EPISODIC ACIDIFICATION AND ASSOCIATED FISH AND AQUATIC INVERTEBRATE RESPONSES IN FOUR CATSKILL MOUNTAIN STREAMS:

An Interim Report of the Episodic Response Project

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply metric units	*by*	*To obtain inch-pound units*
micrometer (µm)	0.00004	inch
centimeter (cm)	0.3937	inch
meter (m)	3.281	foot
square meter (m^2)	0.093	square foot
kilometer (km)	0.621	mile
square kilometer (km^2)	0.3861	square mile
square meter (m^2)	10.76	square foot
liter (L)	0.2642	gallon
milliliter (mL)	0.0338	fluid ounce
cubic meter per second (m^3/s)	35.31	cubic foot per second
degree Celsius (°C)	(1.8 x °C) + 32	degree Fahrenheit
hectare (ha)	2.471	acre
gram (g)	0.0353	ounce

Other Abbreviations

microsiemens per centimeter at 25°C (µS/cm)
microequivalents per liter (µeq/L)
milligrams per liter (mg/L)
micrograms per liter (µg/L)

Water Year

The 365-day period from October 1 through September 30 of the following year.

FOREWORD

Recent studies of the effects of acid rain on aquatic systems in the United States, Canada, and Europe have revealed that streams may undergo significant temporary acidification and other chemical changes during high flows caused by rainstorms and snowmelt, and that these changes may have detrimental effects on fish and other aquatic biota. To address concerns over the potential for episodic acidification of aquatic ecosystems in the United States, the U.S. Environmental Protection Agency in 1988 developed the Episodic Response Project (ERP), the major objectives of which are to:

1. Identify the magnitude, duration, and frequency of episodic chemical changes that accompany snowmelt and rainstorms in streams of the United States,
2. Determine whether episodic chemical changes in streams have long-term effects on fish populations,
3. Obtain new data on the processes and factors that determine the severity of episodic chemical changes in streams and their effects on fish populations, and
4. Develop and test episodic chemistry models that can be used to make predictions of regional episodic acidification.

Fieldwork began in September 1988 in cooperation with the Adirondack Lakes Survey Corporation, Pennsylvania State University, and the U.S. Geological Survey, and continued until June 1990. This interim report presents the major results obtained during first two runoff seasons (fall 1988 and spring 1989), which pertain to the first three objectives of the ERP. These results are included in the National Acidic Deposition Assessment Program (NAPAP) State of Science and Integrated Assessment reports, which were presented to Congress in 1990.

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U.S. Environmental Protection Agency
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Abstract

The Episodic Response Project is a multidisciplinary research project designed to assess the role of storm and snowmelt runoff in stream acidification and the associated responses of fish and invertebrates. The study began in October 1988 and is being conducted simultaneously in the Appalachian highlands of central Pennsylvania, the Adirondack Mountains of northern New York, and the Catskill Mountains of eastern New York. Four streams in the Catskill region were selected to represent the following conditions: (1) high acid-neutralizing capacity (ANC) with no acidic episodes annually (ANC less than 0 microequivalents per liter), (2) high ANC with few acidic episodes, (3) moderate to low ANC with few acidic episodes, and (2) low ANC with frequent acidic episodes. Results of the first 9 months of research in the Catskill region indicate that storm and snowmelt runoff are associated with short periods of stream acidification that, if sufficiently severe, lead to fish mortality or emigration away from acidic reaches. Increased discharge coincided with decreased pH and increased total aluminum concentrations in all four streams. Peak aluminum concentrations ranged from 228 μg/L (micrograms per liter) in the high-ANC stream to 658 μg/L in the most acidic stream studied. Mortality of brook trout in bioassay cages was significant immediately after high flows in the most acidic stream but not in the high-ANC stream. Brook trout movement in the acidic stream, as tracked by radiotelemetry techniques, was generally toward downstream refuges with higher pH than the study reach. Invertebrate populations in the acidic streams were lower, and families less diverse, than in the high-ANC stream.

INTRODUCTION

The Acid Precipitation Act of 1980 prompted extensive research on acidic deposition and its effects in the United States. This research has included regional surveys to assess the current state of surface-water acidification across major geographic regions (Linthurst and others, 1986; Landers and others, 1987; Lynch and Dise, 1986) as well as many site-specific studies to define processes of acidification within individual watersheds (Chen and others, 1983; Galloway and others, 1983; Driscoll and others, 1986; Murdoch, 1991). The information gathered to date has allowed statistical assessments of the acidity of lakes and streams within the regions that are likely to be most severely affected by acidic deposition. Regional surveys of surface-water chemistry during fall and spring have provided an indication of the percentage of lakes and streams that become acidic—that is, their acid-neutralizing capacity (ANC) becomes less than zero (Linthurst and others, 1986; Kaufmann and others, 1988, Murdoch and Barnes, 1989). In addition, models have been developed that predict long-term trends in stream and lake acidification and changes that might be expected if current rates of acidic deposition decrease (Chen and others, 1980; Cosby and others, 1985).

Most of the research to date on the effects of acidic deposition on surface-water chemistry has been aimed at defining the processes and extent of gradual, chronic acidification of lakes and streams. Research on individual watersheds in Europe and North America, however, has shown that stream and lake acidity can change within days or hours as a result of rainstorms or melting snow (Galloway and others, 1980; Lynch and others, 1986; Murdoch, 1991). These acidic "episodes" contribute a major part of the annual hydrogen and aluminum yield of streams and can, for short periods, be toxic to aquatic life (Gagen and Sharpe, 1987). The available data on episodic acidification pertain only to specific lakes and streams, however, and do not reveal the regional extent of these phenomena.

Few research programs have been designed to investigate the combined physical and chemical factors that cause acidic episodes and their effects on fish (Thornton and others, 1987). Research on both chronic and episodic acidification has focused on "biologically relevant" changes in water quality (changes that cause fish mortality or morbidity) rather than on the fish themselves, largely because the direct assessment of fish response in the field is difficult. Laboratory experiments and field bioassays have shown that fish morbidity and mortality result from episodic as well as chronic lake and stream acidification (VanWinkle and others, 1986). Field studies also have shown that the response of fish populations to acidification is variable (Gunn, 1986). Laboratory experiments overestimate the fish mortality or morbidity resulting from given chemical changes because the laboratory environment constrains avoidance behavior (Thornton and others, 1987).

Sensitivity of fish to hydrogen-ion and aluminum concentrations in streams has been shown to depend on the species and life stage (Walter Kretzer, Adirondack Lake Survey Corporation, written commun., 1987), but little is known about how fish detect and use chemically tolerable refuge areas during episodic acidification. As a result, the effects of acidic episodes on fish in streams and lakes are poorly understood and have been studied in only a few locations. The threshold values of "biologically relevant" chemical concentrations in natural systems are largely unknown, and the factors that constitute "biologically relevant" chemistry have not been experimentally defined in the field.

Objectives

The Episodic Response Project (ERP) is a continuing research project (data collection ended June 1, 1990) funded by the U.S. Environmental Protection Agency (USEPA) to address the above questions on the effects of acidic deposition on fish. The ERP has four objectives; which are to:

1. Define the magnitude, duration, and frequency of episodic chemical changes in streams that accompany snowmelt and rainstorms,

2. Ascertain the extent to which episodic chemical changes in streams affect fish populations and note the frequency of episodes that cause these effects,

3. Obtain information on processes and factors that influence the severity of episodic chemical changes in streams, and

4. Provide data needed to model the regional extent of episodic stream acidification in the Catskills and the fish-population response.

Although episodic acidification is a potential problem in many parts of the United States, research costs required limitation of the study to a few high-priority regions. The project is addressing streams in three regions known to have been affected by acidic deposition—the northern Appalachians of western Pennsylvania, the Catskill Mountains of southeastern New York, and the Adirondack Mountains of northern New York (fig. 1). A combination of technical approaches is being used to integrate the chemical, biological, and modeling research goals.

Purpose and Scope

This report describes the research done from September 1988 through June 30, 1989 in the Catskill Mountain region, with reference to data collected thereafter where such data help clarify results. The report (1) presents preliminary findings on the stream hydrology and chemistry during a range of flow conditions and the response of fish and aquatic insects to stream acidification, and (2) gives a preliminary analysis of the processes that cause these episodes.

Acknowledgments

The U.S. Geological Survey (USGS) thanks the Frost Valley YMCA, the Balsam Lake Anglers' Club, and the Tison family for allowing access to the streams observed during this study. Special thanks are extended to Dr. William Kelly III, of Claryville, N.Y., whose advice and services helped initiate the fish-monitoring effort.

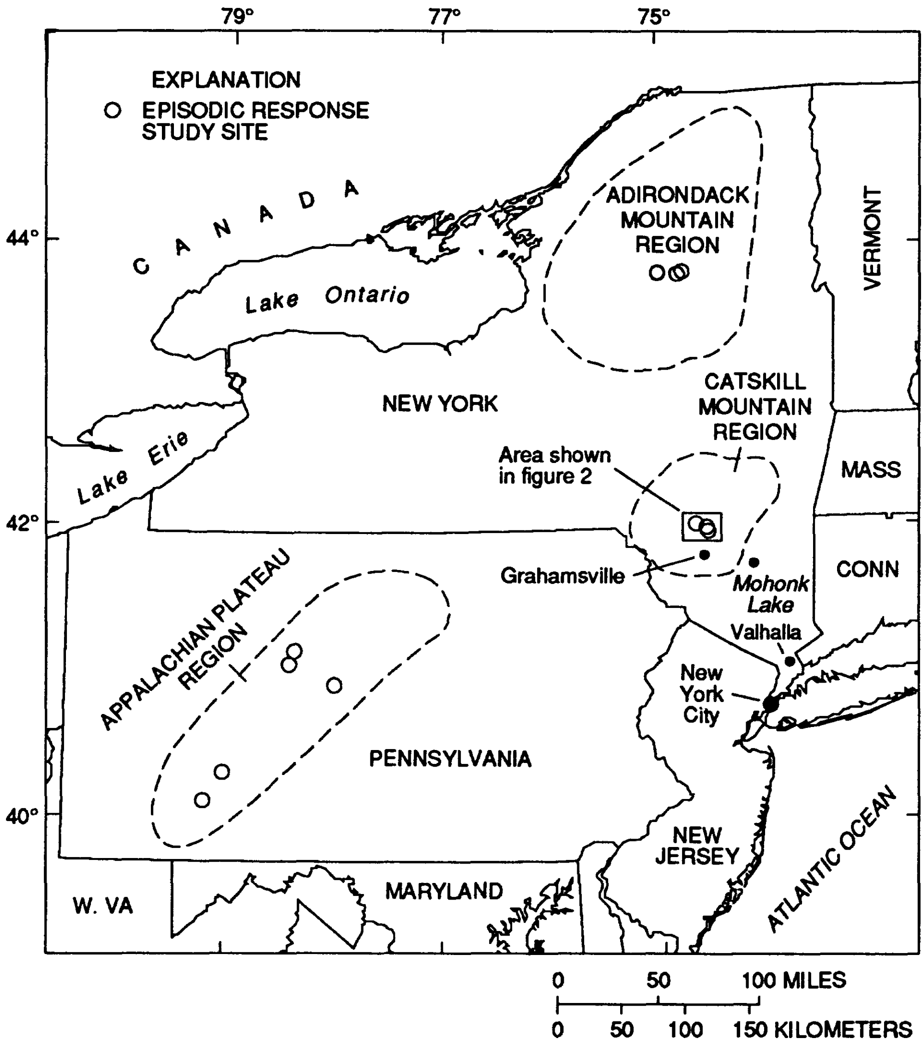

Figure 1. Location of the three regions of the Episodic Response Project.

RESEARCH WATERSHEDS

Four headwater streams (fig. 2) were selected for the stream-chemistry monitoring program—Biscuit Brook and High Falls Brook (both tributaries to the West Branch Neversink River), the upper reaches of the East Branch Neversink River, and Black Brook (a tributary to the Beaverkill). Physical characteristics of the streams are summarized in table 1. These streams cover the range of base-flow acid-neutralizing capacity (ANC) values of interest in episodic acidification research, 0 to 200 μeq/L (microequivalents per liter) and are hydrologically responsive to precipitation. The East

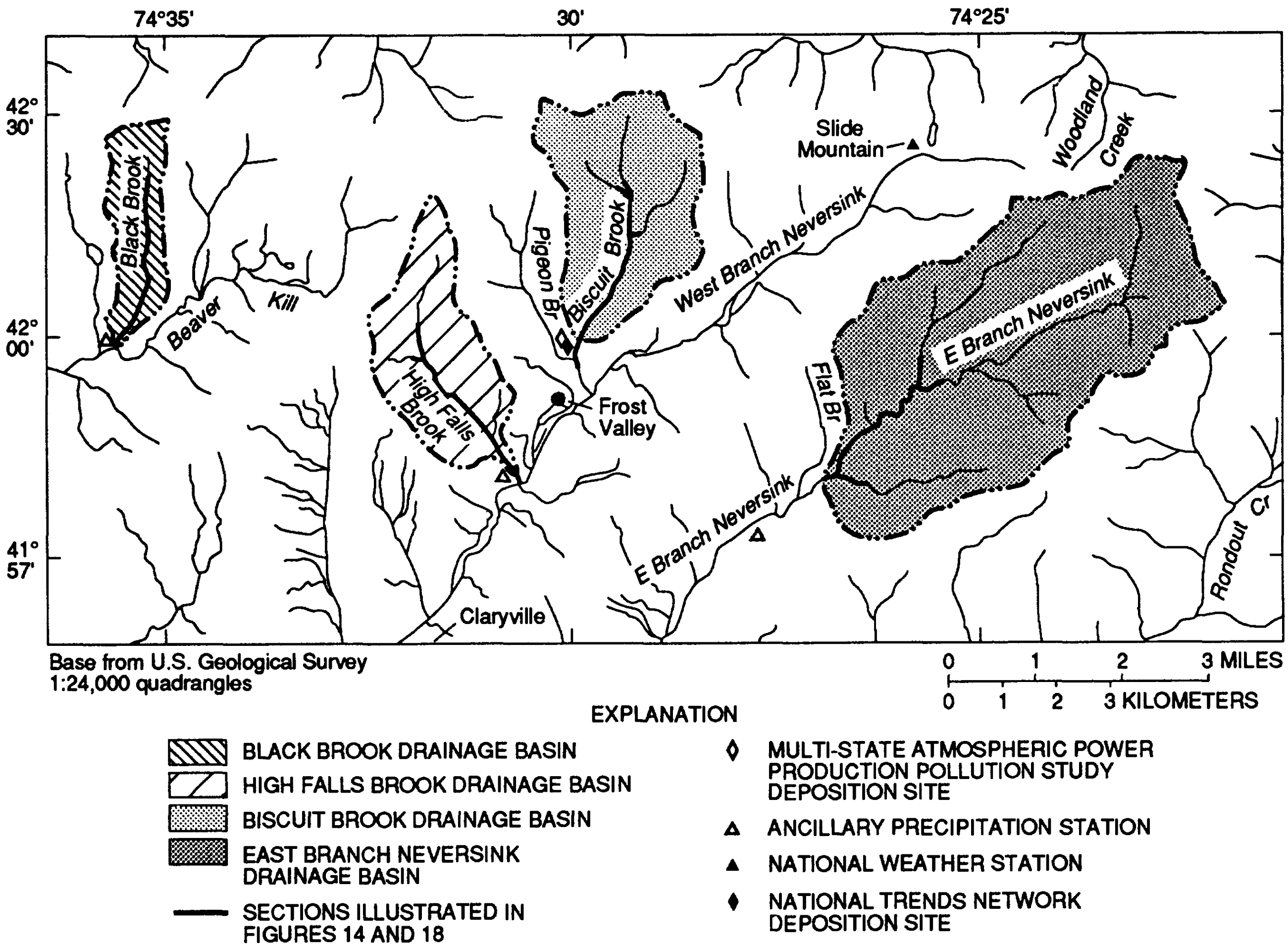

Figure 2. Locations of monitoring sites in the four watersheds. (General location is shown in fig. 1)

Table 1.--Physical characteristics of the four study watersheds above stream gage.
[Locations are shown in fig. 1; m, meters; km, kilometers; km^2, square kilometers]

	Black Brook	High Falls Brook	Biscuit Brook	East Branch Neversink River
Quadrangle ($7\frac{1}{2}$minute)	Seager	Claryville	Claryville	Peekamoose
Stream gage:				
Latitude	42°00'42"	41°58'40"	41°59'43"	41°58'01"
Longitude	74°36'13"	71°31'21"	74°30'05"	74°26'54"
Elevation (m)	681	591	628	651
Stream:				
Order	1	2	2	2
Length (km)	3.73	4.88	4.54	8.42
Slope (m/km)	45	60	45	26
Watershed:				
Maximum elevation (m)	1140	1170	1120	1280
Minimum elevation (m)	680	590	630	650
Relief (m)	460	580	490	630
Area above gage (km^2)	3.65	7.10	9.84	23.1

Branch Neversink River, which was monitored during this study at both its main stem and its major tributary for spawning (Flat Brook, fig. 2) is acidic most of the year (ANC less than 0), yet it contains a brook trout population during the summer base-flow period. Biscuit Brook contains healthy brook trout and sculpin populations despite several acidic episodes each year. Black Brook and High Falls Brook are well-buffered trout streams that have not become acidic (ANC always greater than 0) during observed episodes, although High Falls Brook has large declines in ANC during storms. Both streams were considered to be "control streams" during the first 9 months of the study because ANC did not fall below 0 μeq/L during the observed storm and snowmelt flows. The four streams therefore provide a variety of conditions for assessing fish response to acidic episodes.

All of these streams except Black Brook have been monitored by the USGS since 1983 for monthly flow and stream chemistry as part of the original long-term monitoring program funded by the USEPA (Murdoch and Barnes, 1989). Stream chemistry was monitored over several storms in 1985 at Biscuit Brook as part of an earlier USEPA-funded project. Both Biscuit Brook and High Falls Brook were included in the USEPA national stream survey as "special interest" sites.

Climate

The Catskill Mountain region has cold winters and moderately cool to warm summers. Average annual air temperature calculated from 32 years of data at the National Weather Service station at Slide Mountain (National Oceanic and Atmospheric Administration, 1950-85) was 15 °C. The area has an average of 127 freeze-free days per year, based on 19 years of data. Average annual precipitation during the same period at that station, which is near the center of the study area (fig. 2) was 157 cm. Average annual snowfall, as calculated from data collected at the Mohonk Lake weather station in the southern Catskills (fig. 1), is approximately 170 cm (Tornes, 1979). Heavy dew is common during the early morning throughout the freeze-free period.

Precipitation volume is variable within the Catskill Region; the greatest annual amounts occur in the central, high elevations that contain the four study streams. Short-term local variations in amount of precipitation are large because of localized storms. Precipitation in water year 1989 (October 1988 through September 1989) was typical for the region, although seasonal distribution was not typical, and precipitation was concentrated in June and July.

Physiography and Geology

The Catskill Mountains structurally form the northeastern end of the Appalachian Plateau (Rich, 1934) and are the uplifted remnants of a massive Devonian delta that fed into a shallow inland sea to the west. The high ridges are predominantly erosional remnants, and the physiography suggests that the relief is due largely to stream action.

The region has been divided geographically into three northwest-southeast-trending parallel ranges or escarpments that form the divides between the major Catskill river basins (fig. 2). The escarpment character of the northern and central Catskills is caused by a general 3° southwestward dip of the bedrock. The southern escarpment is irregular with no clear structural control, but the drainage is strongly controlled by structure. The two ridges are separated by a gently plunging syncline oriented northwest-southeast.

The upper reaches of the East and West Branches of the Neversink River and the Beaverkill (fig. 2) are essentially parallel to the strike of the underlying bedrock (Rich, 1934). These southern Catskill drainages are asymmetrical, with much longer tributaries entering from the north than from the south. Biscuit Brook, High Falls Brook, and Black Brook are typical of these southward-draining tributaries.

The bedding planes of the Catskill region bedrock are nearly horizontal. In most places the bedrock is fractured by three nearly perpendicular joint sets, one of which is parallel to the bedding plane (Parker and others, 1964). Joints at oblique angles are also common. The joint fractures were zones of weakness along which quarrying by glacial ice occurred; this resulted in a topography of many flat surfaces adjacent to vertical cliffs. Ground water in bedrock is transmitted primarily along these joint fractures. In many areas, tills of low permeability overlie the bedrock and prevent water from entering the joint systems. Yields of bedrock wells range from 0 to 38 liters per second (Parker and others, 1964), but exceptionally high yields appear to be associated with fault or unusually large joints. The bedrock is therefore considered a poor to moderately good aquifer with a wide variability of yield over short distances (Parker and others, 1964).

Headwater basins in the Catskill Mountains of New York are generally characterized by steep gradients, thin soils with extensive bedrock outcrop, and bedrock or large cobbles in stream channels. Gradients are generally steeper than in comparable Adirondack Mountain streams, and Catskill streams typically flow through fewer wetlands and ponds than Adirondack streams.

