samples will be collected frequently at the beginning and end of the experiment, and less frequently once steady-state concentrations are reached. The tracer experiment will be done on each reach during at least two contrasting seasonal conditions. Precipitation will be sampled at a collector along each stream reach to account for direct deposition during the experiment. Additionally, the wells and tributaries will be sampled frequently during the tracer experiments.

The mass flux of the conservative tracer will be compared with the mass flux of nitrate to determine how much of the storage or release of nitrate is physical; the difference between total storage or release and physical storage or release will be attributed to biological processes. If rainfall is significant during any of the tracer experiments, the data will be used to determine how the ratio of physical to biotic uptake or release varies with flow.

Results of the mass-balance calculations and tracer experiments will identify which stream reaches are sources or sinks of nitrate. Physical and biological characterization of the stream reaches in which these processes have been identified, and subsequent analysis through the GIS data base, will enable extrapolation of the results to other parts of the Neversink watershed.

The nitrogen cycle in streams is complex and has several potential sources and sinks, many of which are difficult to quantify. The approach discussed above assumes that processes such as uptake by aquatic macrophytes are negligible in a mass-balance calculation for nitrate, if, for example, the stream channel contains large quantities of moss, but the approach may have to be revised. Detailed observations of each stream reach, and examination of the effects of varying seasonal conditions on nitrate transport, may suggest changes in the approach. A few select analyses of stream water, ground water, and periphyton for  $^{15}\text{N}/^{14}\text{N}$  ratios could provide additional information on nitrogen transport, and if these analyses provide information on stream-channel nitrate cycling, further sampling and analysis will be done.

## Work Element 2. Aluminum

*Hypothesis.*—Aluminum is removed from solution in the Neversink River in reaches where stream-water pH increases significantly over a short distance.

*Objectives.*—(1) To determine whether aluminum is removed from solution in the Neversink River channel in selected stream reaches where pH at the upstream end is less than 5.5 during the sample-collection period and increases more than 0.5 pH units in less than 800 m, and (2) to determine the temporal and spatial variability of aluminum removal or its release from the substrates in selected reaches of the Neversink River during spring and fall.

*Approach.*—Initially, reconnaissance sampling of the Neversink River watershed will be done to select two stream reaches in which base-flow pH at the upstream end is usually less than 5.5 and increases by at least 0.5 pH units within a distance of 800 m. At least four sampling locations will be selected within and just downstream from each reach. Samples will be collected from these sites as quickly as possible on a given day in the early spring and again in the fall. Discharge will be measured at the upstream and downstream ends of each reach as the samples are collected.

Samples will be analyzed for all major chemical constituents, three fractions of dissolved aluminum (total monomeric, organic monomeric, and total), and fluoride. An attempt will be made to select sampling locations that coincide with stream-gaging locations. Discharge measurements will be used to calculate an instantaneous aluminum mass balance for each reach.

Data from all sampling sites will be entered into the GIS data base as a point coverage, the identifying values of which will be directly related to the water-quality and streamflow data collected along the specified stream reaches. The uptake and release of aluminum in relation to stream-water quality will be analyzed through the digital data base.

An equilibrium thermodynamic model (ALCHEMI or WATEQ) will be used to calculate saturation indices for the common aluminum-bearing minerals that are likely to control aluminum activity in solution. The saturation indices will provide a reference state against which changes in aluminum concentrations in relation to pH can be compared. If the saturation indices and mass-balance fluxes indicate that aluminum is precipitating from solution as pH increases, an additional experiment will be performed in which stream sediment from another location will be placed in Nyltex<sup>1</sup> bags and submerged for several months at selected locations above and within the stream reach. At the end of the experiment, the bags will be removed and the sediment dried, and a series of extractions will be performed to identify the forms of exchangeable and solid-phase aluminum (McKeague and others, 1971). A clean sediment sample that has not been submerged will be compared with the other samples; the presence of significant amounts of aluminum in the sediment in a stream zone in which mass-balance and equilibrium thermodynamic calculations indicate aluminum is precipitating will help to confirm the results.

## Topic E. Nitrogen Cycling

The cycling of nitrogen within forest ecosystems is extremely complex and involves many plant and microbially mediated biochemical reactions, as well as chemically controlled transformations and physical

transport mechanisms. One method of evaluating the net result of these processes is to compare nitrogen inputs in the ecosystem with the outputs. Because changes in the nitrogen cycle could alter stream-water quality, a nitrogen-monitoring program will be established in Winnisook watershed, the source watershed of the West Branch Neversink River (fig. 1). Annual nitrogen input-output budgets will be estimated for subbasins within the Winnisook Watershed and for the entire watershed. Because the Winnisook watershed faces northwestward and drains the highest elevations of the West Branch Neversink watershed, atmospheric deposition is likely to be greater here than elsewhere in the Neversink basin. Therefore, if forest ecosystems in the Neversink basin are approaching nitrogen saturation, the first effects on water quality would be seen in the Winnisook watershed.

Development of chemical input-output budgets requires definition of ecosystem boundaries. In this study, watershed divides will serve as lateral boundaries, and the top of the forest canopy and bottom of the solum will serve as upper and lower boundaries. Because neither bedrock nor till in the Neversink basin contain significant quantities of nitrogen, and because nitrogen-fixing plant species are rare, nitrogen can be introduced into the system only through atmospheric deposition.

To measure the amount of material deposited from the atmosphere is extremely complicated. Atmospheric deposition occurs by three principal mechanisms: (1) wet deposition, including rain and snow; (2) dry deposition or the direct deposition of particles (such as salts, acid aerosols) and gases (such as sulfur dioxide and nitrogen oxides) onto vegetation surfaces, and (3) cloud-water deposition of nonprecipitating cloud droplets onto vegetation immersed in cloud or fog. All three contribute significantly—wet deposition tends to dominate in areas far from the nitrate-emission sources, whereas dry deposition tends to dominate in areas close to those sources; cloud-water deposition can dominate in areas frequently exposed to fog or low clouds, such as mountain tops and seacoasts. Of the three, only wet deposition is easily and routinely measured; dry deposition must be estimated from air concentrations and deposition velocities, which are determined from hydrodynamic models that are sensitive to topographic and canopy variations. Cloud-water deposition is estimated from collectors that simulate the forest canopy. Throughout most of the eastern U.S.,

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<sup>1</sup> Use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Government.

the amount of nitrogen contributed in dry deposition is equal to or greater than the amount contributed in wet deposition, even in rural areas; therefore, measurements fail to account for at least half of the total deposition (Lindberg, 1992; Lovett, 1992).

The difficulty in estimating total deposition is increased in mountainous terrain by the highly variable meteorological and forest-canopy characteristics. For example, high elevations in the Catskill Mountains can result in (1) larger amounts of precipitation than at lower elevation, (2) greater wind speeds, which enhance dry and cloud-water deposition, (3) coniferous rather than deciduous forest, which increases the deposition of some particles and gases but can decrease the deposition of other gases, and (4) an increased amount of time in which the forest is within clouds (Lovett and Kinsman, 1990). Together these factors result in atmospheric-deposition rates at high elevations that can be more than four times greater than those at nearby low elevations (Lovett and Kinsman, 1990).

