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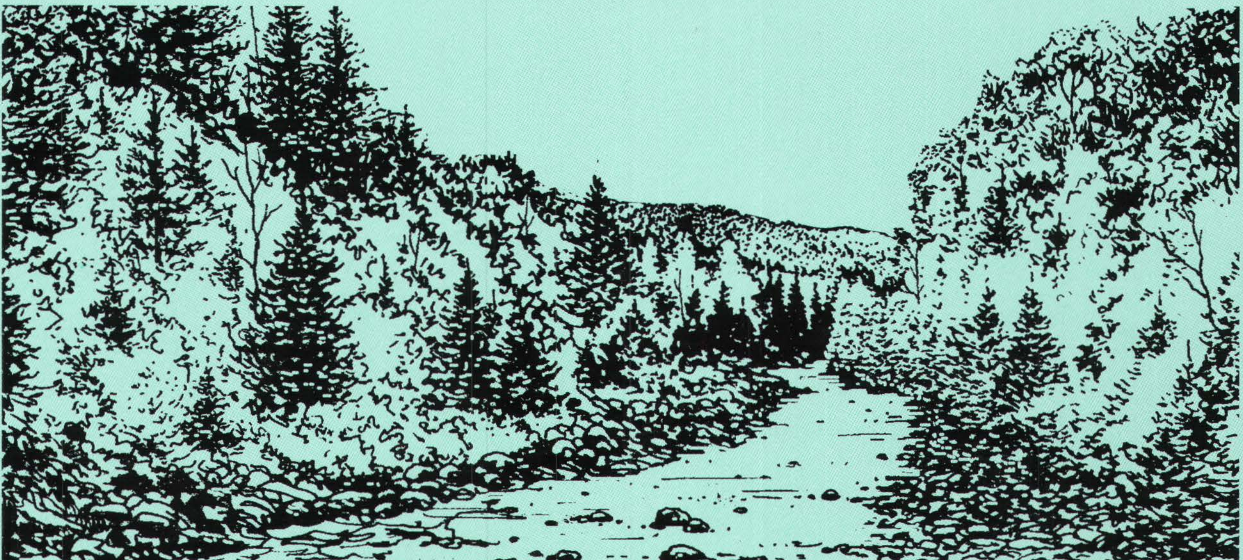
Environmental Characteristics and Water Quality of Hydrologic Benchmark Network Stations in the Eastern United States, 1963–95



U.S. Geological Survey Circular 1173–A

Environmental Characteristics and Water Quality of Hydrologic Benchmark Network Stations in the Eastern United States, 1963–95

By M. Alisa Mast *and* John T. Turk

U.S. GEOLOGICAL SURVEY CIRCULAR 1173–A

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
Charles G. Groat, Director

U.S. GOVERNMENT PRINTING OFFICE : 1999

Free on application to the
U.S. Geological Survey
Information Services
Box 25286
Denver, CO 80225–0286

Library of Congress Cataloging-in-Publications Data

Mast, M. Alisa.
Environmental characteristics and water quality of hydrologic benchmark network stations in the eastern United States / by M. Alisa Mast and John T. Turk.
p. cm. -- (U.S. Geological Survey circular : 1173–A)
Includes bibliographical references (p.).
Supt. of Docs. no.: I 19.4/2:C1173–A
1. Hydrology--Atlantic States. 2. Hydrology--Southern States. 3. Water quality--Atlantic States. 4. Water quality--Southern States. I. Turk, John T. II. Title. III. Series.
GB705.A85M38 1998
551.48'3'0974--dc21
98–28319
CIP
ISBN 0–607–90196–9

FOREWORD

In 1962, Luna Leopold, Chief of the U.S. Geological Survey's Water Resources Division from 1957 to 1966, stated, "We are engaged in great national programs of water control and development. An expanding population demands ever-increasing supplies of the natural resources which are to be found in or upon the landscape—soil, water, minerals, food, timber, and fiber. By his works, by his extractions, man's mark upon his environment becomes ever deeper, his effects more indelible." He proposed that the Geological Survey "establish a network of 'hydrologic bench marks' in areas which are as free as possible from man-induced changes." In 1963, the U.S. Geological Survey established the Hydrologic Benchmark Network to provide long-term measurements of streamflow and water quality in areas that are minimally affected by human activities.

Circular 1173, titled "Environmental Characteristics and Water Quality of Hydrologic Benchmark Network Stations in the United States, 1963–95" consists of a series of four individual circulars that include stations in the (A) Eastern, (B) Midwestern, (C) West-Central, and (D) Western United States. This series describes the hydrologic and chemical characteristics of each of the 58 stations that have been included in the network. Trends in discharge, pH, and major dissolved ions also are examined. This circular provides information to assist scientists in the interpretation of these unique data sets. The information collected in these benchmark watersheds is a legacy that will increase in scientific value over the coming decades. This circular is intended to enhance the value of that legacy by providing a context of information about those watersheds and their hydrology.

Robert M. Hirsch

Robert M. Hirsch
Chief Hydrologist

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
cubic meter per second (m^3/s)	35.31	cubic foot per second
hectare (ha)	2.471	acre
kilometer (km)	0.6214	mile
liter (L)	0.2642	gallon (US)
meter (m)	3.281	foot
meter per kilometer (m/km)	5.291	foot per mile
microequivalent per liter calcium (µeq/L)	0.0200	milligram per liter calcium
microequivalent per liter magnesium (µeq/L)	0.0122	milligram per liter magnesium
microequivalent per liter sodium (µeq/L)	0.0230	milligram per liter sodium
microequivalent per liter potassium (µeq/L)	0.0391	milligram per liter potassium
microequivalent per liter ammonium (µeq/L)	0.0140	milligram per liter ammonium (as nitrogen)
microequivalent per liter alkalinity (µeq/L)	0.0500	milligram per liter alkalinity (as $CaCO_3$)
microequivalent per liter sulfate (µeq/L)	0.0480	milligram per liter sulfate
microequivalent per liter chloride (µeq/L)	0.355	milligram per liter chloride
microequivalent per liter fluoride (µeq/L)	0.0190	milligram per liter nitrite plus nitrate (as nitrogen)
micromole per liter silica (µmol/L)	0.0602	milligram per liter silica
micromole per liter aluminum (µmol/L)	26.981	microgram per liter aluminum
micromole per liter iron (µmol/L)	55.847	microgram per liter iron

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$^\circ F = 9/5\,(^\circ C) + 32$$

Additional abbreviations used in this report:

microsiemens per centimeter at 25 degrees Celsius (µS/cm)
milliequivalents per 100 grams (meq/100 g)
milligrams per liter (mg/L)
year (yr)
micrometer (µm)

Environmental Characteristics and Water Quality of Hydrologic Benchmark Network Stations in the Eastern United States, 1963–95

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Abstract

The Hydrologic Benchmark Network was established in 1963 to provide long-term measurements of streamflow and water quality in areas that are minimally affected by human activities. These data were to be used to study time trends and to serve as controls for separating natural from artificial changes in other streams. The network has consisted of as many as 58 drainage basins in 39 States. This report describes the environmental characteristics and water quality at 16 benchmark basins in the Eastern United States. The basins and physiographic provinces are as follows: the Wild River, Maine, in the New England Province; Esopus Creek, New York, and Young Womans Creek, Pennsylvania, in the Appalachian Plateaus; Buffalo River, Tennessee, in the Interior Low Plateaus; Falling Creek, Georgia, and Holiday Creek, Virginia, in the Piedmont Province; Cataloochee Creek, North Carolina, Little River, Tennessee, and Tallulah River, Georgia, in the Blue Ridge Province; and Blackwater River and Sipsey Fork, Alabama, Cypress Creek, Mississippi, McDonalds Branch, New Jersey, Scape Ore Swamp and Upper Three Runs, South Carolina, and Sopchoppy River, Florida, in the Coastal Plain. The information in this report was compiled to aid in the application and interpretation of historical water-quality data collected as part of the U.S. Geological Survey Hydrologic Benchmark Network program.

The 16 Hydrologic Benchmark Network streams discussed in this report primarily drain forested areas that have a variety of land-use activities ranging from recreational use and timber harvesting on publicly owned land to agriculture and residential development on privately owned land. In most of the basins, stream-water chemistry seems to be controlled by the interaction of acidic precipitation with the underlying soils and bedrock. Land use had a minimal effect on stream-water chemistry at the gaging stations, except for Esopus Creek in New York and Falling Creek in Georgia. The chemistry of Esopus Creek was strongly affected by the application of deicing salts to roads and effluent from a wastewater-treatment facility in the basin, and the chemistry of Falling Creek was affected by industrial wastewater discharge from a settling pond in the headwaters of the basin. Temporal trends in water-quality constituents were observed at several of the stations and were attributed to either environmental or method-related factors. Upward trends in sodium and chloride concentrations in Esopus Creek in New York and the Buffalo River in Tennessee probably were related to increases in residential population in the basins. Downward trends in sulfate concentrations were observed at the Wild River in Maine and Esopus Creek stations and were consistent with regional declines in atmospheric sulfur dioxide emissions since 1970. Interpretation of the historical sulfate data, however, is complicated by several changes in analytical methods during the period of record. Significant trends in stream-water calcium concentrations were observed at several of the stations and were attributed to environmental or method-related factors.

INTRODUCTION

In 1962, L.B. Leopold, then Chief Hydrologist of the U.S. Geological Survey (USGS), proposed to establish a network of hydrologic benchmarks to make long-term measurements of various hydrologic characteristics in areas that were free from the effects of human activities (Leopold, 1962). The main purpose of the network was to provide a long-term hydrologic data base to be used to study temporal trends in hydrologic characteristics and to serve as controls for separating natural from manmade changes in other streams. The Hydrologic Benchmark Network (HBN) was started in 1963, and sites were selected on the basis of four criteria: (1) No manmade storage, regulation, or diversion was to exist in the basin; (2) ground water in the basin was not to be affected by pumping from wells; (3) conditions were to be favorable for accurate measurement of streamflow and water quality; and (4) the potential was to be small for special natural changes, such as beaver activity, overgrazing or overbrowsing, or extensive fire (Cobb and Biesecker, 1971). Most of the stations selected for the network were located in areas virtually free of human activities, such as national parks, wilderness areas, or nature preserves. However, such undisturbed areas no longer existed in many parts of the country, and the decision was made to include basins where logging or agriculture was practiced under the assumption that stations in such basins would still yield useful information as long as the land use did not change (Lawrence, 1987). Most stations in the HBN were established by the late 1960's and, after a few changes in the 1970's and 1980's, the network eventually consisted of 57 streamflow stations and one lake-stage station in 39 States (fig. 1). Following an evaluation of the HBN program in the early 1990's, eight stations were discontinued and two stations were

Figure 1. Map showing locations of gaging stations in the Hydrologic Benchmark Network.

replaced for the following four reasons: (1) The sites were operated as discharge-only stations during the period of record (Tallulah River, Ga.; Swiftcurrent Creek, Mont.; and Little Vermillion River, S. Dak.), (2) poor discharge records were collected at the station (Honolii Stream, Hawaii, replaced by Kahakuloa Stream, Hawaii), (3) substantial changes in land use occurred during the period of record (Upper Three Runs, S.C.), or (4) water quality at the gage was strongly affected by upstream human activities (Esopus Creek, N.Y., replaced by Biscuit Brook, N.Y.; Falling Creek, Ga.; South Hogan Creek, Ind.; North Fork Whitewater River, Minn.; and Elk Creek, Iowa). Because of budgetary restrictions, water-quality sampling was decreased at all HBN stations in October 1986 and discontinued in October 1997.

The original network design to study temporal trends was first used to test whether changes in acidic deposition from the atmosphere were causing regional trends in surface-water chemistry (Smith and Alexander, 1983). This attempt to ascribe surface-water trends to environmental changes revealed a lack of ancillary data for the HBN, particularly for precipitation quality and quantity. Because temporal trends in surface-water chemistry may exist at many of the HBN stations, it is necessary to determine whether environmental factors, such as precipitation chemistry and land use, or changes in analytical methods could have caused the observed trends. However, documentation of environmental characteristics and method-related effects is minimal for most HBN stations, and hydrologic characteristics other than stream discharge and chemistry were seldom measured. In addition, if the HBN is to be useful as a control for separating natural from manmade changes in other streams, an understanding of the natural and manmade factors that affect water quality in these basins is needed. In 1990, the USGS undertook an evaluation of the HBN program to provide detailed information for sites in the network and to determine the suitability of each site with regard to the original design criteria.

Purpose and Scope

This report describes the environmental characteristics and water quality of 16 HBN stream basins in the Eastern United States. These stream basins, in order of presentation, are: Blackwater River, Ala.; Sipsey Fork, Ala.; Sopchoppy River, Fla.; Falling Creek, Ga.; Tallulah River, Ga.; Wild River, Maine; Cypress Creek, Miss.; McDonalds Branch, N.J.; Esopus Creek, N.Y.; Cataloochee Creek, N.C.; Young Womans Creek, Pa.; Buffalo River, Tenn.; Little River, Tenn.; Scape Ore Swamp, S.C.; Upper Three Runs, S.C.; and Holiday Creek, Va. The following information is presented for each HBN basin: (1) An overview of the basin characteristics, including physiography, geology, soils, vegetation, land ownership, basin access, and land use; (2) an analysis of the historical water-quality records for the gaging station in each basin for the period of record through water year 1995, including data quality, water-quality characteristics, and time-series trends; and (3) an interpretation of the intrabasin variability in surface-water chemistry for selected tributary streams in each basin sampled between December 1990 and October 1991. This report is intended to provide a framework of information to aid in the application and interpretation of water-quality data collected as part of the HBN program.

Previous Work

Although the HBN has been in existence for more than 30 years, only a few studies have assessed or analyzed data for the entire network. Brief descriptions of the HBN drainage basins and water-quality characteristics of the streams were compiled by Cobb and Biesecker (1971). Biesecker and Leifeste (1975) compared water-quality constituents for undisturbed HBN stations with constituents for major streams that drain similar hydrologic regions of the United States. Smith and Alexander (1983) examined time trends in pH, alkalinity, and sulfate at 47 HBN stations to investigate the long-term effects of acidic deposition on water quality in undeveloped basins. Lins (1986) used a principal-component analysis to determine whether patterns in stream sulfate at 30 stations in the network could be used as analogues for regional patterns in sulfate deposition from the atmosphere. Lawrence (1987) presented a compilation of streamflow characteristics for 58 HBN stations, including an analysis of time trends in streamflows for the period of record through water year 1980.

Few process-level investigations have been conducted by the USGS in the individual network drainage basins. One exception is for McDonalds Branch in New Jersey, which was the site of an acidic deposition study from 1984 through 1988 (Lord and others, 1990; Johnsson and Barringer, 1993). The

Biscuit Brook Basin, N.Y., which replaced the Esopus Creek Basin in 1991, has been the site of several biogeochemical investigations (Murdoch, 1991; Murdoch and Stoddard, 1993). Site-specific investigations were more limited in scope at other HBN stations. Hainly and Ritter (1986) collected samples from tributary streams in the Esopus Creek Basin, N.Y., and Young Womans Creek Basin, Pa., to determine the representativeness of water quality at the basin outlet compared to water quality in headwater areas of these basins. Several observation wells and rain gages were installed in the Holiday Creek Basin, Va., in the early 1970's to investigate rainfall-runoff relations, but the project was not completed (Edward Knuckles, U.S. Geological Survey, oral commun., 1994). Buell (1985) investigated time-series trends in water-quality constituents at Falling Creek, Ga., in order to evaluate the effects of land use on water quality in similar basins.

Acknowledgments

The authors express their appreciation to employees of the U.S. Department of Agriculture Forest Service and Natural Resources Conservation Service (formerly the Soil Conservation Service), National Park Service, Piedmont National Wildlife Refuge, Appomattox-Buckingham State Forest, Lebanon State Forest, New York City Department of Environmental Protection, Pennsylvania Department of Environmental Resources, Pinelands Commission, Sproul State Forest, Susquehannock State Forest, and the USGS who provided information for this study. The authors also express gratitude to USGS employees Donald H. Campbell, David W. Clow, Kathleen K. Fitzgerald, George P. Ingersoll, Wendy O. Meyer, Anthony J. Ranalli, Norman E. Spahr, and Amy Swancar for technical assistance and data collection.

METHODS

Historical water-quality records for stations in the HBN are available from the USGS National Water Information System (NWIS). Water measurements made at HBN stations have included a comprehensive suite of about 85 characteristics, including physical properties, major dissolved constituents, trace elements, radiochemical constituents, nutrients, and biological constituents (Alexander and others, 1996). Data for 63 of these characteristics were recently compiled on a CD-ROM for 1962 through 1994 (Alexander and others, 1996). The parameter codes used in NWIS and the periods of record of physical properties and water-quality constituents retrieved for this report are listed in table 1. In addition to those items listed in table 1, fluoride data (code 00950) were retrieved for Falling Creek, Ga., and total aluminum (code 01106), total iron (code 01046), and dissolved organic carbon (code 00681) data were retrieved for McDonalds Branch, N.J. The following modifications were made to the data before statistical and graphical analyses were performed: (1) Alkalinity concentrations stored under parameter code 00410 before 1981 were combined with alkalinity concentrations stored under parameter code 90410 to obtain a continuous record of laboratory alkalinities; (2) dissolved and total nitrite plus nitrate and dissolved and total ammonium were combined to obtain more continuous records of these two nutrient species; (3) concentrations reported as less than were set equal to the reporting limit for the time-series plots and charge-balance calculations; (4) concentrations reported as zero were retained in the data files; (5) concentrations were converted from units of milligrams per liter to microequivalents per liter, except silica, aluminum, and iron, which were converted to units of micromoles per liter by using the conversion factors listed at the front of this report; and (6) outliers greater than five standard deviations from the mean were removed from the data sets. All periods of record discussed in this report refer to the water year defined as October 1 through September 30 unless otherwise indicated.

The quality of chemical analyses was checked on the basis of ion balance, which was calculated as the total cation charge minus the total anion charge divided by the total charge in solution. The cation charge was calculated as the sum of the hydrogen ion (calculated from field pH measurements), calcium, magnesium, sodium, and potassium concentrations and the anion charge as the sum of laboratory alkalinity, chloride, and sulfate concentrations. Ion balance was calculated only for samples that had complete chemical analyses. The inorganic nitrogen species—nitrite plus nitrate and ammonium—were excluded from the calculation because neither of these species was measured during the entire period of record. Omission of these constituents from the ion-balance calculation was not expected to produce a substantial bias because concentrations were usually

Table 1. Parameter codes and periods of record for physical properties and water-quality constituents retrieved from the U.S. Geological Survey National Water Information System

Parameter	Parameter code	Period of record
Discharge, instantaneous	00060, 00061	1963–95
Specific conductance, field	00095	1963–95
Specific conductance, laboratory	90095	1981–95
pH, field	00400	1963–95
pH, laboratory	00403	1981–95
Calcium, dissolved	00915	1963–95
Magnesium, dissolved	00925	1963–95
Sodium, dissolved	00930	1963–95
Potassium, dissolved	00935	1963–95
Ammonium, dissolved	00608, 71846	1969–79,[b] 1980–95
Ammonium, total	00610, 71845	1971–79,[b] 1981–82, 1986–92
Alkalinity, laboratory	00410,[a] 90410, 00417	1963–95
Alkalinity, field	00410,[a] 39086, 00419	1985–95
Bicarbonate, field	00440, 00450, 00453	1965–78,[b] 1986–95
Sulfate, dissolved	00945	1963–95
Chloride, dissolved	00940	1963–95
Nitrite plus nitrate, dissolved	00631	1974–77,[b] 1980–95
Nitrite plus nitrate, total	00630	After 1971[b]
Silica, dissolved	00955	1963–95

[a] Prior to 1981, laboratory alkalinity data were stored under parameter code 00410.

[b] Not reported at all stations for entire period indicated.

at or near the reporting limit of the analytical methods. The water-quality records also were inspected for bias that may have been introduced by sampling or analytical methods and were compared to the chronology of activities and analytical methods that were used by USGS laboratories (Durum, 1978; Fishman and others, 1994) and to operational guidelines for the HBN that were documented in a series of USGS technical memoranda available at URL http://water.usgs.gov/public/admin/memo/. Summary statistics of physical properties and water-quality constituents were calculated from the historical water-quality records at each station. Spearman rank correlation coefficients (rho values) were calculated to measure the strength of monotonic associations among discharge and the major solutes. Values of rho fall between −1.0 to 1.0 with a value of zero indicating no correlation between constituents.

Temporal trends in stream discharge and water-quality constituents were calculated by using the computer program, Estimate Trend (ESTREND), which was written by Schertz and others (1991). ESTREND uses two trend-detection techniques—the nonparametric seasonal Kendall test and the parametric Tobit test (Schertz and others, 1991). The seasonal Kendall test for uncensored data was used when less than 5 percent of the observations were censored. The seasonal Kendall test for censored data was used when more than 5 percent of the observations were censored. In cases where a large number of detected concentrations fell between multiple reporting limits, as often occurred for the nitrite plus nitrate concentrations, the Tobit test was used to calculate the trend. Trends were calculated by using unadjusted concentrations and flow-adjusted concentrations. Removal of flow-related variability in the water-quality data not only improved the power of the statistical test but decreased the possibility that the observed trends were an artifact of the sampling discharge record (Hirsch and others, 1982; Schertz and others, 1991). Automated procedures are provided in ESTREND to adjust concentrations for flow-related variability. Flow adjustment was not made if the concentration-discharge model was not significant at the 0.10 probability level (Schertz and others, 1991) or if the data were highly censored. Because the minimum sampling frequency at most HBN stations was quarterly, trends were calculated by using four 3-month seasons beginning in mid-December, except for the Tallulah River in Georgia, which was tested by using two 6-month seasons per year. Trends were considered statistically significant at the 0.01 probability level. The ESTREND procedure also computes a trend slope, which represents the median rate of change in discharge or concentrations for the selected period of record. Interpretation of the trends was aided by the use of a locally weighted scatterplot smoothing technique (LOWESS), which graphically smooths the pattern of the data over time (Schertz and others, 1991). The LOWESS curves are presented in the time-series plots only in cases where the trend in discharge or the unadjusted concentration was statistically significant at the 0.01 probability level.

Stream chemistry at each HBN station was compared to precipitation chemistry at the closest National Atmospheric Deposition Program (NADP) station. The NADP is a monitoring network of almost 200 stations nationwide that provides long-term records of weekly precipitation chemistry. Sampling, analytical, and quality-assurance protocols for the NADP network are summarized in Peden (1983). Annual volume-weighted mean (VWM) concentrations for the NADP stations presented in this report were obtained at URL http://nadp.sws.uiuc.edu/NADP/.

In addition to the historical water-quality records and NADP data, stream samples were collected at the gaging stations and from several major tributary streams in each basin between December 1990 and October 1991 to evaluate the spatial variability of surface-water chemistry as a function of subbasin characteristics, particularly geology and land use. The selection criteria for each sampling site are listed in tables throughout the report. Visits to each HBN drainage basin were scheduled during low-flow periods, and samples generally were collected for 1 to 3 days. Grab samples were collected in 2-L polyethylene bottles and filtered within 12 hours of collection. When possible, field measurements of dissolved oxygen, water temperature, and stream discharge were made at the time of sample collection. Measurements of pH were made within 12 hours of collection on unfiltered sample aliquots by using an electrode designed for low ionic-strength waters. The pH electrode was calibrated with pH 4 and pH 7 buffer solutions, then checked against a dilute sulfuric acid standard (pH 4.75) and deionized water. Samples for chemical analysis were filtered through a 0.45-µm filter and preserved within 12 hours of collection. Samples were analyzed for pH, specific conductance, major cations and anions, silica, and alkalinity at the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo., by using methods developed for low-ionic-strength waters (Friedman and Fishman, 1989). Chemical data for the synoptic samples are stored in NWIS.

ENVIRONMENTAL CHARACTERISTICS AND WATER QUALITY OF HYDROLOGIC BENCHMARK NETWORK STATIONS

Blackwater River near Bradley, Alabama (Station 02369800)

Site Characteristics and Land Use

The Blackwater River HBN Basin is in the Coastal Plain physiographic province (Atwood, 1940) in southern Alabama (fig. 2). The HBN basin drains 227 km^2 of rolling terrain that is interspersed with sinkholes and bays, some of which hold water year-round. The USGS gaging station is 1.6 km east of Bradley, Ala., at an elevation of 37 m and at latitude 31°01'39" and longitude 86°42'36". The basin encompasses the headwaters of the main stem of the Blackwater River, which flows south into the Gulf of Mexico. The channel length of the river upstream from the gage is about 21 km and has an average stream gradient of 1.5 m/km. The main channel is perennial, and mean monthly discharge ranges from 2.3 m^3/s in October to 7.4 m^3/s in March. Average annual runoff from the basin was 59 cm from 1968 through 1995 (U.S. Geological Survey, Water Resources Data, Alabama). Climate of the area is influenced by moist tropical air from the Gulf of Mexico, which results in long, hot summers with cool, short winters. Average daily air temperatures range from 9.1°C in winter to 26.2°C in summer. Precipitation averages 150 cm annually and is fairly evenly distributed throughout the year; July generally is the wettest month and October the driest (Cotton, 1989). Less than 5 percent of winters have measurable snowfall.