Bedrock Composition

Little research has been done on the petrology of the central Catskill bedrock (Ethridge, 1977). The bedrock generally consists of 60 percent sandstone and interspersed conglomerates, and 40 percent mudstone or siltstone. Quartz forms approximately 39 percent of the bedrock material, and rock fragments from metamorphic terrain to the northeast constitute 48 percent of the detrital fraction (Ethridge, 1977). Mineral composition in the Catskill region is fairly uniform. Muscovite is a common accessory mineral, and amphibole is present in small quantities (Ethridge, 1977). Calcite and hematite are the primary cement materials, but most bedrock is uncemented (Way, 1972). Way (1972) reported pyrite and calcite in the shale along Route 17 to the south of the study area and along Route 28 to the northeast; thus small amounts of both minerals may be present in the watersheds.

Ground water from bedrock wells is low in dissolved solids, and the low specific conductance in streams of the study area, generally less than 30 μS/cm (microsiemens per centimeter at 25° C during base-flow periods suggests slow chemical weathering of the bedrock (Parker and others, 1964).

Surficial Deposits

The surficial deposits of the Catskill Mountains are more varied than the bedrock. Glacial deposits in the headwater valleys are a combination of continental-glacier-derived material oriented in the direction of regional ice movement, and reworked or secondarily scoured alpine-glacier deposits oriented perpendicular to each valley.

Little information on till distribution and chemistry in the Catskills is available. Rich (1934) reported thick drift and thinner ground moraine from repeated glaciations in most of the upper Beaverkill and upper East Branch Neversink valleys and pockets of thick drift in the lower High Falls and Biscuit Brook basins. Recent alluvial deposits on modern flood plains extend above the monitoring stations in the Beaver Kill and East Branch Neversink basins. Glacial striae and stratified deposits indicate that the continental ice sheet flowed downvalley in the valleys of the Beaverkill and both branches of the Neversink. All valleys studied were last occupied by local glaciers moving downslope.

Morainal loops are common in the Catskills (Rich, 1934); they consist of unstratified drift deposited at the end of local valley glaciers and are concave upvalley. They were reported by Rich midway up the Biscuit Brook basin and in the headwaters of the East Branch Neversink and Beaverkill basins. Many glacial deposits in the headwaters are thin, and many streams are incised to bedrock.

Glacial deposits in the East Branch Neversink valley (fig. 2) have been reported to be older than Wisconsinan (Rich, 1934), and dissection of till by streams is more advanced than would be expected unless the area were exposed longer than other valleys to the north. The postglacial flood plains are wide, and tributary alluvial fans are large.

The surficial geology of the upper Biscuit and High Falls Brook basins was not mapped by Rich, but a preliminary reconnaissance done as part of the ERP study indicates that ground moraine and bedrock outcrop predominate, and that morainic loops are present, in all four watersheds.

Surficial material in the Catskills consists primarily (at least 90 percent) of local rock and sediment (Parker and others, 1964). The percentage of exotics, particularly carbonate-bearing sediments, probably varies locally, however, and could be a significant factor in explaining the chemical differences among streams.

Soils

The soils of the Catskill Mountains are generally categorized in the Arnot-Oquaga-Lackawanna association, which are excessively drained to well-drained soils mainly on steep slopes (Tornes, 1979). Soils in the basins studied are varied but are predominantly shallow boulder soils on steep slopes and thus are conducive to rapid precipitation runoff; they also are moderately to extremely acidic.

The East Branch Neversink watershed contains mainly Lackawanna soils, which are moderately permeable in their upper layers but contain a fragipan of very low permeability at depths of 45 to 90 cm. Runoff from these soils is rapid. The Biscuit Brook and High Falls Brook watersheds contain mainly Arnot and Oquaga soils, which are well drained and moderately permeable with no fragipan and range from 35 to 60 cm in thickness. Black Brook contains Wellsboro soils on gentle slopes near the stream channel; these are deep, bouldery loam soils that contain a fragipan below a depth of 50 cm. Alluvial deposits are present in the flood plain of Black Brook and the East Branch Neversink near the respective gaging stations.

The soils derive their character largely from the surficial materials on which they have developed. Differences in the thickness and permeability of the soils and of surficial deposits among the four watersheds may be a significant factor in differences in stream chemistry.

APPROACH

Monitoring began in October 1988. The research has focused on (1) the episodic changes in chemical and flow conditions that cause a decline in fish abundance in a given stream reach through fish movement or mortality, (2) the relation between stream discharge and stream chemistry, and (3) the frequency and duration of threshold flow values or chemical concentrations that affect fish survival.

The results described herein are preliminary and do not necessarily reflect the second year of data collection. The research plan is designed to address the four objectives listed previously and described in detail in Thornton and others (1987), through continued monitoring of (a) stream chemistry and discharge, (b) precipitation chemistry and volume, (c) soil-water chemistry and volume, and (d) fish-population behavior in the four selected headwater streams. All methods used during the first 9 months of study are described in detail in Kilkelly Environmental Associates (1988) and Peck and others (1986).

Physical and Chemical Monitoring

Stream-monitoring stations were installed from August through October 1988 at Biscuit Brook, High Falls Brook, Black Brook, and the East Branch Neversink River. Instrumentation at each station was housed in a heated shelter equipped with battery power and recharged by photovoltaic cells. Collection of physical and chemical data at each station included the following:

1. Hourly measurements of stream stage during base flow and quarter-hourly measurements during storm flows by a pressure transducer, and measurements of pH, water and air temperature, and specific conductance by a USGS minimonitor attached to a data logger.
2. Collection of stream-water samples manually each week and by sequential automated samplers during high-flow periods.

3. Collection of snow-core samples biweekly from five sampling stations near each stream gage in the Biscuit Brook, Black Brook, and East Branch Neversink River watersheds.

4. Regular measurements of streamflow by standard USGS procedures (Rantz and others, 1982) for calibration and revision of the stage-to-discharge relations.

Each station was visited at least weekly for routine sampling and discharge measurements, data collection, and instrument-calibration checks. Grab samples were collected in 2-liter bottles at midstream near the monitoring sensors. Automated sampler bases were installed such that the sampling strainers were in well-mixed flow during periods of high discharge. The automated collection tube was removed every 6 months and replaced with a clean tube to minimize the effects of algal buildup on sample quality. Grab samples were sent to a field laboratory at Biscuit Brook and were filtered and preserved within 24 hours for analysis. Samples from the automated samplers were retrieved within 24 hours and generally filtered within 3 days of collection. All samples were kept chilled at 4 °C until processing.

All stream-water samples were initially filtered through 0.4-µm polycarbonate membrane filters for all aliquots except those to be analyzed for aluminum, which were filtered through 0.1-µm polycarbonate filters, and those to be analyzed for pH, ANC, specific conductance, and oxygen isotope analysis, which were not filtered. After experiments proved comparability of results from membrane and fiber filters, and comparability of results from 0.2-µm and 0.1-µm filtration for aluminum, the Catskill ERP switched in June 1989 to 0.2-µm filters for aluminum and 0.4-µm fiber filters for other filtered constituents. The change of methods was at the request of the USEPA to provide consistent filtration methods among the study regions.

Precipitation chemistry and volume in the lower Biscuit Brook watershed were monitored on a storm-by-storm basis with an automated wet-dry collector and a weighing-bucket rain gage. Samples were weighed in the field laboratory and transferred raw to a 250-mL (milliliter) container, stored at 4 °C, and shipped monthly to the analytical laboratory at Battelle Pacific Northwest Laboratories in Richland, Wash., for analysis as part of the Multi-State Atmospheric Power Production Pollution Study (MAP3S). The precipitation-monitoring station, which is central to the study watersheds, is 30 m northwest of the National Trends Network Station (NTN) at Biscuit Brook (fig. 2), where composite sampling of precipitation has been done weekly since 1983. Two additional weighing-bucket rain gages were installed— one at Black Brook and one at the East Branch Neversink River— and data were retrieved weekly. Daily precipitation and temperature data were also collected at the National Weather Service stations at Claryville and Slide Mountain (fig. 2).

Aliquots of each stream-water sample were prepared for analysis for major cations and anions (Ca, Mg, Na, K, SO_4, Cl, NO_3), dissolved organic carbon (DOC), silica, total dissolved aluminum, pH, ANC, and specific conductance. Precipitation and snow samples were analyzed for major ions, pH, and specific conductance. Aliquots for organic and inorganic monomeric aluminum analysis were prepared from selected samples during high-discharge periods. Aliquots for oxygen-isotope ratios were prepared from selected samples of steam water, snow cores, and precipitation.

Biologic Monitoring

Fish-population data were collected during the fall and spring periods of the study. Fall data were obtained with a battery-powered backpack electroshocker designed by the New York State Department of Environmental Conservation. Generator-powered backpack electroshockers were used during the spring estimates to avoid battery failures. Study reaches were blocked at 100-m intervals with seine nets to minimize the escape or migration of fish to and from the study reach.

Captured fish were weighed, measured for length, and marked before reintroduction to the stream. During the spring, native populations of brook trout (*Salvelinus fontinalis*) in each stream were mixed with brook trout from the West Branch Neversink River (hereafter referred to as the common-source fish) and restocked at 80 percent of the reach's carrying capacity.

Efficiency tests on electroshocking methods and sampling bias were conducted several times throughout the study. To conduct the test, a 50-m-long section of a stream was blocked at each end with seine nets and cleared of fish by several electroshocking passes. The reach was then restocked with a known number of marked brook trout, and three or four more electroshocking passes were made. Data from shock-efficiency tests were used to compute error bars on population estimates for the study reaches. At least three passes were made at each stream per population estimate, and the need for additional passes was determined by the Zippin calculation method (Everhart and others, 1975).

Fish movement in the East Branch Neversink River (acidic) and High Falls Brook (high ANC) was monitored by radiotelemetry techniques during April 13-28, 1989. Radio transmitters were placed in the stomachs of 30 adult brook trout, which were held for 48 hours in cages before release to the two study reaches. Fish position was recorded daily and, if daily movement exceeded 25 m, water samples were collected from both the initial and final position. Samples were analyzed for pH, specific conductance, ANC, total dissolved aluminum, and occasionally for major ions and aluminum species.

Bioassay experiments in which brook trout yearlings and sculpin were held in cages within each study reach were conducted during the late fall 1988 and spring 1989. Each experiment lasted 15 to 30 days, depending on mortality or ice conditions. Initially 21 brook trout and 21 sculpin were placed in each stream, with approximately seven fish in each of six 4-liter nalgene jugs modified with screen sides. The experiments were continued until greater than 10-percent mortality occurred in High Falls Brook or Black Brook, or 90 percent mortality in any study stream. Several bioassay experiments included trout and sculpin native to that stream as well as those collected at the well-buffered common-source stream.

Surveys of brook trout and sculpin populations were conducted on all study streams during the summer of 1989 to assess their longitudinal distribution above and below the study reaches. Surveys entailed two electroshocking passes on selected 100-m-long reaches, and the presence or absence of young-of-the-year was noted.

Invertebrate samples were collected with Surber[1] samplers. The sampler encloses a 1-square-foot (0.09-m^2) area of the stream channel with a metal box, which is attached to a fine meshed net that extends from the collector downstream. Bed materials within the box are carefully cleaned of organisms, and the fraction that is smaller than cobble size is turned repeatedly with a trowel to suspend invertebrates and allow them to drift downstream into the collection net. A total of five Surber samples were collected randomly across the stream channel at each station during each collection period. Individual surber samples were then sorted until 100 organisms were collected; these organisms were identified to the family level, and the remaining sample was stored for future analysis.

Laboratory Operations

Aliquots for chemical analysis were sent from the field laboratory directly to the analytical laboratories. Analyses for pH, ANC, specific conductance, and selected major anions (SO_4, Cl, NO_3) were done at the USGS laboratory in Albany, N.Y., and analyses for selected major cations (Ca, Mg, Na, K), DOC, silica, and total dissolved aluminum were done at the New York City Department of Environmental Protection Laboratories in Grahamsville and Valhalla (fig. 1). Analyses for organic monomeric and total monomeric aluminum were done in the laboratory of Dr. Brian Dempsey at Pennsylvania State University, and analyses for oxygen-isotope ratios were done at the USGS isotope laboratory in Reston, Va.

Samples at each laboratory were checked against log-in sheets and, if unpreserved, stored at 4 °C before analysis. Analyses for pH, specific conductance, ANC, and major anions were run as soon as samples were received and were done within the specified holding times except during periods of peak sample loads. Analyses for DOC were conducted immediately upon receipt of samples. Preserved

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[1] Surber samplers are a combination square frame and net device for collecting organisms from a 0.09-m^2 area of a stream bed

samples were generally run within specified holding times except during peak sample loads (Peck and others, 1986).

Quality Assurance and Control

Quality-assurance and control procedures for field and laboratory operations were in accordance with the ERP field-methods manual (Kilkelly Environmental Associates, 1988) and the quality-assurance plan (Peck and others, 1986). Field quality-assurance methods included duplicate measurements, collection of field blanks, processing of field audit samples, calibration and audit checks on field instrumentation, processing of samples collected at other ERP regions, and data-recording checks by pairs of field technicians. All field data were plotted against warning and control limits established by the ERP, and samples falling outside those limits were reanalyzed. Sampling and monitoring instruments and containers were carefully cleaned between use, then filled with deionized water, and allowed to soak for 48 hours. After this soak, the water in 10 percent of the sample bottles was checked for specific conductance values greater than 2 µS/cm, and if this limit was exceeded, all containers were recleaned.

Laboratory quality-assurance methods included duplicate measurements, analysis of blanks and laboratory splits of samples, analysis of quality-assurance check samples every 10th sample, spiked samples for cation analyses, and analysis of audit samples from USEPA, USGS, and the Long-Range Transboundary Air Pollution Program (LRTAP). Analytical results were then tested through anion-versus-cation balances, measured-versus-theoretical conductance balances, and temporal plots of each constituent. Samples that deviated by more than 10 percent from unity in these balances or showed anomalous concentrations in relation to temporal plots were reanalyzed. Results of the quality assurance and control program are presented in the appendix.

HYDROLOGY

The steep gradients and thin soils of the Catskill region result in "flashy" hydrologic conditions, limited storage of water in watershed soils, and low base flows. Peak flows that exceed 3.5 $(m^3/s)/km^2$ (cubic meters per second per square kilometer) have been observed during some spring high flows since 1983 (Murdoch, 1991). Comparison of wet years with dry years at Biscuit Brook indicates that base flow is similar from year to year, and that the main differences among years are in the magnitudes and frequency of stormflows (Murdoch, 1991). The magnitude of stormflow is closely related to antecedent moisture conditions and precipitation volume during individual storms (Murdoch, 1991).

Precipitation

Volume-weighted annual precipitation pH at the NTN station near Biscuit Brook (fig. 2) remained near 4.3 during 1984-89 (Murdoch, 1991, and U.S. Geological Survey, 1989, unpublished data). Sulfate was the dominant anion, and hydrogen the dominant cation; these represented a mean of 61 and 68 percent of the anion and cation equivalents, respectively. Differences in chemical loadings to the study watersheds may have been the result of local differences in precipitation volume.

Precipitation volume in the Catskills during water year 1989 was similar to (5 cm greater than) the 10-year average for the region (table 2), but the seasonal distribution and type of precipitation was atypical. Rain in the last quarter of 1988 fell mostly from late October through November; early October and December were dry (fig. 3). Unusually mild temperatures and low precipitation volume from January through mid-March resulted in record-low snowpack accumulations. Most of the precipitation was retained in the watershed as ice that formed a thick cover over most of the watershed. Precipitation and warm temperatures during mid- and late March removed most ice from the watersheds. April was again dryer than normal, with no rainfall during its second half. Much greater-than-normal precipitation fell during May and June. The Catskills received more than 35 cm of rain in four major storms during the first 15 days of May.

Table 2.--Annual and 10-year average precipitation at the National Weather Service station at Slide Mountain, water years 1980-89

[Precipitation values are in centimeters. Location is shown in fig. 2]

Water Year	Precipitation	Water Year	Precipitation
1980	142.0	1985	131.2
1981	154.6	1986	149.5
1982	138.0	1987	169.3
1983	162.3	1988	130.7
1984	167.4	1989	158.9

10-year mean = 150.4

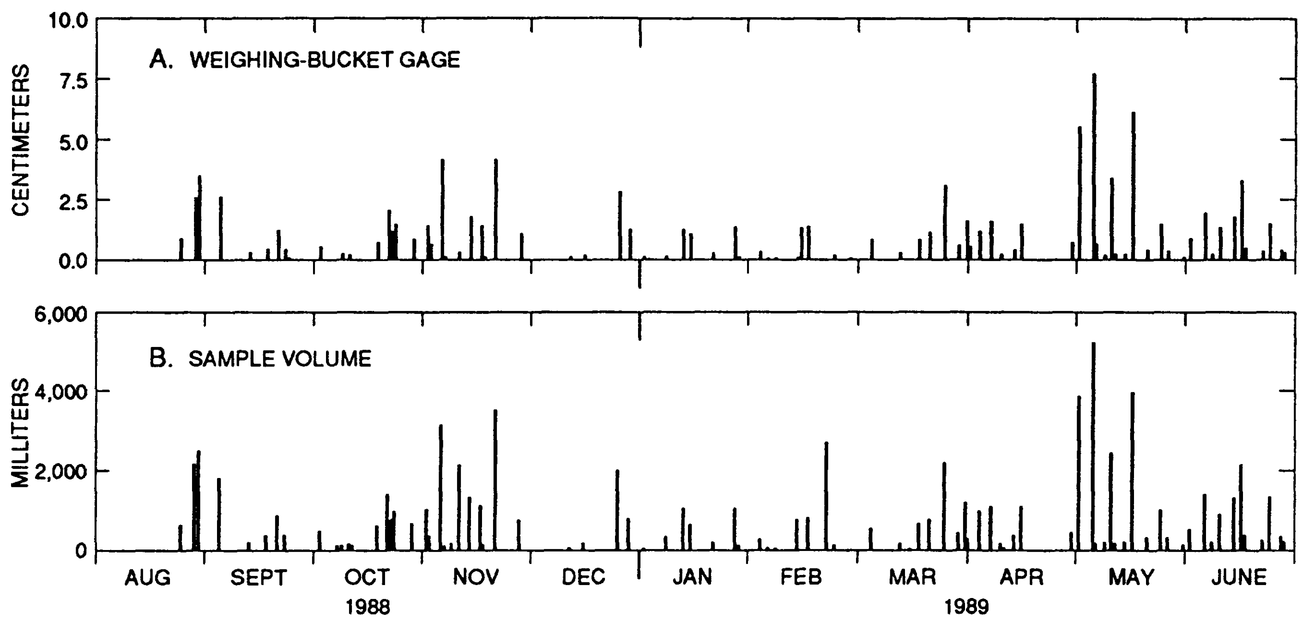

Figure 3.--Precipitation volume at Biscuit Brook as determined from (A) weighing-bucket rain-gage data, and (B) sample volume, August 1, 1988 - June 30, 1989.

Streamflow

Catskill streams during water year 1989 had typical flows in the fall but lower-than-normal flows during spring snowmelt, and above-normal flows during heavy rains in May and June (table 3). Winter precipitation was below normal and was primarily freezing rain; thus the hydrologic response during spring melt was driven primarily by melting ice rather than melting snow. More than 35 cm of rain fell in the first 2 weeks of May after a dry April and created stormflows with peaks exceeding those in the spring melt period.

Hydrographs for all four streams suggest sharp increases and steep recessions to base flow after storms (fig. 4, p. 13). Estimates of the percentage of streamflow contributed by ground water indicate the ground-water contribution in the streams with high ANC (High Falls Brook and Black Brook) to be about 10 percent greater than in Biscuit Brook and 20 percent greater than in the East Branch

Neversink, the most acidic stream studied (table 4). The estimates were computed by the USGS HYSEP (Hydrologic Separation) model, which compares results of three graphical flow-separation techniques. The percent ground-water contribution to total runoff in each stream is therefore consistent with observed differences in stream chemistry and indicates that small ground-water contributions to streamflow correlate with low stream pH values.

Flow-duration curves for each stream, illustrating the percentage of days each year that a given discharge was equaled or exceeded, were compared with the flow-duration curve for 35 years of record at the USGS streamflow-gaging station on the Neversink River (fig. 5). Results indicate that the lowest base-flow discharges per square kilometer were at Biscuit Brook, the stream with intermediate ANC. Low flows of High Falls Brook (high ANC) were similar to those of East Branch Neversink (low ANC), and the East Branch Neversink had more sustained medium and high flows than the other streams. Low flows of Black Brook were between those of High Falls Brook and Biscuit Brook during each season. This comparison suggests that the main hydrologic difference among the study streams is in the medium and high flows; flows of less than 40-percent duration were greatest in the East Branch Neversink (low ANC), and flows of less than 10 percent flow durations were greater in Biscuit Brook (moderate ANC) and the East Branch Neversink than in Black Brook or High Falls Brook (high ANC).