Nitrogen is an essential nutrient for plant and microbial growth, and several processes can effectively immobilize nitrogen within the forest canopy and rooting zone. For this reason, nitrogen inputs tend to greatly exceed outputs in undisturbed forest ecosystems. Mechanisms for ecosystem loss of nitrogen include (1) release of gaseous compounds to the atmosphere (primarily as  $N_2O$  or  $N_2$ ), (2) transport in both dissolved and particulate forms by surface water, and (3) infiltration into the soil. In undisturbed, forested watersheds with well-drained soils, most nitrogen is lost as dissolved  $NO_3^-$  or  $NH_4^+$  through surface-water transport (Likens and others, 1977); therefore, measuring nitrogen losses in streamflow is simpler than estimating nitrogen inputs by atmospheric deposition. Outputs in surface water can be quantified through continuous flow measurements and periodic chemical analysis of stream water leaving the watershed. The frequency of sampling depends on the magnitude of temporal variation in stream-water nitrate concentrations.

### Work Element 1. Quantifying Nitrogen Budgets

*Hypothesis.*—Low-order watersheds in the Never-sink basin are approaching nitrogen saturation.

*Objective.*—To (1) quantify annual nitrogen inputs and outputs in subbasins, (2) evaluate elevational patterns of nitrogen cycling, and (3) obtain baseline

conditions necessary to identify future changes.

*Approach.*—Because total atmospheric deposition of nitrogen is difficult to measure, a combination of atmospheric and ecosystem measurements will be used to evaluate the elevational patterns of deposition. Precipitation will be collected with an automatic wetfall-only collector, air samples will be collected with a filter-pack system, and throughfall deposition (the deposition of chemicals in water that drips through the forest) will be collected with a network of funnel collectors under selected forest stands.

A reference site for measurement of wet and dry deposition will be established lower in the basin, at about 730 m elevation. The site will be in a clearing with AC electric power and will contain an automatic precipitation collector (for chemical analysis) and an air-quality-measurement system. The system consists of a flow-controlled pump that draws air at 3 to 5 L/min through a three-stage filter pack that traps atmospheric particles and the gases  $HNO_3$  and  $SO_2$  on specially treated filters. The filter pack will be installed on a tiltable 5-m mast, and the pump and flow controller will be placed in a weatherproof enclosure. In addition, wind speed and direction, temperature, relative humidity, duration of foliar wetness, and solar radiation will be measured with a meteorological measurement system and data logger. The meteorological data will allow (1) estimation of dry deposition from the measured atmospheric concentrations through a dry-deposition model in common use throughout the U.S. (Hicks and others, 1986), and (2) determination of how concentrations of airborne pollutants are related to the wind direction and, presumably, the general source areas of the pollutants.

Chemical deposition is more difficult to measure than atmospheric chemical concentrations, and methods of measuring the deposition of dry particles, gases, and cloud droplets are not well established and are the subject of current research (Hicks, 1986; Lovett and others, 1992). One method of measuring atmospheric deposition that appears to be gaining considerable support is collection of throughfall (Lindberg and Garten, 1988), but because forest canopies take up atmospheric N, measurement of throughfall probably underestimates total nitrogen deposition. This does not apply to sulfur, however; recent research indicates that forest canopies neither take up nor release significant quantities of sulfur in rain that flows over them (Lindberg and Garten, 1988). If the rain washes off sulfur



deposited as gases, particles, and cloud droplets, as well as that deposited in rain, then the total atmospheric deposition of sulfur (wet + dry + cloud) can be directly measured by the collection of throughfall. A strong correlation has been shown between the amount of  $\text{SO}_4^{2-}$  in throughfall and the total sulfur deposition as estimated by independent methods (Lindberg, 1992, fig. 2). Collection of throughfall to measure atmospheric deposition in remote, mountainous areas is advantageous because the measurement does not rely on models of deposition velocity that are sensitive to variations in topography, and collectors do not require electricity.

Measurements of throughfall-deposition of sulfur will be used to estimate elevational patterns of total nitrogen deposition that cannot be measured directly without installation of air-quality-monitoring equipment throughout the watershed. Previous research suggests that elevational patterns of sulfur deposition are similar to those of nitrogen (Lovett and Kinsman, 1990). In this approach, a relation will also be developed between nitrogen deposition in throughfall and in dryfall at the base of the watershed. This information will then be integrated with the throughfall-deposition measurements at other locations to evaluate spatial patterns of total nitrogen deposition and to estimate annual nitrogen deposition at a subbasin scale and whole-watershed scale.

Throughfall will be collected in 80 funnel collectors placed in clusters of five along a line from the base of the watershed to the top. The throughfall solutions will be collected weekly during spring, summer, and fall, and returned to the laboratory for analysis for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{SO}_4^{2-}$ . The five samples from each cluster will be composited into one sample before analysis to minimize analytical costs. During winter (November 1 through April 1), samples will be collected biweekly in frame-supported polyethylene bags. Total throughfall flux of each constituent will be calculated as the product of concentration and water volume for each site and sampling period. Incident precipitation will also be measured year-round by a standard wet-only collector in the open area at the base of the watershed and in a small clearing near the top, and analyzed for nitrogen and sulfur.

Losses of nitrogen from Winnisook Watershed will be calculated from flow measurements and biweekly sampling described in Topic A, Work Element 1.

Samples will also be collected during storms to monitor changes in concentrations that often occur during changes in flow. Biweekly water samples will be analyzed for dissolved  $\text{NO}_3^-$  and  $\text{NH}_4^+$ ; storm samples will be analyzed for these constituents and total suspended N. All sampling-location data and water-quality data will be maintained in the GIS data base and will be used to quantify nitrogen inputs and outputs and to analyze spatial patterns of nitrogen deposition in the watershed.

Nitrogen inputs and outputs will be monitored for 4 consecutive years; efforts will be made to resume measurements 5 to 10 years later. Quantifying nitrogen inputs and outputs will provide detailed baseline information that will be useful in evaluating any future changes that might result from changes in atmospheric deposition or climate. The nitrogen-budget data will also be compared with data from other sites in the Northeast to investigate the status of Winnisook watershed in relation to similar sites that receive different amounts of atmospheric deposition.

## **Topic F. Water Quality and Its Effects on Aquatic Biological Communities**

Catskill rivers have historically supported self-sustaining brook trout (*Salvelinus fontinalis* Mitchell) populations. Since the mid-1960's, however, acidic deposition has degraded water quality and adversely affected aquatic communities in several Catskill rivers, including the Neversink (Colquhoun and others, 1984; Murdoch and others, 1991; Stoddard and Murdoch, 1991). Much of the East Branch of the Neversink River, as well as many low-order reaches in the West Branch, lack viable populations of indigenous fish species such as brook trout (U.S. Geological Survey, unpublished data, 1992). Although fish can be found in most reaches of the Neversink River, juvenile age classes are commonly missing, community diversity typically is low, fish condition is poor, and natural reproduction appears to occur only in well-buffered tributaries. In the East Branch of the Neversink River, prey species such as the slimy sculpin (*Cottus cognatus* Richardson) now are found only in a few low-order tributaries. Aquatic macroinvertebrate communities have also been affected in most reaches of the Neversink River (U.S. Geological Survey, unpublished data, 1992).