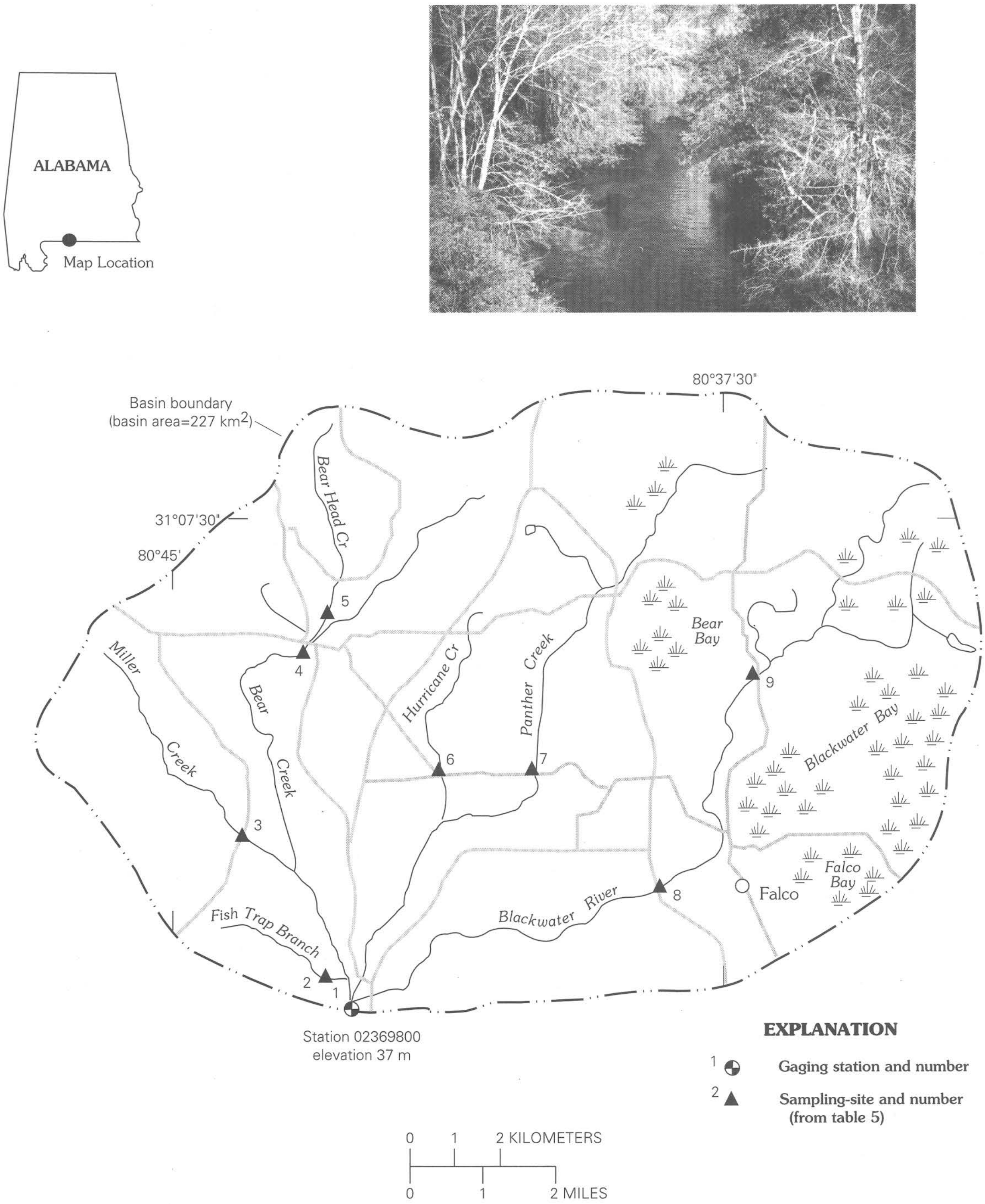

Figure 2. Map showing study area in the Blackwater River Basin and photograph of the stream channel near the gage.

The basin lies in the Outer Coastal Plain Mixed Forest ecoregion, which is characterized by temperate evergreen forests (Bailey and others, 1994). Vegetation communities and soil types are closely related to the two major landform types in the basin—pine hills and bays. The pine hills landform covers more than 75 percent of the basin and consists of upland ridges with gently sloping side slopes. The pre-logging vegetation of the pine hills was a parklike forest composed of more than 75 percent longleaf pine with an understory of wire grass. Secondary species, such as slash pine, southern red oak, and post oak, began to increase in numbers after the area was logged around the turn of the century. Soils in the pine hills are mapped in the Benndale-Orangeburg-Troup association and are developed in unconsolidated fluvial sediments and have a loam or sandy clay loam subsoil (Cotton, 1989). These soils tend to be highly permeable and acidic (pH 4.5 to 6.0) and have a low organic-matter content (less than 4 percent). The bay landform, which is found in the eastern half of the basin, has very little topographic relief and is almost entirely composed of wetlands. Bay vegetation is dominated by sweet bay, bull bay, and red bay with secondary species, such as swamp tupelo, slash pine, pond pine, sweet gum, and water oak. Soils are mapped in the Doravon association and are developed in highly decomposed acidic organic matter. These soils tend to be deep, very poorly drained, and have a mucky peat subsoil (Cotton, 1989).

Bedrock in the basin includes gently dipping, unconsolidated fluvial sediments of the Miocene Catahoula Sandstone and the Paynes Hammock Sand (Cagle, 1963). Both units consist of light gray to white sand, sandy clay, and clay deposits with subordinate beds of gravel. The sandstones are composed of fine- to coarse-grained, subangular to rounded quartz with limonite cement in some layers. The clay is predominantly kaolinite, but mica and lignite are common in some places.

The Blackwater River Basin drains parts of Escambia and Covington Counties and is entirely in the boundaries of the Conecuh National Forest. About 10 percent of land in the northeast corner of the basin also is in the boundaries of the Blue Springs Wildlife Management Area. About 32 percent of land in the National Forest boundary is owned by private individuals or logging companies. More than 150 km of forest and county roads provide vehicle access to most areas of the basin.

Current land cover in the basin is 89 percent forest land, 10 percent agricultural land, and 1 percent residential development (Ray Albright, U.S. Department of Agriculture Forest Service, written commun., 1996). The principal land-use activity on both Federal and private land is timber production. Other land-use activities in the basin include cattle grazing, row-crop farming, road networks, rural residences, and recreation. The only discernible shift in land use during the past 30 years has been the conversion of some farm land into forest land (Ray Albright, written commun., 1996). The residential population of the basin has remained relatively stable since the HBN station was established, although recreational use, particularly hunting, has increased significantly during the past 10 years. Forest management policies of the National Forest are directed at maintaining the health and abundance of the major pine species and providing habitat for the endangered red-cockaded woodpecker. Pines are harvested on an 80- to 120-year rotation with some intermediate thinning at 20 to 30 years. Tractor logging is the sole harvest method in the basin. Most cuts in the Conecuh National Forest range from 2 to 30 ha in size and are primarily shelterwood or seedtree cuts, although clearcutting was more prevalent in the past. Clearcutting is the most common harvesting method used on private land, and cuts may exceed 200 ha in size (Ray Albright, written commun., 1996).

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for this report includes 95 water-quality samples that were collected from November 1976 through September 1995. Sampling frequency ranged from six to nine samplings per year from 1977 through 1982 and quarterly from 1983 through 1995, although no samples were collected in 1984. Samples were analyzed at the Central Laboratory in Atlanta, Ga., from 1976 through 1985 and at the NWQL in Arvada, Colo., from 1986 through 1995. Daily discharge records for the Blackwater River (station 02369800) are available beginning in October 1967, and records of daily water temperature at the gage are available for October 1967 through September 1969. A precipitation gage was operated at the site in the late 1960's and early 1970's, but the data were not published.

Calculated ion balances for 80 samples with complete major ion analyses are shown in figure 3. Ion balances ranged from –45 to +47 percent, and more than 40 percent of the samples had calculated values outside the ±10 percent range. This wide range of values is not unexpected considering the difficulties in making precise analytical measurements at the low solute concentrations typical of this station. The mean charge balance of all samples was 3.7 percent, indicating an excess of measured cations over anions in solution. Considering the tealike color of stream water at this site, it is reasonable to assume that the anion deficit is because of the presence of unmeasured organic anions.

Time-series plots of the major dissolved constituents were inspected for evidence of method-related effects (fig. 3). Several notable patterns were observed in the base cation and sulfate concentrations. For example, several extremely high sulfate concentrations were reported during the late 1980's. This pattern coincides with the use of a turbidimetric titration for sulfate analysis at the NWQL between March 1986 and December 1989 (Fishman and others, 1994). In 1989, the NWQL determined that sulfate concentrations can be overestimated by this technique and changed the method to ion chromatography (Office of Water Quality Technical Memorandum No. 90.04, *Turbidimetric Sulfate Method*, issued December 21, 1989, at URL http://water.usgs.gov/public/admin/memo/). The bias was most pronounced in dilute waters, although it was not consistent among samples and appeared to be influenced by factors such as color and turbidity (Schertz and others, 1994). Calcium, magnesium, and sodium concentrations all had a similar pattern of high scatter in the early part of the record and low scatter after 1983. This pattern coincides with a change in the analysis method for major dissolved cations and trace inorganic constituents beginning in water year 1983 from atomic absorption (AA) spectroscopy to inductively coupled plasma (ICP) spectroscopy (Office of Water Quality Technical Memorandum No. 82.18, *National Water-Quality Networks*, issued September 28, 1982, at URL http://water.usgs.gov/public/admin/memo/). The observed temporal patterns in calcium, magnesium, and sodium, therefore, probably reflect a difference in the precision of these two analytical methods. Changes in field procedures also may have introduced bias into the historical data set.

The time-series plot of field pH measurements in figure 3 shows a definite downward shift in the field pH values in the early 1980's. This coincides with the release of a memorandum in early 1981 that provided guidelines for obtaining accurate pH measurements in low-conductivity waters (Office of Water Quality Technical Memorandum No. 81.08, *Electrodes for pH Measurement in Low-Conductivity Waters*, issued February 10, 1981, at URL http://water.usgs.gov/public/admin/memo/). Although it was not required that measurements at HBN stations were made according to these guidelines, it is likely that many field offices changed the procedures and equipment they used for pH measurements shortly after this memorandum was issued.

Median concentrations and ranges of major constituents in stream water collected at the HBN gaging station and VWM concentrations in wet-only deposition measured at the Quincy NADP station in Florida, about 230 km southeast of the basin, are presented in table 2. Wet-precipitation chemistry at the NADP station is dilute and slightly acidic, with a VWM pH of 4.8 during the 11 years of record. The dominant cations in precipitation were hydrogen, which contributed 41 percent of the total cation charge, and sodium and ammonium, which contributed 28 and 13 percent, respectively. Sulfate was the dominant anion, contributing 49 percent of the total anions, and chloride and nitrate accounted for 29 and 22 percent, respectively. These results indicate that solutes in precipitation at the nearby NADP station probably are a mixture of strong acids derived from anthropogenic emissions of sulfur and nitrogen compounds and salt derived from marine aerosols (Fu and Winchester, 1994).

Stream chemistry in the Blackwater River is very dilute and slightly acidic; specific conductances ranged from 15 to 42 µS/cm and were slightly acidic, and the median pH was 4.9. Organic acids, leached from vegetation in wetlands, give the stream water a tealike color and probably are the dominant source of stream-water acidity. The major cation in stream water was sodium and the dominant anion was chloride. The low concentration of the major weathering products, particularly alkalinity and divalent cations, is attributed to the lack of weatherable minerals in the underlying quartz-rich sediments. The median chloride concentration in

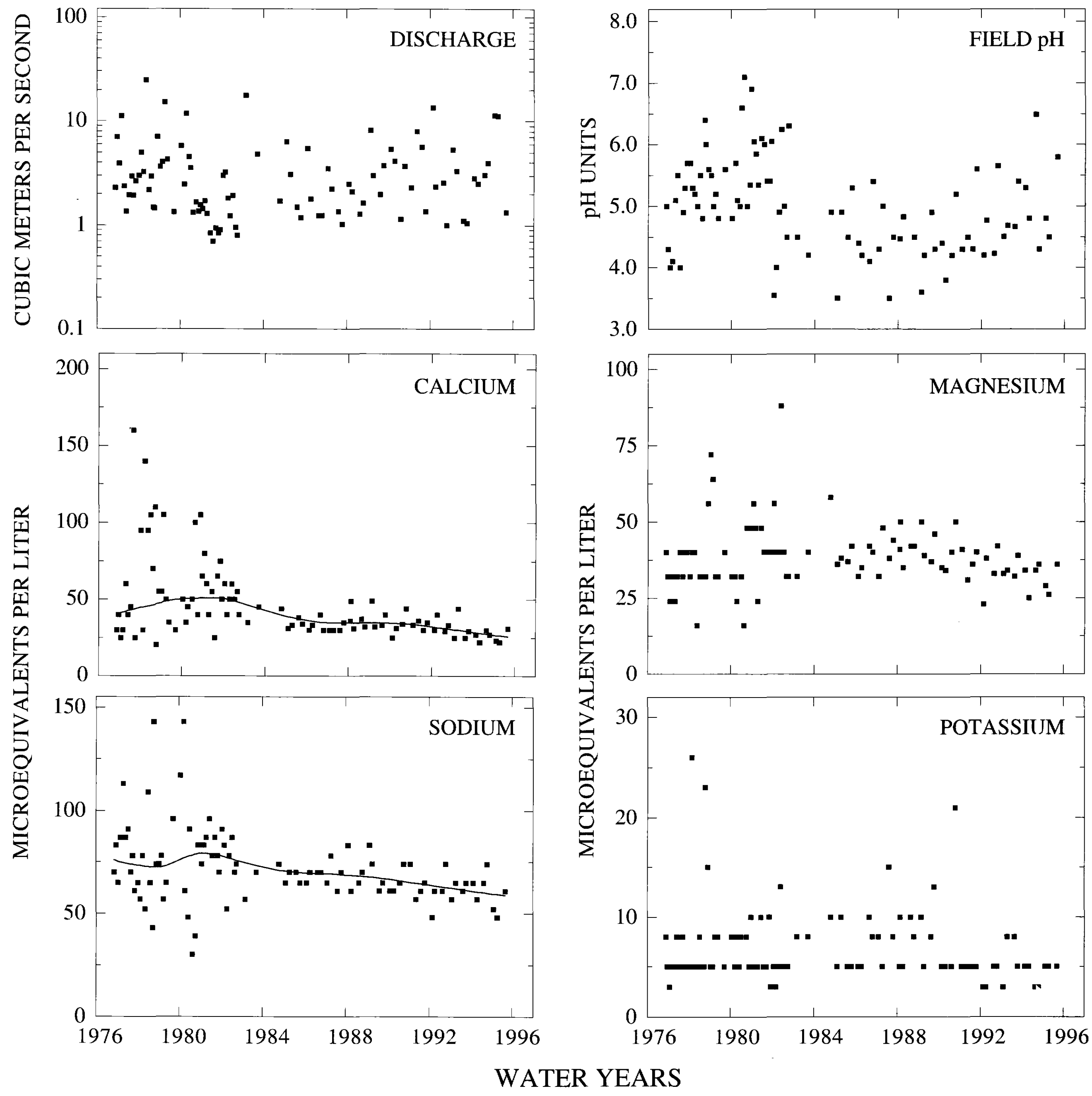

Figure 3. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Blackwater River, Alabama.

stream water was 82 µeq/L, which is about six times larger than the VWM concentration of 12 µeq/L in precipitation. On the basis of the difference between average annual runoff and precipitation, evapotranspiration can account for no more than a threefold increase in the concentration of precipitation, indicating that stream-water chloride is derived from sources other than wet deposition. Considering the proximity of this station to the Gulf of Mexico and the almost equal concentrations of sodium and chloride, it seems plausible that dry deposition of marine aerosols is an important source of chloride (and sodium) in stream water at this station. The median concentration of sulfate in stream water was 35 µeq/L

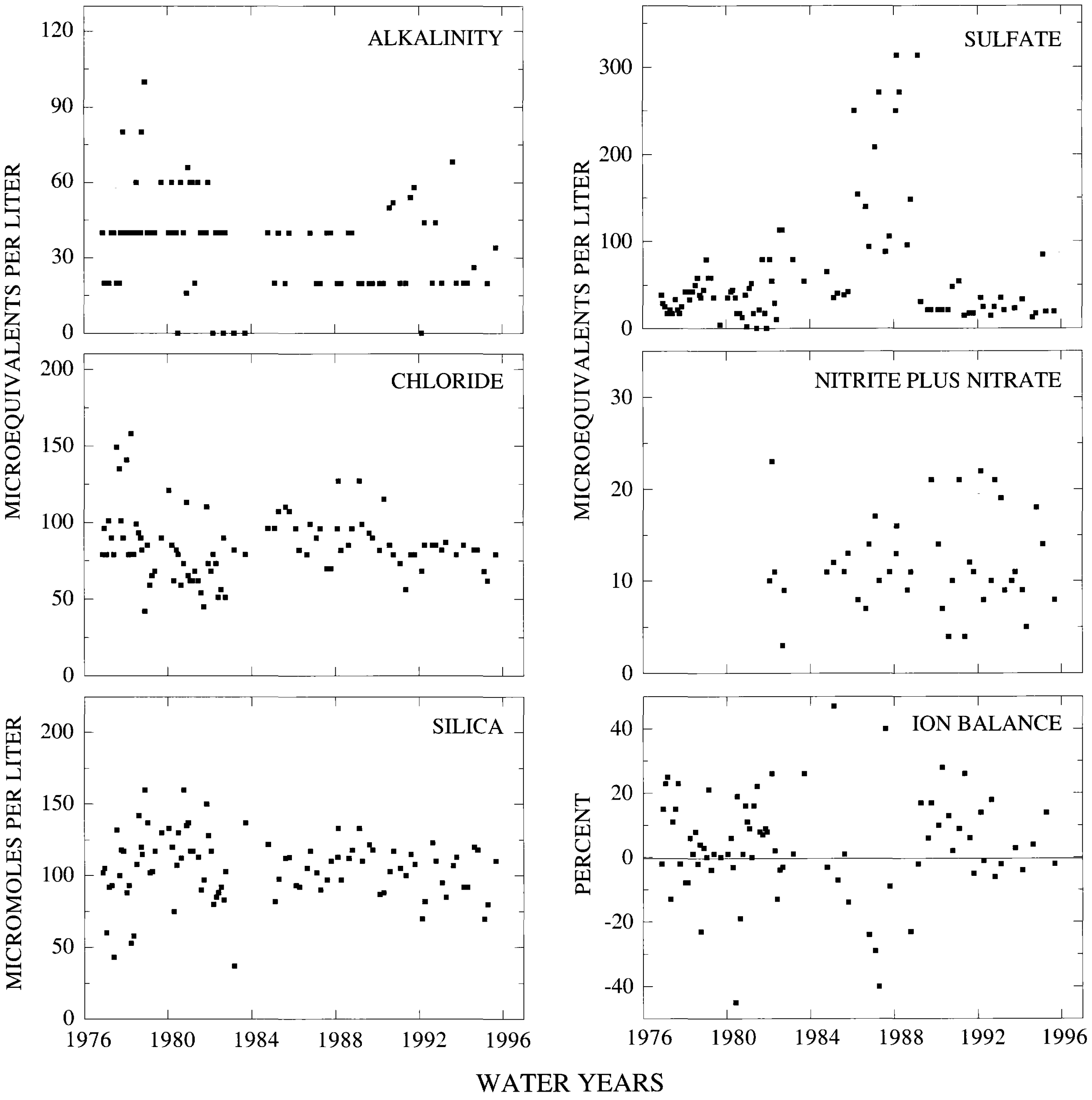

Figure 3. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Blackwater River, Alabama—Continued.

compared to 20 μeq/L in precipitation, which is somewhat smaller than expected, considering the combined effects of evapotranspiration and inputs in dry deposition, which indicates a substantial amount of sulfate is retained in the basin. The retention of sulfate by the basin may be because of sulfate adsorption on soils or, alternatively, sulfate reduction in the large areas of the basin covered by wetlands. The basin also retains most atmospheric nitrogen inputs, based on the smaller concentrations of both nitrate and ammonium in stream water compared to precipitation. In addition, these low stream-water concentrations indicate that upstream agricultural activities have little or no effect on inorganic nitrogen concentrations at the gage.

Table 2. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ion concentrations measured in water-quality samples from Blackwater River, Alabama, November 1976 through September 1995, and volume-weighted mean concentrations in wet precipitation collected at the Quincy Station, Florida

[Concentrations in units of microequivalents per liter, discharge in cubic meters per second, specific conductance in microsiemens per centimeter at 25 degrees Celsius, and silica in micromoles per liter; n, number of stream samples; VWM, volume-weighted mean; inst., instantaneous; spec. cond., specific conductance; <, less than; --, not reported]

Parameter	Stream water						Precipitation
	Minimum	First quartile	Median	Third quartile	Maximum	n	VWM[a]
Discharge, inst.	0.71	1.4	2.4	4.0	25	94	--
Spec. cond., field	15	20	23	27	42	90	--
pH, field	3.5	4.4	4.9	5.5	7.1	93	4.8[b]
Calcium	<5.0	30	36	50	160	94	3.5
Magnesium	<8.0	32	38	41	88	95	2.8
Sodium	30	61	70	78	140	95	11
Potassium	<2.6	5.1	5.1	7.7	26	95	.7
Ammonium	<.7	1.4	1.4	1.4	10.7	45	5.0
Alkalinity, laboratory	<20	<20	40	40	100	86	--
Sulfate	<21	21	35	58	310	92	20
Chloride	42	73	82	96	160	93	12
Nitrite plus nitrate	<.3	7.1	7.1	14	23	49	9.2[c]
Silica	35	89	100	120	160	94	--

[a] Data are volume-weighted mean concentrations for 1983–94.

[b] Laboratory pH.

[c] Nitrate only.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and discharge (table 3). Discharge was poorly correlated with most dissolved constituents, with the exception of weak inverse correlations with alkalinity ($r = -0.437$) and magnesium ($r = -0.442$). Correlations among the solutes also were weak with the exception of a positive correlation between pH and alkalinity ($r = 0.540$). The lack of correlations among most parameters probably is because of the narrow range of solute concentrations measured at this station. The quartz-rich sediments underlying the basin are relatively unreactive and produce dilute soil and ground waters that are not significantly different in composition from the incoming precipitation. Hydrologic characteristics of the basin also may contribute to maintaining a constant stream-water composition. The highly permeable soils result in rapid infiltration of precipitation into the ground-water system, which in turn provides a constant source of stream water throughout the year.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are shown in table 4. Statistically significant downward trends were observed for calcium and sodium at the 0.01 confidence level. Trends in both calcium and sodium were similar for unadjusted and flow-adjusted concentrations, indicating that trends were not driven by variations in stream discharge. The LOWESS curves in figure 3 show that most of the decrease in calcium and sodium occurred around the mid-1980's. As discussed previously, this pattern probably was caused by a change in analytical procedure in 1983. A more detailed examination of the data revealed that calcium and sodium concentrations continued to decrease through the latter part of the record. Calculation of trends for the period 1984 through 1995 showed statistically significant downward trends not only for calcium ($p = 0.005$) and sodium ($p = 0.011$) concentrations, but for magnesium ($p = 0.007$) and chloride ($p = 0.002$) concentrations as well. Because these trends occurred after the change in analytical method, it is possible that they were caused by environmental factors, such as changes in land use or precipitation chemistry. A recent study reported significant downward trends in calcium and magnesium concentrations at many NADP stations in the Southeast between 1980 and 1992 (Lynch and others, 1995). The only substantial change in land use during the period of record was a slight decrease in the amount of agricultural land.

Table 3. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ion concentrations, Blackwater River, Alabama, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; Si, silica]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	−0.503								
Ca	−.277	0.339							
Mg	−.442	.163	0.388						
Na	−.281	.263	.473	0.500					
K	.036	−.053	.211	.347	0.230				
Alk	−.437	.540	.295	.332	.143	0.092			
SO_4	.113	−.372	−.031	.134	.241	.120	−0.293		
Cl	.175	−.375	−.186	−.026	.087	.098	−.368	0.266	
Si	−.182	.264	.314	.342	.328	.314	.182	−.198	0.229

Table 4. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major ion concentrations, Blackwater River, Alabama, November 1976 through September 1995

[Trends in units of microequivalents per liter per year, except discharge in cubic meters per second per year, pH in standard units per year, and silica in micromoles per liter per year; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	0.02	0.454	--	--
pH, field	−.02	.060	−0.02	0.040
Calcium	−1.2	.000	−1.2	.000
Magnesium	<.1	.589	−.1	.490
Sodium	−.9	.000	−1.0	.000
Potassium	<.1	.325	(b)	--
Alkalinity, laboratory	<.1[a]	.029	--	--
Sulfate	−.3	.541	(b)	--
Chloride	−.2	.494	(b)	--
Nitrite plus nitrate[a]	.1	.313	--	--
Silica	−.4	.303	−.2	.375

[a] Calculated using a trend test for censored data.

[b] Flow model not significant at $\alpha = 0.10$.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling of January 15, 1991, are given in table 5; locations of sampling sites are shown in figure 2. Discharge at the gage was 3.7 m^3/s compared to the median daily discharge of 3.8 m^3/s for January (Lawrence, 1987), indicating that the basin was sampled during normal flow conditions for that time of year. Solute concentrations measured at the gage (site 1) during the synoptic sampling were generally between the first- and third-quartile concentrations at the gage during the entire period of record except for magnesium and sulfate, which were both larger than the third-quartile concentrations (table 2). Tributary streams were similar in composition to the gage, with sodium and chloride the dominant ions, and most were acidic (pH 3.82 to 5.37). All but one sample had positive ion balance (−2.1 to 11.5), inferring the presence of unmeasured organic anions. This organic component probably is the source of most stream-water acidity, although some acidity also may be derived from strong acid inputs in precipitation.