Table 3.--Mean monthly discharge of Biscuit Brook, October 1, 1983 to September 30, 1989, and monthly discharge from October 1, 1988 to September 30, 1989 .

[Values are in cubic meters per second]

Month	1983-89	1989
October	6.1	3.0
November	10.5	14.2
December	9.2	5.1
January	5.4	2.3
February	7.2	4.6
March	15.1	13.7
April	15.8	11.4
May	15.2	29.8
June	5.0	7.7
July	3.5	3.01
August	3.1	1.6
September	6.0	7.5

Table 4.--Percentage of total annual flow contributed by ground water in the Catskill streams, as computed from graphic interpolation models.

[Locations are shown in fig. 2]

Stream	Contribution of ground water as a percentage of flow
Black Brook	76.84
High Falls Brook	75.41
Biscuit Brook	67.9
East Branch Neversink	57.04

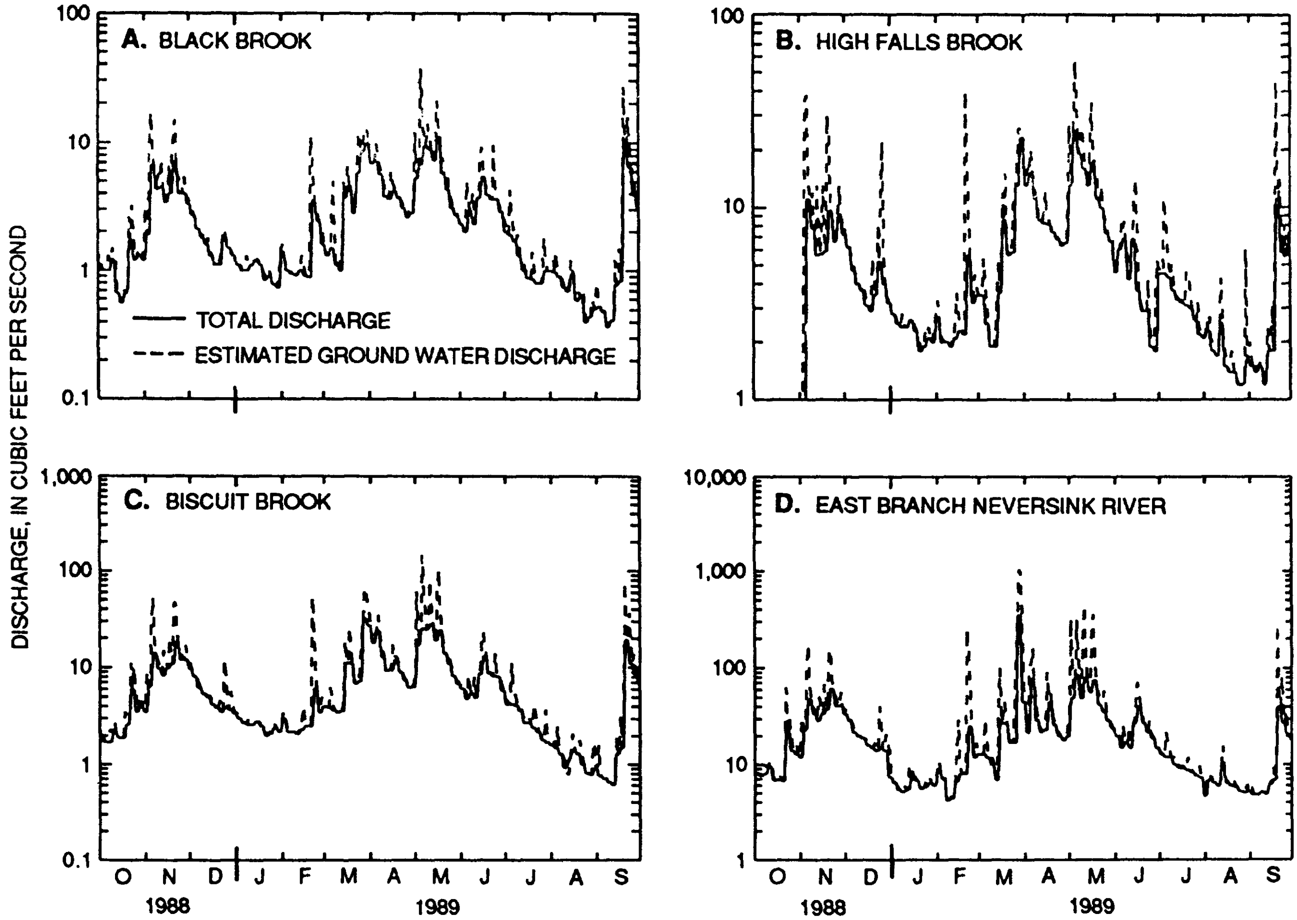

Figure 4.--Hydrographs for the four streams studied, water year 1989.

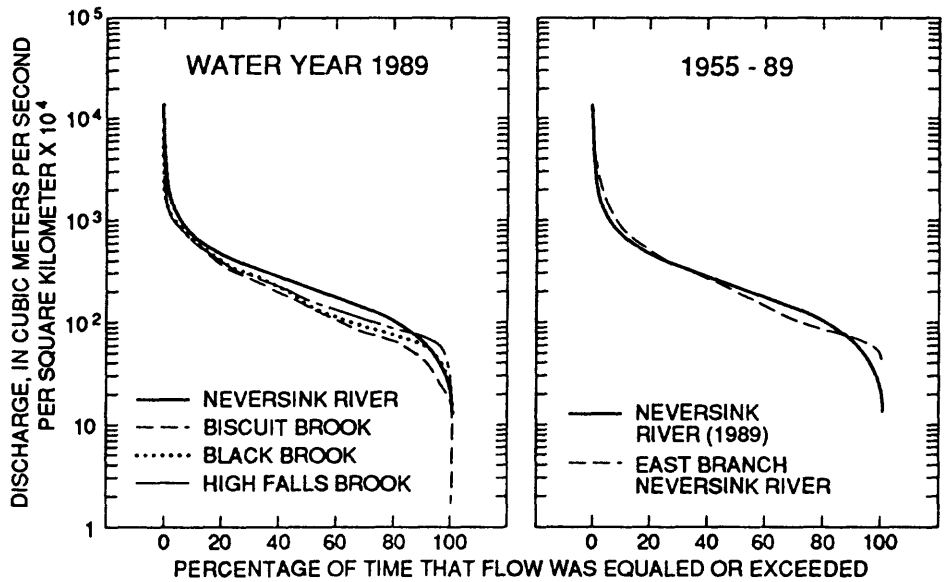

Figure 5.--Flow-duration curves of discharge of the four streams (1989) and the Neversink River at Claryville (1955 to present).

WATER CHEMISTRY

Stream water and precipitation were monitored weekly and during storms by analysis of water samples, and stream water was monitored continuously for pH and specific conductance by onsite sensors. Monitoring by sensors was intermittent during the fall and winter of 1988-89 as a result of calibration difficulty and malfunctions, but the sensors generally were calibrated at all stations after early spring of 1989. Results presented here focus on seasonal trends and the episodic acidification of spring and early summer 1989.

Chemical Deposition

Volume-weighted average concentrations of major constituents in precipitation collected from September 1988 through June 1989 at the MAP3S station (fig. 2) were similar to data collected over the preceding 5 years at the NTN monitoring station at Biscuit Brook (table 5). These values are also similar to those observed at other NTN stations in the Northeast, indicating relatively uniform concentrations of major constituents in precipitation across the region (Murdoch, 1991). Annual precipitation volumes are greater than in other parts of the Northeast,however, which results in greater chemical loading at Biscuit Brook they observed at other monitoring stations.

Table 5.--Average volume-weighted concentrations of major constituents in precipitation at the National Trends Network (NTN) (5-year average) and Multi-State Atmospheric Power Production Pollution Study stations at Biscuit Brook, October 1988 through June 30, 1989

[Locations shown in fig. 2. All values in microequivalents per liter except pH, in units]

Constituent	5-year average	1989
Sum of base cations	11.61	12.78
Hydrogen	51.94	48.5
Ammonium	12.91	14.25
Sulfate	49.57	39.58
Nitrate	26.95	25.39
Chloride	4.97	8.25
pH	*4.3	4.3

* Average pH was computed from average hydrogen ion concentration.

Concentrations of selected anions and cations in precipitation varied from storm to storm within each season, which makes seasonal patterns in concentrations difficult to discern (fig. 6A, p. 16). Generally, concentrations of all constituents selected were lower during December and January than during the other months. Sulfate and nitrate concentrations appear to have some seasonal characteristics; the highest sulfate concentrations were in the fall and early summer, and those of nitrate were in the fall and spring. Chloride concentrations were more seasonally uniform than sulfate and nitrate, but concentrations during individual storms were significantly above average during late November and late February. Seasonal variability of cation concentrations was less clear than for anions, except for the relatively lower winter concentrations mentioned above, and a cluster of storms with higher-than-average potassium concentrations during May and June.

Nitrate and ammonium deposition (mass per unit area) was greatest during storms of November 1988; and was also high during storms in late February and May 1989 (fig. 6B). One storm in late November also delivered large quantities of all other major constituents; otherwise, the deposition of the other constituents was fairly uniform during storms in the fall.

Concentrations of constituents in rainfall during major increases in streamflow were generally lower than concentrations in the streams, which indicates significant interaction between rain water and watershed materials before rain water entered the streams.

Mean Concentrations in Streams

Comparison of the volume-weighted mean base-flow concentrations of major constituents in the four streams indicates that the greatest difference among the streams was in calcium concentrations, and this difference parallels the differences in base-flow ANC and aluminum values (table 6). Concentrations of nitrate during base flow are similar among all streams except Black Brook, which had nearly double the concentration of the others. Hydrogen and aluminum concentrations at base flow were inversely related to calcium and ANC concentrations in all streams, and all other constituent concentrations were similar among the streams. Sulfate and nitrate concentrations were lowest in the most acidic streams (Biscuit Brook and the East Branch Neversink), which further illustrates that differences in stream pH result from differences in the availability of alkalinity sources in the watershed, not concentrations of sulfate and nitrate.

Table 6.--Volume-weighted mean concentrations and standard deviations of major constituents at base flow in the four study streams.

[Values in microequivalents per liter except as indicated: µS/cm = microsiemens per centimeter, µg/L = micrograms per liter, mg/L = milligrams per liter. ANC = acid-neutralizing capacity. Locations are shown in fig. 2]

Constituent or Characteristic	Black Brook (high ANC)		High Falls Brook (high ANC)		Biscuit Brook (med.ANC)		East Branch Neversink (low ANC)	
	Concentration	Standard deviation	Concentration	Standard deviation	Concentration	Standard deviation	Concentration	Standard deviation
pH (units)	6.3		6.4		5.9		4.9	
Hydrogen	0.49	0.29	.38	0.35	1.27	2.7	13.0	5.8
Sum of base cations	287	30	274	53	210	26	144	20.6
Calcium	206	25	192	35	140	19	69	7.5
Sulfate	135	8.5	136	9.6	134	12	122	6.5
Chloride	18.2	2.3	17.1	2.6	16.7	4.3	15.5	2.4
Nitrate	49.0	13	28.8	11.3	26.9	14	27.0	13.9
Acid-neutralizing capacity	92.5	33	84.3	34	22.8	14	-4.1	11.2
Dissolved organic carbon (mg/L)	1.63	.67	2.13	1.0	2.36	2.5	1.36	1.3
Silica (mg/L)	2.18	.38	2.12	.51	1.95	.32	2.27	.32
Aluminum (µg/L)	.05	.03	12.0	35	68.1	53	196.0	87
Specific conduct-ance (µS/cm)	35.3	5.0	32.0	3.3	26.2	3.1	25.7	2.8

Relations between Ion Concentrations and Stream Discharge

Concentrations of major ions in streams are strongly related to discharge in the Catskill Mountains. Base-flow sulfate concentrations (fig. 7A, p. 18) are similar among the four streams, and all streams show similar rates of dilution with increases in discharge. Data from Biscuit Brook show a consistent sulfate-to-discharge relation over a 6-year record. Base-cation concentrations (fig. 7B) also decrease with discharge at all streams, but the initial concentrations and rates of dilution differ greatly. Black

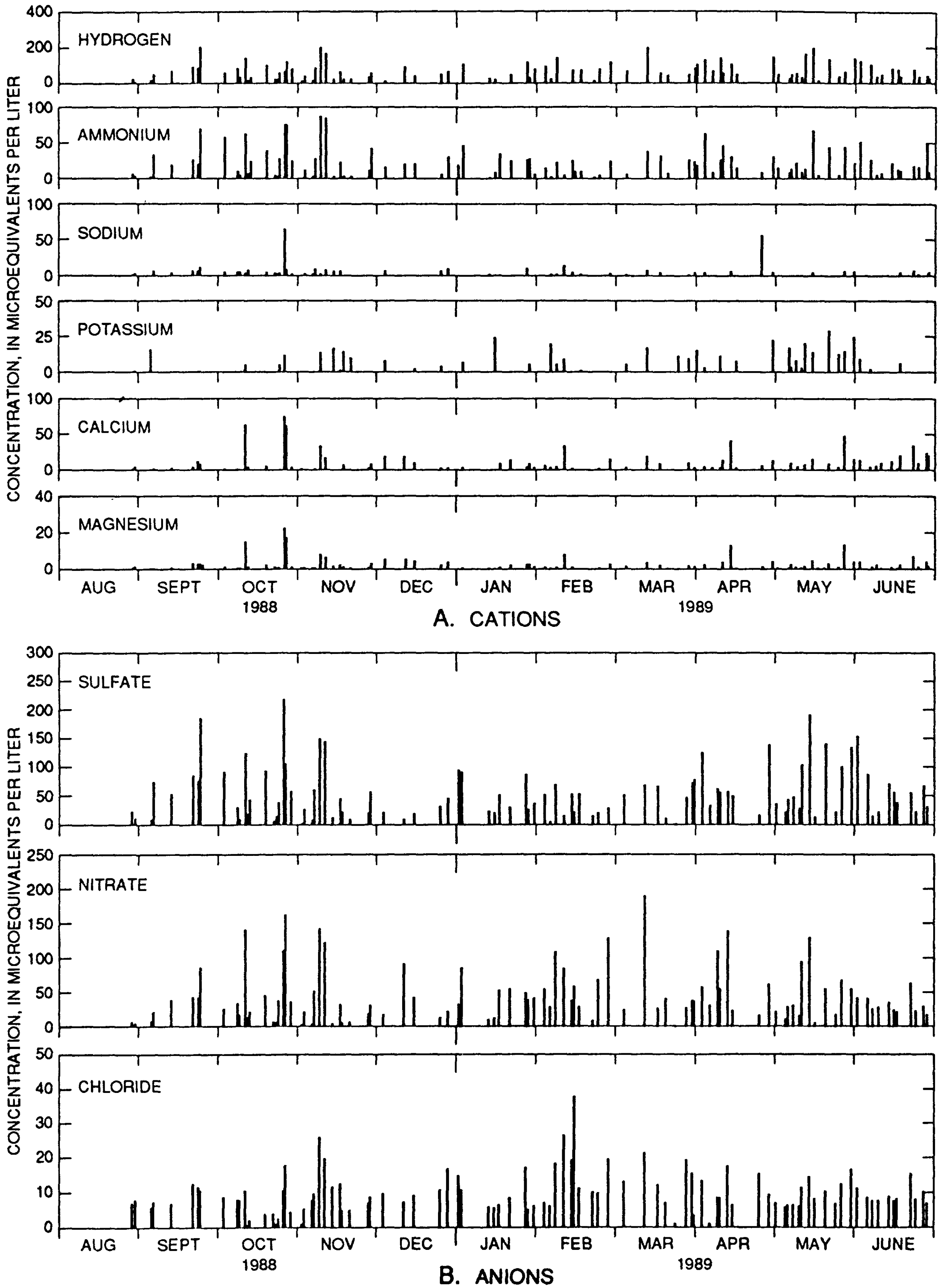

Figure 6A.--Concentrations of major ions in precipitation at Biscuit Brook, August 1988-July 1989.

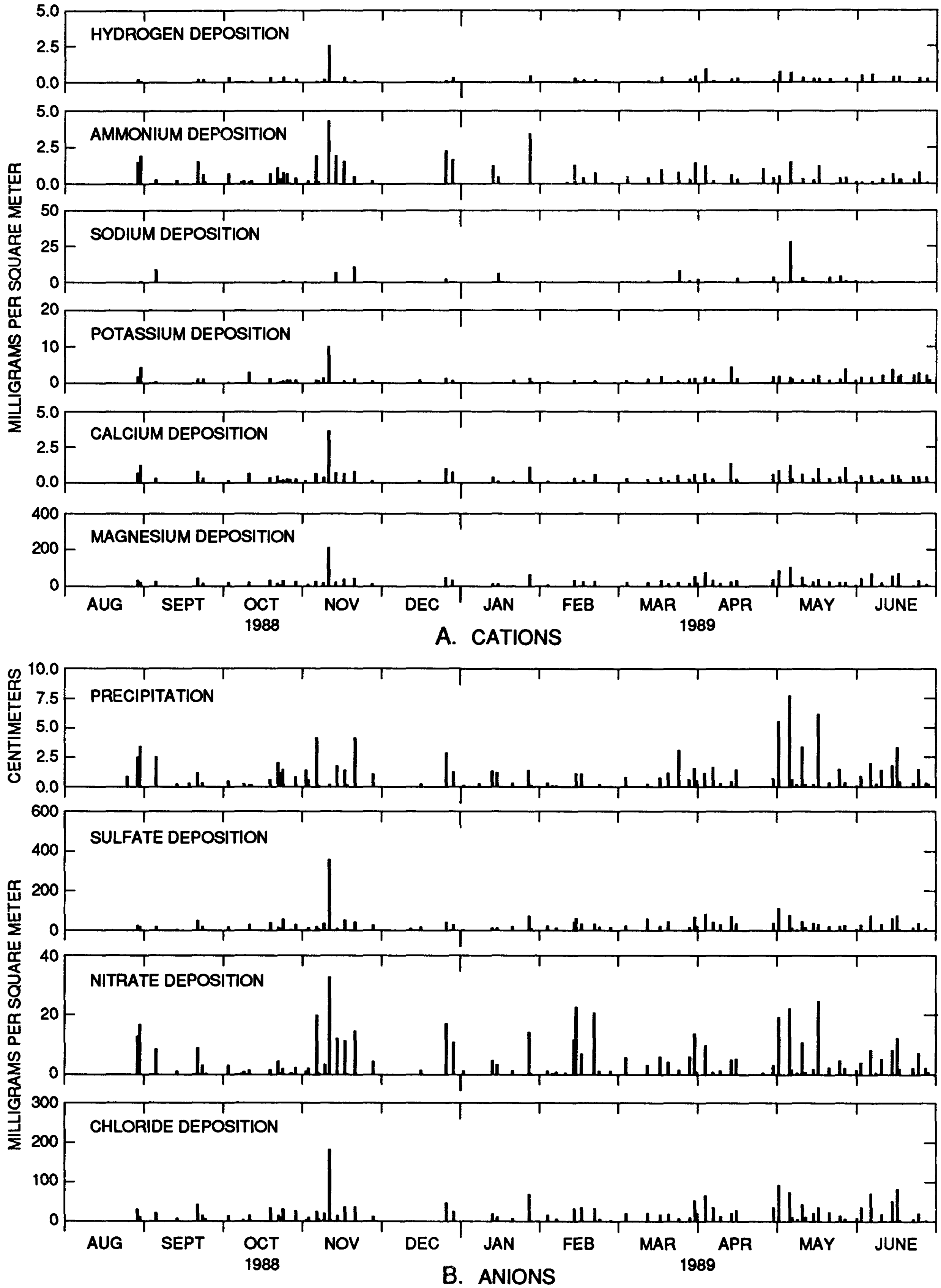

Figure 6B.--Deposition (mass per unit area) of major ions in precipitation at Biscuit Brook, August 1988-July 1989.

Brook and Biscuit Brook have similar rates of dilution with increased discharge but have different concentration ranges. The East Branch Neversink has the lowest base-flow concentrations and the lowest rate of base-cation dilution. High Falls Brook has base-flow concentrations similar to those in Black Brook but also a much more rapid dilution rate. Base-cation concentrations at High Falls Brook during peak discharge approach those in the East Branch Neversink. The greater range of base-cation concentrations at High Falls Brook than at Black Brook correlates with the wider range of pH at High Falls Brook than at Black Brook.