## Effects of Acidification on Fish and Invertebrate Populations

Laboratory toxicity experiments and field investigations have demonstrated that low pH and high aluminum concentrations, alone and in combination, can be toxic to fish (Schofield and Trojnar, 1980; Baker and Schofield, 1982; Parkhurst, 1987; Mount and others, 1988; Baker and Christensen, 1991). The inorganic form of aluminum is biologically available and therefore is usually the fraction most highly correlated with inhibition of brook trout growth and increased mortality during laboratory toxicity tests (Driscoll and others, 1980; Baker and Schofield, 1982; Mount and others, 1988). Inorganic aluminum concentrations also appear to be a primary factor limiting fish survival and populations in acidified lakes and streams (Parkhurst, 1987; Schofield and Driscoll, 1987; Johnson and others, 1987; Baker and others, 1990).

Surface-water acidification also affects aquatic macroinvertebrates and their benthic communities. Unlike fish species, however, invertebrate mortality tends to be most related to ambient pH levels (Raddum, 1980; Baker and others, 1990). The response to acidification differs greatly among invertebrate species because of wide differences in their physiology, life-history strategies, and ecology (Havas, 1981; Pratt and Hall, 1981; Hall and others, 1987; Raddum and Fjellheim, 1984). This range in species tolerances tends to mediate community responses associated with acidification, although changes in structure and function (species replacements) are often noted (Baker and others, 1990). Because macroinvertebrate species have short generation times, and many species are sensitive to acidic conditions, they are excellent bioindicators of acidification trends (Raddum and Fjellheim, 1984; Okland and Okland, 1986).

## Mechanisms of Fish Stress and Mortality

Inorganic aluminum and  $H^+$  invoke stress and mortality in fish through several interrelated physiological mechanisms. Concentrations of inorganic aluminum above  $5 \mu\text{mol/L}$  and/or pH below 6.0 can alter blood-ion balances, which can lead to osmoregulatory damage to essential tissues and organs (Daye and Garside, 1976; Packer and Dunson, 1972; Gagen and Sharpe, 1987). Both low pH (below 4.5) and elevated aluminum concentrations (above  $11 \mu\text{mol/L}$ ) can cause suffocation from excess production of mucus,

erosion or expansion of membrane, and accumulation of aluminum precipitates at the gill surface (Packer 1979; Schofield and Trojnar 1980; Leivestad 1981; Cleveland and others, 1986).

Sensitivity of organisms and degree of toxicity of surface waters often changes as a result of complex hydrogeochemical interactions within watersheds. For example, calcium seems to enhance brook trout tolerance to toxic levels of inorganic aluminum and  $H^+$  by increasing efficiency of Na regulation (Mount and others, 1988). Increased concentrations of dissolved organic carbon can also decrease the toxicity of aluminum and  $H^+$  in streams by increasing the organic fraction of monomeric aluminum and decreasing the biologically available inorganic fraction (Baker and Schofield 1982; Parkhurst, 1987).

In streams where acidic tributaries with elevated dissolved aluminum concentrations mix with waters that have a positive acid-neutralizing capacity, oversaturation with respect to the controlling mineral phase may occur; oversaturation with respect to dissolved aluminum can result in significant fish mortality at pH and aluminum levels that would be nonlethal under equilibrium conditions (Schofield and Trojnar, 1979; Cleveland and others, 1986; Parkhurst, 1987). During oversaturation conditions, aluminum can readily sorb to gill tissue and result in suffocation and, under extreme conditions, precipitating aluminum has been shown to disrupt benthic macroinvertebrate communities (McKnight and Feder, 1984). Although evidence from laboratory experiments indicates that aluminum solubility affects fish mortality, it has not been investigated under natural conditions. Preliminary sampling suggests that oversaturation of aluminum with respect to a controlling mineral phase occurs in several locations in the Neversink basin.

## Use of Biological Indices in Characterizing Water Quality

Stream-water quality has traditionally been defined in terms of measured chemical concentrations and laboratory tests in which levels of reconstituted toxins are kept constant throughout the experiment. This approach often poorly represents conditions in natural systems, however, because (1) stream-water chemistry can change significantly over a few hours (Murdoch and others, 1991), whereas water samples are seldom collected more often than weekly, and (2)

water chemistry can vary over distances of 10 m or less (U.S. Geological Survey, unpublished data, 1992), whereas sampling is seldom done over sufficiently short distances to detect these local changes. These spatial and temporal variations in water quality can affect survival of fish and macroinvertebrate populations. Because mortality is a function of the duration and frequency of exposures, as well as the toxin concentration, local variations can provide refuges wherein individuals and populations can avoid toxic conditions.

To overcome the difficulty in accurately characterizing water quality from chemical analyses of water samples and relating chemistry to results from laboratory toxicity tests, biological indices have been developed that relate factors such as population density and biomass of key species or species assemblages to those that would be expected in natural (unpolluted) conditions. One commonly used index is the Index of Biological Integrity (IBI) developed by Karr and others (1986). In this approach, a score is developed for a particular site, whereby a number from 1 to 5 is assigned to each of 12 operationally defined measurements that reflect characteristics of the fish community. The 12 measurements are divided into three general categories: (1) fish-community richness and composition, (2) trophic composition of community, and (3) fish abundance and condition. Water quality is evaluated through a comparison of the total score with scores that were previously developed for similar habitats considered to be pristine. The IBI of Karr and others (1986) was specifically developed for large rivers but could be useful for evaluating effects of episodic acidification in headwater streams.

### Work Element 1. Aquatic Toxicity

**Hypothesis.**—Survival of biota in streams in which aluminum toxicity varies on a temporal and spatial basis can be predicted by Al-solubility relations.

**Objective.**—To determine the effect of Al-solubility relations on fish and macroinvertebrate condition and mortality.

**Approach.**—Toxicity tests on brook trout (*Salvelinus fontinalis*), midge larvae (*Chironomus tentans*), and one endemic species of mayfly in the genus *Ephemeroptera* will be conducted twice each year at 7 to 11 sites on the Neversink River. Water chemistry will be monitored frequently at each site during test periods.

The effect of spatial differences in stream chemistry on fish and macroinvertebrate mortality at each site will be assessed during spring and fall periods. Relations between organism mortality and concentrations of biologically important constituents, principally Al, will be developed. Because aluminum concentrations and speciation and streamflow during base-flow conditions are relatively stable, the effects of differing watershed characteristics on aluminum solubility and toxicity can be defined.

Effects of fluctuations in toxicant concentrations on organism survival will be assessed through a comparison of results of toxicity tests at sites that experience severe acidification episodes. The concentration of many chemical constituents can change sharply in less than 1 hour and generally is related to stream discharge. Because mortality resulting from changing water quality is related to several factors, it will be correlated with various statistics that quantify either magnitude, duration, or frequency of fluctuations in the concentration of selected toxins. Toxicity tests will be done in conjunction with water-sampling operations associated with the investigation of in-stream aluminum chemistry (topic E). Additional water samples and flow measurements will be taken, as needed, to ensure that all water-chemistry fluctuations during toxicity tests are measured.