The analyses presented in table 5 indicate there was little spatial variability in surface-water chemistry at the time of the synoptic sampling. This invariance probably is because of the unreactive nature of the underlying quartz-rich sediments, which produce dilute soil and ground waters that are not significantly different in composition from the incoming precipitation. The one spatial pattern that does emerge from the data appears to reflect the distribution of landform types in the basin. This can be seen by comparing the chemistry of streams that drain bay areas in the eastern one-half of the basin (sites 7–9) with the chemistry of streams that drain pine hills landscape in the western one-half of the basin (sites 2–6). In general, the bay streams were more acidic and had larger sulfate concentrations and larger charge imbalances than the pine hill streams. These results probably reflect differences in the relative contributions of surface runoff and ground-water discharge to streamflow in these two areas of the basin. Human activities in the basin appeared to have a small but perceptible effect on

Table 5. Physical properties and major ion concentrations from surface-water sampling sites in the Blackwater River Basin, Alabama, collected January 15, 1991

[Site locations shown in fig. 2; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; concentrations in microequivalents; Si, silica in micromoles per liter; <, less than; --, not measured]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria[a]	Remarks
1	02369800	3.68	32	4.52	39	49	74	6	<10	79	93	11	130		
2	310159086425800	.045	32	5.37	50	79	96	16	<10	77	140	13	120	LU	Farming in subbasin
3	310337086440500	--	32	4.41	25	41	74	3	<10	94	90	1	150	LT	Undeveloped, pine hills
4	310556086431000	--	24	4.87	31	38	74	6	<10	60	87	6	120	LU	Some farming
5	310556086431100	.032	29	4.67	16	22	83	2	<10	63	82	1	150	LT	Undeveloped, pine hills
6	310421086411800	.051	16	5.02	13	14	61	10	<10	14	73	<0.7	110	LT	Undeveloped, pine hills
7	310423086400200	.31	35	4.67	49	75	78	10	<10	123	96	4	140	MT, LT	Undeveloped, pine hills
8	310259086382100	.74	62	3.92	49	60	83	5	<10	110	120	8	130	LU, LT	Drains large wetland area
9	310533086365700	.16	63	3.82	31	54	91	4	<10	170	87	<0.7	16	LT	Drains large wetland area

[a] Criteria used in selection of sampling sites: LT = landform type, MT = major tributary, LU = land use.

surface-water chemistry during the sampling period. For example, the subbasins with agriculture or residential development, such as Fish Trap Branch (site 2) and Blackwater Creek near Falco (site 8), had elevated concentrations of chloride compared to streams that drain relatively undisturbed subbasins (sites 3, 5, 6, 7, and 9). Nitrate concentrations were very low at all sampling sites but also were slightly elevated in Fish Trap Branch (site 2) and Blackwater Creek near Falco (site 8).

Sipsey Fork near Grayson, Alabama (Station 02450250)

Site Characteristics and Land Use

The Sipsey Fork HBN Basin lies in the Cumberland Plateau section of the Appalachian Plateaus physiographic province in northwestern Alabama (fig. 4). The topography is characterized by a gently rolling plateau that is dissected by a well-developed drainage pattern with canyonlike bluffs and narrow flood plains. The Sipsey Fork drains 239 km^2 of this deeply dissected terrain and ranges in elevation from 165 to 325 m. The USGS gaging station is 7.2 km west of Grayson, Ala., at latitude 34°17'07" and longitude 87°23'56". Sipsey Fork is a southeast-flowing tributary of the Black Warrior River with a channel length of 17 km upstream from the gage and an average stream gradient of 5.3 m/km. The main channel is perennial, and mean monthly discharge is strongly seasonal, varying from 0.52 m^3/s in August to 10.7 m^3/s in March. Average annual runoff from the basin was 62 cm for the period 1967 through 1995 (U.S. Geological Survey, Water Resources Data, Alabama). A distinguishing hydrologic characteristic of the Sipsey Fork is its rapid flow response to precipitation events. This rapid response is the result of a combination of basin characteristics including steep topography, deeply incised stream channels, and shallow soils (U.S. Department of Agriculture, 1988). Climate of the area is characterized by long, moderately hot summers and short, mild winters (Smalley, 1979). Average monthly temperatures range from 5°C in January to 25.5°C in July, and the area has an average frost-free period of 220 days per year. Average annual precipitation is 145 cm, which is fairly evenly distributed throughout the year; March is the wettest month and October the driest (Smalley, 1979). Snowfall seldom exceeds a few centimeters and usually melts within a few days.

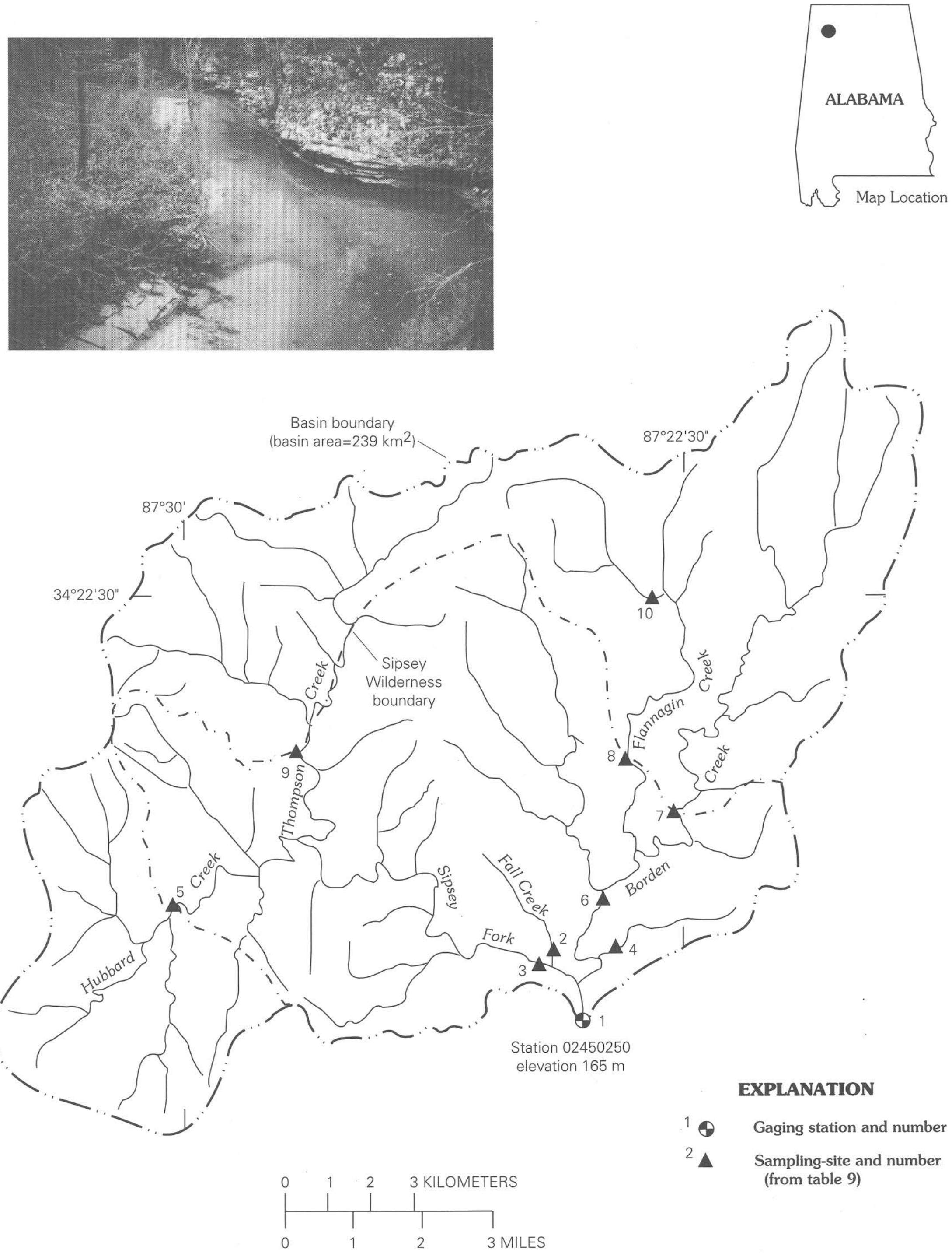

Figure 4. Map showing study area in the Sipsey Fork Basin and photograph of the stream channel near the gage.

The Sipsey Fork Basin is at the northern extent of the Southern Mixed Forest ecoregion (Bailey and others, 1994) and supports a wide diversity of plant communities and species because of the variety of landforms, soils, and moisture conditions found in the area (U.S. Department of Agriculture, 1988). Dry ridgetop sites and uplands are covered by hardwood and pine forest types dominated by white oak, chestnut oak, blackgum, hickories, shortleaf pine, Virginia pine, and southern red oak. Understory species include sassafras, huckleberry, big leaf magnolia, dogwood, and persimmon. The cool and moist conditions in the cove and canyon areas provide suitable habitat for Appalachian flora. Common overstory species in these areas are hemlock, yellow poplar, river birch, red maple, beech, and white oak. Understory species include oak-leaf hydrangea, big leaf magnolia, viburnum, dogwood, and box elder. Most soils in the area are highly leached Ultisols belonging to the Montevallo-Enders-Townley soil association (Harkins, 1981). Soils in the southern and northwestern part of the basin are primarily shaley silt loams that have developed in sandstone and shale of the Pottsville Formation. They tend to be deep and moderately permeable and contribute to sustaining streamflow during dry periods in late summer. In contrast, soils in the northeastern part of the basin are developed primarily in limestone and tend to be thin and rocky. These soils are significantly less permeable than soils elsewhere in the basin and are one cause for the flashy behavior of the stream during storm events (U.S. Department of Agriculture, 1988).

Bedrock in the basin consists of gently dipping, marine, sedimentary rocks of Late Mississippian and Early Pennsylvanian age (Schweinfurth and others, 1981). The oldest unit is the Bangor Limestone, which principally crops out along drainages in the northeastern part of the drainage basin. The unit is described as a white to light gray limestone having several zones of interbedded shale and claystone. Overlying the Bangor Limestone are the Parkwood and Pottsville Formations, which crop out in the northwest and central sections of the basin. The Parkwood Formation consists of interbedded sandstone, shale, mudstone, siltstone, claystone, and carbonaceous shale and contains several thin but nonpersistent coal beds. The Pottsville Formation consists of a cliff-forming, coarse-grained, pebbly sandstone separated by interbedded layers of shale and fine-grained sandstone.

The Sipsey Fork Basin drains parts of Lawrence and Winston Counties in northwestern Alabama and is entirely in the boundaries of the William B. Bankhead National Forest. Almost 40 percent of the National Forest land is in the Sipsey Wilderness, and 72 km of the river corridor including the Borden Creek tributaries are designated components of the National Wild and Scenic River System. The entire basin also is in the boundaries of the Black Warrior Wildlife Management Area, which is under the jurisdiction of the Alabama State Division of Game and Fish. Private holdings, which account for about 9 percent of the land, tend to be concentrated along the northern and western basin boundaries. Nonwilderness areas of the basin are accessible by way of several gravel and paved roads. The wilderness is almost entirely encircled by roads, although access into the interior is limited to foot trails. The lower section of river is generally floatable by canoe for between 20 and 60 days each spring.

Most forests in the basin were logged at some time during the past century, although small patches of virgin timber still remain in inaccessible canyons where farming and logging are impractical. Natural occurrences also have left their mark on the forest communities during the past century, including the southern pine beetle infestation, American chestnut blight, fires, and tornadoes. Since the establishment of the HBN station, land-use activities in the basin have been limited primarily to timber production and recreation. Logging occurs in nonwilderness areas of the basin in small clearcut and thinning operations on a 60-year rotation for pines and a 100-year rotation for hardwoods. About 500 ha of forest land was harvested in the basin from 1992 through 1995 in plots that ranged from 4 to 84 ha in size (James Ramey, Forest Service, written commun., 1996). The Sipsey Wilderness was established in 1975 and is used primarily for back-country recreation, averaging more than 10,000 visitors per year. The management objective for the wilderness is to maintain the system of natural processes that governs the distribution of plant communities and to allow these natural processes to operate freely. Guidelines for managing components of the Wild and Scenic River System include maintaining the existing free-flowing character of the river, preventing degradation of existing water quality, and preserving natural scenic values. The only recreational facility in the basin is a picnic area near the gage. The Forest Service has operated an aerosol sampler in the basin since 1989 as part of an interagency network to monitor visibility in National Parks and Wilderness Areas (Sisler, 1996).

Historical Water-Quality Data and Time-Series Trends

The HBN data set analyzed for this report includes 160 water-quality samples that were collected from November 1967 through September 1995. Sampling frequency was monthly from 1968 through 1970, bimonthly from 1971 through 1982, and quarterly from 1983 through 1995. Although not documented, samples in the early part of the record probably were analyzed at a USGS laboratory in Tuscaloosa, Ala., which was operated until 1973 (Durum, 1978). After the establishment of the Central Laboratory System, samples were analyzed at the Central Laboratory in Atlanta, Ga., from 1973 through 1985 and at the NWQL in Arvada, Colo., from 1986 through 1995. Daily discharge records for Sipsey Fork (station 02450250) are available beginning in October 1966. A precipitation gage was operated for several years in the basin, but the data were not published.

Calculated ion balances for 117 samples with complete major ion analyses are shown in figure 5. Ion balances ranged from −30 to +11 percent, and more than 95 percent of the samples had calculated values within the ±10 percent range, indicating that the analyses are of high quality. The mean charge balance of all samples was −1.2 percent, indicating that the measured cations nearly balanced with the measured anions in these waters. Time-series plots of the major dissolved constituents were inspected for evidence of method-related effects (fig. 5). For example, sulfate concentrations were slightly elevated during the period 1983 through 1988. This pattern coincides with the use of a turbidimetric titration for sulfate analysis at the NWQL between March 1986 and December 1989 (Fishman and others, 1994). In 1989, the NWQL determined that sulfate concentrations can be overestimated by this technique and changed the method to ion chromatography in 1990 (Office of Water Quality Technical Memorandum No. 90.04, *Turbidimetric Sulfate Method*, issued December 21, 1989, at URL http://water.usgs.gov/public/admin/memo/). The bias was most pronounced in dilute waters, although it was not consistent among samples and appeared to be influenced by factors such as color and turbidity (Schertz and others, 1994). The time-series plot of calculated ion balances shows a distinct shift to more negative values around 1983. Although the exact cause of the shift could not be identified, it was coincident with a network-wide change in the analytical procedure for cations and metals from AA spectroscopy to ICP spectroscopy in 1983 (Office of Water Quality Technical Memorandum No. 82.18, *National Water-Quality Networks*, issued September 28, 1982, at URL http://water.usgs.gov/public/admin/memo/).

Median concentrations and ranges of major constituents in stream water collected at the HBN gaging station and VWM concentrations in wet-only precipitation measured at the NADP site at Sand Mountain Experimental Station about 120 km east of the basin are presented in table 6. Wet-precipitation chemistry at the NADP station is dilute and acidic with a VWM pH of 4.6 during the 11 years of record. The dominant cations in precipitation were hydrogen and ammonium, which accounted for 51 percent and 25 percent of the total cation charge, respectively. Sulfate was the dominant anion, contributing 64 percent of the total anions, whereas nitrate and chloride contributed 23 and 12 percent, respectively. The low pH and predominance of strong acid anions indicate that precipitation at the nearby NADP station probably is affected by anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain.

Stream water in the Sipsey Fork is moderately concentrated and well buffered; specific conductances ranged from 9 to 136 µS/cm and alkalinities generally were between 500 and 780 µeq/L. The dominant ions in stream water were calcium and alkalinity, which are produced by weathering of carbonates in the underlying limestone. The median chloride concentration in stream water was 39 µeq/L, which is about six times larger than the VWM concentrations of 6.2 µeq/L in precipitation. On the basis of the difference between average annual runoff and precipitation, evapotranspiration can account for roughly a twofold increase in the chloride concentration of precipitation. This difference indicates that some stream-water chloride may be derived from sources other than wet deposition, such as salt in the underlying sedimentary rocks or possibly dry deposition of marine aerosols. The median concentration of sulfate in stream water was 83 µeq/L compared to 33 µeq/L in precipitation. Concentration by evapotranspiration and additional inputs from dry deposition can account for most of this difference, indicating that sulfate behaves relatively conservatively in the basin. Biomass appears

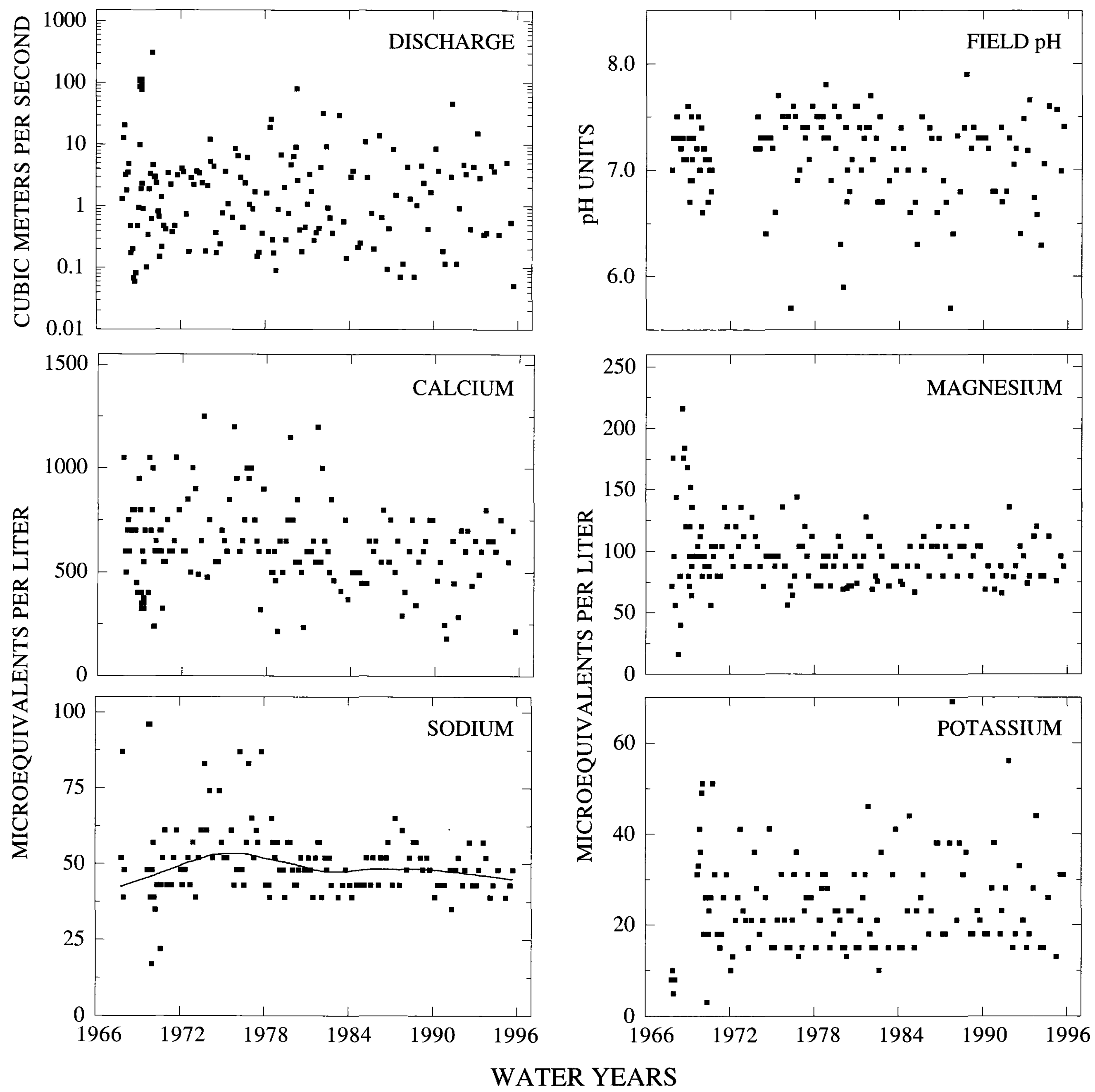

Figure 5. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Sipsey Fork, Alabama.

to be an important sink for nitrogen species based on the smaller concentrations of both nitrate and ammonium in stream water compared to precipitation.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 7). Most solutes were weakly correlated with discharge with the exception of potassium (rho = –0.753). Among the solutes, only calcium and alkalinity were strongly correlated (rho = 0.910). The strong correlation between potassium and discharge is somewhat difficult to explain. Potassium is a common constituent of marine clays and may be released from the weathering of clay-rich units in the Pottsville Formation. The strong correlation between calcium and alkalinity clearly reflects the weathering of limestone, but the lack of correlation with discharge was somewhat unexpected. A more detailed examination of the data revealed that calcium

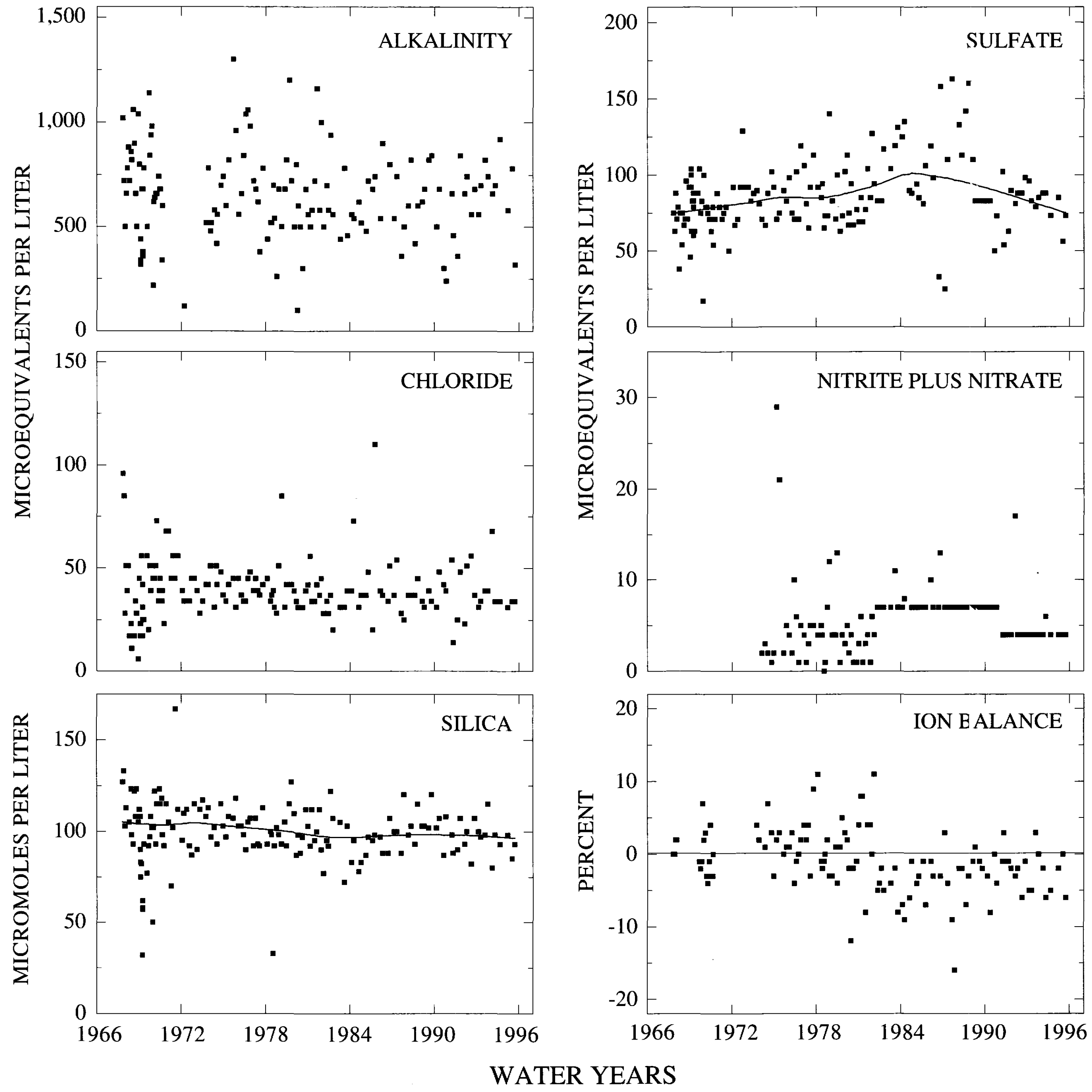

Figure 5. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Sipsey Fork, Alabama—Continued.

and alkalinity were in fact correlated with flow, but the pattern was more complex. Instead of the more common monotonic relation, calcium and alkalinity concentrations were highest around 0.6 m^3/s and decreased with both decreasing flows below this level and increasing flows above this level. Differences in soil characteristics in the basin may provide at least one explanation for this observed pattern in stream chemistry. The highly permeable soils in the southern and northwestern parts of the basin are the dominant source of streamflow during dry periods in late summer. Because these soils are formed in sandstones and shales, they produce dilute waters, which may explain the decrease in calcium and alkalinity concentrations when flows are less than 0.6 m^3/s. During wetter

Table 6. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ion concentrations measured in water-quality samples from Sipsey Fork, Alabama, November 1967 through September 1995, and volume-weighted mean concentrations in wet precipitation collected at the Sand Mountain Experimental Station, Alabama

[Concentrations in units of microequivalents per liter, discharge in cubic meters per second, specific conductance in microsiemens per centimeter at 25 degrees Celsius, pH in standard units, and silica in micromoles per liter; n, number of stream samples; VWM, volume-weighted mean; inst., instantaneous; spec. cond., specific conductance; <, less than; --, not reported]

Parameter	Stream water						Precipitation VWM[a]
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge, inst.	0.05	0.37	1.6	4.1	310	160	--
Spec. cond., field	9.3	66	80	92	136	145	--
pH, field	5.7	7.0	7.2	7.4	7.9	144	4.6[b]
Calcium	180	500	600	750	1,250	156	3.5
Magnesium	16	80	96	100	220	156	1.7
Sodium	<17	43	48	57	96	135	5.5
Potassium	2.6	17	23	31	69	135	.7
Ammonium	<14	<14	<14	29	310	60	12
Alkalinity, laboratory	100	500	660	780	1,300	144	--
Sulfate	17	71	83	95	160	156	33
Chloride	5.6	31	39	45	110	158	6.2
Nitrite plus nitrate	<3.6	<3.6	<7.1	<7.1	29	99	12[c]
Silica	6.5	89	95	110	170	155	--

[a] Data are volume-weighted mean concentrations for 1984–94.