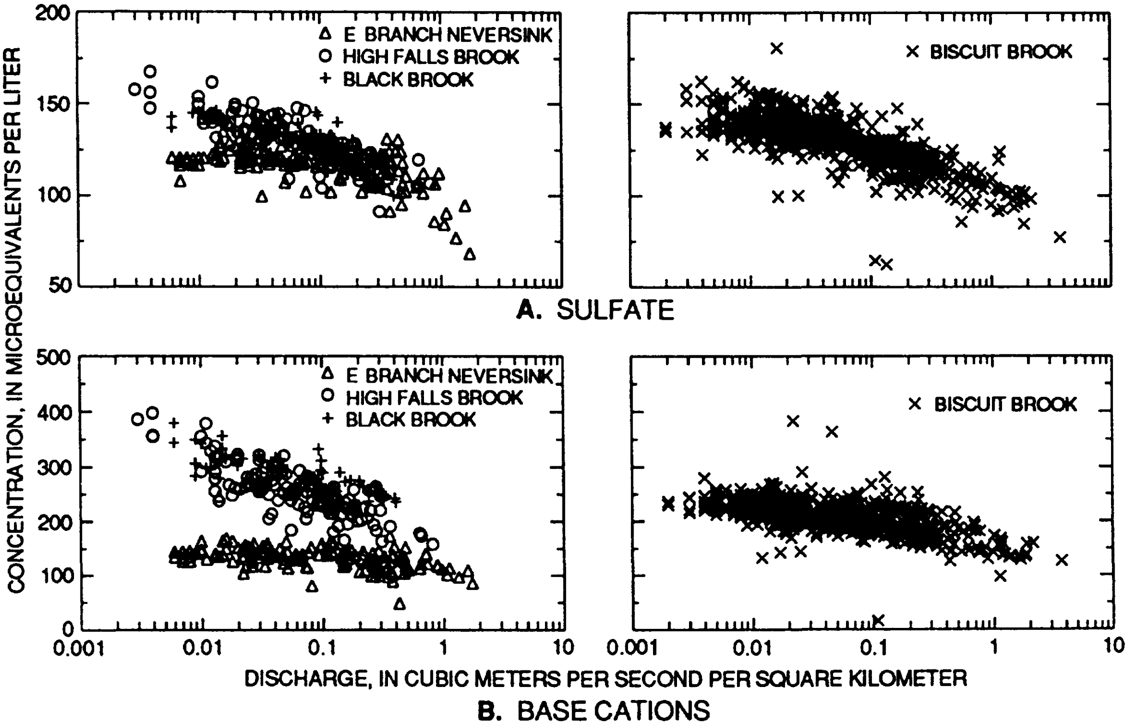

Figure 7.--Relation of ion concentrations to discharge in the four study streams: A. Sulfate. B. Base cations

Seasonal Stream Chemistry

Concentrations of aluminum, nitrate, ANC, and pH in water samples from the four streams during 1988-89 (fig. 8, p. 20) indicate that the lowest pH and ANC and the highest aluminum concentrations generally occurred during November 1988 and late spring 1989. The mid-winter peaks in aluminum and decreases in ANC concentrations and pH recorded at all streams were the result of dilution by rain on ice and snow. Lowest pH and highest aluminum values were found during the November 5 storm in 1988 and the May storms of 1989. Aluminum concentrations in Black Brook during the November 5 storm were three times the next-highest peak. Seasonal controls on stream chemistry are minor, however, in comparison to antecedent moisture conditions or precipitation during individual storms, and these latter factors can cause minimum annual pH and ANC and high aluminum concentrations to occur during any season (Murdoch, 1991).

Base-flow nitrate concentrations gradually increased in Biscuit Brook, High Falls Brook, and the East Branch Neversink during the study period, from a minimum during October 1988 to a peak during

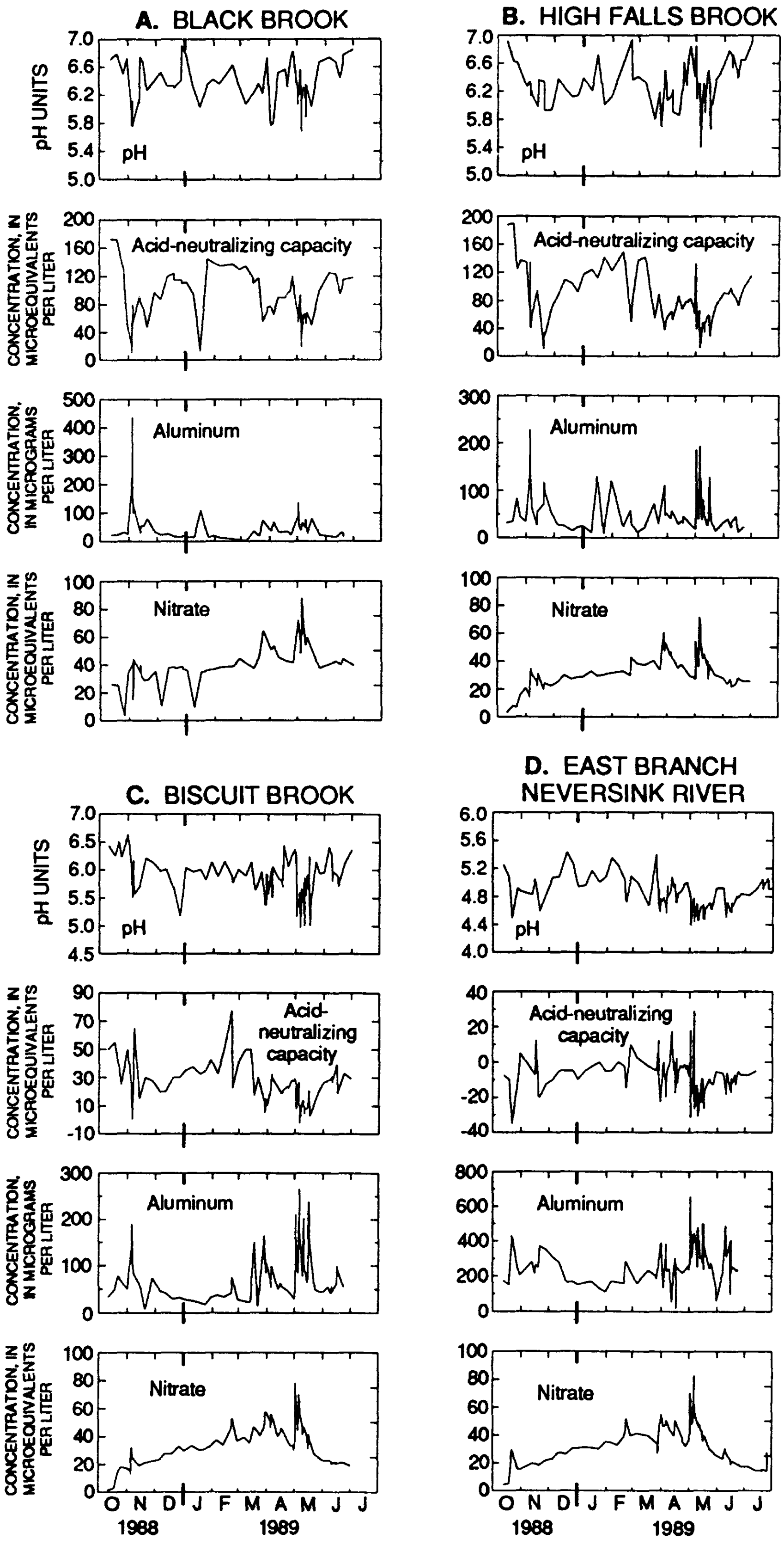

Figure 8.--pH, acid-neutralizing capacity, and concentrations of aluminum and nitrate in the four study streams during the first 9 months of study.

May 1989. Black Brook maintained a higher nitrate concentration during the fall than the other streams, which suggests a more sustained source of nitrate within its watershed. Peak nitrate concentrations were similar among the streams, whereas base-flow nitrate concentrations were lowest in the most acidic stream (East Branch Neversink).

Spring Snowmelt, 1989

The 1989 spring meltwater-runoff period began with a high discharge of short duration on February 21 and continued through a small rainstorm in early April. The most sustained high flows occurred from March 27 through April 2, a period of high air temperatures but little precipitation (fig. 9, p. 22). The winter had been a period of mild temperatures and low precipitation, which resulted in record low snowpack accumulations. The precipitation that did occur was primarily freezing rain, and water retention was greatest in the East Branch Neversink watershed, where high elevation allowed some snowpack development. As a result, spring discharge was substantially greater in the East Branch Neversink than in the other three streams, and chemical changes there were also more pronounced.

The meltwater flow of February 21 came suddenly after a period of below-freezing air temperatures that prohibited the use of the automatic samplers for sample collection, but hand samples collected during that storm indicate the range of chemical changes. The data show that major dilution occurred, probably as a result of runoff over frozen ground, and acidification was only minor (as evidenced by a moderate decrease in pH and an increase in aluminum and nitrate concentrations). For example (fig. 9), large decreases in sulfate, total base cations, and ANC concentrations occurred in High Falls Brook, but these decreases were associated with minor increases in nitrate and aluminum concentrations, and the minimum pH was above 6.3. Discharge quickly receded to base flow after this episode and remained low until mid-March.

The high flow of late March was caused mainly by melting ice, and the chemical characteristics, therefore, were not typical of changes related to spring snowmelt in the region. For example, nitrate concentration at the East Branch Neversink, which typically increases with discharge during the spring (Murdoch and Barnes, 1989), was initially diluted before increasing during the highest flows of the melt period in late March (fig. 9). A short dilution period also could have occurred in the other streams at that time. ANC concentrations in the East Branch Neversink increased from negative values (by Gran's titration) to slightly above zero at the beginning of the same high-flow period before decreasing to negative values as discharge increased.

Stream pH values exceeded 6.0 at High Falls and Black Brooks during the entire melt period, and pH at Biscuit Brook remained at or slightly less than 6.0. The East Branch Neversink had minimum pH values (4.3) during late March, a decrease from a maximum of 5.4 in mid-March. Maximum concentrations of total dissolved aluminum for the period were less than 150 µg/L at all streams except the East Branch Neversink, where peak values were about 400 µg/L.

Chloride concentrations increased slightly over the period of spring melt at Black Brook but were relatively stable in the other streams during that time. Dilution of chloride occurred during the late February and late March high flows in the East Branch Neversink but recovered quickly to former levels after the peak discharge.

ANC concentrations remained well above zero at High Falls and Black Brooks for the entire melt period and slightly above zero at Biscuit Brook. ANC concentrations in Biscuit Brook during 1984-89 typically became negative during the spring (Murdoch, 1991). Negative ANC values at the East Branch Neversink coincided with increases in aluminum, DOC, and nitrate concentrations.

Organically bound aluminum formed only a small percentage of the total monomeric aluminum observed (fig. 9). Aluminum concentrations increased slightly in Black and High Falls Brooks, and concentrations in Biscuit Brook increased to about 150 µg/L. Organic aluminum accounted for a greater proportion of the total dissolved aluminum in Biscuit Brook than in the East Branch Neversink during this period.

The spring snowmelt of 1989 in the Catskills can therefore be summarized as being smaller than normal (Murdoch, 1991). Both the highest runoff per square kilometer and most acidic chemical conditions occurred in the East Branch Neversink, which can probably be attributed to a greater accumulation of snow and ice than in the other watersheds. Biscuit Brook, the moderately buffered stream of the study, did not become as acidic as has been observed in the previous six spring periods (Murdoch, 1991; USGS, unpublished data on file in the New York office of the USGS), and dissolved organic compounds formed complexes with a large percentage of the dissolved aluminum.

Storm of May 1 - 17, 1989

The highest discharges recorded in the four streams from October 1988 through June 1989 occurred during four rainstorms between May 1 and May 17 (fig. 10, p. 24). More than 35 cm of rain fell during this period, and the greatest rainfall intensities and stream discharges occurred during the second and fourth storms. The resulting discharges showed more severe pH and ANC declines and aluminum increases than those of the spring melt period. The relation between stream chemistry and discharge differed from storm to storm, however, as a result of the storms' rapid succession. Over the course of the four storms, each stream had a unique pattern of chemical characteristics that possibly reflectedthe hydrologic differences among the watersheds. Results of chemical analyses of streamwater collected on these dates indicate the effect of antecedent moisture conditions and short-term storage on the relations of discharge to chemistry at all four streams.

Nitrate

Nitrate concentrations in Black Brook and High Falls Brook had the greatest increase during the second storm, which suggests that discharges resulting from that storm were great enough to flush out the nitrate that had accumulated in the watershed from deposition and biological activity over the winter and been retained over the mild spring (fig. 10). Biscuit Brook and the East Branch Neversink, which are "flashier" than the other streams, had the greatest nitrate concentrations during the first storm, and, during the second storm, they showed a decrease in the nitrate concentration as a function of discharge, which indicates a depletion of nitrate sources in the watershed. All streams showed this "washout" characteristic by the third storm, when each stream showed little change in nitrate concentration as discharge increased. Nitrate deposition was assumed to be similar among the streams because the precipitation volume was similar in each storm; therefore, differences in stream response probably indicate watershed differences.

Base Cations

The sum of base cations (Ca+Mg+Na+K) in the East Branch Neversink and High Falls Brook underwent little dilution with increased discharge after the first storm, which indicates a major stable source of base cations in these watersheds during saturated conditions. In contrast, Black Brook, which has the highest base-cation concentrations at base flow, was significantly diluted during the first three storms of the period. Biscuit Brook showed successively greater base-cation dilutions with discharge from one storm to the next, but the concentrations increased during the first storm, which suggests a depletable source of base cations in that watershed.

Sulfate and Chloride

Sulfate and chloride concentrations generally decreased with increasing discharge at all four streams during the four-storm period, although the chloride concentration in the East Branch Neversink appears to have increased slightly during the first storm . All streams showed an overall decrease in chloride concentrations over the period, which suggests some depletion of chloride sources.

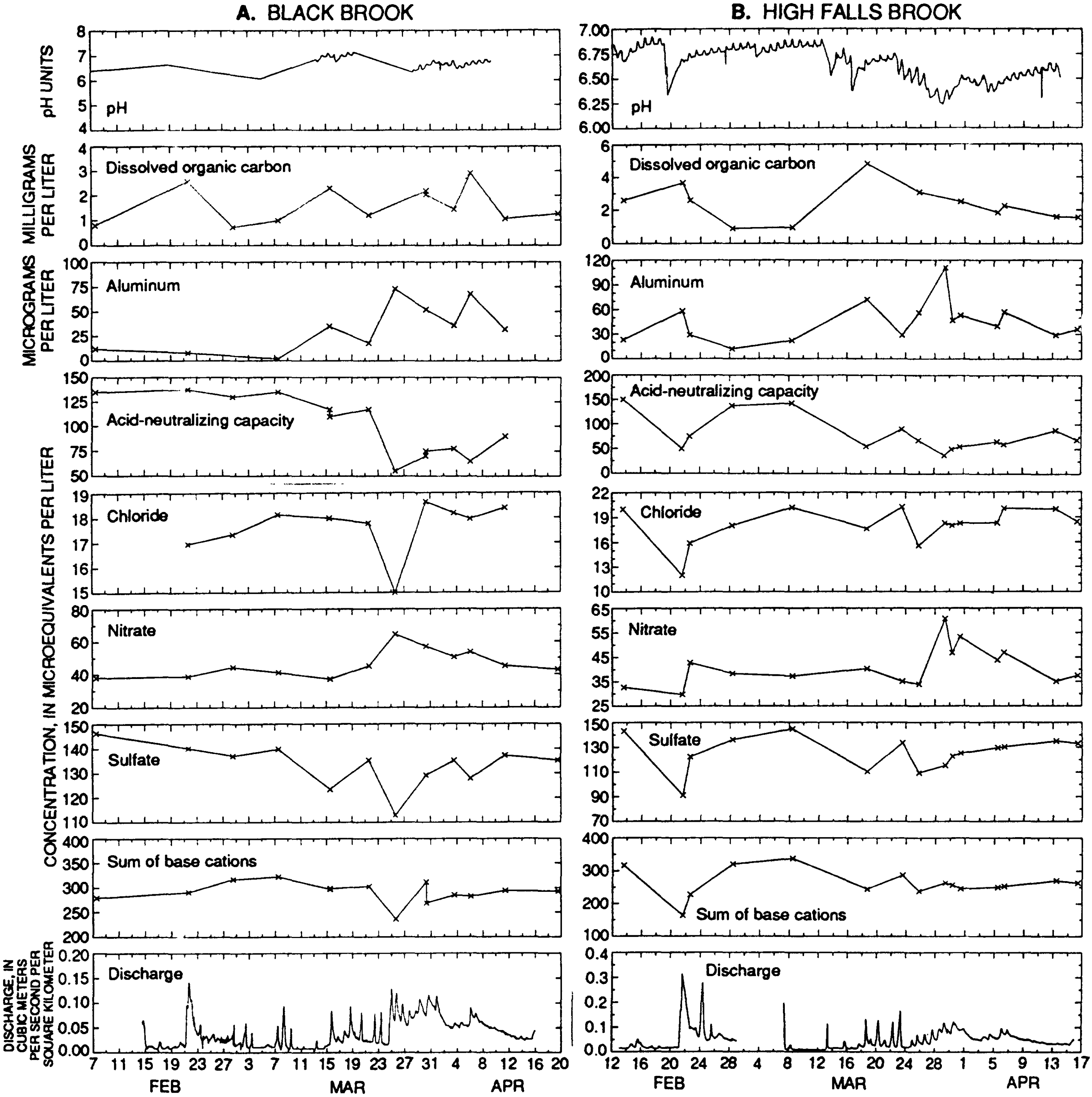

Figure 9.--pH, acid-neutralizing capacity, concentrations of selected constituents, and discharge in Black Brook and High Falls Brook during the spring snowmelt of 1989.

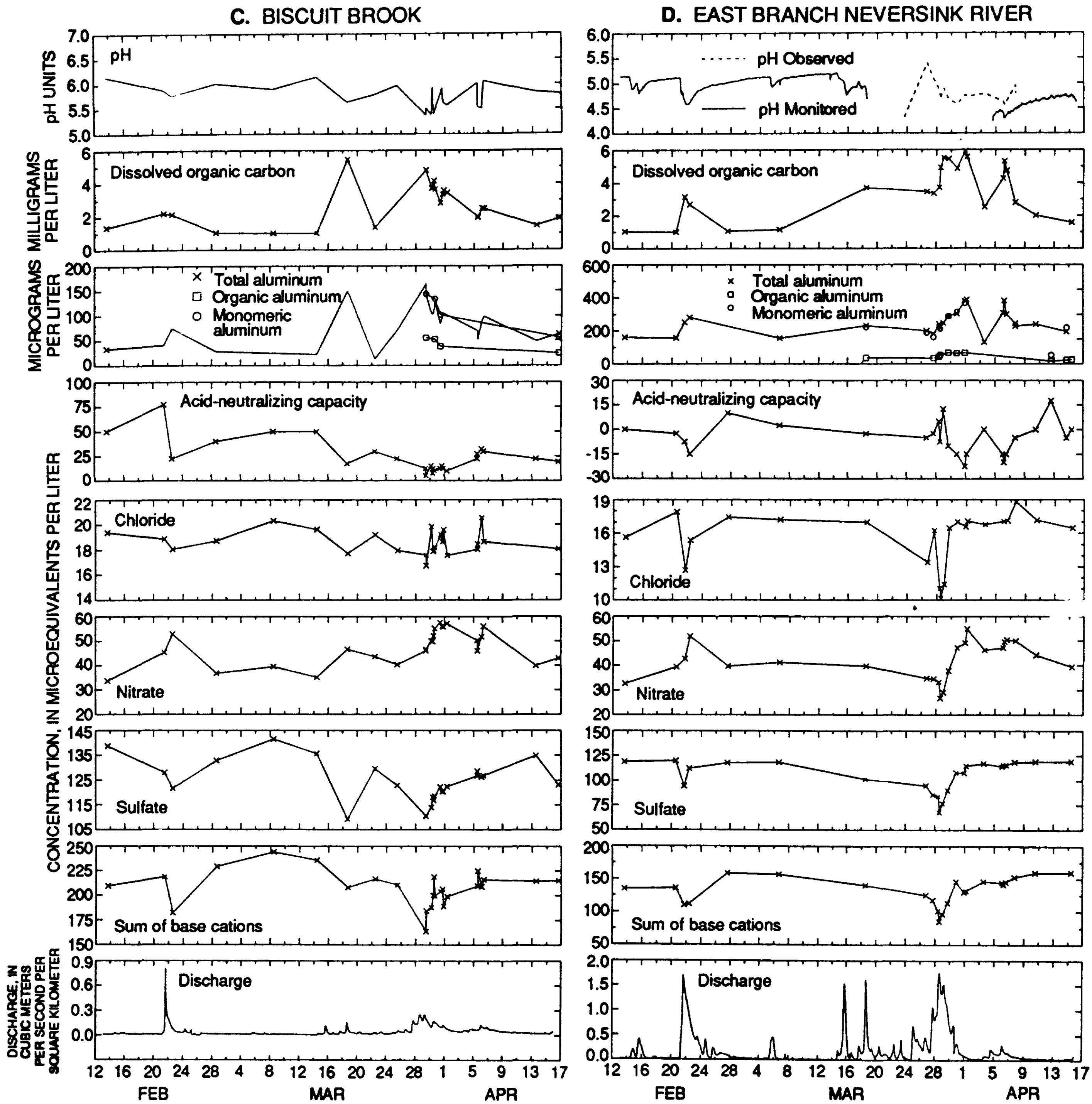

Figure 9 (continued).--pH, acid-neutralizing capacity, concentrations of selected constituents, and discharge in Biscuit Brook and East Branch Neversink River during the spring snowmelt of 1989.