The water-quality sampling sites and bioassay locations will be entered into the GIS data base as point coverages, and the effect of aluminum solubility and other water-quality factors on fish and macroinvertebrate mortality will be analyzed through the digital data base. The correlations developed by these analyses will be used to predict mortality rates of fish and macroinvertebrate species in the remainder of the Neversink watershed.

Because brook trout are the most common game fish in the upper reaches of the Neversink River and have intermediate sensitivity to acidification, they will be used in all fish-toxicity tests. Young-of-the-year fingerling trout will be used for each test (age = <1 year). All brook trout will be obtained from East Branch tributaries to ensure a common-pool source of fish and minimize effects that differing heredity and (or) exposure histories could have on tolerance and mortality. In each test, 20 to 30 brook trout will be placed in each of four or five plastic, screen-sided jugs installed in holding cages in slow-moving water protected by channel structures. At each site, the fish

will be exposed to water for at least 30 days and will be checked daily during exposure periods.

One or more insect species will be used to assess the effects of acidification on the benthic macroinvertebrate community. Midge larvae (*Chironomus tentans* (Fabricius)) tests will use late instar larvae from cultures maintained by the New York State Department of Environmental Conservation (NYSDEC) at the USGS laboratory in Albany. At least 20 larvae will be added to three screen-sided polyethylene containers and placed adjacent to the brook trout cages at each site. Because the chironomid larvae emerge from the water (as adults) after about 30 days (at 25°C), the test duration might be shorter than the trout tests. The life spans of most mayfly and stonefly species are much longer than that of chironomids, and some species are highly sensitive to acidification. Therefore, if sufficient numbers can be collected with minimal stress and damage to individuals, toxicity tests will be conducted on at least one endemic macroinvertebrate species. Response of *Chironomus tentans* and a readily available indigenous species will be compared with bioassay information reported in the literature to assess their representativeness as water-quality indicators.

## Work Element 2. Integrity of Biological Communities

**Hypothesis.**—Biological indices reflect the spatial and temporal variability of water chemistry in the Neversink River.

**Objective.**—To measure and evaluate standard and integrated biological-community indices that characterize spatial and temporal variations in water quality in the Neversink River.

**Approach.**—Fish and macroinvertebrate communities will be sampled in conjunction with water sampling at representative mainstream and tributary sites throughout the Neversink River basin to characterize present conditions. Sampling locations and water-quality measurements will be entered into the GIS data base. Standard measures and indices will be compared with indices that integrate selected physical, chemical, and biological measures (hereafter referred to as integrated indices) to identify those that correlate best with water quality and most effectively predict biological consequences of chronic and episodic acidification. Spatial information on fish and macroinvertebrate-community characteristics (measures and indices) will be incorporated into the spatial watershed model.

Standard biological measures and indices to be evaluated include: community diversity and richness, indicator species, species assemblages, fish condition, fish and macroinvertebrate-population densities and biomass, fish-age distribution, and fish-growth rates. Indices that integrate several biological and chemical measurements that reflect acidification will also be developed and refined if possible. These will include the IBI (Karr and others., 1986), the Ephemeroptera-to-Plecoptera Ratio, and the biological multimetric profile (R. Bode, New York State Department of Environmental Conservation, unpublished data), and the Biological Monitoring Working Party system (BMWP) (Armitage and others, 1983). Variability of fish communities could be a result of stream or site differences in food supply, physical habitat quality, competition, availability and use of refuges, predation and fishing pressures, and fecundity. Several of these factors will be investigated directly through macroinvertebrate inventories, special fishery surveys (that assess use of refuges), and physical-habitat characterizations. Physical characteristics of sampling sites will be examined to determine whether differences in fish and macroinvertebrate communities might also be related to differences in physical habitats. For example, the riverine Habitat Suitability Index (HSI) (Raleigh, 1982) represents a measure of suitability for several physical stream characteristics known to affect the survival and growth of embryo, fry, juvenile, and adult brook trout.

Fish sampling will be done at most sites at which a streamflow gage has been installed and water samples are routinely collected for chemical analyses (fig. 2). Water-quality and fish characteristics will be entered into the GIS data base as point coverage. Several ungaged sites will be selected for additional sampling. Fish communities will be sampled annually at low flows in late July and early August; some mid-spring and late-fall fish surveys will also be conducted at several sites to assess seasonal fish movement and use of refuges. Fish populations will be sampled by electroshocking in seine-blocked 50- to 100-m reaches. Three passes will be used to collect as many individuals as possible. After each pass, the length and weight of individual fish will be measured and recorded, with species counts, on field forms. Growth and survival rates for each fish species will be determined from frequency distributions of body length. Population levels and confidence limits will be estimated by the Moran-Zippin proportional model (Zippin, 1958).

Macroinvertebrate populations at selected sites will be sampled by a standard Surber sampler. One or two inventories will be done at gaged sites in conjunction with midsummer fishery inventories, and results will be entered into the GIS data base. At each sampling location, three replicate samples will be collected by stirring up stream substrate within the Surber grid to force debris and macroinvertebrates into a downstream net. Specimens and organic debris collected in this manner will be separated from coarse rock, gravel, and sand by rinsing in a sieve-bottomed bucket (500 mm) and then preserved in 80-percent ethanol. The remaining material will be inspected for large macroinvertebrates. Specimens will be taken to a processing laboratory for sorting, identification as to genus (and species when possible), and enumeration.

At gaged sites, stream-chemistry and flow data will be provided from routinely collected water samples and stage-to-discharge relations. At ungaged sites of special interest, water samples will be collected, and discharge will be measured during fish surveys. At these sites, additional water samples will also be collected periodically to develop concentration-to-discharge relations that can be used to predict chemical concentrations from flow. Statistics of biologically important chemical constituents will be summarized on an annual basis for comparison with community-integrity indices. These data will be maintained in the GIS data base of sampling sites.

Basic water-quality statistics will be supplemented with integrated indices such as the ASI, which calculates brook trout mortality levels from aluminum, acidity, and calcium concentrations (Ingersoll and others, 1988; Baker and others, 1990). The ASI will be compared with observed mortality (results of onsite toxicity tests), inorganic Al, and biotic community indices to evaluate its association with and its potential ability to predict biological-community integrity. All biological measures and indices will be correlated with the concentration of selected chemical constituents to evaluate their ability to quantify the quality of stream waters. All measures of biologic and water quality will be entered into the GIS data base and used to develop a conceptual model of biological diversity in the Neversink basin. Relations between water quality and various indices will enable development of spatial models that describe aquatic species and community distributions in the Neversink River. These models can ultimately be used to develop strategies to monitor

changes in water quality and to predict the changes in ecosystems that could result from differing rates of atmospheric deposition of acids within the Neversink watershed.

## **GEOGRAPHIC INFORMATION SYSTEM (GIS) SUPPORT ACTIVITIES**

Geographic Information Systems comprise computer hardware and software that are designed to collect, manipulate, manage, analyze, and display spatially referenced data. ARC/INFO, developed by the Environmental Systems Research Institute (ESRI), organizes geographical data through a relational and topological model. This GIS used for the Neversink watershed Study relates the location and topology of map features to attribute, or descriptive, data at a scale of 1:24,000. The following coverages will be developed:

*Watershed Boundaries.*—Drainage-basin and sub-basin boundaries of the Neversink watershed have been delineated on USGS topographic quadrangle maps. These boundaries will then be digitized, edge-matched, and edge-joined.