[b] Laboratory pH.

[c] Nitrate only.

Table 7. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ion concentrations, Sipsey Fork, Alabama, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; Si, silica]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	0.094								
Ca	.203	0.294							
Mg	–.486	.169	0.490						
Na	–.356	.071	.323	0.643					
K	–.753	–.191	–.126	.604	0.367				
Alk	.050	.288	.910	.609	.347	0.011			
SO_4	.050	.035	.060	.220	.171	.096	0.050		
Cl	–.044	.033	.267	.263	.394	.051	.222	0.208	
Si	.007	.109	.156	.287	.356	.128	.175	.000	0.118

periods of the year, soils in the northeast section of the basin begin to contribute a greater proportion of streamflow. Because these soils are formed in limestone, they produce higher alkalinity waters than the sandstones, which causes a positive relation between discharge and calcium and alkalinity concentrations for flows below 0.6 m^3/s. At flows above 0.6 m^3/s, the concentrations of both constituents were inversely related to discharge, probably because of dilution.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents from 1967 through 1995 are shown in table 8. Statistically significant trends were detected in sodium, sulfate, and silica concentrations at the 0.01 confidence level. Trends in the flow-adjusted sodium and silica concentrations were similar to the unadjusted concentrations, indicating that the trends were not caused by variations in stream discharge. The trend in flow-adjusted sulfate concentrations was not calculated because the flow model was not significant at the 0.1 confidence level. The LOWESS curve in figure 5 shows a pattern of increasing sulfate concentrations until the mid-1980's, followed by a slight decrease in concentration in the 1990's. One possible explanation for the trend in stream-water sulfate is a change in atmospheric deposition. Estimates of sulfate deposition in the Southeast indicate that deposition increased significantly between 1960 and 1980 (Husar and others, 1991). Lynch and others (1995) have found that sulfate concentrations at NADP stations in the Southeast have been declining since 1980. Although the pattern in stream-water sulfate appears to mimic the temporal trend in atmospheric deposition, sulfate concentrations during the late 1980's may have been biased by the analytical procedure, thus complicating the interpretation of sulfate trends at this station. The LOWESS curves for sodium and silica indicate that most of the change in concentrations occurred during the early part of the record and concentrations have been fairly stable since the 1980's. Declines in stream-water sodium and silica probably cannot be attributed to increases in acidic deposition. A more plausible cause of the trends in sodium and silica may be a change in land use. Although most of the basin is now designated as wilderness, these areas of the basin may have been subjected to logging prior to establishment of the wilderness in 1975.

Table 8. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major ion concentrations, Sipsey Fork, Alabama, November 1967 through September 1995

[Trends in units of microequivalents per liter per year, except discharge in cubic meters per second per year, pH in standard units per year, and silica in micromoles per liter per year; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	<0.01	0.693	--	--
pH, field	–.01	.172	–0.01	0.216
Calcium	–3.3	.026	–3.6	.025
Magnesium	<.1	.603	<.1	.853
Sodium	–.2	.006	–.2	.014
Potassium	<.1	.465	<.1	.516
Alkalinity, laboratory	1.0	.524	1.6	.354
Sulfate	.6	.002	([a])	--
Chloride	<.1	.449	<.1	.685
Nitrite plus nitrate[b]	([b])	--	--	--
Silica	–.4	.005	–.3	.005

[a]Flow model not significant at $\alpha = 0.10$.

[b]Insufficient data to calculate trend.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling conducted December 6 and 7, 1990, are shown in table 9; location of sampling sites in the basin are shown in figure 4. During the synoptic sampling, discharge at the gage was 0.8 m^3/s compared to the median daily discharge of 2.5 m^3/s for December (Lawrence, 1987), indicating that the basin was sampled during low-flow conditions for that time of year. Concentrations measured at the gage (site 1) during the synoptic sampling were generally within the median to third-quartile range measured at the gage during the entire period of record (table 6). The tributary streams spanned a wide range of concentrations that bracketed the concentrations at the gage. For example, the alkalinity at the gage was 760 μeq/L, whereas the alkalinities of the tributaries ranged from 46 μeq/L at site 4 to 2,440 μeq/L at site 8. A similar pattern is apparent for calcium, which ranged from 65 μeq/L at site 4 to 2,600 μeq/L at site 8. Ion balances for the synoptic samples ranged from –1.1 to 3.8 percent, indicating that organic anions did not contribute significantly to the ionic content of stream water during the sampling period.

The wide range of solute concentrations measured during the synoptic sampling can be explained by the distribution of different bedrock types in the basin. For example, the tributaries with the highest alkalinity concentrations (sites 6–10) drain areas of the basin underlain by limestone, whereas sites with low alkalinities (sites 2–5) drain areas underlain primarily by sandstone and shale. Calcium and magnesium had the same relationship with rock type, with waters that drain limestone having significantly larger concentrations of calcium and magnesium than those that drain areas of sandstone and shale. A similar relationship between stream chemistry and geology was observed by Ward (1992) in a longitudinal survey of the water chemistry in the Sipsey Fork Basin conducted in June 1991. Controls on spatial variability in the other solutes are more difficult to discern. Sodium and silica concentrations were very uniform among the sites and did not appear to reflect the distribution of bedrock types. Both sulfate and chloride were slightly elevated in streams that drain limestone (sites 6–10) compared to those that drain sandstone (sites 2–5). Because it is unlikely that atmospheric deposition rates would differ significantly between the tributary basins, these results suggest that small amounts of chloride and sulfate may be released by the limestone bedrock. Nitrate concentrations in all

Table 9. Physical properties and major ion concentrations from surface-water sampling sites in the Sipsey Fork Basin, Alabama, collected December 6–7, 1990

[Site locations shown in fig. 4; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; concentrations in microequivalents; Si, silica in micromoles per liter; <, less than; --, not measured]

Site	Site name	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria[a]	Remarks
1	02450250	0.79	98	7.61	750	110	48	25	760	140	51	8.6	98		
2	341750087242300	.008	35	6.43	110	80	52	26	48	180	39	<.7	120	LU, BG	Wilderness, sandstone
3	341750087242500	.45	43	7.06	240	88	48	26	220	100	48	9.3	100	MT, BG	Mostly sandstone
4	341754087234200	.011	25	6.26	65	74	39	24	46	120	39	<.7	110	BG	Sandstone only
5	341826087301200	.18	29	6.67	80	69	48	26	61	92	54	19	93	BG, LU	Sandstone, some development
6	341947087223700	.15	210	7.95	2,100	160	52	21	1,970	200	70	7.1	100	MT, BG	Limestone bedrock
7	341834087234000	.25	230	8.08	2,300	170	57	21	2,080	230	100	14	97	BG, LU	Limestone, some development
8	342019087231700	.045	260	8.06	2,600	200	52	19	2,440	230	100	7.1	98	BG	Limestone
9	342027087281600	.057	100	7.60	800	120	57	25	830	120	45	<.7	98	BG	Mixed lithology
10	342224087225300	.014	240	7.72	2,400	220	61	20	2,240	230	110	14	110	BG, LU	Limestone, some development

[a] Criteria used in selection of sampling sites: BG = bedrock geology, MT = major tributary, LU = land use.

tributaries were very low, although tributaries that drain nonwilderness areas of the basin (sites 5, 7, and 10) had slightly larger nitrate concentrations than streams that drain the wilderness area (sites 2 and 4). The nonwilderness tributaries have slightly more human activity (logging, rural residences) in their basins that could contribute small amounts of nitrate to stream water. Ward (1992) reported relatively high nitrate concentrations in Hubbard Creek that were attributed to logging activity upstream from the sampling site. However, Ward (1992) also reported relatively high nitrate concentrations for the Bee Branch tributary despite the fact that this tributary drains an area entirely in the wilderness boundary.

Sopchoppy River near Sopchoppy, Florida (Station 02327100)

Site Characteristics and Land Use

The Sopchoppy River HBN Basin is in the Apalachicola Coastal Lowlands section of the Coastal Plain physiographic province in the Panhandle of Florida (fig. 6). The Sopchoppy River drains 265 km^2 of flat, sandy terrain with shallow, swamplike areas and poorly defined drainages that range in elevation from 3.0 to 34 m. The USGS gaging station is 7.5 km north of Sopchoppy, Fla., at latitude 30°07'45" and longitude 84°29'40". The Sopchoppy River originates at the confluence of several small creeks in the northern part of the basin then flows south through a narrow, incised valley before reaching the gage. The channel length of the incised section is about 15 km and the stream gradient in this reach ranges from 0.6 to 0.8 m/km. The main channel is perennial, and discharge generally peaks twice annually, once in January and February when evapotranspiration rates are low and again in July and August when precipitation is heaviest. Mean monthly discharge ranges from 1.8 m^3/s in November to 8.8 m^3/s in February and 8.9 m^3/s in August. Average annual runoff from the basin was 67 cm from 1964 through 1995 (U.S. Geological Survey, Water Resources Data, Florida). A distinguishing hydrologic characteristic of the river is its rapid response to precipitation events because of surface runoff from the large areas of the basin covered by wetlands (U.S. Department of Agriculture, 1995). Climate of the area is characterized by warm, humid summers and short, mild winters. Air temperatures are moderated by the Gulf of Mexico, and average monthly air temperatures range from 12.2°C in January to 27.4°C in July.

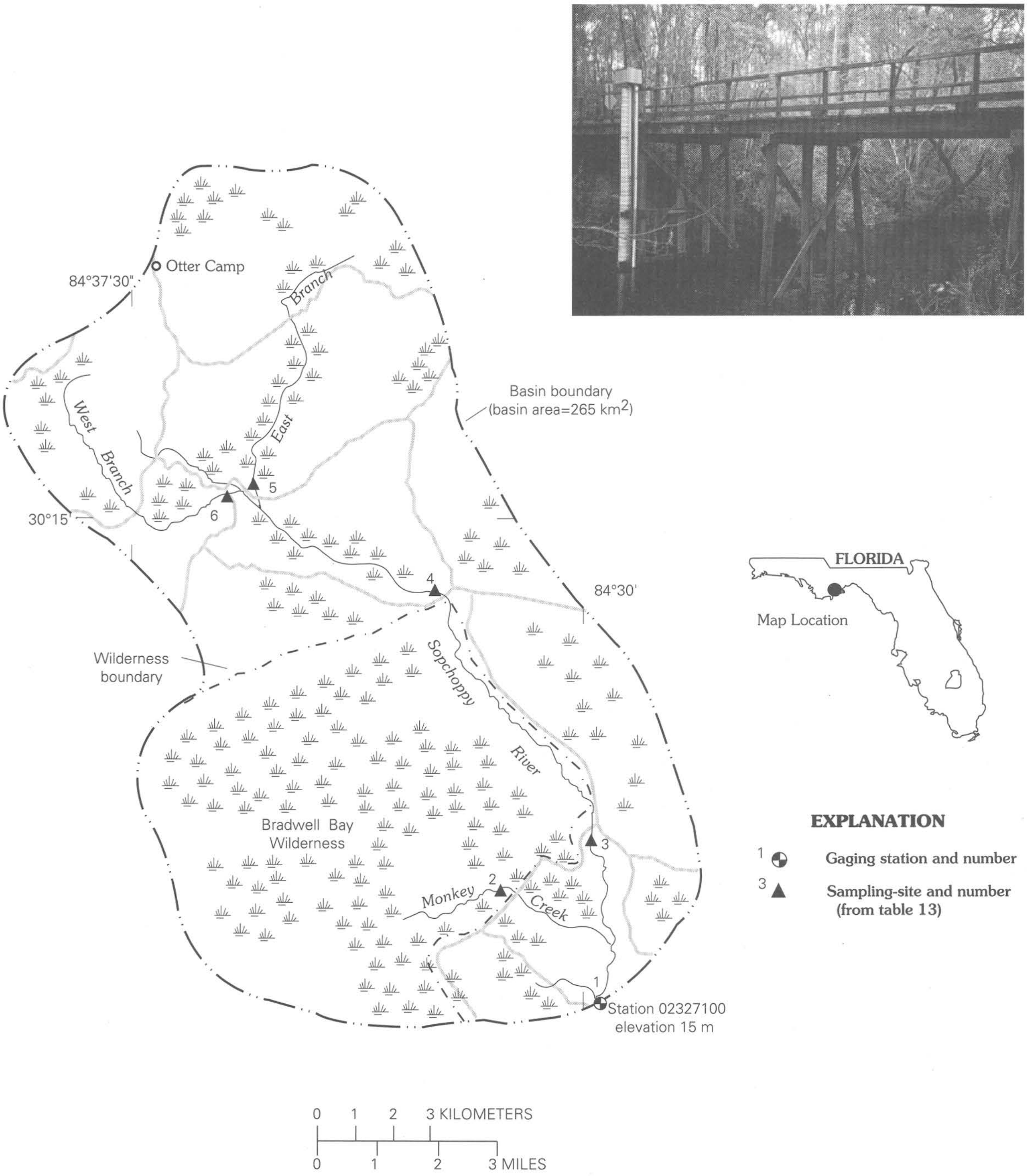

Figure 6. Map showing study area in the Sopchoppy River Basin and photograph of the stream channel at the gage.

Precipitation averages 145 cm annually and is heaviest from June through September when rain can fall as frequently as every other day (Allen, 1991).

The basin lies in the Outer Coastal Plain Mixed Forest ecoregion (Bailey and others, 1994), and the dominant vegetation communities are pine-palmetto flatwood, titi swamp, and bay swamp (Clewell, 1981). The pine-palmetto flatwoods grow in flat, sandy areas were the ground is saturated to the surface only during periods of rain. The dominant species are slash pine and longleaf pine with a ground cover of wire grass and saw palmetto. The titi swamp community, which covers most of Bradwell Bay, is a tangle of shrubs and small trees including black titi, fetterbush, swamp Cyrillas, and little-leaf Cyrillas. The bay swamp community grows in swampy depressions scattered among the flatwoods. The dominant species is sweet bay with a ground cover of sphagnum moss. Soils in the basin are classified as Ultisols and are mapped in the Leon-Scranton-Rutlege and Croatan-Dorovan soil associations (Allen, 1991). The Leon-Scranton-Rutlege association includes soils developed in sandy marine sediments underlying broad flatwoods areas (Allen, 1991). These soils are composed almost entirely of sand, are very poorly drained, and have an organic-stained subsoil. In areas dominated by these soils, the water table is typically 25 to 100 cm below the land surface. The clay mineralogy is dominated by smectite, a 14Å intergrade mineral, and kaolinite. Soils belonging to the Croatan-Dorovan association are found in swamps and depressions, including the entire Bradwell Bay, where the water table is at or above the soil surface 5 to 8 months of the year (Allen, 1991). A typical soil profile has a surface layer of dark, well-decomposed organic matter overlying a subsoil of dark sand and clay.

The basin is underlain by flat-lying limestone of the Miocene St. Marks Formation, which crops out along the bed and bank of the Sopchoppy River in the southern one-half of the basin (Rupert and Spencer, 1988). The St. Marks Formation is described as a cream-colored, partly recrystallized limestone that is in places slightly dolomitic and stained with limonite (Cameron and others, 1977). The St. Marks Formation comprises the upper portion of the Floridan aquifer system that is the source of most domestic water in Wakulla County. In most areas of the basin, the limestones are covered by 6 to 9 m of unconsolidated marine sediments of Pleistocene and Holocene age. These surficial deposits are composed of quartz sand, silt, clay, muck, and peat and have been mapped in detail by Cameron and others (1977).

The Sopchoppy River Basin drains the western part of Wakulla County and is entirely in the boundaries of the Apalachicola National Forest. The Bradwell Bay Wilderness encompasses 89 km^2 of National Forest land on the west side of the river. Two small parcels of private land, totaling less than 500 ha, also lie in the National Forest boundary. Nonwilderness areas of the basin are accessible by several forest roads; however, the poorly drained soils in the area may limit vehicle access during wet periods of the year. Access to the wilderness is limited to roads around the perimeter and foot trails in the interior. During all but the driest times of the year, the river is navigable by small boat downstream from the wilderness boundary. Boat travel upstream from the wilderness boundary is more difficult because of swampy and densely vegetated conditions along the river.

Land-use activities in the Apalachicola National Forest are related to timber harvest and prescribed burning, which are conducted primarily for the management of wildlife habitat rather than the commercial value of the timber (John Cameron, Forest Service, written commun., 1996). Timber harvests are conducted on a 60-year rotation in small patches that average 20 ha in size. Swamps and lowlands along the river corridor are considered unsuitable for cutting, and logging is generally restricted to drier upland areas. The Apalachicola National Forest is currently in the process of revising its Land and Resource Management Plan (John Cameron, written commun., 1996). Under the revised plan, the rotation lengths for timber harvesting will increase to 120 years for longleaf pine and 100 years for slash pine. Prescribed burning is conducted on 3-year cycles to maintain a fire climax forest system. The basin is in an area that has frequent lightning strikes; as a consequence, many species of plants and animals have adapted to fire as the primary force driving forest succession. The most substantial change in land use that has occurred since the establishment of the HBN station was the creation of the Bradwell Bay Wilderness in 1975—one of the first wilderness areas established in the Eastern United States. All segments of the river corridor in the HBN basin have been recommended by the Forest Service for inclusion in the National Wild and Scenic River System, but designation is still pending.

Historical Water-Quality Data and Time-Series Trends

The HBN data set analyzed for this report includes 252 water-quality samples that were collected from April 1964 through August 1995. Sampling frequency progressively increased from 2 samplings in 1965 to 10 in 1968. Sampling frequency was monthly from 1969 through 1982 and quarterly from 1983 through 1995. Although not documented, water-quality samples in the early part of the record probably were analyzed at a USGS laboratory in Ocala, Fla. (Durum, 1978). After establishment of the Central Laboratory System, samples were analyzed at the Central Laboratory in Atlanta, Ga., from 1973 through 1985 and at the NWQL in Arvada, Colo., from 1986 through 1995. Daily discharge records for the Sopchoppy River (station 02327100) are available beginning in June 1964. The gage was operated as a crest stage station from 1961 through 1964. Records of daily water temperature at the gage are available from June 1964 through September 1979. Daily water-level measurements are available for a ground-water well located 200 m east of the gage (station 300740084293001) from January 1967 through September 1986. Daily precipitation amount has been measured at two locations—the gage and Otter Camp (station 301830084370001)—since February 1966.

Calculated ion balances for 230 samples with complete major ion analyses are shown in figure 7. Ion balances ranged from –54 to +46 percent, and only 55 percent of the samples had calculated values within the ±10 percent range. This wide range of values reflects the difficulty in making precise analytical measurements at the low solute concentrations typical of this station. The mean charge balance of all samples was 6.8 percent, indicating that the samples had an excess of measured cations over anions. Because the Sopchoppy River is considered a black-water river, deriving the tealike color of its water from dissolved organic matter, the observed anion deficit can be explained by the presence of unmeasured organic anions.

Time-series plots of the major dissolved constituents were inspected for evidence of method-related effects (fig. 7). Several patterns are evident in the sulfate records. The unusually high sulfate concentrations reported in the 1980's are coincident with the use of a turbidimetric titration for sulfate analyses at the NWQL between March 1986 and December 1989 (Fishman and others, 1994). In 1989, the NWQL determined that sulfate concentrations can be overestimated by this technique and changed the method to ion chromatography in 1990 (Office of Water Quality Technical Memorandum No. 90.04, *Turbidimetric Sulfate Method*, issued December 21, 1989, at URL http://water.usgs.gov/public/admin/memo/). The bias was most pronounced in dilute waters, although it was not consistent among samples and appeared to be influenced by factors such as color and turbidity (Schertz and others, 1994). Assuming ion chromatography produced unbiased sulfate concentrations, these results indicate that analytical methods used prior to 1967 and between 1973 and 1983 also may have introduced a positive bias. As with the turbidimetric technique, these earlier methods may have been susceptible to color interferences caused by the high organic content of stream water at this station.

Median concentrations and ranges of major dissolved constituents in stream water collected at the HBN gaging station and VWM concentrations in precipitation measured at the Quincy NADP site about 25 km north of the basin are presented in table 10. Precipitation chemistry at the NADP station is dilute and slightly acidic with a VWM pH of 4.8 during the 11 years of record. The dominant cations in precipitation were hydrogen, which contributed 41 percent of the total cation charge, and sodium and ammonium, which contributed 28 and 13 percent, respectively. Sulfate was the dominant anion, accounting for 49 percent of the anion charge, and chloride and nitrate accounted for 29 and 22 percent, respectively. These results indicate that precipitation at the nearby NADP station probably is a mixture of both strong acids derived from anthropogenic emissions of sulfur and nitrogen compounds and salt derived from marine aerosols (Fu and Winchester, 1994).