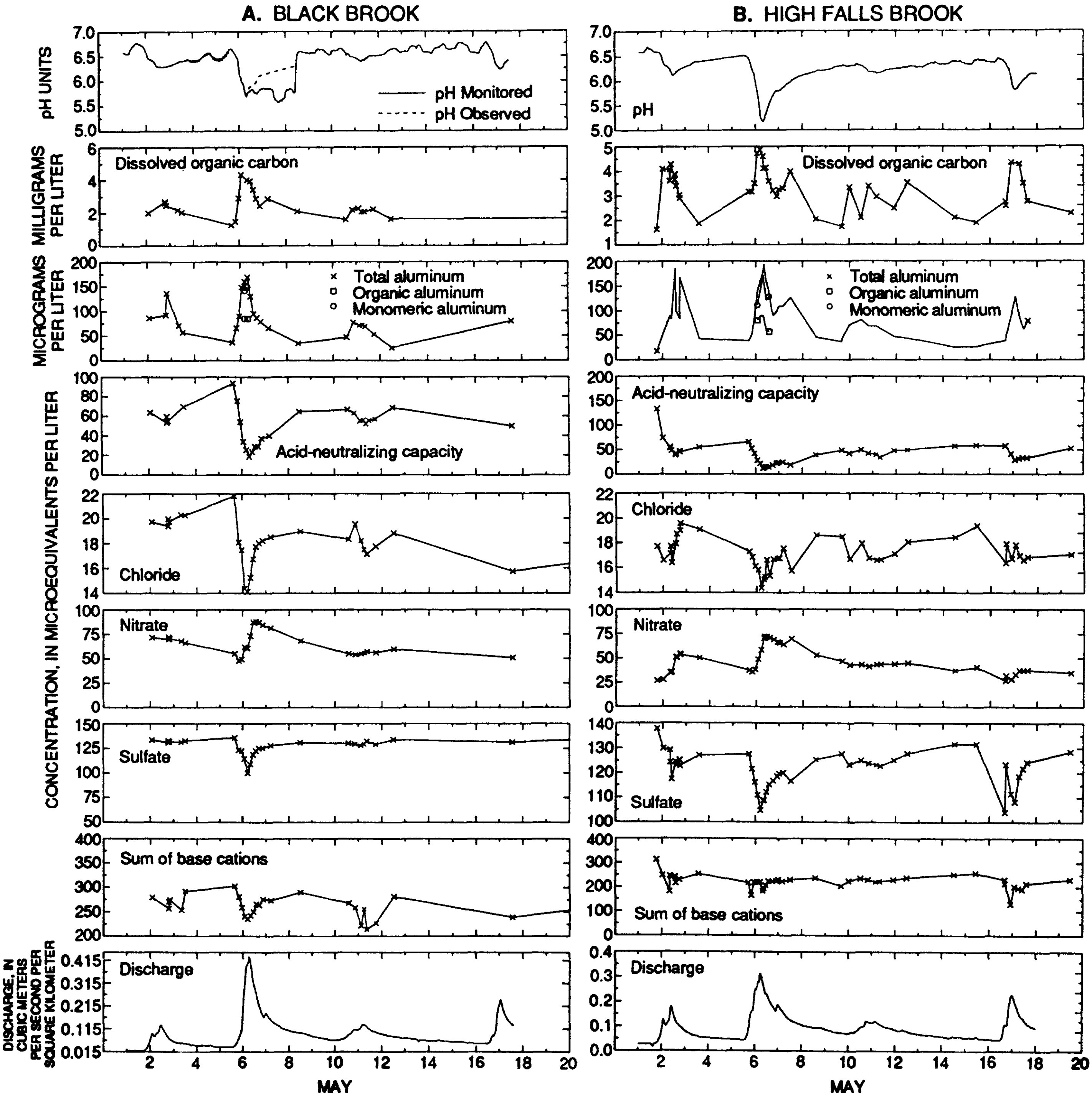

Figure 10.--pH, acid-neutralizing capacity, concentrations of selected constituents, and discharge in Black Brook and High Falls Brook during the storm of May 1 - 17, 1989.

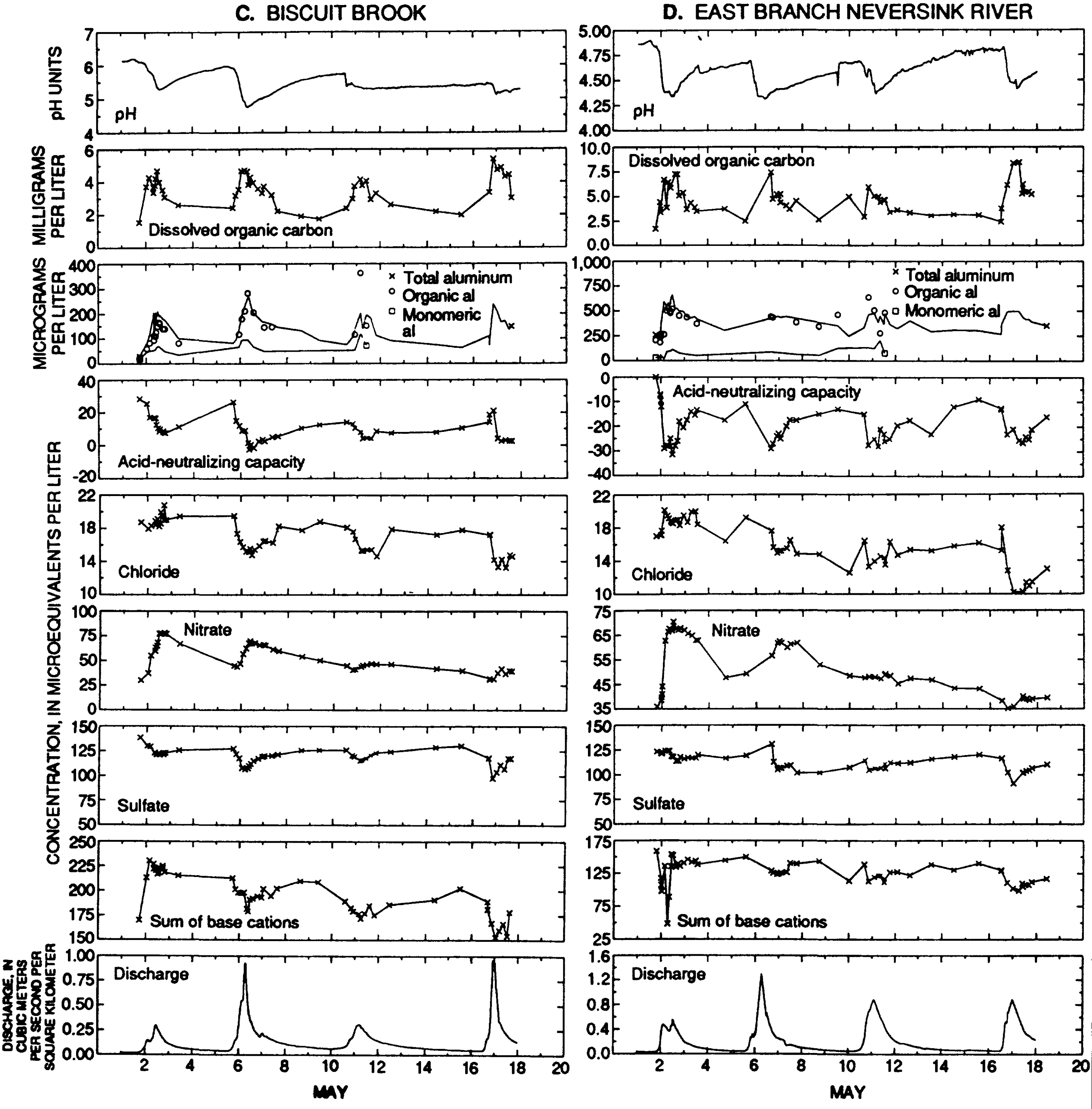

Figure 10.--pH, acid-neutralizing capacity, concentrations of selected constituents, and discharge in Biscuit Brook and East Branch Neversink River during the storm of May 1 - 17, 1989.

Acid-neutralizing Capacity

ANC concentrations and pH decreased with increased discharge at all four streams during all storms. The greatest decreases were associated with the highest discharges except at the East Branch Neversink, where ANC and pH depressions were similar among all storms.

Aluminum

Aluminum concentrations increased with increasing discharge at all streams, and the differences in maximum concentrations among the streams correlated with differences in pH. Concentrations of total monomeric aluminum were generally similar to those of total dissolved aluminum (fig. 10). Organic monomeric aluminum formed a greater percentage of the total dissolved aluminum in High Falls Brook and Black Brook than in the more acidic streams, and within each stream, inorganic aluminum species formed an increasing proportion of the total dissolved aluminum as flow increased (fig. 11). These comparisons suggest that, as stream acidity increases, the proportion of the inorganic aluminum

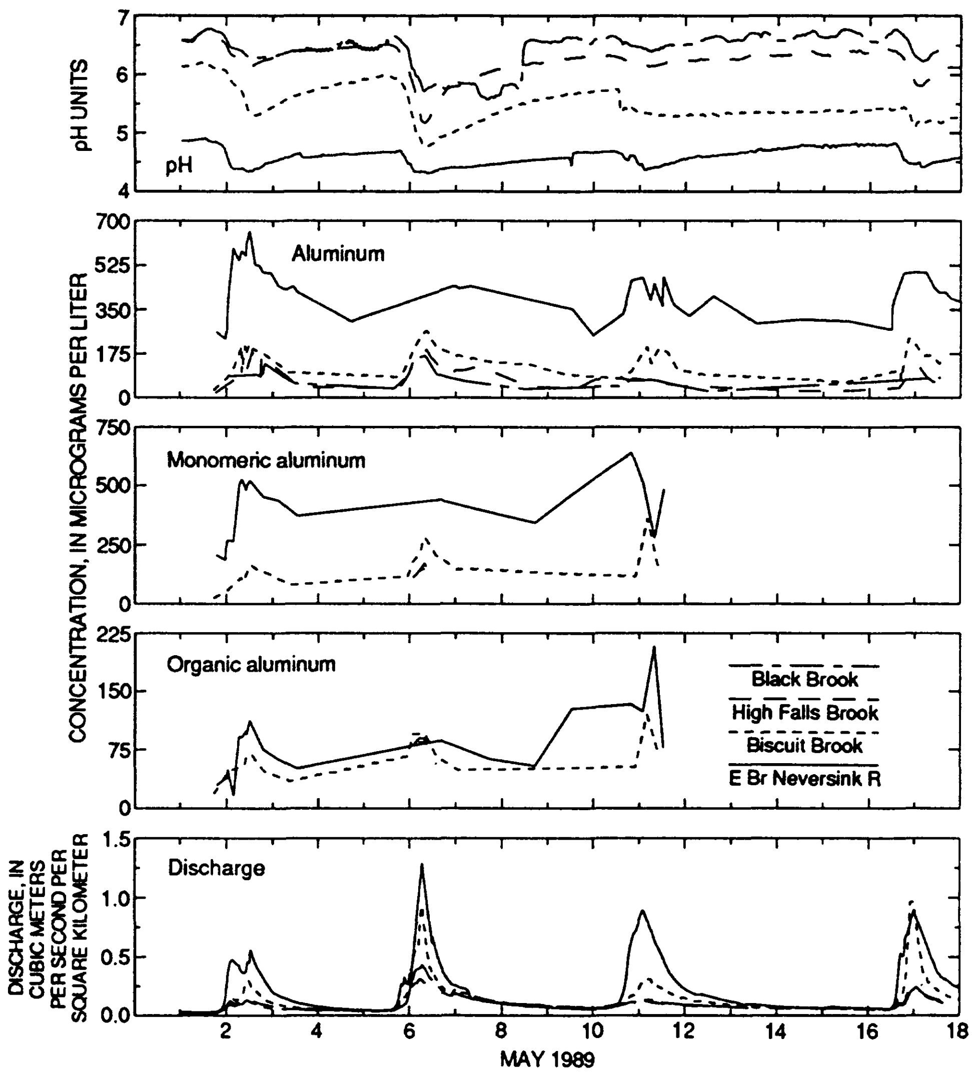

Figure 11.--Stream pH, total dissolved aluminum and aluminum species concentrations, and discharge of the four study streams during storm of May 1 - 17, 1989.

increases in relation to organically bound aluminum. The data also suggest that total dissolved aluminum in Biscuit Brook and the East Branch Neversink includes a more toxic form of aluminum than at High Falls and Black Brooks (fig. 11). Organically bound aluminum concentrations were similar among the streams during the peak flow of May 6, despite differences in pH and total dissolved aluminum concentrations (fig. 11). The data therefore indicate a similar capacity among the streams for organic complexation of aluminum in stream water. When this capacity is exceeded, as in the East Branch Neversink, the free-aluminum concentration increases. Both pH and ANC are negatively correlated with discharge (x = 0.0001), and total dissolved aluminum is positively correlated with discharge (x = 0.0001).

Dissolved Organic Carbon

Dissolved organic carbon (DOC) increased during all storms at all four streams. Acidity from organic acids can significantly decrease stream pH when ANC is low (Steven Gherini, Tetra Tech Inc., oral commun., 1990). Estimates of approximately 5.0 μeq/L of acidity per milligram of organic acids have been reported from analysis of field data and laboratory experiments (Harold Hemond, Massachusetts Institute of Technology, oral commun., 1990). The importance of DOC as an acidifying agent appeared to increase as other strong acids were depleted in the succession of storms observed. The largest observed changes in DOC were in the East Branch Neversink, where peak DOC concentrations exceeded 7 mg/L (figs. 9, 10).

BIOLOGIC RESPONSE TO EPISODIC ACIDIFICATION

The fish and invertebrate experiments of the Episodic Response Project were designed to provide quantitative evidence of fish and aquatic invertebrate mortality or avoidance behavior that directly results from episodic acidification of stream water. Previous studies have shown that episodic acidification can cause significant mortality of fish held in field bioassay cages (Sharpe and others, 1983; Johnson and others, 1987). Likewise, mortality of free-ranging adult fish as a result of episodic acidification has been reported in the northeastern United States (Gagen and others, 1989). Avoidance behavior, such as the movement of fish to less acidic microhabitats during acidic episodes, has not been documented, however. Neither avoidance behavior nor mortality in the Catskill Mountain streams had been documented before this study, and the distribution of invertebrates in relation to stream acidity was unknown. The study therefore was designed to address these issues through bioassay experiments with brook trout (*Salvalinus fontinalis*) and sculpin (*Cottus cognatus*), radio-tracking of adult brook trout, population estimates of all fish species present in specific study reaches, and population surveys of fish and invertebrates to assess distribution along the length of each study stream. The periods of each of these experiments and the corresponding stream discharges and pH are indicated in figure 12.

Fish-Population Estimates and Results of Transfer Experiments

Initial population estimates indicate that differences in standing populations of brook trout in the four streams are generally correlated with stream pH, calcium, and ANC concentrations (tables 6, 7). Trout populations in the spring and summer of 1989 were comparable in both biomass and numbers in the East Branch Neversink (median pH 4.8), and native sculpin were absent (fig. 13, p. 30). High Falls Brook (median pH 6.6) had many more trout and sculpin than Biscuit Brook (median pH 5.9) in the fall of 1988 and again in the summer of 1989 (fig. 13A), but the two brooks had similar trout populations during the spring of 1989. The differences in fall data probably result from sampling-efficiency differences resulting from equipment failure, and also from the accessibility of spawning areas in High Falls Brook. The fall population estimate for High Falls Brook may include trout that migrated into

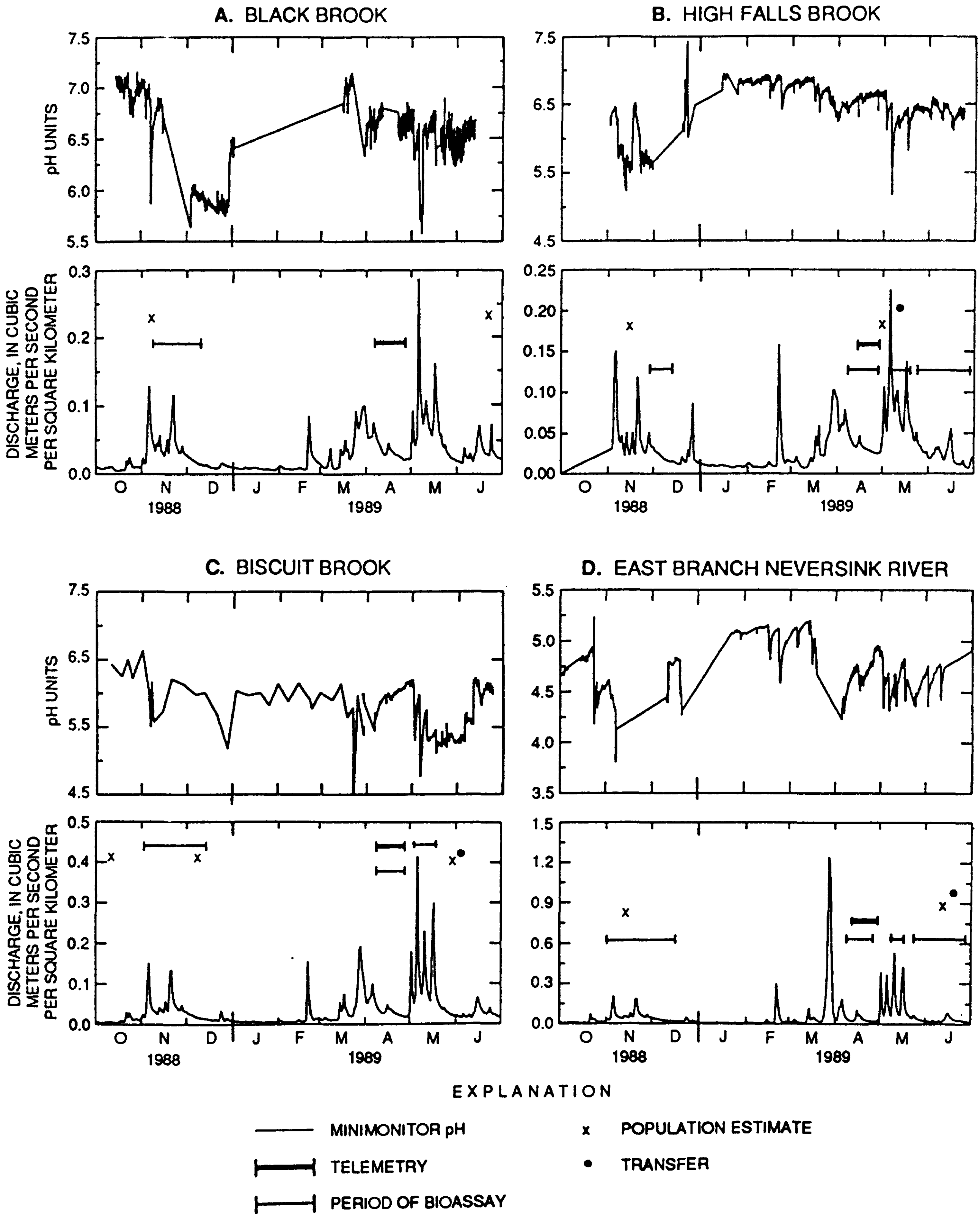

Figure 12.--Temporal variation in pH and discharge of the four study streams and periods of biologic experiments.

Table 7.--Trout and sculpin populations in 200-meter-long study reaches before transfer experiments, and pH and aluminum concentration from October 1, 1988 through June 30, 1989.