*Hydrography.*—Surface water and related features—streams, ponds, reservoirs, springs, and aqueducts—in the Neversink watershed and vicinity will be digitized from stable-base USGS topographic quadrangle maps that are reproduced by the New York State Department of Transportation. Arcs and polygons in each coverage will be coded to correspond to USGS Digital Line Graph (DLG) attribute coding standards. The coverages will be edge-matched, edge-joined, and appended into a single coverage.

*Land Use/Land Cover.*—Stable-base land-use/land-cover maps from the Land Use and Natural Resources Inventory are available from the Cornell Laboratory for Environmental Applications and Remote Sensing. The maps will be scanned on a Tektronix autovectorizing scanner at the USGS GIS Research Laboratory in Reston, Va. The vectorized data will then be converted to ARC/INFO polygon coverages. Each polygon will be coded according to the Land Use and Natural Resources Inventory classification. The coverages will be edge-matched, edge-joined, and appended into a single coverage.

*Hypsography.*—Topographic contours from USGS topographic quadrangle maps will be isolated from

other map features so that contours can be scanned. The New York State Department of Transportation will use these separations to prepare negatives of maps with contours and their elevation values, in feet. The negatives will then be scanned with a Tektronix auto-vectorizing scanner at the USGS GIS Research Laboratory in Reston, Va. The vector data will be converted to ARC/INFO line coverages, which will be edited and coded to correspond with the source materials.

**Soils.**—Soil surveys produced by the Soil Conservation Service (SCS) will be recompiled onto 7.5-minute topographic quadrangles. These maps will then be digitized at the Soil Information Systems Laboratory at Cornell University, and the accuracy will be maintained according to SCS national digitizing standards. These data will be converted to ARC/INFO polygon coverages, and the Soils Attribute Data Base will reside in the PAT (polygon attribute table) of each coverage.

**Wetlands.**—Wetlands data are available from two sources: (1) regulatory wetlands maps that have been digitized by the New York State Department of Environmental Conservation Habitat Inventory Unit, as required by the Freshwater Wetlands Act (Article 24 of the Environmental Conservation Law), and (2) wetlands maps that were generated by the Cornell University Laboratory for Environmental Applications and Remote Sensing from the interpretation of aerial photographs as part of the Land Use and Natural Resources Inventory. These data will be evaluated to determine which will be most useful for the Neversink data base. Data from the Cornell Laboratory will be scanned and coded with polygon attributes that correspond to the source materials.

**Forested Land.**—Forested-land data from the Land Use and Natural Resources Inventory will be acquired from the Cornell University Laboratory for Environmental Applications and Remote Sensing. The forested lands are classified as brushland, natural forest, and plantations. After these data have been scanned and converted to ARC/INFO polygon coverages, the forests within each of these categories will be further classified as hardwood or coniferous through use of aerial photographs.

**Sampling Sites.**—All sampling sites will be represented in point coverages containing unique identifying values that are consistent with all relational data bases. The variables measured at each of the sites will be directly related to their geographic location in the

Neversink watershed. This data base will enable spatial analysis and display of physical, chemical, and biological data.

## DELIVERABLES

Products resulting from this project will be (1) a conceptual spatial model of factors that control stream chemistry, (2) a basinwide characterization of the effects of acidic deposition on stream chemistry, and (3) nitrogen input-output budgets for Winnsboro watershed.

1. *Conceptual Spatial Model.*—The major product resulting from the research and data-collection programs within this project will be a conceptual model that spatially relates watershed factors that control stream chemistry within the Neversink basin. This will be the first spatial model of stream chemistry to describe natural processes and effects of acidic deposition at scales greater than those of small watersheds. Historically, little or no information on water quality was collected in intermediate-size watersheds such as the Neversink before degradation by acid deposition or other forms of pollution. Goals of remediation efforts, therefore, are often set without complete information on the cost and benefits associated with various levels of water-quality improvement. Because the Neversink basin is relatively undeveloped (with respect to other Catskill watersheds), the Neversink spatial model will be useful in developing a Catskill watershed-management plan. By providing a control with which other watersheds can be compared, the Neversink model can be used as a foundation for a management model that incorporates a variety of development scenarios. Many of the new approaches that will be needed to build the Neversink spatial model will also be used to evaluate the effects of disturbance.

2. *Characterizing Effects of Acidic Deposition.*—In addition to providing information on natural watershed processes, this project will provide a basinwide characterization of the effects of acidic deposition. Whereas previous research has shown that acidic deposition is affecting stream-water quality within parts of the Neversink basin, this project will document the extent of the spatial and temporal effects of acidic deposition, including effects on the distribution of fish and aquatic invertebrate populations.

3. *Nitrogen Budgets.*—Through this project, a monitoring program will be established to evaluate the

current status of nitrogen cycling within the headwaters of the basin. If forested watersheds in the Catskills are approaching nitrogen saturation,  $\text{NO}_3^-$  concentrations in stream water could increase from current levels without an increase in atmospheric deposition  $\text{HNO}_3$ . This would likely increase the acidity of surface waters in the Neversink basin and possibly increase nitrogen concentrations in the reservoir. Water- budget data for 4 years of the project will provide baseline information that could be compared with future budget data to assess changes over time.

Information on the current status of nitrogen cycling in the Catskills is also relevant to forest-harvesting practices. Old-growth forests tend to be less productive than younger forests and therefore less efficient at immobilizing nitrogen. Timber harvesting to establish uneven-aged forests could increase nitrogen retention within the terrestrial environment and result in improved water quality; conversely, it could result in acute acidification of surface waters for 2 or 3 years until vegetation is reestablished (Lawrence and others, 1987). The effect of timber harvesting on the nitrogen cycle within the Neversink basin is being studied in detail through another USGS project being done in cooperation with the New York City Department of Environmental Protection. That project is being designed such that the results can be applied to the Neversink spatial model.

In addition to the research activities associated with the spatial model in this project, several data-collection activities will be implemented, both to support research tasks and to provide basic information on water quality and flow characteristics within the basin. A basinwide GIS data base will result from this work.

Upon completion of data collection and interpretation, results of this project will be compiled in a final report comprising interpretive discussions of each of the six research topics described herein; results of each research topic also will be published individually in a peer-reviewed scientific journal. The final report will synthesize the information from each journal article to provide a detailed description of the Neversink spatial model and will include a compilation of all data collected and will be published in a USGS interpretive series. A report detailing analytical and quality-control procedures used in this project by the Albany laboratory will be published as a USGS open-file report.