Stream water in the Sopchoppy River has a bimodal chemical composition that is strongly related to stream discharge. For example, at flows below 0.28 m^3/s (25 percent of samples), the average specific conductance is 180 µS/cm, but for flows above 0.28 m^3/s, the average specific conductance drops to only 45 µS/cm. A similar bimodal pattern also is observed for pH, calcium, magnesium, and alkalinity as shown in figure 7. The predominance of calcium, magnesium, and alkalinity at flows below 0.28 m^3/s indicates that ground water from limestones of the underlying St. Marks Formation is the dominant source of streamflow under base-flow conditions. In contrast, hydrogen, sodium, chloride, and sulfate are typically the dominant ions at higher flows. Under

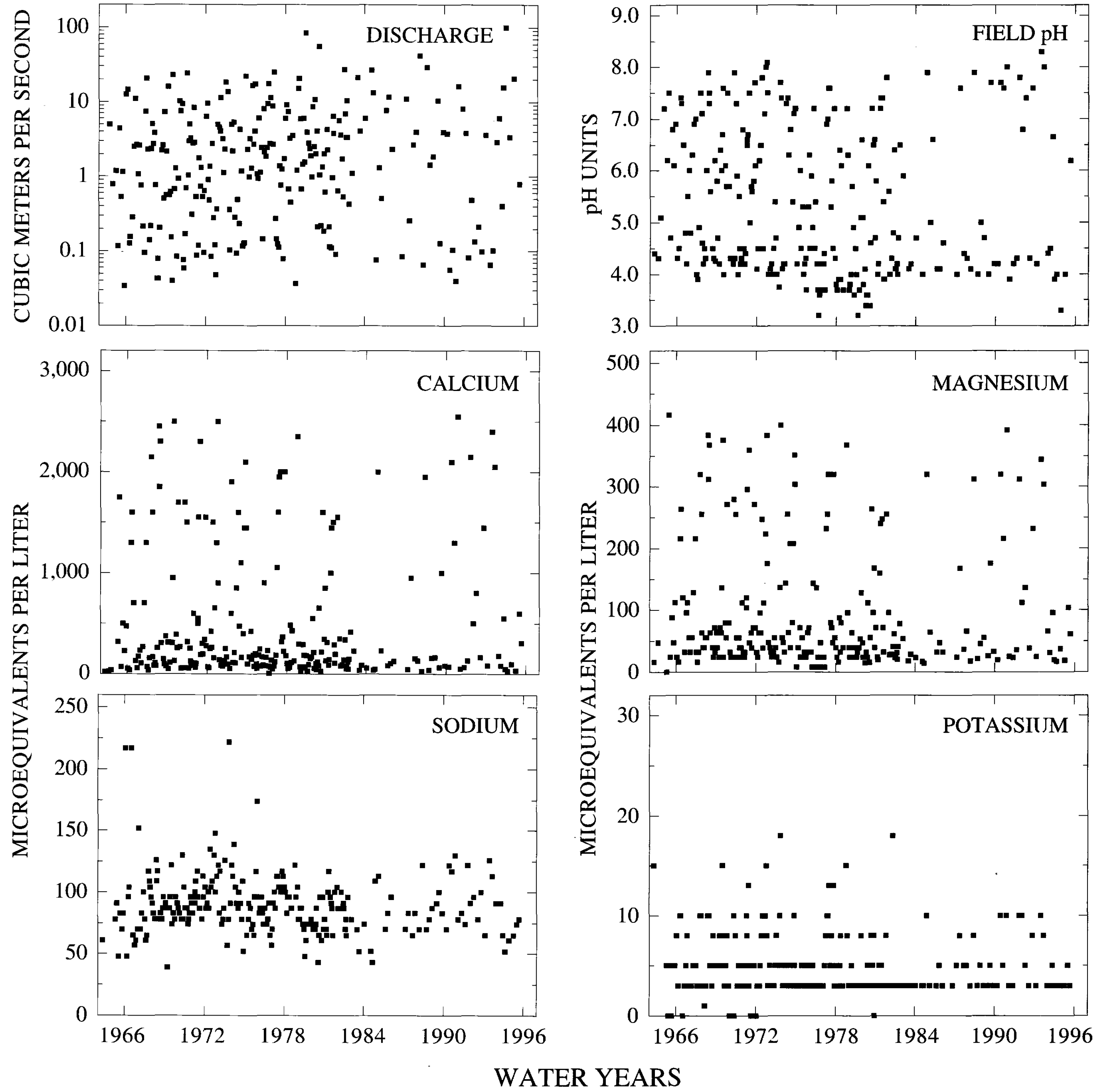

Figure 7. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Sopchoppy River, Florida.

these hydrologic conditions, the chemistry of stream water is more similar to the composition of precipitation, which reflects surface runoff from large wetland areas in the basin. The median chloride concentration in stream water was 130 µeq/L, which is nine times larger than the VWM concentration of 12 µeq/L in wet precipitation. On the basis of the difference between average annual runoff and precipitation, evapotranspiration can account for about a twofold increase in the chloride concentration of precipitation, indicating that a considerable amount of stream-water chloride is derived from sources other than wet deposition. Considering the proximity of this site to the Gulf of Mexico, it seems likely that a substantial amount of stream-water chloride (and sodium) is derived from dry deposition of marine aerosols (Pollman and Canfield, 1991). The

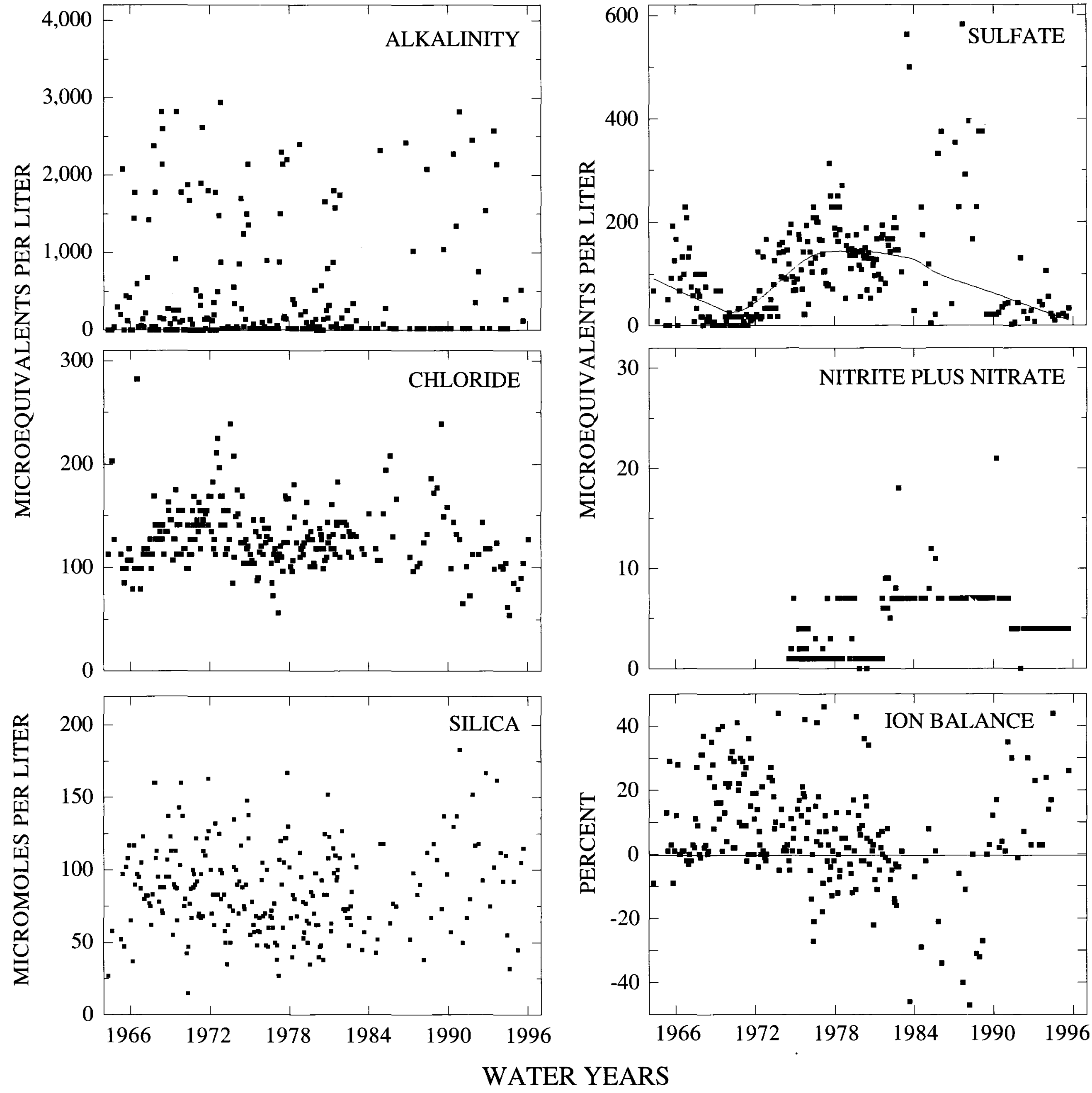

Figure 7. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Sopchoppy River, Florida—Continued.

median concentration of sulfate in stream water was 83 μeq/L, which probably is somewhat overestimated because of analytical artifacts discussed previously. Assuming that sulfate concentrations measured by ion chromatography are unbiased, the median sulfate concentration at this station may be closer to 30 μeq/L. This concentration is only slightly larger than the VWM concentration of 20 μeq/L in precipitation and may indicate that some of the atmospherically deposited sulfate is retained in the basin. Possible mechanisms of sulfate retention include adsorption on basin soils or sulfate reduction in the extensive wetland areas of the basin.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 11).

The weathering-derived constituents—calcium, magnesium, alkalinity, and silica—were strongly correlated with discharge ($0.844 > r > 0.968$). These strong associations with flow are consistent with the idea that base flow from the underlying St. Marks Formation is diluted with surface runoff from wetland areas during periods of high flow. Among the solutes, the strongest correlations were found between calcium and magnesium (rho = 0.967) and calcium and alkalinity (rho = 0.915), and the weakest correlations were found between sulfate and chloride. Strong correlations between calcium, magnesium, and alkalinity are consistent with the weathering stoichiometry of calcite and dolomite in the bedrock. The poor correlations with chloride and sulfate are consistent with the idea that these two solutes are derived primarily from atmospheric sources.

Table 10. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ion concentrations measured in water-quality samples from Sopchoppy River, Florida, April 1964 through August 1995, and volume-weighted mean concentrations in wet precipitation collected at the Quincy Station, Florida

[Concentrations in units of microequivalents per liter, discharge in cubic meters per second, specific conductance in microsiemens per centimeter at 25 degrees Celsius, and silica in micromoles per liter; n, number of stream samples; VWM, volume-weighted mean; inst., instantaneous; spec. cond., specific conductance; <, less than; --, not reported]

Parameter	Stream water						Precipitation
	Minimum	First quartile	Median	Third quartile	Maximum	n	VWM[a]
Discharge, inst.	0.03	0.37	1.9	5.1	99	249	--
Spec. cond., field	19	38	46	70	290	249	--
pH, field	3.2	4.2	4.9	6.6	8.3	248	4.8[b]
Calcium	5	80	180	550	2,550	249	3.5
Magnesium	<8.0	25	48	110	420	247	2.8
Sodium	39	74	87	100	220	246	11
Potassium	<2.6	2.6	2.6	5.1	18	245	.7
Ammonium	<14	34	43	54	239	111	5.0
Alkalinity, laboratory	<20	<20	40	440	2,940	247	--
Sulfate	<21	21	83	150	580	249	20
Chloride	54	110	130	140	280	248	12
Nitrite plus nitrate	<.7	<3.6	<7.1	7.1	21	84	9.2[c]
Silica	15	63	81	100	180	248	--

[a] Data are volume-weighted mean concentrations for 1984–94.

[b] Laboratory pH.

[c] Nitrate only.

Table 11. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ion concentrations, Sopchoppy River, Florida, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; Si, silica]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	–0.904								
Ca	–.967	0.917							
Mg	–.911	.902	0.967						
Na	–.664	.671	.679	0.723					
K	–.651	.702	.701	.735	0.577				
Alk	–.896	.886	.915	.884	.617	0.677			
SO_4	.359	–.347	–.314	–.296	–.271	–.166	–0.352		
Cl	–.045	–.075	–.031	–.042	.178	–.178	–.084	0.153	
Si	–.845	.844	.876	.885	.707	.553	.770	–.358	0.107

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents from 1964 through 1995 are shown in table 12. The only statistically significant upward trend was observed in the unadjusted sulfate concentrations at the 0.01 confidence level. The LOWESS curve in figure 7 shows a pattern of increasing sulfate concentrations between 1970 and 1980, followed by a period of low concentrations in the 1990's. This pattern in stream-water sulfate is somewhat consistent with trends in sulfate deposition in the region since the 1960's. Estimates of sulfate deposition in the Southeast show a substantial increase in deposition between 1960 and 1980 (Husar and others, 1991). Between 1980 and 1992, substantial declines in sulfate concentrations were observed at many NADP stations in the Southeast (Lynch and others, 1995). Although trends in stream-water sulfate appear to mimic deposition trends, it is perhaps more likely that the pattern reflects changes in analytical methods during the period of record. As discussed previously, some analytical methods used prior to 1990 probably introduced a substantial positive bias, which greatly complicates the interpretation of sulfate trends at this station.

Table 12. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major ion concentrations, Sopchoppy River, Florida, April 1964 through August 1995

[Trends in units of microequivalents per liter per year, except discharge in cubic meters per second per year, pH in standard units per year, and silica in micromoles per liter per year; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	−0.01	0.641	--	--
pH, field	<.1	.902	−0.1	0.741
Calcium	.3	.694	.9	.360
Magnesium	<.1	.705	.2	.552
Sodium	<.1	.898	−.2	.545
Potassium	<.1[a]	.119	--	--
Alkalinity, laboratory	−1.6	.821	--	--
Sulfate	2.8[a]	.007	--	--
Chloride	<.1	.687	<−.1	.921
Nitrite plus nitrate	([b])	--	--	--
Silica	.4	.278	.5	.049

[a] Calculated using a trend test for censored data.

[b] Insufficient data to calculate trend.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling of January 11, 1991, are shown in table 13; locations of sampling sites in the basin are shown in figure 6. During the synoptic sampling, discharge at the gage was 6.51 m^3/s compared to the median daily discharge of 7.6 m^3/s for January (Lawrence, 1987), indicating that the basin was sampled during normal flow conditions for that time of year. Concentrations measured at the gage (site 1) during the synoptic sampling were generally within the first-quartile to third-quartile range measured at the gage during the entire period of record (table 10). The tributary and upstream sites were similar in composition to the stream at the gage. All samples are very dilute, with specific conductances below 83 µS/cm, and acidic, with pH values that ranged from 3.72 to 4.29. Organic acids probably are the main source of acidity in these waters, although some acidity may be derived from strong acid inputs in precipitation. The presence of organic acids in surface waters is supported by the observation that all samples had positive ion balances (18 to 40 percent). As discussed previously, this acidic condition in stream-water chemistry at the gage occurs during wetter periods of the year when streamflow is dominated by surface runoff from the wetlands. This hydrologic condition probably also is the reason that little spatial variability in surface-water chemistry was observed at the time of the synoptic sampling. A large component of surface runoff in streamflow would tend to mask any spatial variations in stream chemistry that might reflect basin characteristics, such as geology. A weak spatial pattern that does emerge from the chemical data is that stream chemistry of the headwater samples (sites 4, 5, and 6) tends to be more dilute and more acidic than the downstream samples (sites 1 and 3). This pattern may reflect a shift in the relative contributions of surface runoff and base flow with downstream position along the river. The one sampling site that does not appear to follow this general pattern is Monkey Creek (site 2), a small tributary that drains the large wetland of Bradwell Bay. This site has a low pH and calcium concentration like the headwater sites, but has sulfate, sodium, and silica concentrations similar to the downstream sites.

Table 13. Physical properties and major ion concentrations from surface-water sampling sites in the Sopchoppy River Basin, Florida, collected January 11, 1991

[Site locations shown in fig. 6; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; concentrations in microequivalents; Si, silica in micromoles per liter; <, less than; --, not measured]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria[a]	Remarks
1	02327100	6.51	51	4.29	170	62	100	3.3	<10	96	100	<0.5	90		
2	300930084312200	--	83	3.72	48	49	100	4.6	<10	180	96	<.5	100	MT, LU	Downstream from wilderness
3	301012084295400	--	67	3.95	110	54	110	3.3	<10	140	130	<.5	110	MT	Downstream from wilderness
4	301353084321900	--	57	3.94	55	38	100	4.6	<10	79	100	<.5	90	MT	Upstream from wilderness
5	301518084352300	--	65	3.81	70	38	96	4.1	<10	71	96	<.5	92	MT, LU	Some logging
6	301521084355300	--	51	3.88	18	25	78	3.6	<10	31	79	<.5	83	MT, LU	Some logging

[a] Criteria used in selection of sampling sites: MT = major tributary, LU = land use.

Falling Creek near Juliette, Georgia (Station 02212600)

Site Characteristics and Land Use

The Falling Creek HBN Basin is in the southern part of the Piedmont physiographic province in central Georgia (fig. 8). The basin drains 187 km^2 of rolling terrain that ranges in elevation from 113 to 244 m. The USGS gaging station is 8 km east of the town of Juliette, Ga., at latitude 33°05'59" and longitude 83°43'25". Falling Creek is a south-flowing tributary of the Ocmulgee River with a channel length of about 18 km upstream from the gage and an average stream gradient of 3.8 m/km. The main channel is perennial, and average daily discharge ranges from 0.31 m^3/s in September to 4.2 m^3/s in February. Average annual runoff was 30 cm from 1965 through 1995 (U.S. Geological Survey, Water Resources Data, Georgia), of which almost 60 percent occurs during the 20 to 30 storm events each year (Rose, 1996). Climate of the area is temperate with warm, humid summers and mild winters (Payne, 1976). Precipitation averages 122 cm annually and is fairly evenly distributed throughout the year except for the fall months that are slightly drier (Plummer, 1983). Average daily air temperatures range from 7.3°C in January to 26.6°C in July. Freezing occurs on slightly more than one-half the days between December and February, although snowfall is rare (Payne, 1976).

The basin lies in the Southern Mixed Forest ecoregion (Bailey and others, 1994) and is covered by second-growth pine and mixed pine-hardwood forest types. Pine forests, which naturally reforested previously farmed or logged areas, are composed of loblolly pine with an understory of dogwood and redbud. Hardwood forest types are concentrated along the creek bottoms and in small, sheltered, upland valleys. The lowland hardwood species are predominantly sweetgum, water oak, and willow oak, and the upland hardwood stands are dominated by white oak, post oak, red oak, and hickory. Most soils in the basin are classified as Ultisols and are mapped in the Davidson series (Payne, 1976), which includes well-drained soils that have formed in residual material weathered from mafic crystalline rocks. A typical soil profile has a dark reddish-brown surface layer of loam (18 to 30 cm) that is underlain by dark-red clay subsoil that extends to a depth of almost 2 m. Soils are moderately to strongly acidic (pH 5.1 to 6.0) and have a low organic-matter content (Payne, 1976). Soil mineralogy is dominated by detrital plagioclase, potassium feldspar, pyroxene, biotite, hornblende, and quartz and pedogenic kaolinite with minor amounts of vermiculite (Rose, 1994). Soils are underlain by a layer of saprolite as much as 30 m thick that is the primary source of base flow to the stream (Rose, 1996).

Bedrock in the basin consists of interlayered felsic and mafic gneiss of Precambrian age. The felsic gneiss accounts for about one-third of the bedrock and

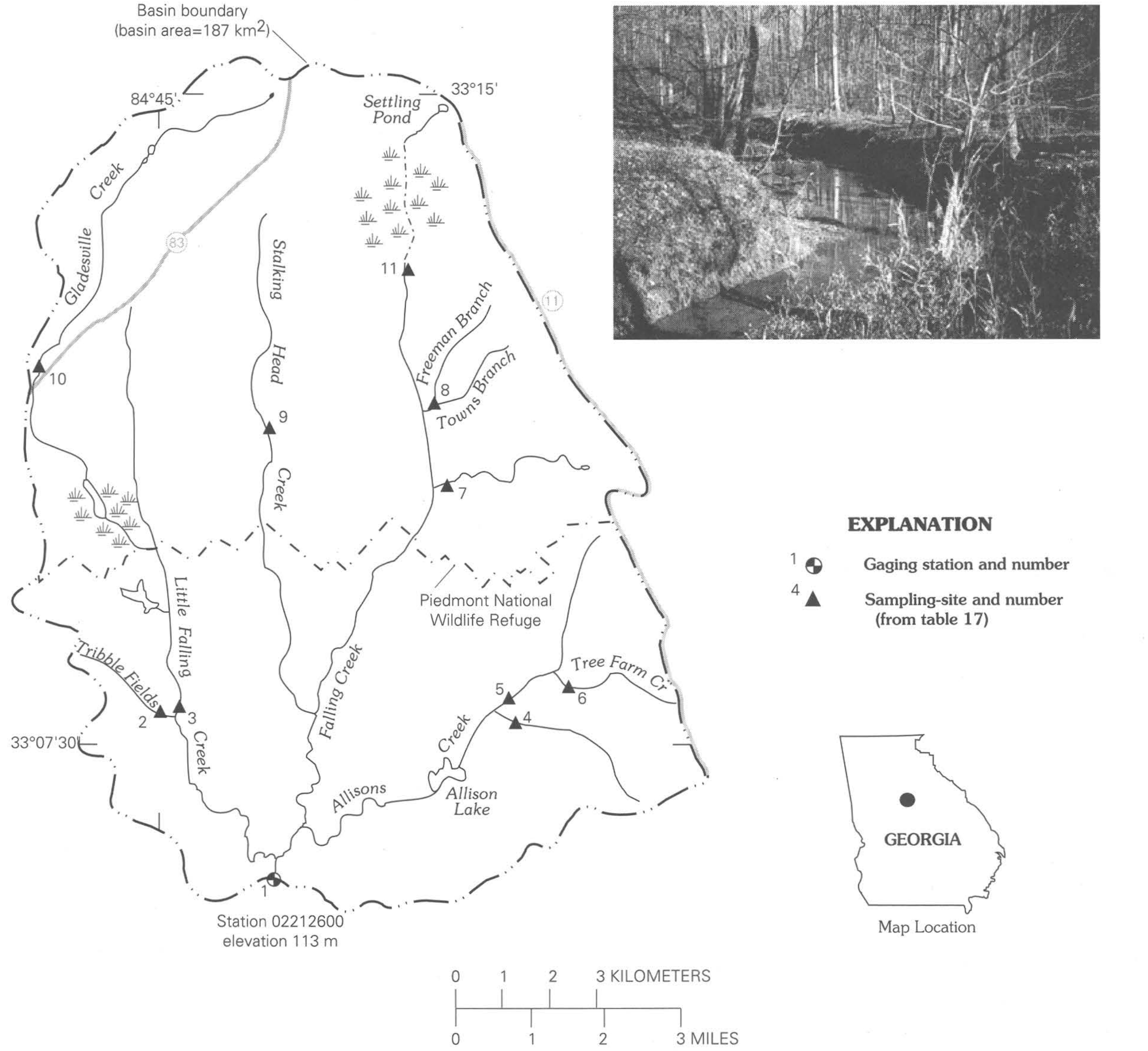

Figure 8. Map showing study area in the Falling Creek Basin and photograph of a typical tributary stream.

consists of oligoclase, microcline, and quartz with accessory biotite, muscovite, garnet, sphene, magnetite, zircon, apatite, and epidote (Matthews, 1967). The primary minerals of the mafic gneiss include hornblende, andesine, and quartz with accessory epidote, magnetite, and apatite. The mafic gneiss weathers to an orange-red saprolite with a boxwork structure. Ultramafic rocks also are present in the basin including a large body of gabbro (12 km by 1.5 km) mapped along the northern basin divide roughly parallel to State Highway 83 (Vincent and others, 1990). The gabbro consists primarily of plagioclase, clinopyroxene, orthopyroxene, and olivine.

The Falling Creek Basin drains parts of Jasper and Jones Counties in central Georgia. Sixty percent of the basin is in the boundaries of the Oconee National Forest and 40 percent is in the boundaries of the Piedmont National Wildlife Refuge (PNWR). The PNWR is part of the National Wildlife Refuge System administered by the U.S. Fish and Wildlife Service, and the refuge headquarters is located just inside the southern basin boundary. About one-half the land in the National Forest boundary is owned by private individuals or logging companies. Most areas of the basin are accessible by the 50 km of Forest Service and county roads that traverse the area. The PNWR is open year-round for general public use, although some roads in the refuge may be closed during hunting season or in bad weather.

Public land in the basin was purchased by the Federal Government in the mid-1930's after almost 100 years of cotton farming had left severely eroded lands and nutrient-depleted soils. The PNWR was established in 1939 to develop techniques for reclaiming depleted areas and to restore suitable habitat for native animals (Riley and Riley, 1979). Current (1997) land cover in the basin is more than 95 percent forest and the dominant land use is for timber harvest, wildlife habitat, and recreation. Management policies of the PNWR are designed primarily to provide habitat for the endangered red-cockaded woodpecker. Pine forests in the refuge are managed on an 80-year rotation in stands of 4 to 12 ha, and hardwood stands are left to develop naturally (Ronnie Shell, Piedmont National Wildlife Refuge, oral commun., 1994). The refuge also manipulates water levels in natural wetlands, beaver ponds, and manmade ponds to improve food sources for birds. Pine forests in the Oconee National Forest are harvested on a 60-year rotation in a checkerboard pattern by clearcutting 12-ha parcels or thinning slightly larger areas (John Moore, Forest Service, oral commun., 1994). Some logged areas are left to revegetate naturally, whereas others are reseeded. Logging on private land has increased significantly during the past decade with clearcutting being the primary method of removal (John Moore, oral commun., 1994). Logging on private land has increased significantly during the past decade with clearcutting being the primary method of removal (John Moore, oral commun., 1994).

Other manmade features in the basin include several gravel pits and feldspar mines that were operated until the early 1980's and have since been revegetated or turned into ponds. A feldspar-processing plant, located just outside the northeast basin boundary, has discharged industrial wastewater into a settling pond at the head of Falling Creek for more than 30 years. The ore processing involves the use of hydrofluoric and sulfuric acids that generate acidic wastewater (Georgia Department of Natural Resources, 1985). The wastewater is treated with a caustic rinse to raise the pH then pumped into the settling pond. Discharge from the settling pond has been identified as a point source of both suspended sediment and chemical contamination to Falling Creek (Georgia Department of Natural Resources, 1985). A sample collected from the outlet of the settling pond in 1985 had a pH of 7.1 and fluoride and sulfate concentrations of 13.8 mg/L (730 μeq/L) and 50 mg/L (1,040 μeq/L), respectively (Georgia Department of Natural Resources, 1985). The impact of the industrial wastewater on the chemistry of Falling Creek is the reason this station was removed from the HBN in 1994.

Historical Water-Quality Data and Time-Series Trends

The chemical data set analyzed for this report includes 187 water-quality samples that were collected from October 1967 through June 1994 when the site was removed from the HBN. Water-quality samples were collected as frequently as monthly from 1968 through 1982 and quarterly from 1983 through 1994. Although not documented, water-quality samples in the early part of the record probably were analyzed at one of the three USGS laboratories (Raleigh, N.C.; Ocala, Fla.; Tuscaloosa, Ala.) that provided analytical services in the Southeastern Region (Durum, 1978). After establishment of the Central Laboratory System, samples were analyzed at the Central Laboratory in Atlanta, Ga., from 1973 through 1985 and at the NWQL in Arvada, Colo., from 1986 through 1994. Daily discharge records for Falling Creek (station 02212600) are available beginning in July 1964. Continuous records of water temperature at the gage were published from August 1965 through September 1979.

Calculated ion balances for 175 samples with complete major ion analyses are shown in figure 9. Ion balances ranged from –27 to +12 percent, and more than 85 percent of the samples had calculated values within the ±5 percent range, indicating that the analyses were of high quality. The mean charge balance of all samples was 0.2 percent, indicating that unmeasured constituents, such as organic anions, do not contribute significantly to the ion balance of stream water at this site.

Time-series plots of the major dissolved constituents were inspected for evidence of method-related effects (fig. 9). For example, several higher than average sulfate concentrations were reported during the late 1980's. This pattern coincides with the use of a turbidimetric titration for sulfate analyses at the NWQL between March 1986 and December 1989 (Fishman and others, 1994). In 1989, the NWQL determined that sulfate concentrations can be overestimated by this technique and changed the method to ion chromatography in 1990 (Office of Water Quality Technical Memorandum No. 90.04, *Turbidimetric Sulfate Method*, issued December 21, 1989, at URL http://water.usgs.gov/public/admin/memo/). Sulfate and chloride both show a pattern of slightly smaller concentrations during the early 1970's. The fact that both silica and fluoride are missing for these same analyses may be an indication of a change in analytical laboratory during this period of record. The time-series plot of field pH shows an abrupt downward shift in pH around 1974 and many uncharacteristically low pH values during the next 6 years (fig. 9). Although not documented, these low values may have been caused by a change in the pH electrode used by field personnel. Some instrument-electrode systems are known to give erroneous readings when measuring pH in low-conductivity waters, and the electrode commonly is the critical component (Office of Water Quality Technical Memorandum No. 81.08, *Electrodes for pH Measurement in Low-Conductivity Waters*, issued February 10, 1981, at URL http://water.usgs.gov/public/admin/memo/).