	Stream			
Fish data and chemical conditions	East Branch Neversink	Biscuit Brook	High Falls Brook	Black Brook
Fish density (number per square meter)				
Fall 1988				
Brook trout, total	0.44	0.059	0.147	0.233
Sculpin	0	.037	.415	.331
Brown trout	0	.007	.03	0
Spring 1989				
Brook trout, total	.028	.087	.082	.231
Sculpin	0	.67	.162	.618
Biomass (grams per square meter)				
Brook trout	.39	1.47	1.40	2.75
Sculpin	0	.322	.575	2.20
Summer 1989				
Brook trout, total	.035	.126	.197	.528
Sculpin	0	.205	.212	0.9
Fall 1989				
Brook trout, total	.013	.141	.187	.354
Sculpin	0	.136	.215	.623
Biomass (grams per square meter)				
Brook trout, total	.19	1.86	2.07	3.7
Sculpin	0	.569	.75	3.02
Base-flow chemistry, median of samples collected				
pH	4.8	5.9	6.6	6.6
Aluminum (micrograms per liter)	274	96	54	47
Extreme-condition chemistry: maximum and minimum values of samples taken				
pH				
minimum	4.3	4.7	5.2	5.7
maximum	5.7	6.8	7.2	6.9
Aluminum (micrograms per liter)				
minimum	58	7	9	2
maximum	658	266	228	230

the reach. Biscuit Brook contains a dam downstream from the study reach that impedes upstream movement of fish. The differences during the summer are the result of differences in recruitment (successful spawning or immigration) of young of the year. Black Brook (median pH 6.6) contained the highest number of trout per square meter of stream surface and the highest trout biomass during all population experiments; sculpin populations and biomass were also far greater in Black Brook than in the other streams (fig. 13B).

Transfers of marked brook trout and sculpin were completed during the late spring of 1989 and included specimens collected onsite and from the common-source stream (West Branch Neversink River). Recapture rates of marked fish indicate significant movement of fish in and out of the study reaches (fig. 13, table 8). Recapture of marked fish in the spring from the fall marking period was affected by winter dieoff, but that probably does not account entirely for the low percentage of recapture. The percent recapture of fish collected from the common-source stream of high ANC was significantly lower than the percent recapture of fish native to the study streams (table 8). The percent recapture of these common-source fish was lowest in the East Branch Neversink, but was less than 20 percent in all the streams in which the transfers were done. Fish from the common-source stream were not transferred into Black Brook, and recapture rates of marked fish (all trout native to Black Brook) were the highest of the four streams. Recapture of Slimy Sculpin (*Cottus cognatus*) was inhibited by the inherent difficulty in electroshocking this species (Margaret Wilzbach, University of Pittsburgh, oral commun., 1989). Total percent recapture of trout during the summer at the East Branch Neversink (low pH) was similar to that at High Falls Brook (high pH). The recapture experiment of summer 1989 suggests that brook trout and sculpin from the West Branch Neversink (the origin of the common-source fish) will either die or move out when placed in the more acidic East Branch Neversink. No transferred sculpin were recaptured in Biscuit Brook during this period. The highest percent recapture was in Black Brook, where native populations were not disturbed by transferred fish. This, plus the fact that a stream as acidic as the East Branch Neversink has a native trout population, suggests that fish become acclimated to acidic conditions and that differences in the percent recapture of common-source and native trout are the result of differences in acclimatization.

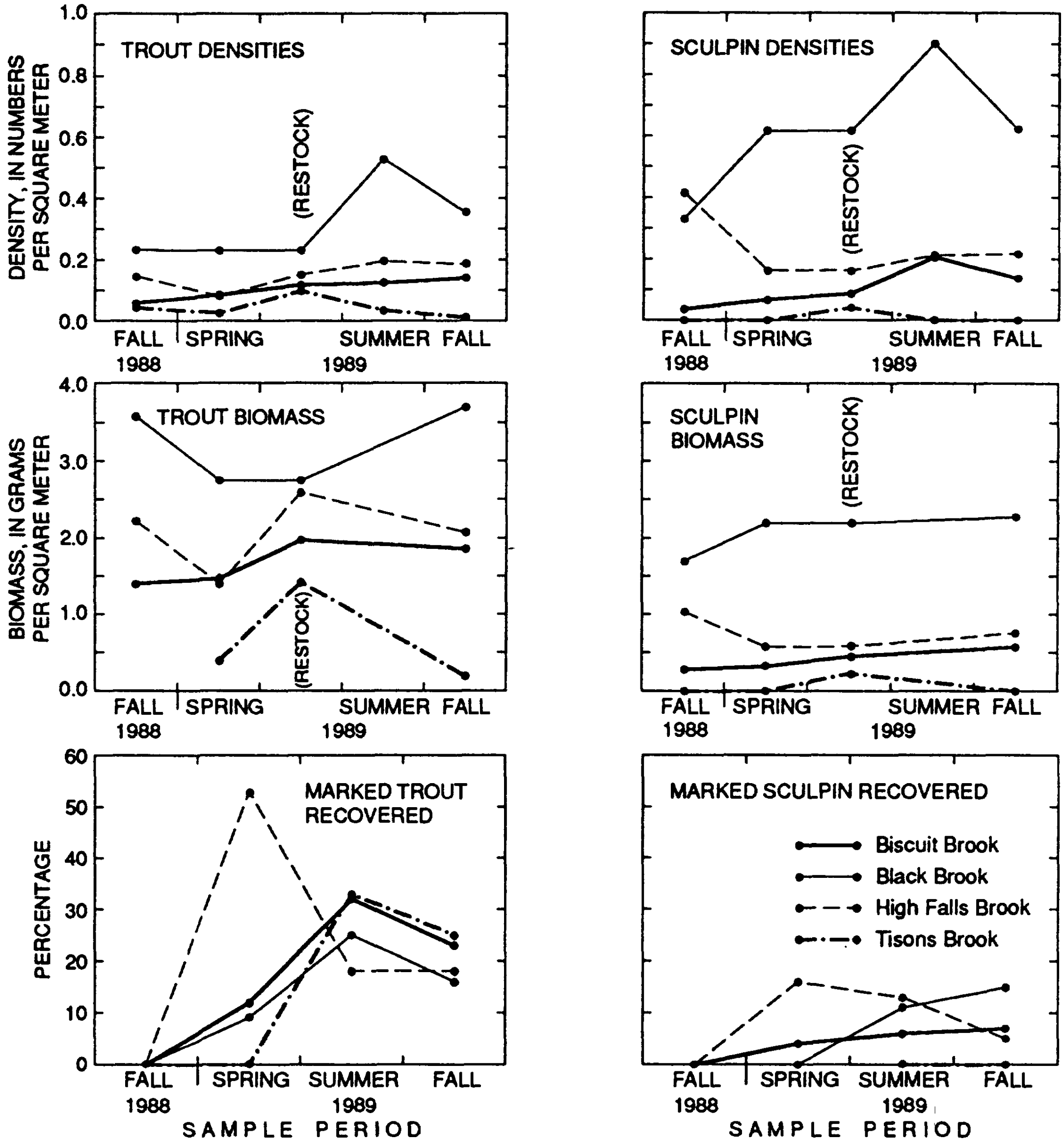

Figure 13.--Number and biomass of marked and total trout and sculpin per square meter of stream surface area in study streams.

Table 8.--Results of mark-and-recapture experiments conducted between fall 1988 and spring 1989 in the study streams.

Fish	Black Brook	High Falls Brook	Biscuit Brook	East Branch Neversink
TROUT				
Common source				
number stocked	0	43	42	50
number recaptured	0	7	5	2
percent recaptured	0	16	12	4
Native				
number stocked	85	40	119	66
number recaptured	45	11	51	26
percent recaptured	53	28	43	39
Total				
number stocked	85	83	161	116
number recaptured	45	18	56	28
Percent recaptured	53	22	35	24
SCULPIN				
Common source				
number stocked	0	0	29	50
number recaptured	0	0	0	0
percent recaptured	0	0	0	0
Native				
number stocked	233	94	92	6
number recaptured	40	17	10	0
percent recaptured	17	18	11	0
Total				
number stocked	233	94	121	50
number recaptured	40	17	10	0
Percent recaptured	17	18	8	0

Fish Distribution Along Stream Profiles

Perhaps more informative than the mark-and-recapture information is the distribution of fish along the length of each of the four stream channels. Longitudinal profiles of the fish populations along each stream were conducted during the summer of 1989 to define the overall habitat suitability and presence of nonacidic refuge areas within each stream. Fish distribution profiles of Black Brook were not conducted during the summer of 1989, but pH values in the headwaters were above 6.0.

High Falls Brook

Results indicate that High Falls Brook (median pH 6.6) supports a large population of adult and juvenile brook trout throughout the length of the stream (fig 14B). A waterfall on High Falls Brook serves as a physical barrier that prevents upstream fish movement, and no brown trout were observed above the falls. Adult and juvenile brook trout were present both below the falls and in the headwaters, however. pH values were above 6.0 along the entire length of High Falls Brook.

Biscuit Brook

Distribution of fish along the length of Biscuit Brook and the East Branch Neversink was more variable than in Black Brook or High Falls Brook (Fig. 14A, B). The headwaters of Biscuit Brook (pH 6.5, and ANC 84.5) support a viable population of adult and juvenile (age 0 to 1 year) brook trout but no sculpin. A tributary downstream of this headwater station (pH 5.9 and ANC 5.0) contained only four adult brook trout and no juveniles in a 60-m-long section. A second tributary (pH 4.6 and ANC 0) supported no fish populations. No sculpin were present from 0.6 km above the gage to the headwaters. A possible explanation for the lack of sculpin in the upper reaches of Biscuit Brook is the influence of the several acidic tributaries on main-stem water quality. A moderate-sized population of adult and young-of-the-year brook trout and sculpin were noted near the gaging station.

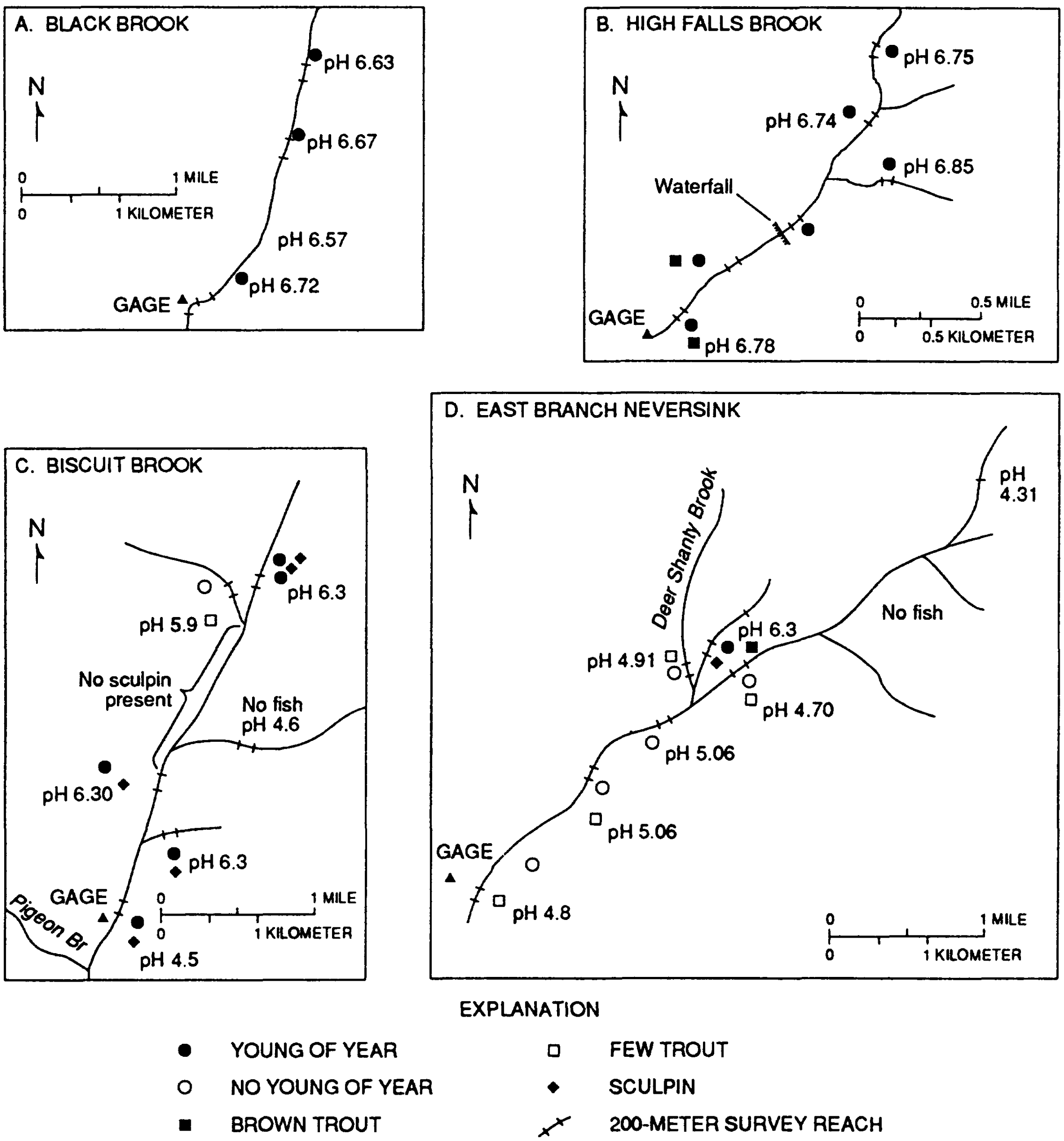

Figure 14.--Longitudinal profiles of fish distribution and pH along the length of the four study streams during August 1989. (Locations are shown in fig. 2.)

East Branch Neversink

The East Branch Neversink River is an acidic stream with a median pH of 4.8 at the gage (pH 4.9 on date of the profile). The study reach supports a sparse population of brook trout 0.64 g/m^2 and no sculpin. A stream-water sample taken in August at the extreme headwaters of the main stream had a pH of 4.3. The pH at most tributary and main-stem sampling reaches was less than 5.1, and no juvenile trout or sculpin, and only a few adult brook trout, were present.

Deer Shanty Brook (pH 4.9), a tributary to the East Branch Neversink (fig. 14D), has a small unnamed tributary with a high pH (6.3) that supports a moderate population of both adult and juvenile brook trout as well as slimy sculpin. This isolated population of sculpin is of special interest because the nearest source of sculpin is in Flat Brook, a tributary nearly 3 km downstream from the gaging station (fig. 2). The main stem East Branch supports sculpin only at the confluence with the West Branch Neversink (Robert Bode and others, New York State Department of Environmental Conservation, written commun., 1988).

Deer Shanty Brook, which is more acidic than its tributary, contained only a sparse population of adult brook trout (fig. 14D). The main-stem East Branch above the confluence with Deer Shanty Brook (pH 4.7) had an even smaller population of adult brook trout. Below this confluence, fish populations were also small and discontinuous to the gage. The profile of the East Branch Neversink therefore illustrates the detrimental effect of stream acidity on brook trout populations.

Fish Mortality

Fish-mortality experiments were conducted by placing fish in bioassay cages near the gage of each study stream. Experiments were conducted at all streams during the late fall of 1988 and April 1989, on three of the streams (Biscuit Brook, High Falls Brook, and the East Branch Neversink) during May 5-17, 1989, and on two of the streams (High Falls Brook and the East Branch Neversink) from May 18 through June 24. The fall 1988 experiments included adult brook trout, sculpin, and native and common-source fingerling brook trout; the later bioassays did not include adult brook trout.

The fall study (November 4 through December 15) began with a large storm that damaged the stream-monitoring and bioassay-cage structures at the East Branch Neversink. Fish mortality the East Branch Neversink during that storm could be attributed either to the lack of an adjustment period for the fish before a large acidic episode or the movement of the cage (fig. 15A). A second acidic episode on November 20 caused no additional mortality. A second bioassay (December 1-15) of common-source brook trout collected from Pigeon Brook (fig. 14C) (pH 6.2), a tributary to Biscuit Brook, had a mortality of 3 out of 21 fish over a 15-day period before ice cover developed and ended the experiment. No significant mortality occurred in experiments at the other streams during this period, except for adult trout in Biscuit Brook, which showed a steady decline over the period of gradual flow recession.

The first spring experiments were begun on April 7, 1989 the earliest that stream conditions allowed. The initial experiment covered a period of 20 days, in which little precipitation and only one small storm occurred (fig. 15B). No mortality of sculpin or common-source trout occurred in either Black Brook or High Falls Brook until the end of the period, when the long holding time in the cages probably began to affect survival. Mortality of common-pool trout began in Biscuit Brook after the small storm of April 16, but no seemingly significant changes in chemistry accompanied the increased discharge. The ambient conditions could have been toxic to brook trout, but the duration of exposure was insufficient to cause higher mortality than was observed. Sculpin in Biscuit Brook showed no mortality until the end of the period.

Significant mortality in both common-source brook trout and sculpin occurred over the same period in the East Branch Neversink, but no mortality of native trout was observed. The number of live common-source trout showed a steady decline that did not appear to accelerate during or after the April 16 storm. Sculpin mortality increased after the storm, however, and concentrations of total dissolved aluminum increased from 200 μg/L to 300 μg/L as pH decreased from 4.7 to pH 4.5.

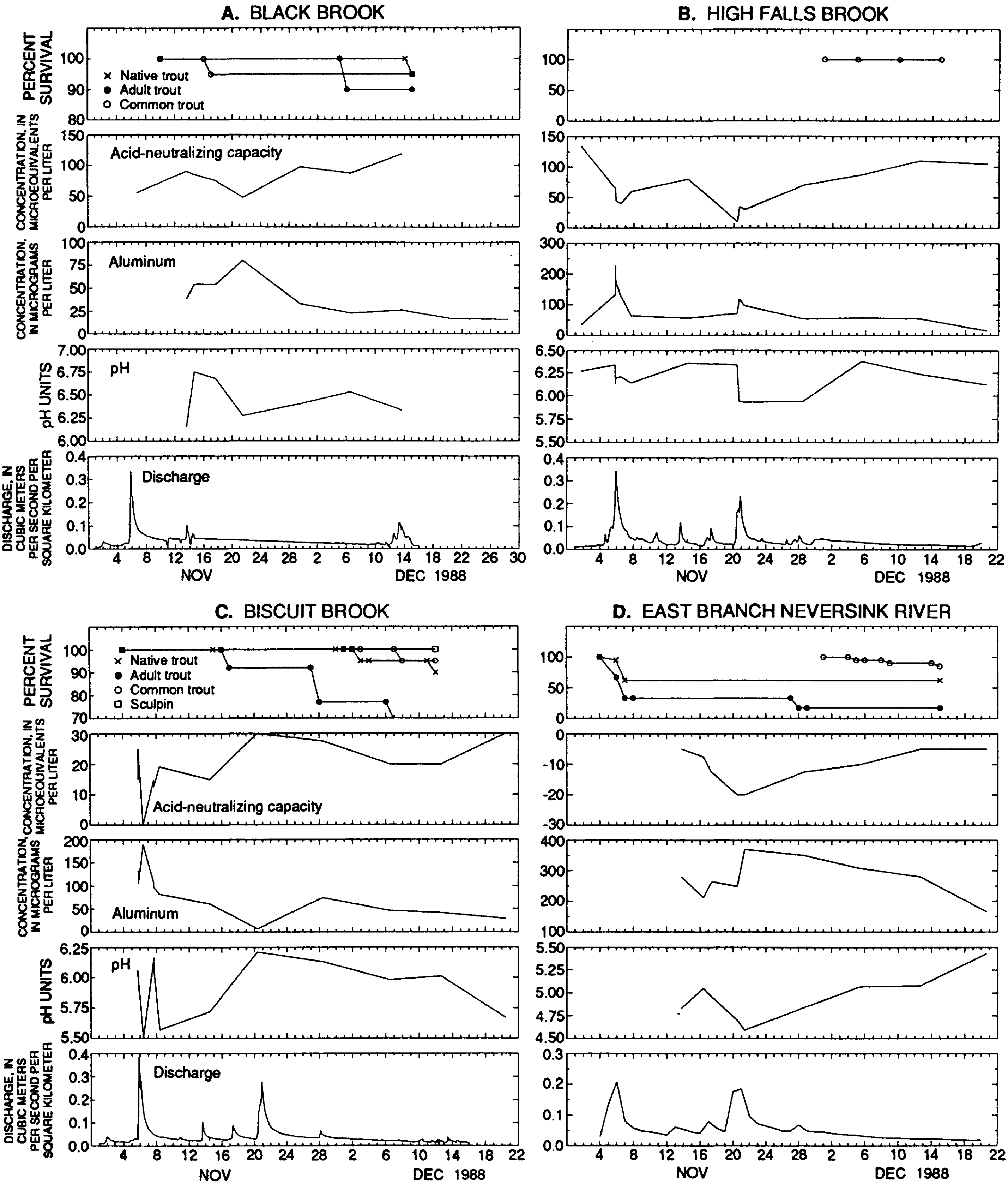

Figure 15A.--Percent survival of brook trout and sculpin, pH, acid-neutralizing capacity and aluminum concentration, and discharge in the four study streams during bioassay experiments, November 4 - December 15, 1988.