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# Appendixes

1. Field Implementation Schedule. ....	32
2. Analytical Methods .....	36
3. Quality Assurance Plan for Streamflow Measurements .....	40
4. Data management .....	41

## APPENDIX 1: FIELD IMPLEMENTATION SCHEDULE

Activity	Starting Date	Completion Date
<b>TOPIC A: SMALL (FIRST-ORDER) WATERSHEDS</b>		
<b>Work Element 1.—Subsurface-Water Residence Time</b>		
1. Installation of a headwater streamflow-gaging station.	April 1991	April 1991
2. Biweekly stream-water collection at 8 locations upstream of gage.	May 1991	June 1991
3. Periodic sets of streamflow measurements taken at all 8 sampling sites.	April 1992	November 1993
4. Identification of seep collection points along an elevated gradient.	April 1992	July 1992
5. Periodic seep-water collection.	May 1992	May 1994
6. Installation of weighing-bucket rain gage.	April 1992	June 1992
7. Installation of 70 throughfall collectors, 5 collectors per plot, at 14 elevations in Winnisook watershed.	April 1992	November 1992
8. Precipitation and stream-water sampling before, during, and after three selected storms.	May 1992	November 1993
<b>Work Element 2.—Hillslope Gradients of Soil Chemistry</b>		
1. Insertion of about 130 mineral-soil bags along an elevational gradient in Winnisook Watershed.	May 1994	May 1995
2. Collection and chemical analysis of about 200 Oa and Bs horizon soil samples along an elevational gradient in a Winnisook watershed.	May 1993	December 1993
3. Collection and chemical analysis of mineral soil bags.	May 1995	August 1995
<b>Work Element 3.—Extrapolation of Relations to Other First-Order Watersheds</b>		
1. Stream-water sampling along elevational gradients of about 15 first-order streams.	November 1991	November 1992
2. Installation of a streamflow-measurement gage in a first-order watershed remote from Winnisook Watershed.	June 1992	July 1991
3. Stream-water sampling along elevational gradients of five first-order watersheds (including the gaged watershed of activity 2, representative of the Neversink River basin. Streams will be sampled at low and high flows.	July 1992	June 1994
4. Sampling of 20 first-order streams at locations just upstream from the confluence of the first adjoining stream. Each of the 20 streams will be sampled at low and high flows .	April 1993	August 1994

Activity	Starting Date	Completion Date
<b>TOPIC B: INTERMEDIATE AND LARGE WATERSHEDS</b>		
<b>Work Element 1.—Spatial Controls at Intermediate and Large Scales</b>		
1. Installation of 5 streamflow gages in intermediate and large watersheds.	April 1991	June 1991
2. Biweekly stream-water sampling at all streamflow gages.	June 1991	June 1994
3. Biweekly stream-water sampling along an elevational gradient of a stream that increases in drainage area from first order to sixth order.	June 1991	July 1993
4. Streamflow measurements at ungaged locations to evaluate tributary effects on chemical transport.	April 1993	October 1994
5. Streamwater sampling along elevational gradients of two additional gaged, intermediate-sized watersheds at high, intermediate, and low streamflows (3 sampling dates).	November 1991	October 1994
<b>Work Element 2.—Effect of Watershed Size on Temporal Variations in Stream Chemistry</b>		
1. Stage-activated automated stream-water sampling at five streamflow-gaging stations during high flows in the spring and fall.	April 1992	April 1994
2. Continuous field pH measurements in a first-order watershed and near the Neversink Reservoir.	June 1992	September 1993
3. Stream-water sampling for suspended-solids analysis in the Neversink River above the reservoir.	April 1992	April 1995
<b>TOPIC C: LANDSCAPE CONTROLS ON STREAM CHEMISTRY</b>		
<b>Work Element 1.—Identifying the Effects of Landscape on Neversink River Water Quality</b>		
1. Stream-water survey sampling to identify four distinct types of landscape for landscape plot studies.	November 1991	November 1992
2. Streamflow measurements on stream reaches affected by hemlock stands.	April 1992	May 1994
3. Bimonthly seep-water sampling at approximate sites within landscape plots.	April 1992	September 1994
4. Biweekly sampling of 10 seeps and 5 stream sites to determine subsurface water residence time.	October 1993	September 1994
<b>Work Element 2.—Modeling the Sources of Landscape Effects on Stream-Water Quality</b>		
1. Installation of Oa- and Bs-horizon soil lysimeters, seepage collectors, and shallow ground-water samplers as needed to sample end members for each type of landscape.	November 1991	November 1993
2. End-member sampling for EMMA model analysis (soil solutions, shallow ground water, and seep water, collected seasonally to monthly).	April 1993	November 1993
3. End-member sampling at locations within the same landscape plots, to test the EMMA model.	May 1993	November 1993

Activity	Starting Date	Completion Date
<b>TOPIC D: NONCONSERVATIVE TRANSPORT OF NITRATE AND ALUMINUM IN STREAM WATER</b>		
<b>Work Element 1.—Nitrate</b>		
1. Reconnaissance stream-water sampling for site selection.	September 1991	November 1991
2. Installation of wells, 2 per site.	May 1992	June 1992
3. Stream-reach mass-balance measurements: collection of 24 stream-water samples and 6 ground-water samples, with flow measurements over a 24-hour period, four times (early spring, late spring, midsummer, and late fall).	April 1992	September 1993
4. Chemical tracer experiments: collection of 36 stream-water and 12 ground-water samples, with flow measurements over a 2- to 5-day period in each of the two experimental stream reaches, in midsummer and late fall.	September 1992	October 1994
<b>Work Element 2.—Aluminum</b>		
1. Reconnaissance stream-water sampling for site selection.	September 1991	November 1991
2. Monthly stream-water sampling of 1 of the experimental reaches, four samples per month.	March 1992	November 1993
3. Stream-reach aluminum speciation measurements, collection of 48 stream-water samples and flow measurements, over about 30 days in early spring, midsummer, and late fall.	July 1992	August 1993
4. Placement of mesh bags of homogeneous sediment in the stream to evaluate precipitation/ dissolution in reaches where disequilibrium conditions occur.	August 1993	May 1994
<b>TOPIC E: NITROGEN CYCLING</b>		
<b>Work Element 1.—Quantifying Nitrogen Budgets</b>		
1. Installation of 80 throughfall collectors in Winnisook watershed	September 1992	April 1993
2. Throughfall collections biweekly during spring, summer, and fall; monthly in winter	May 1993	September 1995
3. Installation of wet-only precipitation collectors at two locations in Winnisook watershed.	May 1993	May 1993
4. Installation of one 5-m atmospheric-deposition-monitoring tower at the base of Winnisook watershed.	May 1992	August 1993
5. Sampling of wet-only precipitation collection.	June 1993	September 1995
6. Air-quality and meteorological measurements from the tower.	August 1993	September 1995
7. Monthly stream-water sampling for analysis of total nitrogen concentration at the gaging station (analysis could be discontinued if results indicate low concentrations).	February 1992	June 1995
8. Streamflow sampling at the gaging station during storms for 1 month in spring and fall. Chemical analysis will include total nitrogen.	April 1992	April 1995

Activity	Starting Date	Completion Date
<b>TOPIC F: WATER QUALITY AND AQUATIC BIOLOGICAL COMMUNITIES</b>		
<b>Work Element 1.—Aquatic Toxicity</b>		
1. Thirty-day onsite fish bioassays at nine sites, run once in spring, summer, and fall.	October 1992	June 1994
<b>Work Element 2.—Integrity of Biological Communities</b>		
1. Fish shocking at 10 sites once per year, and at five sites three times times per year. Streamflow measurements will be taken, and one stream-water sample collected at each site for complete chemical analysis, on each shocking date.	July 1991	June 1994
2. Start of aquatic-invertebrate sampling at 10 sites once per year, and at three sites four times per year.	July 1991	November 1993