Table 14 gives median concentrations and ranges of major constituents in stream water collected at the gage and VWM concentrations in wet-only deposition measured at the Georgia Station NADP station about 65 km west of the basin. Wet-precipitation chemistry at the NADP station is dilute and slightly acidic with a VWM pH of 4.6. During 17 years of record, the dominant cations in precipitation were hydrogen, which contributed 50 percent of the total cation charge, and ammonium and sodium, which contributed 19 and 15 percent, respectively. Sulfate was the dominant anion, accounting for 62 percent of the total anions, whereas nitrate and chloride accounted for 23 and 15 percent, respectively. These data indicate that solutes in precipitation in the basin are primarily a mixture of strong acids derived from anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain.

Stream water in Falling Creek is moderately concentrated and well buffered; specific conductances ranged from 44 to 180 µS/cm and alkalinities generally were between 780 and 1,260 µeq/L. The major cations in stream water were calcium, magnesium, and sodium, and the major anion was bicarbonate. The relatively high concentrations of dissolved calcium, magnesium, sodium, and alkalinity in stream water result from the weathering of mafic minerals in the underlying bedrock and saprolite. Rose (1994) noted that solute flux related to rock weathering from Falling Creek is much greater than other more felsic locations in the region because of the predominance of amphiboles in the mafic gneiss. The median chloride concentration in stream water was 90 µeq/L, which is about 12 times larger than the VWM concentrations of 7.6 µeq/L in precipitation. On the basis of the difference between average annual runoff and precipitation, evapotranspiration can account for no more than a fourfold increase in the chloride concentration of precipitation, indicating that some stream-water chloride must be derived from sources other than wet deposition. The most obvious basin source of chloride is industrial wastewater discharged from the settling pond. The median concentration of sulfate in stream water was 81 µeq/L compared to 32 µeq/L in precipitation. The stream-water concentration is somewhat smaller than would be expected considering the combined effects of evapotranspiration, dry deposition of sulfate, and discharge from the settling pond, indicating that a substantial amount of atmospherically deposited sulfate is retained in the basin. The primary mechanism probably is sulfate adsorption on soils that is generally attributed to the abundance of pedogenic iron and aluminum oxides in the highly weathered soils of the Southeast (Shanley, 1992). The median concentration of fluoride in stream water was 32 µeq/L, which is significantly larger than the concentrations reported at most other HBN stations. Given the low fluoride content of both precipitation (Hem, 1989) and common metamorphic minerals (Deer and others, 1966), these concentrations of fluoride in stream water are almost certainly related to wastewater discharge from the tailings pond.

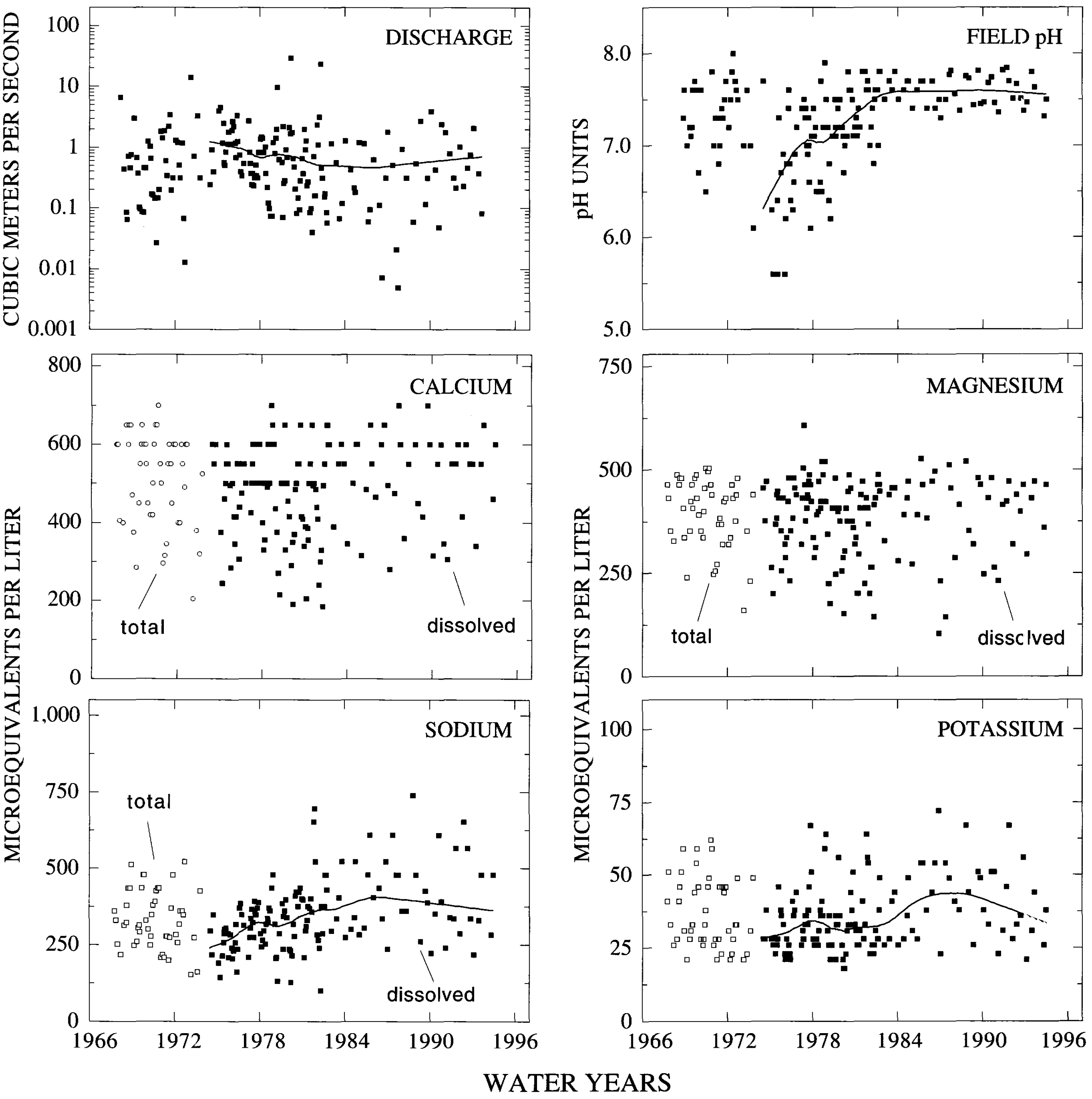

Figure 9. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Falling Creek, Georgia.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 15). Most dissolved constituents had strong inverse correlations with discharge, particularly calcium (rho = –0.845), magnesium (rho = –0.828), sodium (rho = –0.726), and alkalinity (rho = –0.861). Strong correlations between weathering products and flow are consistent with a hydrologic system where weathering-enriched base flow is diluted by waters from shallow or surficial sources during periods of increased discharge. Although fluoride is not a weathering product, it also had a strong inverse correlation with discharge (rho = –0.668). This relation may indicate that discharge from the settling pond has contaminated the local ground-water system as well as the stream.

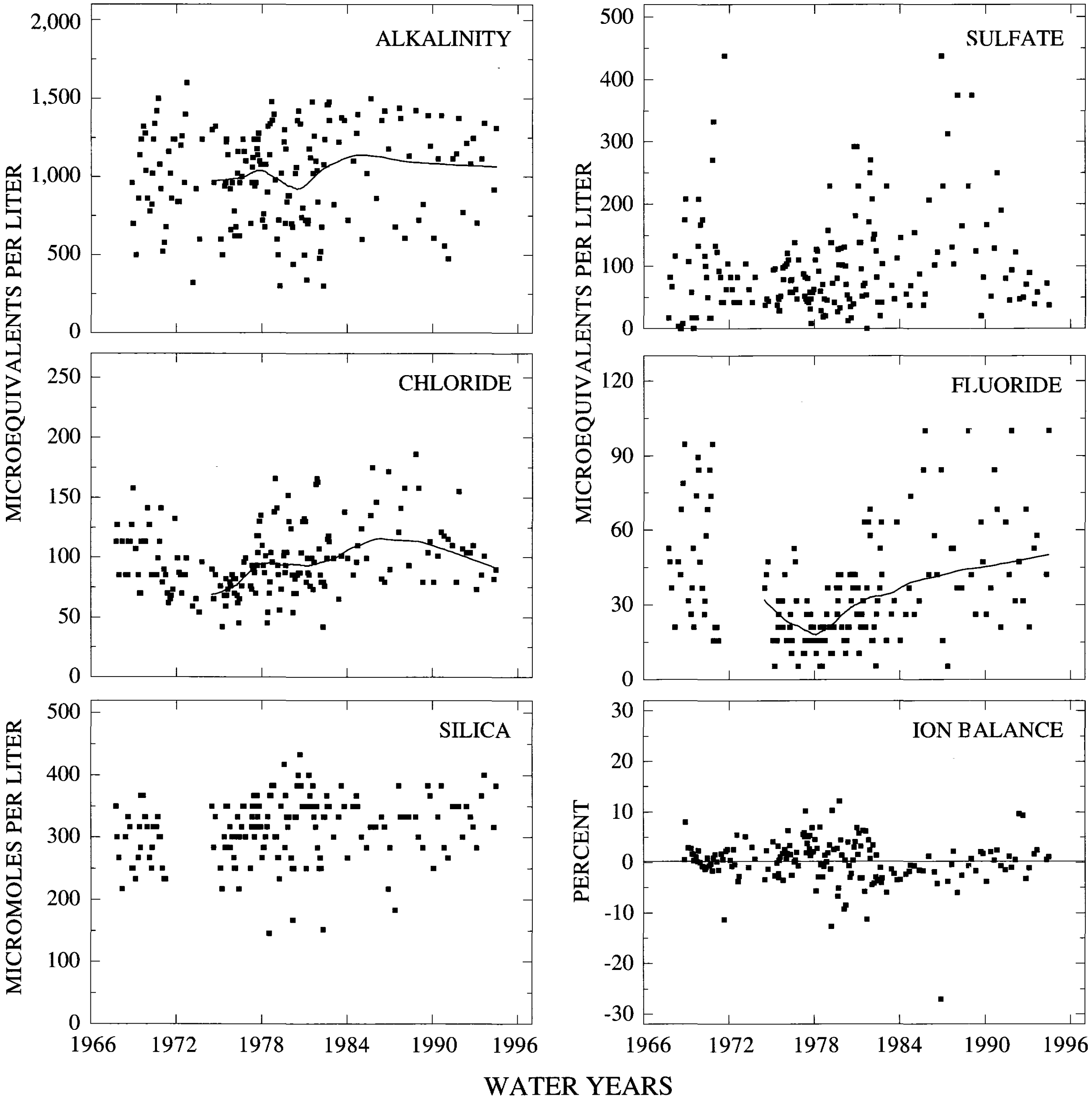

Figure 9. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Falling Creek, Georgia—Continued.

Among the ions, the highest degree of correlation was found between calcium, magnesium, and alkalinity (0.911 < r < 0.953). These strong positive correlations most likely reflect the weathering of amphibole minerals in the mafic gneiss. Significant correlations also were found between chloride and the monovalent cations, sodium (rho = 0.684) and potassium (rho = 0.633), and sulfate and the divalent cations, calcium (rho = –0.594) and magnesium (rho = –0.574). The positive correlations between chloride and the monovalents probably are the result of industrial wastewater input because these constituents do not occur together in common metamorphic minerals. In contrast, the inverse correlations between sulfate and the divalent cations probably are related to hydrologic processes. The implication is that sulfate is

Table 14. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ion concentrations measured in water-quality samples from Falling Creek, Georgia, October 1967 through June 1994, and volume-weighted mean concentrations in wet precipitation collected at the Georgia Station, Georgia

[Concentrations in units of microequivalents per liter, discharge in cubic meters per second, specific conductance in microsiemens per centimeter at 25 degrees Celsius, and silica in micromoles per liter; n, number of stream samples; VWM, volume-weighted mean; inst., instantaneous; spec. cond., specific conductance; <, less than; --, not measured]

Parameter	Stream water						Precipitation VWM[a]
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge, inst.	0.01	0.21	0.54	1.2	30	183	--
Spec. cond., field	44	100	120	140	180	186	--
pH, field	5.6	7.1	7.4	7.6	8.9	165	4.6[b]
Calcium	180	410	500	600	700	187	4.0
Magnesium	110	340	420	470	630	187	2.2
Sodium	100	270	330	400	740	187	7.3
Potassium	18	27	33	43	72	185	1.2
Ammonium	<.7	<.7	1.4	2.9	17	69	9.4
Alkalinity, laboratory	300	780	1,040	1,260	1,600	157	--
Sulfate	<21	45	81	130	440	188	32
Chloride	42	79	90	110	170	187	7.6
Nitrite plus nitrate	<.7	2.1	5.0	7.1	44	151	12[c]
Fluoride	<5.3	21	32	47	100	170	--
Silica	150	280	320	350	430	170	--

[a] Data are volume-weighted mean concentrations for 1978–94.

[b] Laboratory pH.

[c] Nitrate only.

Table 15. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ion concentrations, Falling Creek, Georgia, 1980 through 1994

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; F, fluoride; Si, silica]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	F
pH	-0.618									
Ca	-.845	0.652								
Mg	-.828	.623	0.919							
Na	-.726	.543	.596	0.582						
K	-.631	.504	.542	.520	0.779					
Alk	-.861	.648	.952	.912	.634	0.559				
SO_4	.345	-.290	-.594	-.574	.005	.105	-0.569			
Cl	-.277	.232	.104	.117	.684	.633	.165	0.438		
F	-.668	.643	.663	.691	.764	.795	.661	-.115	0.528	
Si	-.687	.456	.666	.665	.435	.265	.592	-.499	.022	0.426

primarily transported to the stream during high-discharge periods when streamflow is dominated by discharge from the unsaturated zone that apparently is enriched in sulfate and depleted in base cations relative to ground water (Shanley, 1992).

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are shown in table 16. Because many of the chemical analyses in the early part of the record are incomplete, trends were calculated only for the period 1974 through 1994. Statistically significant upward trends were observed in the unadjusted concentrations of pH, sodium, potassium, chloride, alkalinity, and fluoride at the 0.01 confidence level. Discharge had a significant downward trend of –0.2 m^3/s per year at the 0.01 confidence level. The upward trends in potassium and alkalinity were not statistically significant for the flow-adjusted concentrations, indicating that unadjusted trends in these constituents probably were driven by the downward trend in stream discharge. In contrast, the upward trends in pH, sodium, chloride, and fluoride were significant for both the unadjusted and flow-adjusted concentrations, and the trend in sulfate became significant only after the discharge variation had been removed. Increases in stream-water fluoride, sulfate, chloride, and sodium concentrations occurred primarily between 1974 and 1984 (fig. 9) and are almost certainly related to the settling pond based on the chemical composition of discharge from the pond reported by the Georgia Department of Natural Resources (1985). The upward trends in concentration may indicate that chemical loadings from the plant have increased during that time, or alternatively, that there has been a progressive contamination of the ground-water system. The cause of the upward trend in field pH is less clear. Although the trend appears to be consistent with the other chemical changes in stream water, many of the low pH measurements between 1974 and 1980 also can be explained by analytical bias.

Table 16. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major ion concentrations, Falling Creek, Georgia, August 1974 through June 1994

[Trends in units of microequivalents per liter per year, except discharge in cubic meters per second per year, pH in standard units per year, and silica in micromoles per liter per year; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	–0.02	0.003	--	--
pH, field	.03	.000	0.04	0.000
Calcium	2.5	.046	1.0	.454
Magnesium	1.5	.177	–.6	.269
Sodium	8.7	.000	4.1	.000
Potassium	.5	.004	.3	.122
Alkalinity, laboratory	17.5	.001	–2.5	.407
Sulfate	1.2	.103	2.1	.007
Chloride	1.8	.000	1.3	.000
Nitrite plus nitrate	([a])	--	--	--
Fluoride	1.4	.000	1.1	.000
Silica	1.0	.080	<.1	.999

[a] Insufficient data to calculate trend.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling of December 8 through 10, 1990, are presented in table 17; locations of sampling sites are shown in figure 8. Discharge at the gage was 0.28 m^3/s compared to the median monthly discharge of 0.91 m^3/s for December (Lawrence, 1987), indicating that the basin was sampled during low-flow conditions for that time of year. Because of the hydrologic conditions, solute concentrations measured at the gage (site 1) during the synoptic sampling were generally outside the first-quartile to third-quartile range measured at the gage during the entire period of record (table 14). Tributary streams sampled during the synoptic sampling had smaller concentrations than those measured at the gage (site 1) with the exception of the headwaters of Falling Creek (site 11). All samples had ion balances close to zero (range –1.6 to 2.8 percent), indicating that organic anions did not contribute significantly to the ionic content of stream water during the sampling period.

The chemistry of tributary streams sampled during the synoptic sampling supports the hypothesis that the settling pond at the headwaters of Falling Creek is a point source of chemical contamination at the gage. This is clearly demonstrated by comparing dissolved fluoride concentrations among the sampling sites. At site 11, just 3 km downstream from the settling pond, the fluoride concentration was 410 µeq/L compared to less than reporting-level concentrations at the other nine tributaries (sites 2–10). The fluoride concentration of 63 µeq/L at the gage was much smaller than at site 11, but still was elevated compared to background sites in the basin. Other constituents appeared to be affected by the industrial wastewater inputs as well. For example, sodium at site 11 was four times larger and calcium was three times larger than the average concentrations of sodium and calcium at the nine background tributaries (sites 2–10). With the exception of site 3, the average sulfate concentration in the background tributaries was nine times smaller than the sulfate concentration in the headwaters of Falling Creek (site 11). Although not every tributary was sampled during the synoptic sampling, it seems reasonable to conclude that the discharge of industrial wastewater in the headwaters of Falling Creek has a substantial effect on the chemistry of Falling Creek at the gage.

Table 17. Physical properties and major ion concentrations from surface-water sampling sites in the Falling Creek Basin, Georgia, collected December 8–10, 1990

[Site locations shown in fig. 8; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; F, fluoride; concentrations in microequivalents; Si, silica in micromoles per liter; <, less than; --, not measured]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	F	Si	Criteria[a]	Remarks
1	02212600	0.28	7.56	140	500	400	480	59	840	310	140	<7.0	63	350		
2	330754083444500	.008	6.93	100	420	320	260	26	630	250	130	<7.0	<5.0	450	BG	Mafic gneiss
3	330755083444200	.020	6.81	150	550	470	320	22	340	900	170	<7.0	<5.0	330	BG, MT	Gabbro
4	330739083394500	.008	7.26	110	400	320	330	46	870	54	120	<7.0	<5.0	430	BG	Felsic gneiss
5	330757083401400	--	7.13	77	290	220	230	28	550	100	99	--	<5.0	330	BG	Mixed lithology
6	330807083391800	.008	6.99	75	230	180	270	41	360	200	120	--	<5.0	380	BG	Felsic gneiss
7	331032083410900	.022	7.52	100	400	330	280	38	860	56	100	<7.0	<5.0	470	BG	Felsic gneiss
8	331126083411600	--	6.72	85	280	240	250	33	580	100	120	--	<5.0	320	BG	Mafic gneiss
9	331112083432700	.017	7.43	140	550	500	300	36	1,140	100	140	<7.0	<5.0	420	BG, MT	Gabbro
10	331139083464200	.014	7.04	90	310	220	240	33	390	270	160	--	<5.0	250	BG	Mafic gneiss
11	331303083413200	--	7.00	290	1,150	630	1,000	100	940	1,270	260	<7.0	411	330	LU	Settling pond

[a] Criteria used in selection of sampling sites: BG = bedrock geology, MT = major tributary, LU = land use.

In addition to assessing the effects of the settling pond on stream chemistry, sampling sites also were selected to assess geologic controls on spatial variability in surface-water chemistry (table 17). Variability in the composition of the background tributaries does not appear to be strongly related to the distribution of felsic and mafic gneiss as mapped by Ferguson (1978). For example, the alkalinity of streams that drain predominantly felsic gneiss (sites 4, 6, and 7) ranged from 360 to 870 μeq/L and was similar to the range of 390 to 630 μeq/L in streams that drain predominantly mafic gneiss (sites 2, 8, and 10). The other major weathering products—calcium, magnesium, sodium, and silica—also showed no substantial difference in concentration between streams that drain the two types of gneiss. In contrast, the two tributary streams that drain ultramafic rocks (sites 3 and 9) had the highest concentrations of calcium and magnesium, and site 9 had the highest alkalinity among the background sites. Although data are available for only two sites, this pattern may reflect the higher weathering rates of pyroxene and olivine minerals in the gabbro compared to amphibole and feldspar minerals in the gneiss. The sulfate concentration of 900 μeq/L at site 3 was somewhat unexpected and reveals another substantial internal source of sulfate in the basin. The high sulfate concentration at this site is balanced by a lower alkalinity rather than larger concentrations of cations, which is consistent with the consumption of stream-water alkalinity by sulfuric acid produced by the oxidation of pyrite. Numerous sulfide deposits have been mapped in the area, including one deposit in the subbasin of Little Falling Creek (Ferguson, 1978).

Tallulah River near Clayton, Georgia (Station 02178400)

Site Characteristics and Land Use

The Tallulah River HBN Basin is in the Blue Ridge physiographic province in the northeast corner of Georgia (fig. 10). The basin drains 146 km^2 of steep, mountainous terrain that ranges in elevation from 573 m at the gage to 1,676 m at the summit of Standing Indian Mountain. The USGS gaging station is 17 km west of Clayton, Ga., at latitude 34°53'25" and longitude 83°31'50". The Tallulah River is a south-flowing tributary of the Tugaloo River and discharges into Lake Burton reservoir about 2 km downstream from the gage. The reach of the main channel upstream from the gage is about 23 km long and has an average stream gradient of 3.8 m/km. The main channel is perennial, and flow varies strongly with season; mean monthly discharge ranged from 3.1 m^3/s in September to 8.3 m^3/s in March. Average annual runoff, of which between 5 and 20 percent occurs as stormflow (Swift and others, 1988), was 116 cm from 1964 to 1995 (U.S. Geological Survey, Water Resources Data, Georgia). Meteorological data

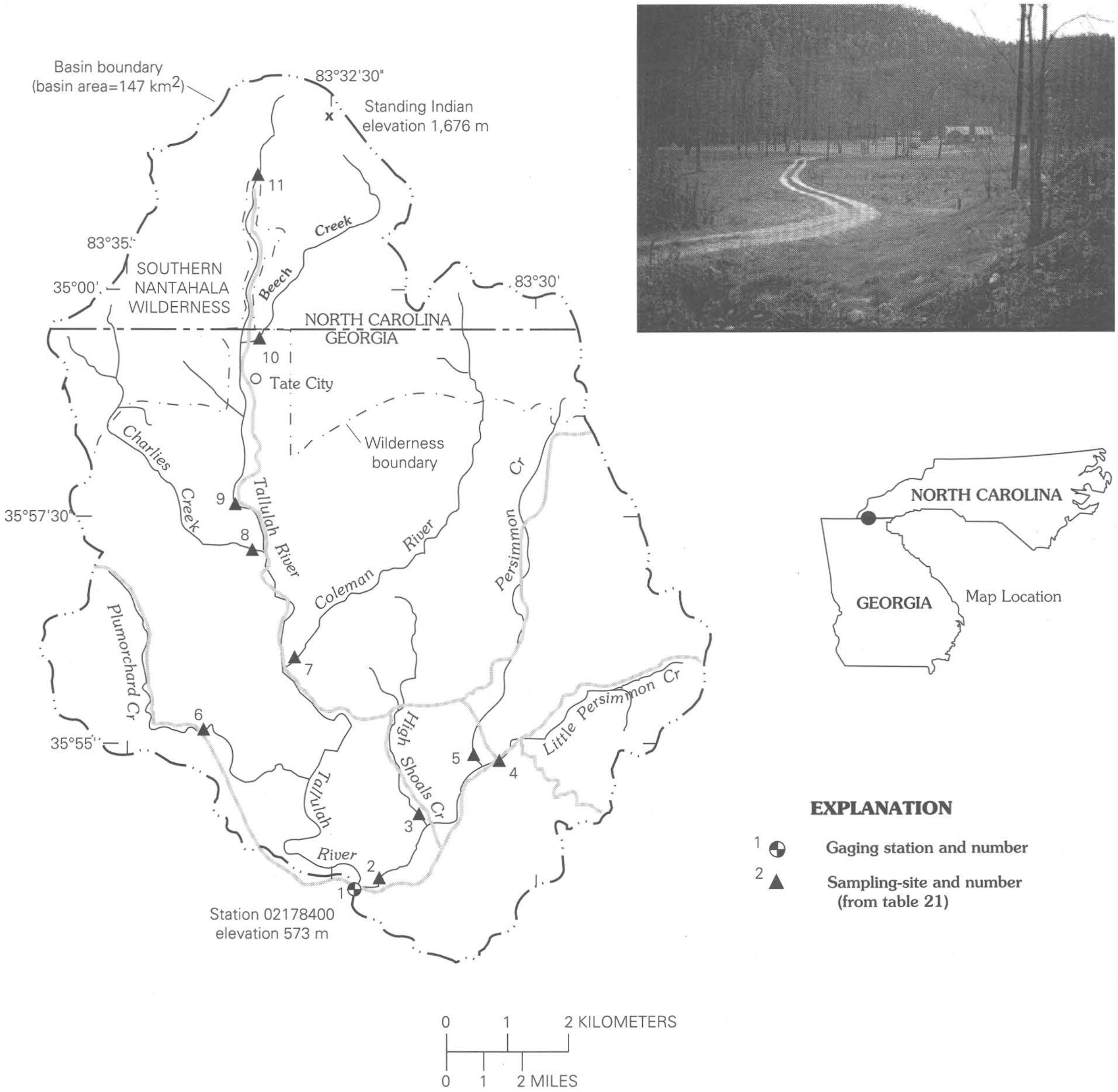

Figure 10. Map showing study area in the Tallulah River Basin and photograph of the basin landscape near Tate City, Georgia.

have been collected since the 1930's at the Coweeta Experimental Forest, 10 km northeast of the basin (Swift and Waide, 1988). Climate of the area is characterized by mild temperatures and large precipitation amounts. Average monthly temperatures range from 3.3°C in January to 21.6°C in July. Average annual precipitation at Coweeta's main weather station (elevation = 685 m) is 182 cm and increases with elevation at a rate of about 5 percent per 100 m. Precipitation is greater in late winter and spring than in late summer and fall with March being the wettest month. Snow comprises as much as 10 percent of the annual precipitation, although heavy snows and long-lasting snowpacks are rare.