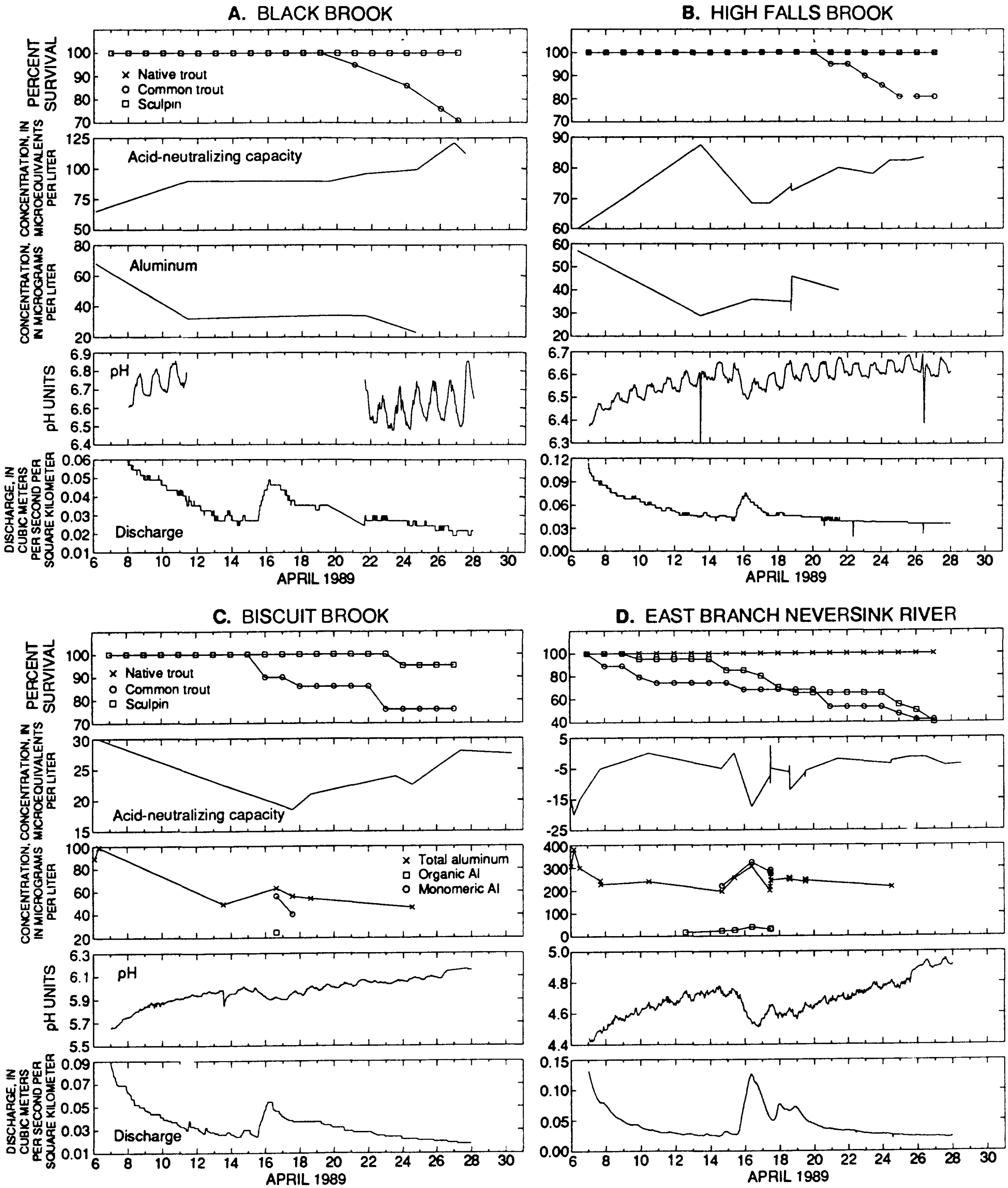

Figure 15B.--Percent survival of brook trout and sculpin, pH, acid-neutralizing capacity and aluminum concentration, and discharge in the four study streams during bioassay experiments, April 5-28, 1989.

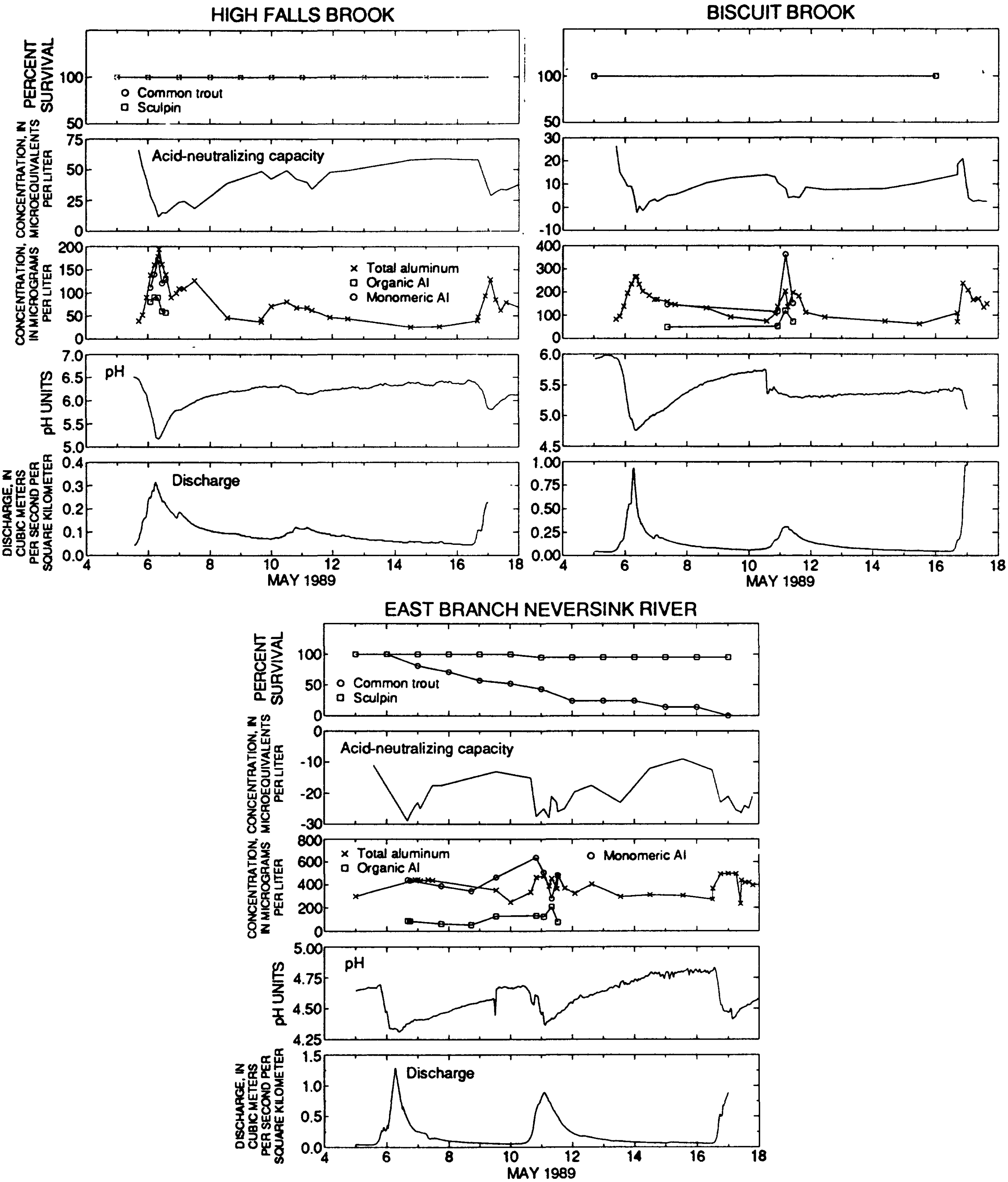

Figure 15C.--Percent survival of brook trout and sculpin, pH, acid-neutralizing capacity and aluminum concentration, and discharge in the four study streams during bioassay experiments, May 5 - 17, 1989.

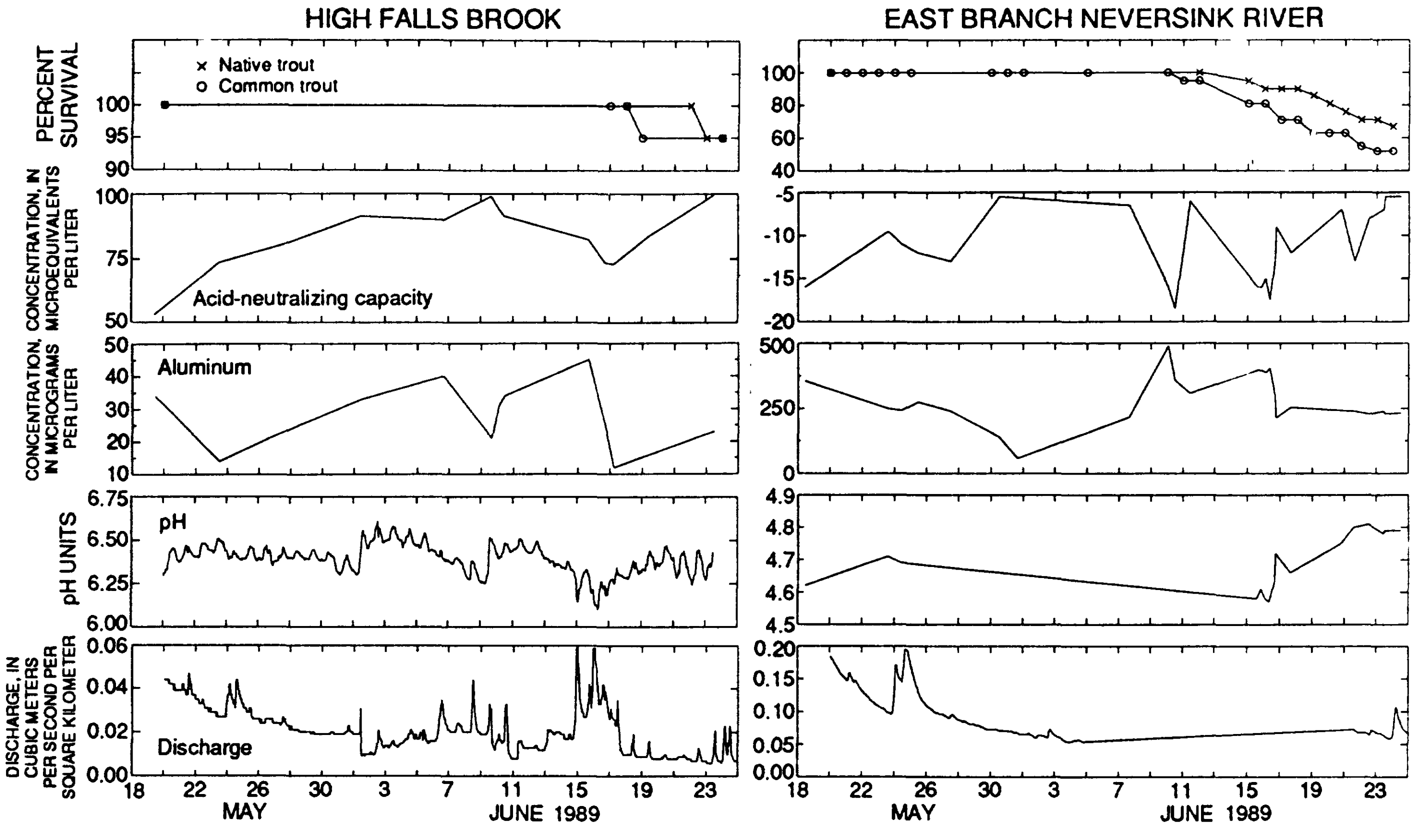

Figure 15D.--Percent survival of brook trout and sculpin, pH, acid-neutralizing capacity and aluminum concentration, and discharge in the four study streams during bioassay experiments, May 18 - June 25, 1989.

The third bioassay was done in High Falls Brook, Biscuit Brook, and the East Branch Neversink from May 5-17, during which time two large storms occurred (fig. 15C). ANC values dropped to near zero in Biscuit and High Falls Brooks during the first storm, and peak aluminum values were 266 and 194 μg/L, respectively. Organically bound aluminum again formed a larger percentage of the total dissolved aluminum at these stations than at the East Branch Neversink and thus lowered the effective toxicity of the dissolved aluminum. No mortality of sculpin or common- source fish occurred during this period in these streams, but mortality of common-source trout in the the East Branch Neversink was 100 percent. pH was less than 4.8, and aluminum concentrations were exceeded 200 μg/L for the entire period. The decline in the number of surviving fish was fairly steady over the period, with only a minor increase in the mortality rates during stormflow. Only one sculpin out of 21 individuals died during the same period.

The fourth bioassay experiment ran from May 18 through June 25 at the East Branch Neversink and High Falls Brook (fig. 15D). The period had a series of much smaller stormflows than the previous month (fig. 15C). pH values exceeded 6.0 in High Falls Brook and ranged from 4.2 to 4.7 in the East Branch Neversink. No mortality of native or common-source trout was observed until the end of the experiment in High Falls Brook. Mortality in the East Branch Neversink began during a stormflow on June 12 and reached 50 percent of the common-source trout and 40 percent for the native trout by the experiment end. The major chemical difference between the first 15 days of the experiment, when no mortality occurred, the second 15 days, when mortality reached 50 percent, and the previous experiment period, when mortality was 100 percent, was that aluminum concentrations were less than 300 μg/L during the first 15 days. Values of pH were similar during the first 15-day period and the second. Therefore the data indicate that aluminum is a major factor in fish mortality and that pH is not necessarily a reliable indicator of aluminum concentrations in Catskill streams.

Plots of average daily percent mortality in all bioassay experiments indicate a much greater mortality of common-source trout than of native trout, and greater mortality of both types of trout in the East Branch Neversink than in the other streams (fig. 16). Ranges of mortality of native and common-source fish are similar in Biscuit Brook, Black Brook, and High Falls Brook, whereas the difference in percent mortality of the two fish types in the East Branch Neversink suggests either acclimatization of the native trout or genetic differences between the two fish groups. The plots of fish mortality suggest similar mortality among the streams in the four experiments, despite a wide range of pH and dissolved aluminum concentrations.

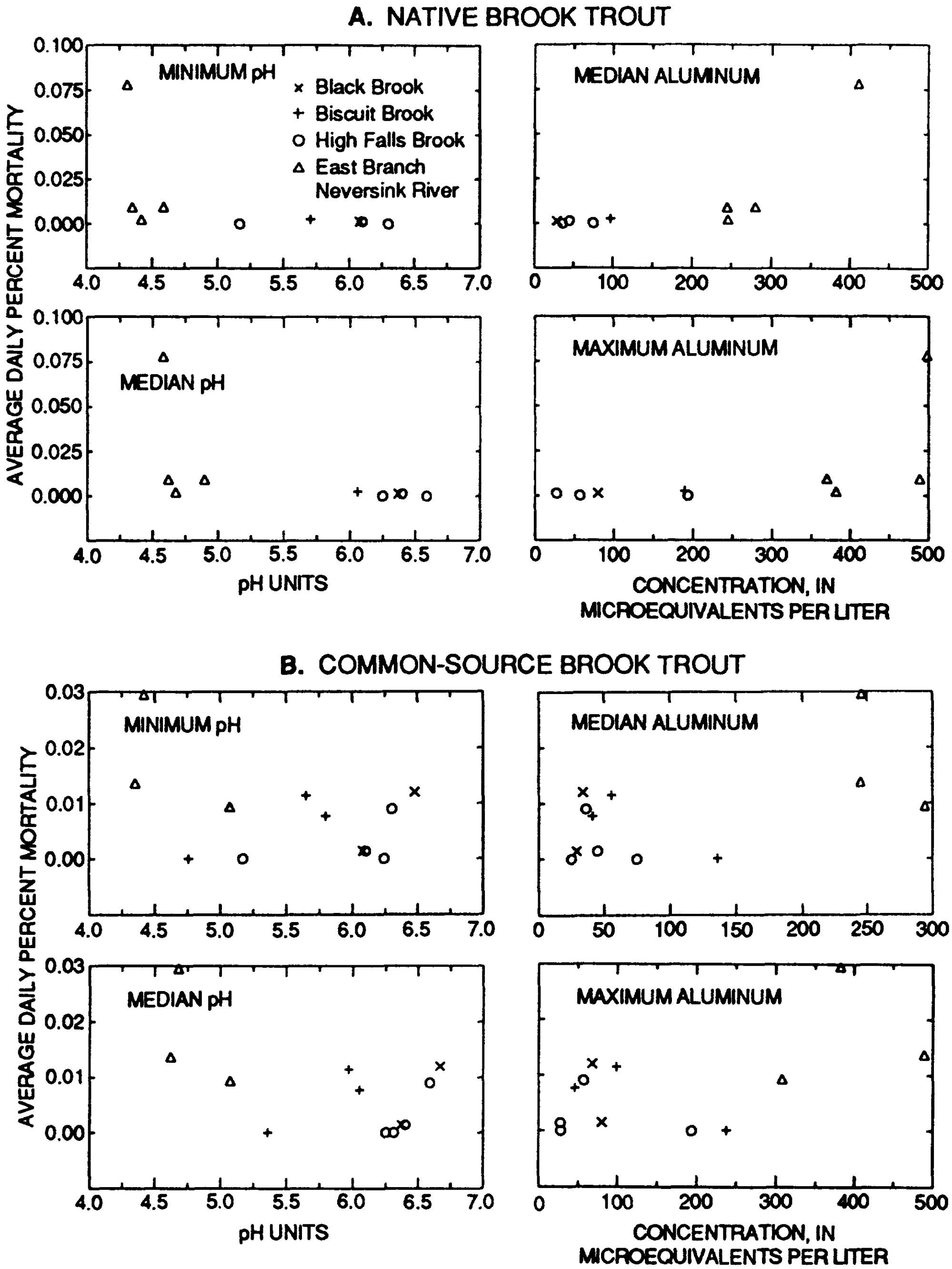

Figure 16.--Average daily percent mortality of native and common-source brook trout in the four streams in relation to pH and dissolved aluminum concentration.

Fish Migration

Radiotelemetry experiments were conducted in the East Branch Neversink and High Falls Brook from April 13 through April 28, 1989, to track the movement of fish during acidic episodes. Radio tags were inserted into the stomach of 30 brook trout, and after 48 hours of observation, the fish were placed in equal numbers in the study reach of a control stream (High Falls Brook) and an acidic stream (East Branch Neversink). The period of observation was short because of the short battery life of the radio tags and regurgitation of the tags by the fish.

An analysis of tagged-fish movement during the spring experiment indicates a significant net downstream movement of trout in the acidic East Branch Neversink, and a small net upstream movement in the well-buffered High Falls Brook (fig. 17). Aluminum concentrations were significantly higher and pH values lower in the East Branch Neversink than in High Falls Brook during the 14 tracking days. The period was one of gradually improving water quality in both streams, however, with no significant acidic episodes.

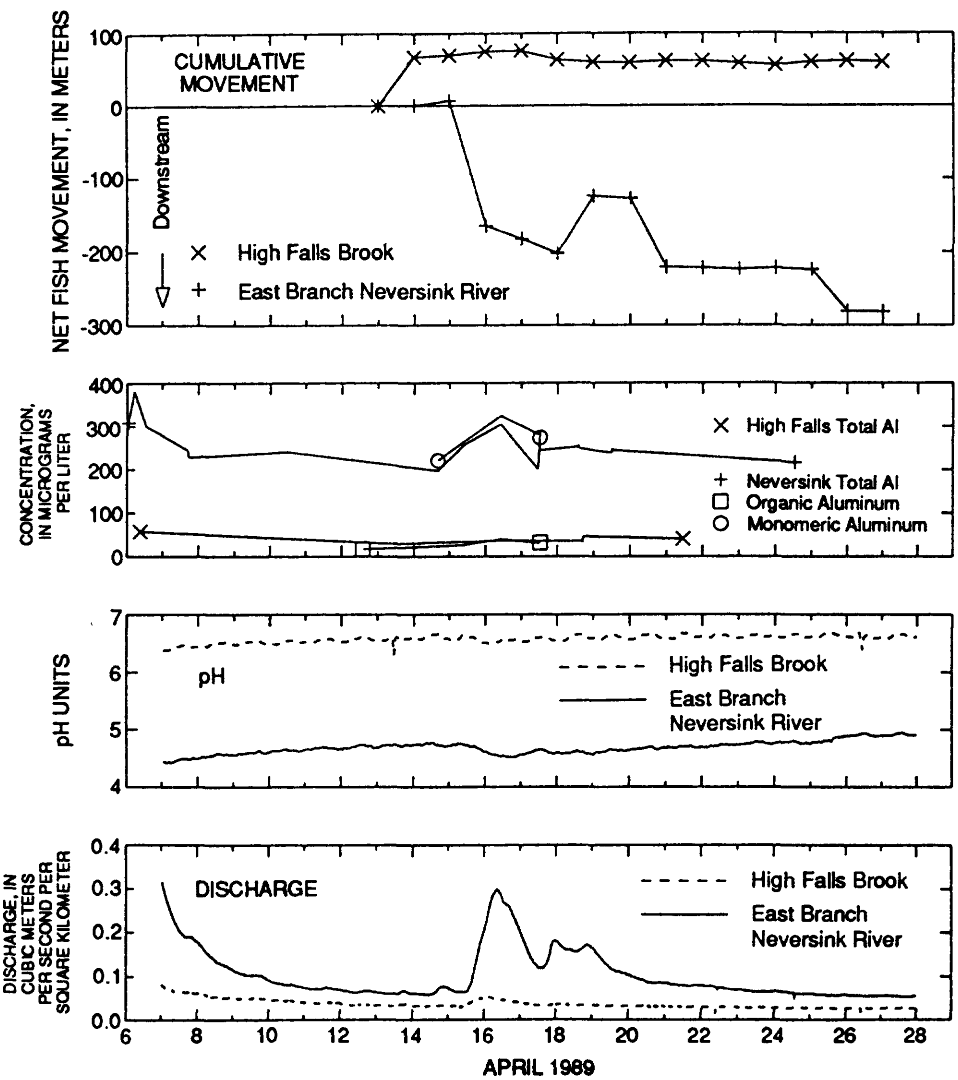

Figure 17.--Net downstream movement of radio-tagged fish, aluminum concentration, and stream pH and discharge during radiotelemetry experiments High Falls Brook and East Branch Neversink River, April 6-28, 1989.