## APPENDIX 2: ANALYTICAL METHODS

### TABLES

2A. Analytical procedures used to measured concentrations of major solutes. . . . .	37
2B. Reporting limits and data quality objectives for accuracy, precision, and blanks . . . . .	38
2C. Analytical procedures for soil chemistry analysis . . . . .	39
2D. Data-quality objectives for accuracy and precision of soil analyses . . . . .	39



## APPENDIX 2: ANALYTICAL METHODS

Solutions collected during this project will include precipitation, throughfall, soil water, ground water, seepage, and stream water. These will be analyzed for all major solutes at the USGS Water Analysis Laboratory in Albany, N.Y. The list of major solutes and the methods used to measure their concentrations are given in table 2A. Quality-assurance procedures used at the Albany laboratory are similar to those used by the U.S. Environmental Protection Agency for analysis of surface waters in acid-deposition studies (U.S. Environmental Protection Agency, 1987). Data-quality objectives and reporting limits for analyses performed in the Albany laboratory are given in table 2B. A report detailing analysis and quality-assurance procedures for the Albany laboratory in this project will be compiled, as will annual summaries of quality-assurance data.

Analysis of suspended-solids samples for total nitrogen and total phosphorus concentrations will be

done by the USGS National Laboratory in Denver, Colo. Total nitrogen and total phosphorus concentrations will be measured by the Jirka method, a modified Kjeldahl block digestion followed by colorimetric detection (Jirka and others, 1976; Patton and Truitt, 1992). Selected precipitation, throughfall, seepage, and stream-water samples will also be analyzed for  $^{18}\text{O}/^{16}\text{O}$  ratios through mass spectrometry at the USGS Isotope Laboratory in Reston, Va.

Analysis of soil samples and mineral-soil bags will be done by a contracting laboratory yet to be determined. Criteria for laboratory selection will include the requirement that analyses be done according to USEPA methods (Blume and others, 1990). All analyses will be done on air-dried soils that have passed through a 2-mm-mesh sieve and meet data-quality objectives listed in table 2C.

**Table 2A.** Analytical procedures used to measure concentrations of major solutes.

Constituent or Property	Method	Reference
$\text{SO}_4^{2-}$ , $\text{NO}_3^-$ , $\text{Cl}^-$	Ion chromatography	Tabatabai and Dick, 1983
pH	Potentiometric	Peden and others, 1986
$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$	Atomic absorption spectrophotometry	Fishman and Friedman, 1989
Si	Automated heteropoly blue colorimetry	American Public Health Association, 1981
$\text{Na}^+$ , $\text{K}^+$	Atomic emission spectrophotometry	Fishman and Friedman, 1989
$\text{NH}_4^+$	Automated flow-injection colorimetric phenate	American Public Health Association, 1981
Dissolved organic carbon	Filtration, total carbon analyzer	U.S. Environmental Protection Agency, 1987
Total aluminum	Atomic absorption graphite furnace	Fishman and Friedman, 1989
Total monomeric Al	Automated flow injection pyrocatechol colorimetry	Peden and others, 1986
Organic monomeric Al	Automated flow injection ion exchange, pyrocatechol colorimetry	Peden and others, 1986
Total F	Ion selective electrode	U.S. Environmental Protection Agency, 1987
Acid-neutralizing capacity	Strong acid titration	Gran, 1952

**Table 2B.** Reporting limits and data-quality objectives for accuracy, precision, and blanks for solution analyses performed by the U.S. Geological Survey laboratory in Albany, N.Y.

[ DQO, data-quality objective.  $\mu\text{mol/L}$ , micromoles per liter. cv, coefficient of variation. ANC, acid-neutralizing capacity. Numbers in "dividing value" column are concentrations that divide high range from low range of precision DQO's. pH and ANC values (in parentheses) are in pH units and microequivalents per liter, respectively. ]

Constituent or property	Report- ing limit (μmol/L)	Accuracy				Precision			Filter and analysis blanks DQO (μmol/L)
		Low-concentration quality-control sample		High-concentration quality-control sample		Low-con- centration range DQO (cv)	Dividing value (μmol/L)	High-con- centration range DQO (cv)	
		DQO (percent error)	Concen- tration (μmol/L)	DQO (percent error)	Concen- tration (μmol/L)				
Br <sup>-</sup>	2.0	10	20	10	150	15	8	10	0.5
Cl <sup>-</sup>	2.0	10	8.5	10	85	15	8	10	0.5
NO <sub>3</sub> <sup>-</sup>	2.0	10	5	10	50	15	5	10	0.3
SO <sub>4</sub> <sup>2-</sup>	2.0	10	8.3	10	83	15	8.3	10	0.3
Ca <sup>2+</sup>	2.0	10	25	10	100	15	10	10	1.0
Mg <sup>2+</sup>	1.0	10	8.2	10	33	15	5	10	0.5
Na <sup>+</sup>	1.0	10	8.7	10	35	15	15	10	1.0
K <sup>+</sup>	1.0	10	5.1	10	20	15	5	10	0.5
NH <sub>4</sub> <sup>+</sup>	2.0	15	7.1	10	17.5	15	5	10	1.0
Total Al	1.0	15	1.8	10	28	15	1	5	0.5
Total mono- meric Al	1.5	10	7.4	10	18.5	15	5	10	0.75
*Organic monomeric Al	1.5	--	--	--	--	15	5	10	0.75
Total Si	6.0	15	35.6	10	107	15	50	10	3
†Dissolved organic carbon	41.0	15	83	10	415	15	83	10	18
Total F	0.5	10	2.0	10	10.0	15	1.5	10	0.2
‡pH	--	10	(4.41)	20	(6.88)	10	(6.00)	20	--
‡ANC	--	10	(-39.9)	10	(125)	10	--	10	--

\* Quality-control samples for organic monomeric Al are unavailable.

† Dissolved organic carbon concentrations are expressed as  $\mu\text{mol C/L}$ .

‡ pH: Values in parentheses are standard pH units. Percent error and coefficient of variation determined from  $[\text{H}^+]$ . Blanks not run for pH.

ANC: Values in parentheses are in microequivalents per liter. For values within  $\pm 20$  microequivalents per liter, an absolute data-quality objective of  $\pm 6$  microequivalents per liter is used for precision, rather than a coefficient of variation of 10 for values outside this range. Blanks not run for ANC.

**Table 2C.** Analytical procedures for soil-chemistry analysis.

Constituent or Property	Method	Reference
H <sub>2</sub> O- and CaCl-exchangeable pH	Potentiometric	Blume and others, 1990
Exchangeable Ca <sup>2+</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Al	Atomic absorption spectro photometry	Blume and others, 1990
Exchangeable acidity	Strong-acid titration	Blume and others, 1990
Total carbon	LECO carbon analyzer	Nelson and Summers, 1982
Total nitrogen	Kjeldahl digestion, automated phenate	U.S. Environmental Protection Agency, 1987
Water-extractable SO <sub>4</sub> <sup>2-</sup>	Ion chromatography	Tabatabai and Dick, 1983
NaH <sub>2</sub> PO <sub>4</sub> -extractable SO <sub>4</sub> <sup>2-</sup>	Ion chromatography	Tabatabai and Dick, 1983

**Table 2D.** Data quality objectives for accuracy (expressed as percent error) and precision (expressed as a coefficient of variation) of soil analyses.