The basin lies in the Central Appalachian Broadleaf Forest ecoregion (Bailey and others, 1994). The four major vegetation communities in the area are distributed in a reasonably predictable pattern controlled by elevation and moisture (Day and others, 1988). The Northern Hardwood forest type is found on slopes and in coves at elevations above 1,200 m and is dominated by yellow birch, basswood, buckeye, northern red oak, yellow poplar, and black cherry. The cove hardwood forests grow primarily along moist ravines at elevations below 1,200 m and are dominated by yellow poplar and hemlock with smaller amounts of red maple, northern red oak, hickory, and black birch. The oak forest type is widely distributed on north-facing slopes at elevations below 1,200 m. Chestnut oak is the dominant species with variable amounts of scarlet oak, northern red oak, and white oak. The oak-pine community type, which is dominated by pitch pine and scarlet oak, is found at lower elevations on dry, south-facing slopes and ridgetops.

Most soils in the basin are classified as Ultisols and are mapped in the Tusquitee-Edneyville-Porters soil association, which includes steep, well-drained loamy soils formed in residuum weathered from schist and gneiss (Carson and Green, 1981). These soils are characterized by a reddish to grayish-brown surface layer of loam (20 cm) overlying a subsoil of yellowish-brown, sandy to clayey loam extending to a depth of 150 cm or more. Chemically, these soils have a high-organic matter content (5 to 15 percent), are moderately acidic (pH 4.74 to 5.13), and have low cation-exchange capacities (Swank and Crossley, 1988). The dominant soil minerals are detrital feldspar, biotite, and garnet and pedogenic kaolinite and gibbsite (Velbel, 1988).

The basin lies in the Southern Appalachian Blue Ridge geologic province and is underlain by rocks of late Proterozoic to early Paleozoic age belonging to the Richard Russell Formation and Coweeta Group (Peper and others, 1991; Hatcher, 1988). Both units contain gneiss, schist, amphibolite, and calc-silicate rocks, but the Richard Russell Formation tends to be coarser grained and more migmatized than the Coweeta Group. The mineralogy of both units is similar and includes quartz, muscovite, biotite, plagioclase, garnet, hornblende, epidote, kyanite, staurolite, and sillimanite. A few lithologic units in the Richard Russell Formation contain sulfide-bearing schists. Extensive isovolumetric weathering of the bedrock has resulted in the formation of a porous, permeable mantle of saprolite over the bedrock that is generally believed to be the primary source of base flow to streams (Velbel, 1988).

The Tallulah River Basin drains parts of Towns and Rabun Counties in northeastern Georgia and Clay County in western North Carolina. Land in the basin is entirely in the boundaries of the Chattahoochee and Nantahala National Forests, of which 32 percent is in the Southern Nantahala Wilderness and 19 percent is privately owned. The main road into the basin enters near the gage and roughly parallels the main channel to within 2.5 km of the northern basin boundary. Paved and gravel roads provide access to most major tributaries, although travel in the wilderness is limited to foot trails. A portion of the Appalachian Trail follows most of the ridgeline in the northern one-half of the basin. The steep, heavily forested slopes make travel off roads and trails difficult.

Logging was important in the history of the area (Douglass and Hoover, 1988), and most of the basin probably was logged at least once prior to the establishment of the Chattahoochee and Nantahala National Forests in the mid-1930's. Current (1997) land cover in the National Forest is almost 100 percent forest, and the primary land-use activities are timber production and recreation. Timber harvesting in the basin during the past 10 years has averaged 140 ha annually (David Jensen, Forest Service, written commun., 1996). The method of cutting used prior to 1990 was largely clearcutting; however, seedtree, shelterwood, group selection, and single tree selection have become the standard during the past 5 years (David Jensen, written commun., 1996). Recreational use has increased significantly during the past 20 years, and campgrounds along the river are in high demand throughout the summer season.

Roads are a major source of sediment loading to streams during storm events. During the last 5 years, the Forest Service has rebuilt bridges and paved or upgraded roads along drainages in an effort to reduce erosion of sediment to surface waters. The most substantial land-use change in the National Forest during the past 30 years was the designation of the Southern Nantahala Wilderness in 1984. Both the Chattahoochee and Oconee National Forests are in the process of revising their current management plans (David Jensen, written commun., 1996). These revisions may result in future increased areas of wilderness in the basin and provide Wild and Scenic designation for some segments of the Tallulah River upstream from the gage.

Private land in the basin is currently 78 percent forested, 17 percent cleared, and 5 percent residential (David Jensen, written commun., 1996) and is concentrated in the Persimmon Creek subbasin, along the valley floor near Tate City, and along the flood plain downstream from the Coleman River confluence. The primary land-use activities in these areas are cattle grazing and hay production with some poultry production, logging, and crop production. Three relatively new residential subdivisions are in the Persimmon Creek subbasin; two have about 20 new houses and the third is currently (1997) being developed (David Jensen, written commun., 1996). There are several small prospects and mines in the basin, but all are inactive (Peper and others, 1991).

Historical Water-Quality Data and Time-Series Trends

The Tallulah River gage was operated by the USGS as a discharge-only station until it was removed from the HBN in 1994. Water-quality samples were collected periodically at the gage from March 1967 through July 1990 as part of a USGS program to monitor pristine surface-water sites in Georgia (James McConnell, U.S. Geological Survey, oral commun., 1996). Samples were collected on a biannual schedule and were analyzed for a suite of chemical constituents similar to those measured at other HBN stations. Partial analyses for an additional 22 samples also are stored in NWIS. These samples were collected as part of a State water-quality assessment program and were analyzed at the Georgia Department of Natural Resources (James McConnell, oral commun., 1996). Daily discharge records for the Tallulah River (station 02178400) are available beginning in July 1964. Records of daily water temperature at the gage from September 1964 through September 1979 also are available.

Calculated ion balances for 48 samples with complete major ion analyses are shown in figure 11. Ion balances ranged from –26 to +7 percent, and less than 65 percent of the samples had calculated values within the ±10 percent range. This wide range of values reflects the difficulty in making precise analytical measurements at the low solute concentrations typical of this station. The average ion balance for all samples was –8.5 percent, and almost 90 percent had negative ion balances, indicating that the samples had an excess of measured anions over cations. Because stream samples at this station generally have low alkalinities, the apparent anion excess probably is because of an overestimation of alkalinity by the fixed-endpoint titration to pH 4.5 (Office of Water Quality Technical Memorandum No. 80.27, *New Parameter Codes for pH, Alkalinity, Specific Conductance, and Carbonate/ Bicarbonate*, issued September 19, 1980, at URL http://water.usgs.gov/public/admin/memo/). For waters with alkalinities around 100 µeq/L, however, the endpoint pH is closer to 5.0, and titration to pH 4.5 may overestimate alkalinity by as much as 25 µeq/L (Barnes, 1964). Because the average alkalinity and anion excess for this station were 140 µeq/L and 30 µeq/L, respectively, a bias in the laboratory alkalinity appears to be a reasonable explanation for the negative ion balances.

Time-series plots of the major dissolved constituents were inspected for evidence of method-related effects (fig. 11). Several patterns are evident in the sulfate and field pH records. For example, sulfate concentrations between 1970 and 1972 were all reported as less than or equal to 42 µeq/L (2 mg/L), which was the reporting limit used by some USGS laboratories during this period of record. The two uncharacteristically high sulfate concentrations apparent near the end of the record are coincident with the use of a turbidimetric titration for sulfate analyses at the NWQL between March 1986 and December 1989 (Fishman and others, 1994). In 1989, the NWQL determined that sulfate concentrations can be overestimated by this technique, and the method was changed to ion chromatography in 1990 (Office of Water Quality Technical Memorandum No. 90.04, *Turbidimetric Sulfate Method*, issued December 21, 1989, at URL http://water.usgs.gov/public/admin/memo/).

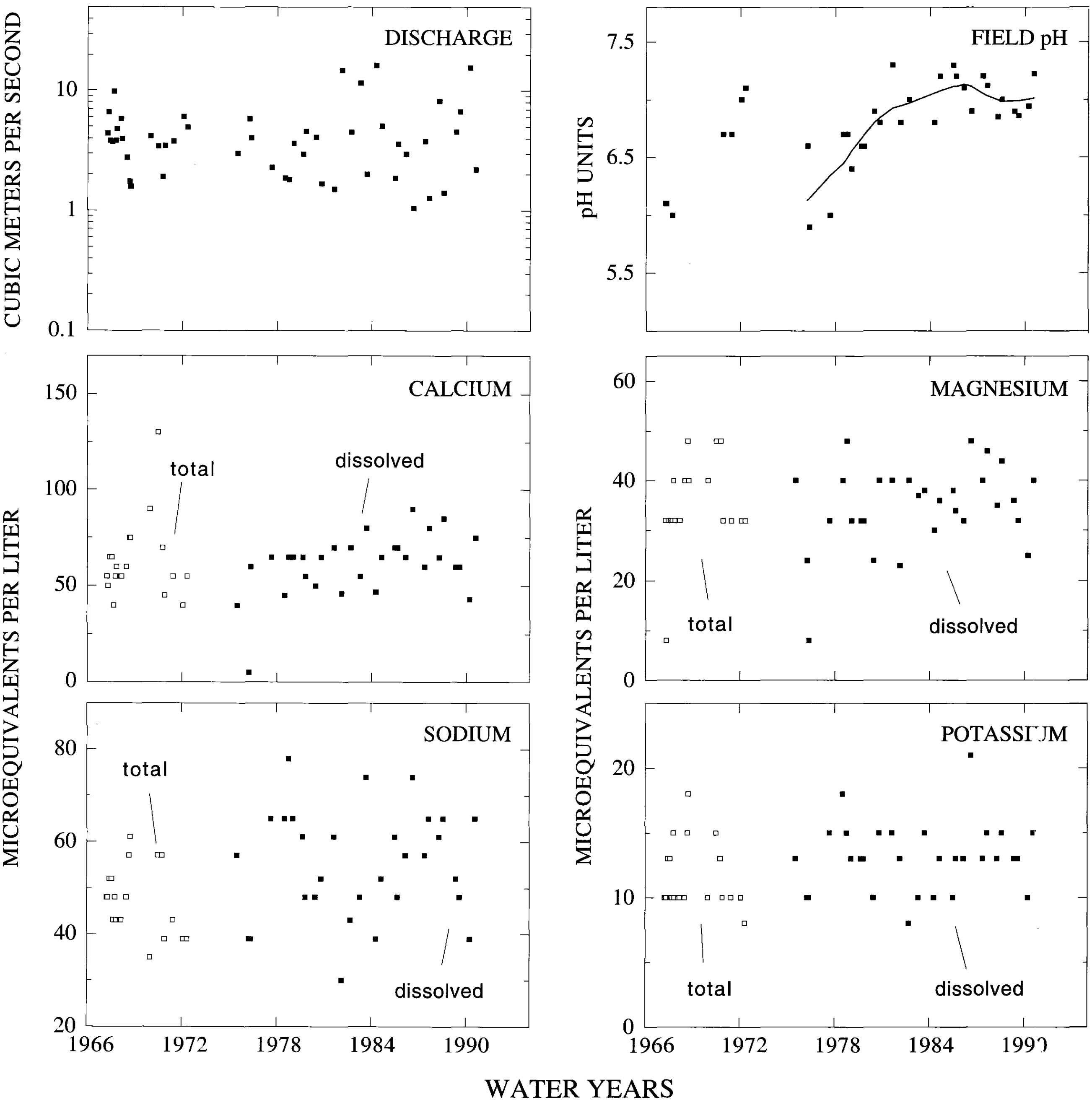

Figure 11. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Tallulah River, Georgia.

The plot of field pH shows several uncharacteristically low values in the first one-half of the record. Interestingly, a similar pattern in field pH also was observed at the Falling Creek HBN station in Georgia (fig. 9). As suggested for that station, the pattern may have been caused by a change in field instrumentation. This is further supported by the fact that both stations were serviced by the same USGS field office.

Table 18 gives median concentrations and ranges of major constituents in stream water collected at the gage and VWM concentrations in wet-only deposition measured at the Coweeta NADP station about 10 km northeast of the basin. Precipitation chemistry at the NADP station is dilute and slightly acidic, with a VWM pH of 4.6 for 17 years of record. The dominant cations in precipitation were hydrogen,

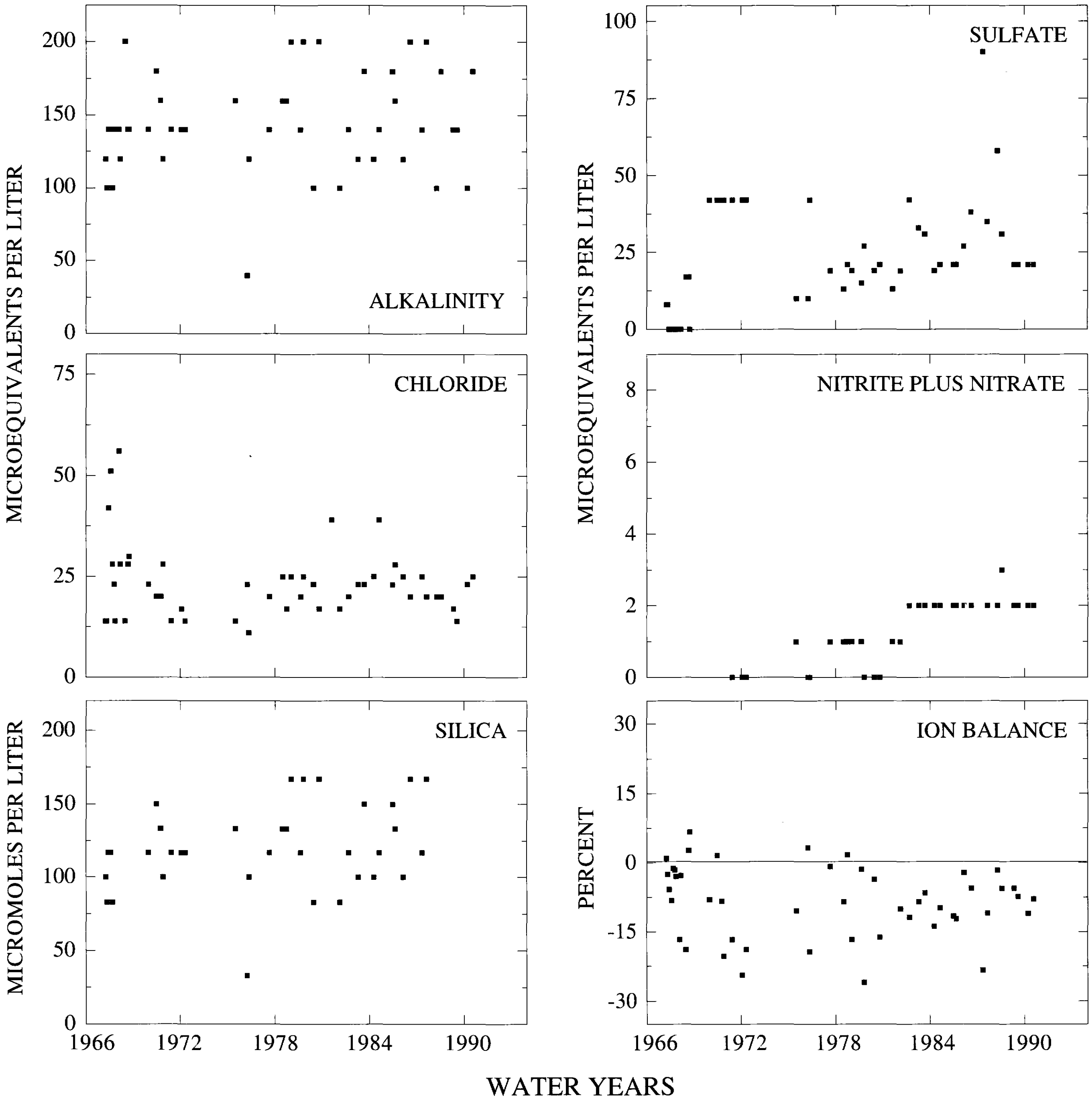

Figure 11. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Tallulah River, Georgia—Continued.

which contributed 58 percent of the total cation charge, and ammonium and sodium, which contributed 18 and 13 percent, respectively. Sulfate was the dominant anion, accounting for 64 percent of the total anion charge, and nitrate and chloride accounted for 25 and 13 percent, respectively. The predominance of these ions indicates that precipitation in the basin is primarily a mixture of strong acids derived from anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain.

Stream water in the Tallulah River is very dilute and poorly buffered; specific conductances ranged from 12 to 25 µS/cm and alkalinities were generally between 120 and 160 µeq/L. The major cations in stream water were calcium and sodium and alkalinity was the dominant anion. The primary source of base cations and alkalinity in stream water probably is weathering of silicate minerals in the underlying gneiss and schist. The median chloride concentration in stream water was 22 µeq/L, which is about four times larger than the VWM concentration of 5.6 µeq/L in precipitation. On the basis of the difference between average annual runoff and precipitation, evapotranspiration can account for no more than a threefold increase in the concentration of precipitation, indicating that a small amount of chloride may be derived from sources other than wet deposition. Swank and Waide (1988) determined that dry deposition from the atmosphere accounted for about 15 percent of the annual chloride input to streams that drain the nearby Coweeta Basin. Alternatively, weathering of hornblende in the bedrock also may contribute small amounts of chloride to surface waters (Peters, 1991), as would some human activities in the basin. The median concentration of sulfate in stream water (21 µeq/L) was smaller than the VWM concentration of 28 µeq/L in wet precipitation. Considering that dry deposition of sulfate in the Southern Blue Ridge has been estimated to be comparable to that of wet deposition (Elwood and others, 1991), it appears that much of the atmospherically deposited sulfate is currently being retained in the basin. The primary mechanism probably is sulfate adsorption on soils, which also acts to buffer surface waters from the effects of acidic deposition (Elwood and others, 1991). The lower concentration of both nitrate and ammonium in stream water compared to precipitation indicates nitrogen also is strongly retained in the basin but also indicates that upstream agricultural activities do not have a substantial effect on nutrient concentrations in stream water at the gage.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 19). Base cations, silica, and alkalinity had strong inverse correlations with discharge, which is consistent with a hydrologic system where weathering-enriched base flow is diluted by waters from shallow or surficial sources during periods of increased discharge. Among the ions, the highest degree of correlation was found between sodium and silica (rho = 0.908), which most likely reflects the weathering of feldspars in the underlying gneiss and schist. As expected, the atmospherically derived constituents showed little correlation with

Table 18. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ion concentrations measured in water-quality samples from Tallulah River, Georgia, March 1967 through July 1990, and volume-weighted mean concentrations in precipitation collected at the Coweeta Station, North Carolina

[Concentrations in units of microequivalents per liter, discharge in cubic meters per second, specific conductance in microsiemens per centimeter at 25 degrees Celsius, and silica in micromoles per liter; n, number of stream samples; VWM, volume-weighted mean; inst., instantaneous; spec. cond., specific conductance; <, less than; --, not measured]

Parameter	Stream water						Precipitation VWM[a]
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge	1.1	2.2	3.7	5.1	16	49	--
Spec. cond., field	12	15	17	20	25	49	--
pH, field	5.9	6.6	6.9	7.1	7.3	34	4.6[b]
Calcium	<5.0	55	60	70	130	49	3.5
Magnesium	8.2	32	34	40	48	49	1.5
Sodium	30	43	52	61	78	49	5.4
Potassium	7.7	10	13	15	21	49	.5
Ammonium	<.7	.7	1.4	2.9	7.1	18	7.8
Alkalinity, laboratory	40	120	140	160	200	48	--
Sulfate	<8.3	<21	21	35	90	49	28
Chloride	11	17	22	25	56	49	5.6
Nitrite plus nitrate	<1.4	3.9	3.9	7.1	79	27	11[c]
Silica	90	130	140	160	180	45	--

[a] Data are volume-weighted mean concentrations for 1978–94.

[b] Laboratory pH.

[c] Nitrate only.

Table 19. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ion concentrations, Tallulah River, Georgia, 1980 through 1990

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; Si, silica]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	–0.262								
Ca	–.682	0.500							
Mg	–.706	.518	0.632						
Na	–.834	.182	.566	0.688					
K	–.702	.137	.347	.583	0.734				
Alk	–.718	.308	.689	.735	.683	0.635			
SO_4	–.385	.532	.632	.465	.184	.215	0.485		
Cl	.173	.387	–.067	.143	.036	.033	.105	–0.001	
Si	–.927	.235	.625	.744	.908	.687	.657	.267	–0.180

the major weathering products with the exception of a positive correlation between calcium and sulfate (rho = 0.632). Although most sulfate is retained in the basin soils, this association indicates that mobilization of sulfate from the basin may be causing the export of soil calcium to the stream (Johnson and Ruess, 1984).

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are shown in table 20. Because many of the chemical analyses in the early part of the record are incomplete, trends were calculated only for the period 1976 through 1994. Statistically significant upward trends were observed for field pH at the 0.01 confidence level and calcium at the 0.05 confidence level. Trends in both constituents were similar for unadjusted and flow-adjusted concentrations, indicating that the trends are not driven by variations in stream discharge. The LOWESS curve for field pH reveals that most of the increase occurred in the late 1970's and early 1980's (fig. 11). As mentioned previously, field pH measurements during this period of record may have been affected by changes in analytical equipment. Thus, the trend in pH is more likely to have been caused by analytical bias than environmental change in the basin. The weak upward trend in calcium and lack of trends in other major constituents are inconsistent with long-term changes in stream chemistry observed at the nearby Coweeta Hydrologic Laboratory. Swank and Waide (1988) reported significant increases in streamwater sulfate and decreases in alkalinity and basin cations in several undisturbed streams at Coweeta. They suggested these changes in stream chemistry indicate that the capacity of these basins for retaining atmospheric sulfate and mobilizing base cations is beginning to decline. One explanation for the difference in trend results between the two sites is that the Tallulah River Basin may be less affected by acidic deposition because it drains a much larger area than the streams at Coweeta. Large basins offer a greater opportunity for buffering of acidic inputs as a result of longer residence times of waters in contact with soil and bedrock (Elwood and others, 1991). Alternatively, detection of trends in stream-water chemistry of the Tallulah River may have been obscured by factors such as analytical bias and low sampling frequency.

Table 20. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major ion concentrations, Tallulah River, Georgia, March 1976 through July 1990

[Trends in units of microequivalents per liter per year, except discharge in cubic meters per second per year, pH in standard units per year, and silica in micromoles per liter per year; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	–0.01	0.929	--	--
pH, field	.08	.008	0.08	0.008
Calcium	1.6	.028	1.2	.030
Magnesium	.5	.168	.4	.199
Sodium	.4	.528	.2	.507
Potassium	<.1	.548	<.1	.825
Alkalinity, laboratory[a]	--	--	--	--
Sulfate	<.1	.365	([b])	--
Chloride	<.1	.385	([b])	--
Nitrite plus nitrate	([a])	--	--	--
Silica	.6	.561	.5	.268

[a] Insufficient data to calculate trend.

[b] Flow model not significant at $\alpha = 0.10$.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling conducted October 27 and 28, 1991, are given in table 21; locations of sampling sites are shown in figure 10. Discharge at the gage was 2.0 m^3/s compared to the median daily discharge of 2.7 m^3/s for October (Lawrence, 1987), indicating that the basin was sampled during normal conditions for that time of year. Solute concentrations measured at the gage (site 1) during the synoptic sampling were generally between the median and third-quartile concentrations at the gage during the entire period of record (table 18). Tributary streams were similar in composition to the gage, with calcium and sodium the dominant cations and alkalinity the dominant anion. All samples had ion balances close to zero (range –2.5 to 4.9 percent), indicating that organic anions probably did not contribute significantly to the ionic content of stream water at the time of sampling.