Water samples collected along the length of High Falls Brook at locations of tagged fish show a relatively uniform chemical quality similar to that of water at the gaging station. No significant springs or tributaries enter between the confluence of High Falls Brook with the West Branch Neversink River and the waterfall 1 km upstream of the monitoring station (fig. 2), whereas the East Branch Neversink study contains several springs, tributaries, and braided channels with numerous backwater pools (fig. 18). Several of the springs and tributaries have significantly higher pH and ANC than does the main channel. The tagged fish were initially released near the confluence of one such spring (pH 6.2), and two fish remained at that junction throughout the experiment in a pool with a relatively high pH. Territorial competition could have forced the other fish to move into the more acidic water in search of other refuges from the acidic water. Whether these fish seek out other alkaline areas or accidently come across them as they move downstream, is unclear, however. At least two of these fish died during this experiment. Fish in the fall 1989 telemetry experiment moved into tributaries with higher pH than the main channel (Kirk Eakin, EA Engineering and Technology, oral commun., 1989).

The largest net downstream movement of tagged fish in the East Branch Neversink occurred during the April 16 stormflow, during which pH decreased only slightly, but monomeric aluminum values rose above 300 μg/L. Organically bound aluminum concentrations in the East Branch Neversink were similar to those in High Falls Brook but formed only a small percentage of the total dissolved aluminum in the East Branch Neversink. Results of this initial telemetry experiment, therefore, suggest a net downstream movement of fish in response to a low-pH episode characterized by high aluminum concentrations. Results from the fall 1989 telemetry experiment support these conclusions over a tracking period longer than the spring 1989 experiment described here. (Kirk Eakin, EA Engineering and Technology, oral commun., 1990).

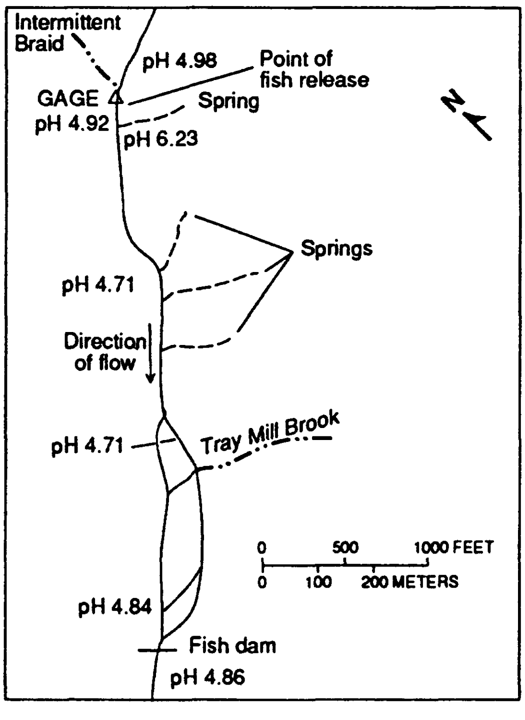

Figure 18.

Longitudinal changes in stream pH along East Branch Neversink River during spring 1989 radiotelemetry experiments. (Location is shown in fig. 2)

Invertebrate Distribution

Samples of stream invertebrate populations were collected by a "roving kick sample" method at two streams in 1988, during which the field technician moves randomly while kicking the bottom of the stream and holding a collection net immediately downstream, and by use of Surber samplers for the collections in 1989. All samples were collected in riffles over sand and gravel, and a subsample of 100 organisms was used for evaluation and assessment.

Results of the invertebrate assessments to the family level indicate that, during the spring, differences among the total number of families in the four study streams are small and do not correlate with differences in stream acidity (fig. 19), although differences emerge within each order. More families of Diptera (true flies) and Ephemeroptera (mayflies) were present in the well-buffered streams than in the acidic streams, and the acidic streams contained a larger number of families in the order Plecoptera (stoneflies) and probably Trichoptera (caddisflies). Platyhelminthus (flatworms), oligocheate (worms), and decapoda (crayfish) were found in small numbers in all streams.

The most significant difference among the streams was in the number of mayfly genera collected at each site; the number collected at the East Branch Neversink was significantly lower than that collected at the other streams (table 9). Mayflies also form a much smaller percentage of the total number of individuals obtained in the East Branch Neversink and Biscuit Brook than in the other three streams.

The East Branch Neversink showed the lowest productivity of the four streams and required five surber samples to collect 77 organisms. The reach contains predominantly a stonefly community. Although the invertebrate community is generally well balanced and includes the insect orders Ephemeroptera, Plecoptera, and Trichoptera, the Ephemeroptera formed only 14 percent of the total organisms collected. The two genera of Ephemeroptera, *Epeorus* and *Ameletus*, have been shown to be acid tolerant in other recent studies (Robert Bode, New York State Department of Environmental Conservation, oral commun., 1989). Biscuit Brook also has a well-balanced community of several families in the major orders of aquatic insects. Its productivity is moderate; only three Surber collections were needed to obtain the 100-specimen subsample. Stoneflies dominate the community, and the stream contains four genera of mayflies, which form 21 percent of the total subsample of individuals.

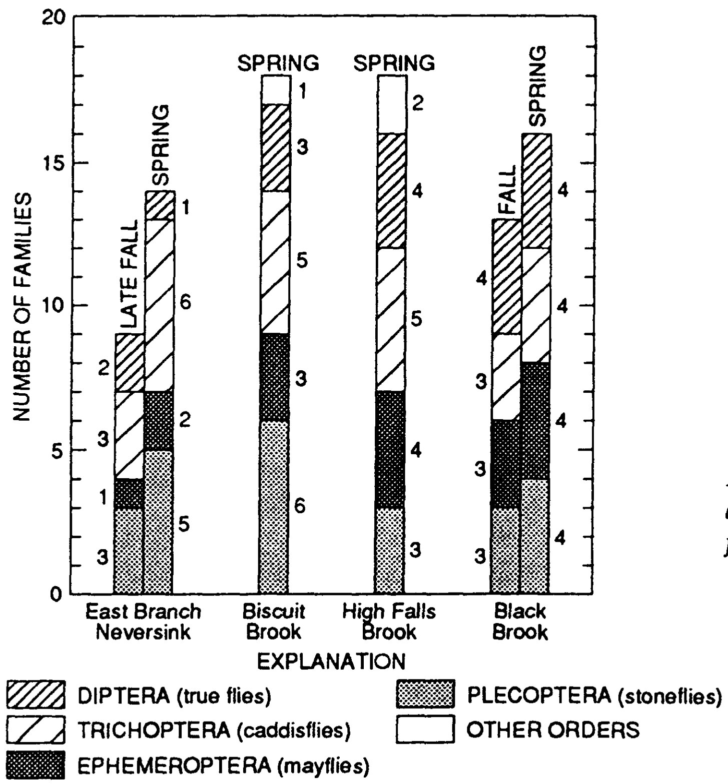

Figure 19.

Number of families represented in the aquatic insect orders detected in the four study streams by season.

High Falls Brook has a benthic community dominated by Ephemeroptera, which constitute 63 percent of the total individuals and are represented by five genera. Qualitatively the stream productivity was neither exceptionally high or exceptionally low compared to other similarly cited streams in the northeast (Robert Bode, New York State Department of Environmental Protection, oral commun., 1990); 2.5 Surber samples were required to obtain the 100-specimen subsample. High Falls Brook is also a well-balanced community with families in all expected aquatic-insect orders. Black Brook had the highest productivity of the four streams; less than one Surber sample supplied the 100-specimen subsample for identification. Ephemeroptera constituted 38 percent of the total number of individuals and comprised five genera. The community is well balanced, and contains families in most major aquatic insect orders.

Table 9.--Percentage of mayflies (Ephemeroptera) among total invertebrates collected, and number of genera represented; spring 1989.

[Locations are shown in fig. 2]

Stream	Percentage of invertebrates represented by mayflies	Number of Mayfly genera
East Branch Neversink	14	2
Biscuit Brook	21	4
Black Brook	38	5
High Falls Brook	63	5

SUMMARY AND CONCLUSIONS

The first 9 months of investigation (October 1988 through June 1989) produced data on chemistry of four streams during stormflows and on the effects of chemical changes on trout and sculpin mortality and behavior, and on aquatic insect populations within the four streams. Hydrologic conditions during this period were typical for the region in the fall but not in the winter or spring. Mild winter temperatures and record-low snowpack development resulted in moderate-to-low stream discharge during the spring snowmelt period. More than 35 cm of rain in the first 17 days of May 1989 created the largest streamflows of the period at a time when discharge is typically receding toward base-flow conditions.

Episodic acidification during increased flows is associated with increases in aluminum and nitrate concentrations. Dilution of total base cations at a rate greater than dilution of sulfate is compensated in the charge balance by a net increase in hydrogen-ion and aluminum concentrations during some high flows. A rapid succession of high-flow periods in early May altered the relations between discharge and chemistry in all streams. Nitrate concentrations in the East Branch Neversink decreased with increased discharge at the beginning of a late-March stormflow, probably when melting ice entered the stream, and increased with increased discharge during other high flows.

Results of the trout and sculpin experiments suggest that the East Branch Neversink River (median pH 4.8) contains an acid-tolerant, sustainable population of brook trout but in smaller numbers than in the other streams. No young-of- the-year were present throughout the main channel of the river at above the monitoring station, indicating that trout in the main stem of the East Branch Neversink originate in tributaries or in less acidic waters downstream of the study reach. Aluminum toxicity was probably the major cause of mortality of caged fish during bioassay experiments in the acidic East Branch Neversink, and trout native to that stream seem to be more tolerant to high aluminum concentrations than are fish moved to that stream from a stream with high ANC and low aluminum concentrations. Trout tracked by radiotelemetry showed a net downstream movement in the acidic East Branch Neversink and a small net upstream movement in the well-buffered High Falls Brook. The results to date therefore suggest that episodic stream acidification is causing fish mortality and at least temporary migration of brook trout to reaches of higher pH in some Catskill streams. The acidic East Branch Neversink had a much smaller in number of organisms than the other streams studied. The orders of aquatic insects were similar among the four streams, but streams with high ANC had more genera of mayflies, and the mayflies in the East Branch Neversink were an acid-tolerant variety.

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APPENDIX

Results of the Quality-Assurance and Control Program

Results of the Episodic Response Project quality-assurance and control program are presented in the following tables. Summary statistics for synthetic (prefix "S" in the sample column) and natural (prefix FN) audit sample analyses are presented in table A-1. The table includes Data-Quality Objectives (for bias, relative bias, precision, and relative precision). Results of analyses of blank samples are presented in table A-2, and results of the Long-Range Transboundary Air Pollution Program (LRTAP) audit program in table A-3. The table of blank-sample data (table A-2) includes mean and median concentrations, standard deviations, and 95-percent confidence intervals for each constituent. The table of LRTAP results (table A-3) includes the rank of the Catskill ERP laboratory results relative to the results from other participating laboratories, and the number of samples flagged for bias for each constituent.

Table A-1.--Results of synthetic and natural audit sample analyses.

Sample[1]	Theoretical value	Number of observations	Bias	Relative bias (percent)	Precision
pH (units)					
S1	4.45	6	0.02	.45	0.100
S2	6.53	5	0.39	5.97	0.344
S4	7.49	6	0.52	6.94	0.348
FN09	6.83	6	0.06	.88	0.448
FN10	5.15	7	-0.26	-5.05	0.430
Data-Quality Objectives:					
Synthetic			0.03		0.03
Natural			0.05		0.10
Acid-neutralizing capacity (microequivalents per liter)					
S1	-39.90	8	-3.80	-9.5	10.68
S2	15.00	6	-5.70	-38.0	13.42
S4	140.00	8	-7.90	-5.6	18.02
FN09	152.3	6	-3.2	-2.1	21.78
FN10	-0.8	7	3.0	375.00	8.06
Data-Quality Objectives:					
Synthetic			2.5	3	2.5
Natural			5.0	5	3.0
Specific conductance (microsiemens per centimeter at 25° C)					
S1	1.4	4	0.6	42.86	.54
S2	17.0	5	-1.3	-7.65	2.96
S4	45.5	5	-.7	-1.54	4.06
FN09	52.1	6	-4.6	-8.83	5.96
FN10	23.5	7	-1.0	-4.26	.96
Data-Quality Objectives:					
Synthetic			1	3	1
Natural			2	5	2
Chloride (milligrams per liter)					
S2	0.80	5	0	0	.06
S3	5.00	8	.19	3.80	.33
S4	15.00	4	1.12	7.47	4.52
FN09	3.96	6	-.02	-.50	.52
FN10	0.30	7	.10	33.33	.266
Data-Quality Objectives:					
Synthetic			.01	3	.01
Natural			.06	5	.06
Nitrate (milligrams per liter)					
S2	0.30	5	0.013	4.33	0.0998
S4	3.00	7	-0.119	-3.97	0.244
S5	6.00	7	-0.103	-6.72	0.645
FN09	1.06	6	-0.152	-14.34	0.102
FN10	0.89	7	0.131	14.72	0.653
Data-Quality Objectives:					
Synthetic			0.006	3	0.006
Natural			0.020	5	0.020

[1] S = Synthetic FN = Natural

Table A-1.--Results of synthetic and natural audit sample analyses. (continued)

Sample	Theoretical value	Number of observations	Bias	Relative bias (percent)	Precision
Sulfate (milligrams per liter)					
S2	2.00	7	0.01	0.50	0.064
S3	6.00	8	-0.12	-2.00	0.144
S4	10.00	5	-0.12	-1.20	0.170
FN09	6.36	6	-0.12	-1.89	0.748
FN10	5.65	7	0.23	4.07	0.176
Data-Quality Objectives:					
Synthetic			0.06	3	0.06
Natural			0.40	5	0.40
Silica (milligrams per liter)					
S2	0.70	3	0	0	0.144
S3	3.00	3	0.02	0.67	0.042
S4	7.00	3	-0.38	-5.43	0.282
FN09	4.07	5	-0.08	-1.96	0.684
FN10	3.47	7	0.22	6.34	0.556
Data-Quality Objectives:					
Synthetic			0.05	3	0.05
Natural			0.06	5	0.06
Dissolved Organic Carbon (milligrams per liter)					
S2	2.50	6	0.20	8.00	0.24
S3	5.00	6	-0.10	-2.00	0.30
S4	10.00	5	0.20	2.00	0.30
FN09	4.42	6	-0.70	-15.84	1.82
FN10	3.31	6	1.00	30.21	2.52
Data-Quality Objectives:					
Synthetic			0.1	5	0.1
Natural			13.3	10	13.3
Calcium (milligrams per liter)					
S2	2.50	7	0.01	0.04	0.206
S3	4.50	7	0.06	1.33	0.458
S4	7.00	7	0.03	0.43	0.442
FN09	5.02	6	-0.68	-13.54	1.154
FN10	1.82	7	-0.04	-2.20	0.116
Data-Quality Objectives:					
Synthetic			0.01	3	0.01
Natural			0.07	5	0.07
Magnesium (milligrams per liter)					
S2	0.50	6	0.02	4.00	0.010
S3	0.80	7	0.01	1.25	0.020
S4	1.50	7	0.03	2.00	0.104
FN09	0.78	6	-0.08	-10.26	0.126
FN10	0.29	7	-0.02	-6.90	0.098
Data-Quality Objectives:					
Synthetic			0.01	3	0.01
Natural			0.07	5	0.07

Table A-1.--Results of synthetic and natural audit sample analyses. (continued)

Sample	Theoretical value (mg/L)	Number of observations	Bias	Relative bias (%)	Precision
Sodium (milligrams per liter)					
S2	0.80	7	0	0	0.070
S3	3.50	7	-0.02	-0.57	0.064
S4	6.00	6	-0.09	-1.50	0.192
FN09	2.59	6	-0.25	-9.65	0.482
FN10	0.57	7	0.01	1.75	0.068
Data-Quality Objectives:					
Synthetic			0.01	3	0.01
Natural			0.07	5	0.07
Potassium (milligrams per liter)					
S2	0.25	7	0.04	16.00	0.220
S3	0.35	7	0	0	0.062
S4	0.60	7	0	0	0.046
FN09	0.47	6	-0.09	-19.15	0.102
FN10	0.32	7	-0.02	-6.25	0.046
Data-Quality Objectives:					
Synthetic			0.01	3	0.01
Natural			0.07	5	0.07
Aluminum, total dissolved (micrograms per liter)					
S2	50	6	12.00	24.00	53.60
S3	400	3	-7.00	-1.75	57.80
S4	750	4	-42.00	-5.60	109.40
FN09	41	5	3.00	7.32	28.40
FN10	187	7	-12.00	-6.42	60.80
Data-Quality Objectives:					
Synthetic			6	3	6
Natural			10	5	10
Aluminum, total monomeric (micrograms per liter)					
S2	50.00	4	-2.00	-4.00	7.8
S3	400.00	4	-17.00	-4.25	20.8
S4	750.00	3	-28.00	-3.73	11.0
FN09	13.00	8	-1.00	-7.69	10.4
FN10	158.00	8	6.00	3.80	18.4
Data-Quality Objectives:					
Synthetic			6	3	6
Natural			10	5	10
Aluminum, organic monomeric (micrograms per liter)					
FN09	7.00	8	1.00	14.28	2.00
FN10	42.00	8	-3.00	-7.14	12.00
Data-Quality Objectives:					
Synthetic			—	—	—
Natural			10	5	10

Table A-2.--Field blank sample results for constituents.

[µeq/L = microequivalents per liter; µS/cm = microsiemens per centimeter; mg/L = milligrams per liter; µg/L = micrograms per liter]

Constituent characteristic	Number of observations	Min.	Max.	Range	Mean	Standard Deviation	Data Quality Objective
Acid-neutralizing capacity (µeq/L)	25	-5.00	12.50	17.50	4.612	3.856	5.0
Specific Conductance (µS/cm)	20	0.10	1.42	1.32	0.674	0.366	1.0
Calcium (mg/L)	17	0.01	0.06	0.05	0.014	0.012	0.02
Magnesium (mg/L)	17	0.01	0.02	0.01	0.011	0.002	0.02
Potassium (mg/L)	17	0.01	1.00	0.99	0.126	0.329	0.02
Sodium (mg/L)	17	0.01	0.03	0.02	0.011	0.005	0.02
Chloride (mg/L)	20	0	0	0	0	0	0.02
Nitrate (mg/L)	20	0	0	0	0	0	0.01
Sulfate (mg/L)	20	0	0	0	0	0	0.10
Silica (mg/L)	24	-0.069	0.300	0.369	0.025	0.084	0.10
Dissolved organic carbon (mg/L)	26	0.160	1.470	1.310	0.408	0.308	0.20
Aluminum, total (µg/L)	25	0.00	25.00	25.00	6.21	6.09	10.00
pH (pH units)	27	5.28	6.85	1.57	5.98	0.413	—

Table A.3.--Summary of bias flags and direction of bias in five Long-Range Transboundary Air Pollution (LRTAP) interlaboratory comparison studies.

[Numbers refer to number of flagged samples. (10 samples per study).
S = Satisfactory, NR = No results reported.]

Constituent characteristic	Study 18 May 1988	Study 19 Aug. 1988	Study 20 Jan. 1989	Study 21 April 1989	Study 22 June 1989
Specific conductance	S	Low on 1	S	S	S
pH	S	Low on 1	S	S	S
Dissolved organic carbon	NR	NR	NR	S	No flags. Slight low bias
Acid-neutralizing capacity	S	S	S	S	S
Nitrate	S	S	Slight low bias	S	S
Sodium	S	NR	NR	S	S
Magnesium	S	NR	S	High on 3. High bias	S
Sulfate	S	S	S	S	S
Chloride	Slight high bias	S	S	S	S
Potassium	S	NR	NR	S	S
Calcium	S	NR	NR	High on 5. High bias	S