Constituent or Property	Accuracy (percent error)	Precision (coefficient of variation)
pH*	15	15
Exchangeable bases	10	10
Exchangeable Al	10	10
Exchangeable acidity	15	15
H <sub>2</sub> O extractable SO <sub>4</sub> <sup>2-</sup>	10	10
NaH <sub>2</sub> PO <sub>4</sub> extractable SO <sub>4</sub> <sup>2-</sup>	10	10
Total carbon	15	15
Total nitrogen	15	15

\* Percent error and coefficients of variation are based on [H<sup>+</sup>]

### APPENDIX 3: QUALITY-ASSURANCE PLAN FOR STREAMFLOW MEASUREMENTS

Field measurements and inspections of gaging-station operations will be done in accordance with guidelines set forth in Rantz and others (1982), Hubbard (1992), and the USGS series, "Techniques of Water-Resources Investigations" (TWRI). For activities not adequately covered by the TWRI's, the Hydrologic Records Unit Chief or the District Surface-Water Specialist will be consulted.

Training of field personnel in standard field practices will be directed by the Data Unit Chief or designees. The instructor will be experienced and knowledgeable. Review and spot checking of field practices, installations, and record computations are the responsibility of the Data Unit Chief or his designees.

All field measurements and inspection notes will be recorded in a specified format as a permanent record. Field notes will be neat, readable, and leave no doubt as to interpretation.

Discharge measurements will be computed in the field and checked against the current rating curve after it has been established. If the measurement exceeds the normal tolerance ( $\pm 5$  percent), a check measurement will be made and computed unless otherwise directed by the Data Unit Chief. Measurements made when the control is affected by ice or other obvious obstructions (such as leaves or other debris) do not require check measurements.

Gaging stations will be inspected and discharge measurements made at least once every 6 weeks.

Inspections and measurements may be made in addition to scheduled visits and planned experiments when the control is affected by debris or ice, or during high flows.

Streamflow records will be computed regularly and will follow a progress chart developed by the Data Unit Chief. Record computation will be done in accordance with Rantz and others (1982) or the appropriate TWRI methods. All computations will be checked and reviewed.

Computer computations, data storage, and updating will follow procedures outlined in the ADAPS and WATSTORE User's Guides (Hubbard, 1992) and checked carefully after each processing step to ensure accuracy and continuity between updates. Flow records for all stations will be checked to ensure that flows follow hydrologically consistent patterns. Sub-basins in the Neversink basin will be compared hydrographically, statistically, and by basin-runoff summaries, and significant variations will be investigated.

All computation, checking, and review functions will be done within the Albany, N.Y. office.

Streamflow data from gaging stations will be published annually. Data collection and analysis will be routinely monitored through project reviews and input from the District specialists prior to report preparation. The project chief is responsible for correct interpretation of data to reach sound conclusions.

## APPENDIX 4: DATA MANAGEMENT

### Computer Resources

The Neversink Watershed Study's computer resources consist of a 400 series Data General (DG) Avilion workstation networked to the New York District's central 6200 series DG server. Several networked personal computers are also available for use by project personnel. The total disk space on the DG workstation and server amounts to about 1.5 gigabytes. The personal computers (PC's) are linked to the DG server through SUN PCNFS networking software and, therefore, have access to the project data base. Several of the PC's are dedicated to capturing data from the chemistry laboratory's test equipment and processing them into the data base; the others are used by project personnel for data manipulation and analysis.

### Data Base

The data-management activities are handled by SAS (Statistical Analysis Software) on the DG network under the UNIX operating system. SAS is also available to project personnel on the PC, in both the DOS and WINDOWS versions. SAS was chosen for its data-handling capabilities as well as for its ability to analyze the data graphically, statistically, and otherwise. The specific data base being used is a modification of one written for the Episodic Response Project (ERP) and is running exclusively on the DG platform. This data base consists of two major components—the field data and the chemistry data. The former consists of one data set, and the latter consists of a data set for each constituent analyzed and a single data set representing the data from each of the individual constituent data sets. The data base also consists of several programs for input/output and analysis that are being or have been modified on an "as-needed" basis.

### Data Capture

Most of the chemistry laboratory's instruments are connected to PC's so that the data they generate can be captured in digital form and entered directly into the data base. Those instruments include a Perkin-Elmer 1100B atomic absorption spectrophotometer, a Dionex DX-100 ion chromatograph, a Radiometer VIT90 video titrator, a Fisher Scientific Accumet 925 pH/ion meter, and a Lachat QuikChem AE flow-injection analyzer. The Dohrmann carbon analyzer has not yet been automated. Those instruments that do not have

associated proprietary software to capture the data (the Radiometer titrator, the Perkin-Elmer atomic absorption spectrophotometer, and the Fisher pH/ion meter) have had custom software written by project personnel for this task. The Fisher pH/ion uses a Quick-Basic program to capture output, whereas the Perkin-Elmer and the Radiometer use the Procomm communication software's Aspect script language. Import of the electronic data files into the data base is done through SAS programming.

As stated above, the Perkin-Elmer and the Radiometer VIT90 use the Procomm Aspect programming language to capture instrument data to a log file. The programs provide a menu-driven system for processing data from the instrument and reside on the local PC. The log files are stored in a directory with the path C:\store\identifier\mmdyy, where "mmdyy" is current date, and "identifier" is either "anc" for the Radiometer or "aa" for the Perkin-Elmer. For the Perkin-Elmer, this program is named aa.asp, and for the Radiometer, this program is named anc.asp. Log files are named after the constituent being analyzed and are suffixed with the run number. For example, the first run of the Radiometer for 01/01/93 would produce the log file C:\store\anc\010193\anc1. These programs also use "C" programs to modify the log files into a format that can be edited by the analyst and be read directly into the SAS data base. The resulting files are named after the current log file name with a ".dat" extension and are stored in the same directory as the given log file.

### Data Verification

Accuracy of the data base is verified through two independent mechanisms, depending on whether the data are input manually or electronically. All written field data are typed into the data base twice. The SAS compare procedure is then run on the data to identify differences in the duplicate data sets. Differences are resolved by referral to the field-data forms. Data that are electronically transferred into the data base are automatically checked for duplicate sample serial numbers and illegal site-identification codes. A separate file containing legal site-identification codes is maintained to ensure that only correct codes are used. Out-of-limits values for each chemical analysis have also been set within the program. Periodically the data-base

manager reviews completed segments of the data base to determine whether any values are missing.

### **Software**

The project's DG has a disk partition dedicated to storage of DG and PC software. The software includes SAS for DOS, SAS for Windows, Exceed X11 GUI, Excel for Windows, and Quick C. Also in this directory is a directory called "work," which includes a PC SAS program directory, an SAS initialization directory, and a storage directory for Lotus "prn" files.

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### **Backup**

Backup procedures currently consist of three measures:

- The complete data base is copied daily from the work-station disk to a disk located on the DG server, through a "crontab" job
- The server disk is backed up to tape weekly by the computer unit of the Albany office.
- The data base residing on the workstation is also backed up to tape once every 3 months.