Visual inspection of the synoptic data indicates that land-use activities explain most of the spatial variation in water quality at the time of the synoptic sampling. Although nitrate concentrations were extremely low at all the sampling sites (less than 17 μeq/L), only tributaries that drain areas of the basin with agricultural activities (sites 2–5) had detectable concentrations of nitrate. These sites also had slightly elevated concentrations of alkalinity, silica, sodium, potassium, and chloride compared to sites that drain largely undeveloped subbasins (sites 6–8, 10, and 11). For example, alkalinity averaged 180 μeq/L and silica averaged 200 μeq/L in the agricultural subbasins compared to 110 μeq/L and 140 μeq/L, respectively, in the forested subbasins. Chloride averaged 24 μeq/L and sodium averaged 92 μeq/L in the agricultural areas compared to 15 μeq/L and 50 μeq/L, respectively, in the forested subbasins. These differences in chemistry indicate that landscape disturbance related to agriculture and possibly septic tank leakage had a minor, although detectable, impact on the chemistry of surface waters during the sampling period. The impact of these disturbed areas on stream chemistry and sediment load, however, may increase disproportionately during periods of high runoff. Abandoned mines and prospects also may affect the chemistry of some surface waters in the basin. For example, Beech Creek (site 10), which was sampled downstream from a mapped mine and mineralized zone, had the highest sulfate and calcium concentration of the forested tributaries. The mine was not sampled during the synoptic sampling, but the slightly elevated concentrations measured in this tributary are consistent with the weathering sulfide minerals in the ore deposit.

Table 21. Physical properties and major ion concentrations from surface-water sampling sites in the Tallulah River Basin, Georgia, collected October 27–28, 1991

[Site locations shown in fig. 10; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; concentrations in microequivalents; Si, silica in micromoles per liter; <, less than; --, not measured]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	Cl	NO_3	SO_4	Si	Criteria[a]	Remarks
1	02178400	1.98	20	7.12	65	41	57	15	150	20	1.4	15	153		
2	345324083314500	.68	24	7.18	75	40	87	19	170	22	5.0	14	190	MT, LU	Agriculture
3	345407083305200	--	31	7.21	110	62	91	31	230	28	16	13	210	LU	Agriculture
4	345447083300300	--	24	7.17	65	37	110	18	170	22	4.3	19	230	LU	Agriculture
5	345448083300700	.28	21	7.21	65	30	78	18	150	22	2.9	12	180	LU	Agriculture
6	345509083335600	.14	14	6.87	41	24	43	11	89	17	<.7	11	120	MT	Rural residences
7	345549083324600	.23	13	6.94	33	19	43	11	83	17	<.7	12	120	MT	Forested
8	345706083331300	.22	15	7.06	44	22	48	13	98	16	<.7	11	130	LU	Forested
9	345739083332700	.40	21	7.20	85	37	57	14	150	17	<.7	33	150	LU	Downstream from Tate City
10	345924083332500	.040	23	7.12	110	33	57	13	160	11	<.7	42	140	BG	Sulfide mineralization
11	350043083332600	.053	20	7.13	90	23	61	13	140	16	<.7	25	140	LU	Wilderness

[a] Criteria used in selection of sampling sites: BG = bedrock geology, MT = major tributary, LU = land use.

Wild River at Gilead, Maine (Station 01054200)

Site Characteristics and Land Use

The Wild River HBN Basin is in the New England physiographic province, in the northeast section of the White Mountains along the Maine and New Hampshire boundary (fig. 12). The basin drains 180 km^2 of steep, mountainous terrain that ranges in elevation from 208 m at the gage to 1,478 m at the summit of Carter Dome. The USGS gaging station is 0.6 km west of the town of Gilead, Maine, at latitude 44°23'27" and longitude 70°58'47". The Wild River is a northeast-flowing tributary of the Androscoggin River and has a channel length of about 24 km. Stream gradients range from 10 m/km in the lower reaches of the main channel to as much as 60 m/km in the steep headwater tributaries. The main channel is perennial, and mean monthly discharge ranges from 1.53 m^3/s during low-flow conditions in September to 14.7 m^3/s in April, when snowmelt combines with spring rains. Average annual runoff from the basin was 89 cm from 1964 through 1995 (U.S. Geological Survey, Water Resources Data, Maine). Climate of the area is classified as humid continental with short, cool summers and long, cold winters. Average daily air temperatures range from –9.0°C in January to 19.0°C in July (Likens and others, 1977). Precipitation averages 119 cm annually, based on a USGS precipitation gage in the basin, and is fairly evenly distributed during the year (Kahl and others, 1991). A seasonal snowpack, which ranges from 150 to 200 cm in depth, develops each winter.

The basin lies in the Adirondack-New England Mixed Forest ecoregion, which is in the transition zone between the boreal spruce-fir forest to the north and the deciduous forest to the south (Bailey and others, 1994). The forest is currently composed of 35 percent hardwoods, 15 percent conifers, and 50 percent mixed forest, which is largely a result of historic logging activities and recent forest management practices (U.S. Department of Agriculture, 1986). The major hardwood species are sugar maple, beech, yellow birch, paper birch, and aspen; conifers are predominantly hemlock, red spruce, and balsam fir. About 5 percent of the basin is covered by bare rock areas on the summits and in steep upland areas. Vegetation in these areas consists of heath, moss, lichen, and stunted spruce and birch. Soils in the basin are mostly well-drained Spodosols that have developed in Pleistocene till and outwash deposits and have textures that range from rocky to sandy loams (Williams and others, 1948). In general, soils are acidic (soil pH 3.3 to 4.6), have low exchangeable bases, and have low sulfate-adsorption capacities (Kahl and others, 1991).

Bedrock in the basin consists of a sequence of complexly deformed and metamorphosed sandstones, siltstones, and shales of Paleozoic age (Hatch and Moench, 1984). The metamorphosed sediments are mapped as a set of northeast-trending folds that are parallel to the drainage pattern and include the Devonian Littleton Formation and the Silurian Madrid, Smalls Falls, Perry Mountain, and Rangeley Formations (Hatch and Moench, 1984). The major rock types are coarse-grained gneisses, mica schists, and impure quartzites that are composed primarily of quartz, plagioclase, biotite, and garnet. Less common rock types include a calc-silicate granofels in the Madrid Formation and a sulfide-bearing schist in the Smalls Falls Formation. The Kinsman Formation, a Devonian quartz monzonite, is mapped along the southern divide of the basin. Pleistocene glacial materials in the basin were deposited by an active ice sheet that persisted in the area until about 14,000 years ago (Thompson and Fowler, 1989).

The Wild River Basin drains parts of Oxford County in Maine and Coos County in New Hampshire. Ninety-seven percent of the basin lies in the Evans Notch Ranger District of the White Mountain National Forest. The remaining 3 percent includes several private holdings near the gage. The area of the basin upstream from the Wild River Campground is part of the Wild River Roadless Area, which is currently pending designation as a wilderness area (U.S. Department of Agriculture, 1986). The Caribou-Speckled Wilderness area was recently established in the northeastern part of the basin and is east of State Highway 113 between Peabody and Speckled Mountains. Access into the basin is by way of two roads, State Highway 113 and Forest Route 12. State Highway 113 is a paved road that enters the basin at the gage and follows the Evans Brook drainage to Evans Notch (fig. 12). Forest Route 12 is an earthen road that parallels the Wild River from the Evans Brook confluence to just upstream from the Wild River Campground. Upstream from the campground, access is provided by more than 60 km

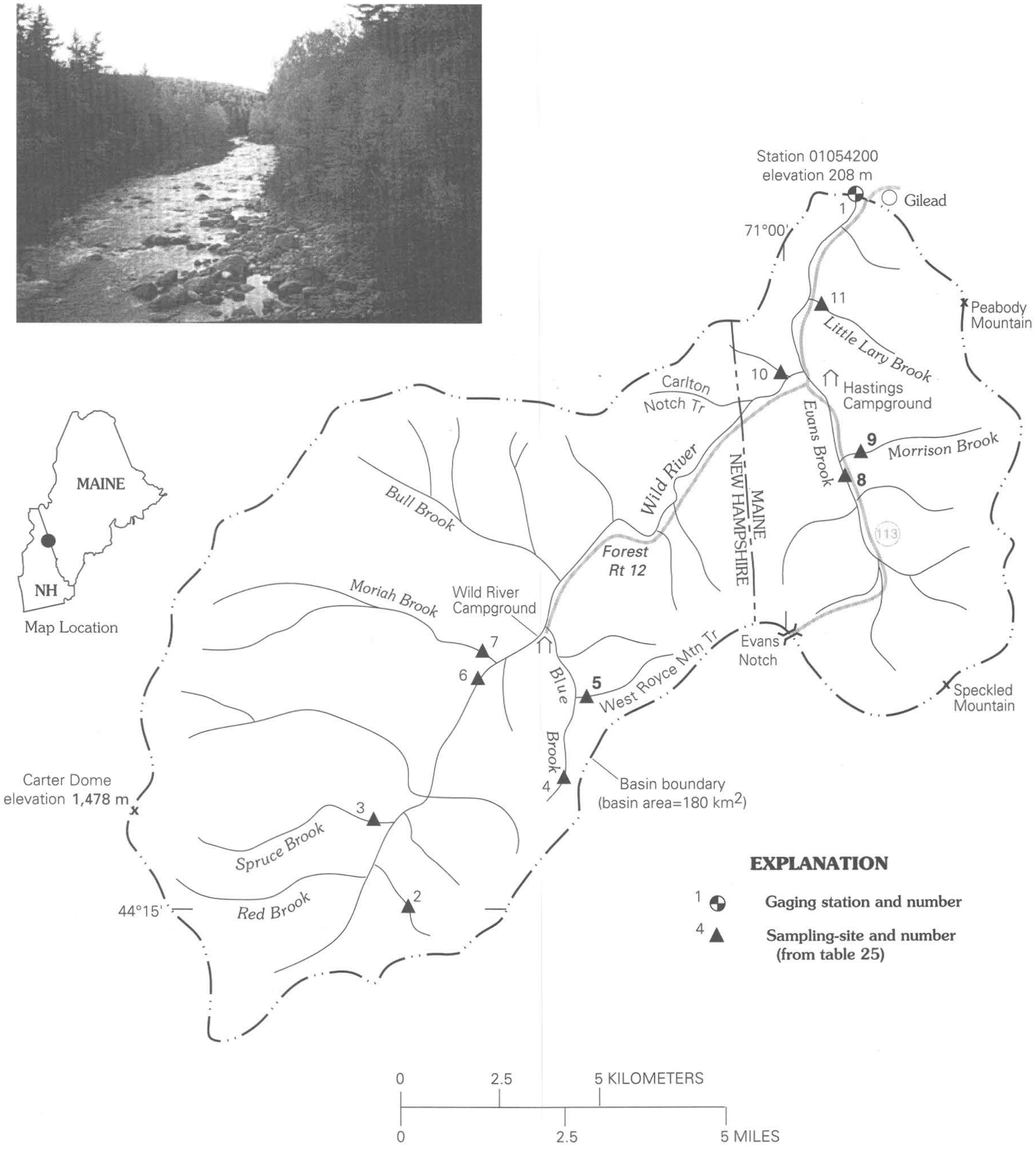

Figure 12. Map showing study area in the Wild River Basin and photograph of the stream channel near the Wild River Campground.

of foot trails that are maintained by the Forest Service and the Appalachian Mountain Club. All roads in the basin are closed during the winter except State Highway 113, which is plowed and salted along a 2-km stretch upstream from the gage. The unplowed section of State Highway 113 is used as a snowmobile trail.

Logging has been important in the land-use history of the Wild River Basin (Wight, 1971). Between 1890 and 1903, a logging railroad was operated along the river as far upstream as Red Brook and along the Bull Brook and Moriah Brook tributaries. During this period, several logging camps and mills were operated in the basin, and more than 300 people lived in the town of Hastings, which was near the current site of the Hastings Campground. Following a large fire in 1903 that destroyed several thousand hectares of timber in the headwater areas of the basin, the Hastings Lumber Company sold its land to the Federal Government, and by 1912 Hastings had become a ghost town. Between 1933 and 1936, the Civilian Conservation Corps constructed State Highway 113 between Gilead and Evans Notch and converted several old railroad grades into hiking trails.

Since 1935, the basin has been administered by the White Mountains National Forest, which manages it primarily for timber, recreation, and wildlife. Logging during the last 35 years has resulted in the thinning or harvesting of about 3,600 ha of forest land in the basin, with cuts that ranged in size from 0.5 to 785 ha (Wayne Millem, written commun., 1994). Since 1980, timber harvesting has been restricted to areas downstream from the Wild River Campground and in the Evans Brook subdrainage. Mining in the White Mountain region has been of minor importance, and no mines are currently in operation. The only known activity in the basin includes three gem-collecting sites near the southern basin divide and a small feldspar quarry near Peabody Mountain that was active from 1938 to 1940 (Gazdik and others, 1988). The Forest Service maintains two campgrounds and five back-country shelters in the basin. Several private cabins are situated along State Highway 113 just upstream from the gage. The Wild River Basin once served as a Forest Service barometer basin, and meteorological data were collected from 1966 to 1972 at a weather station near the Wild River Campground (Richard McKenna, Forest Service, oral commun., 1993).

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for this report includes 162 water-quality samples that were collected from September 1964 through June 1995. Sampling frequency progressively increased from 2 samples per year in 1964 to a maximum of 12 samples per year in 1969. Sampling frequency was reduced to bimonthly from 1971 through 1982 and quarterly from 1983 through 1995. Samples were analyzed at a USGS laboratory in Albany, N.Y., from 1964 through 1977, the USGS Central Laboratory in Atlanta, Ga., from 1978 through 1985, and at the NWQL in Arvada, Colo., from 1986 through 1995. Daily discharge records for the Wild River (station 01054200) are available beginning in July 1964. Daily precipitation amount was measured in the basin from 1990 through 1995 (Wild River Precipitation at Beans Purchase, N.H., station 441852071033101). Records of daily water temperature at the gage are available for July 1964 to September 1983 and November 1992 to September 1993.

Calculated ion balances for 154 samples with complete major ion analyses are shown in figure 13. Ion balances ranged from –41 to +31 percent, and less than 55 percent of the samples had values within the ±10 percent range. This large range of ion balances is not unexpected considering the difficulties in making precise analytical measurements at the low solute concentrations typical of this station. The average ion balance for all samples was –6.7, and almost 80 percent of the samples had negative ion balances, indicating that the samples had an excess of anions over cations. Natural waters commonly have an excess of cations in solution because of the presence of unmeasured organic anions. An anion excess is more difficult to explain than a cation excess and may indicate a bias in one of the analytical measurements. The alkalinity determination probably is the largest single source of error in a major ion analysis (Fishman and Friedman, 1989) and in dilute waters is often overestimated by analytical methods commonly used before 1975 (Kramer and Tessier, 1982). Laboratory alkalinity in HBN samples was determined by a fixed endpoint titration to pH 4.5. For waters with alkalinities below 100 μeq/L, however, the endpoint pH is closer to 5.0, and titration to pH 4.5 may overestimate alkalinity by as much as 25 μeq/L (Barnes, 1964). Because the average alkalinity and anion excess for the Wild River station were 98 μeq/L and 25 μeq/L, respectively, a bias in the laboratory alkalinity appears to be a reasonable explanation for the negative bias in the calculated ion balances.

Time-series plots of the major dissolved constituents were inspected for evidence of method-related effects (fig. 13). Several patterns are evident at the Wild River station. For example, elevated concentrations of calcium and alkalinity were measured in many samples that were collected from 1974 through 1977. A more detailed analysis of the data revealed that the elevated calcium and alkalinity concentrations were not usually reported in the same samples, indicating that they were not related to real changes in stream chemistry. The only documented analytical or procedural change during

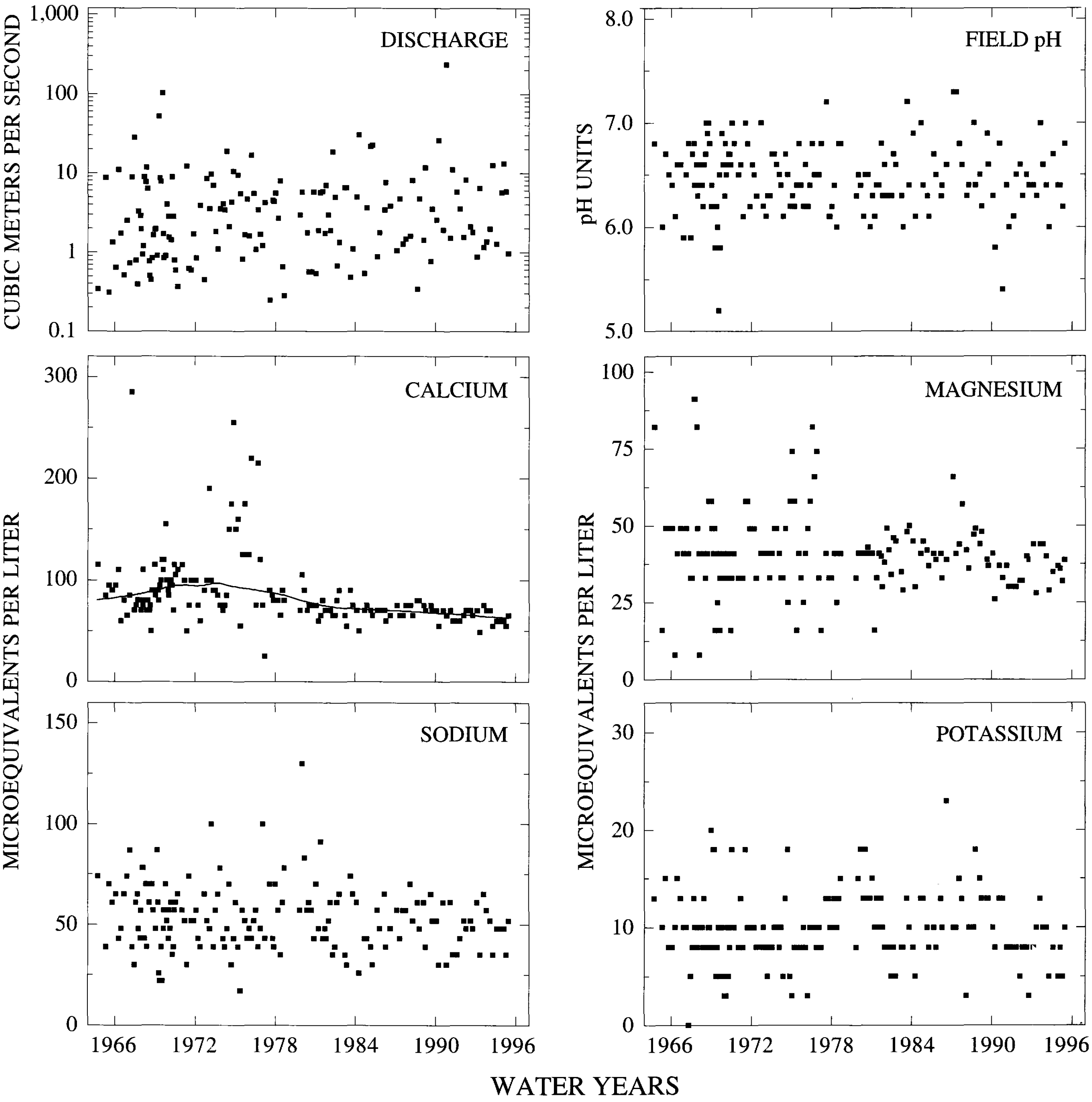

Figure 13. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Wild River, Maine.

this period was the introduction of a polypropylene churn splitter for compositing and splitting samples that was required for use at all HBN stations beginning in water year 1977 (Office of Water Quality Technical Memorandum No. 76.24–T, *Sample Splitter for Water-Sediment Samples*, issued August 16, 1976, at URL http://water.usgs.gov/public/admin/memo/). Although problems with previous sample splitters were not documented by the OWQ, the fact that the anomalous pattern disappeared around the beginning of 1977 indicates that previous splitters or compositing devices may have been a potential source of contamination. Figure 13 also shows a period of elevated sulfate concentrations during the late 1980's. This pattern coincides with the use of a turbidimetric titration method for the analysis of sulfate at the

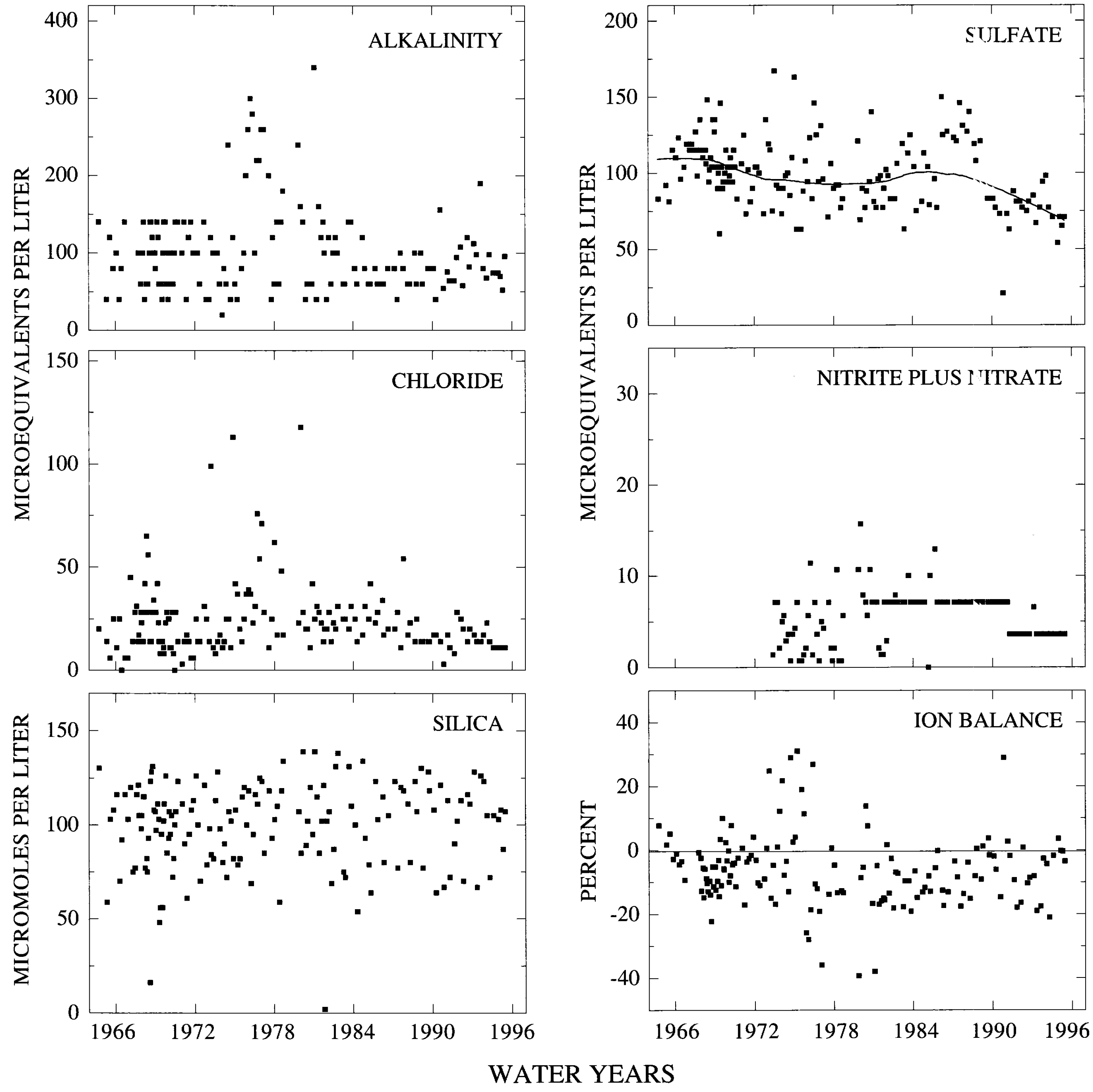

Figure 13. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Wild River, Maine—Continued.

NWQL between March 1986 and December 1989 (Fishman and others, 1994). In 1989, the NWQL determined that sulfate concentrations can be overestimated by this technique and changed the method to ion chromatography in 1990 (Office of Water Quality Technical Memorandum No. 90.04, *Turbidimetric Sulfate Method*, issued December 21, 1989, at URL http://water.usgs.gov/public/admin/memo/). The bias was most pronounced in dilute waters, although it was not consistent among samples and appeared to be influenced by factors such as color and turbidity (Schertz and others, 1994).

Median concentrations and ranges of major dissolved constituents in stream water collected at the HBN gaging station and VWM concentrations in wet-only precipitation measured at the Greenville NADP

Table 22. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ion concentrations measured in water-quality samples from Wild River, Maine, September 1964 through June 1995, and volume-weighted mean concentrations in wet precipitation collected at the Greenville Station, Maine

[Concentrations in units of microequivalents per liter, discharge in cubic meters per second, specific conductance in microsiemens per centimeter at 25 degrees Celsius, pH in standard units, and silica in micromoles per liter; n, number of stream samples; VWM, volume-weighted mean; inst., instantaneous; spec. cond., specific conductance; --, not reported]

Parameter	Stream water						Precipitation
	Minimum	First quartile	Median	Third quartile	Maximum	n	VWM[a]
Discharge, inst.	0.25	1.1	2.7	6.5	240	163	--
Spec. cond., field	15	20	22	25	36	162	--
pH, field	5.2	6.3	6.4	6.7	7.3	162	4.6[b]
Calcium	25	70	75	95	285	162	3.0
Magnesium	8.0	33	41	46	91	163	1.4
Sodium	17	43	52	61	130	162	3.8
Potassium	<2.0	8.0	10	13	23	163	.4
Ammonium	<.7	.7	.7	2.7	14	75	6.7
Alkalinity, laboratory	20	66	98	120	340	155	--
Sulfate	21	83	99	120	170	162	26
Chloride	<3.0	14	21	29	120	160	3.9
Nitrite plus nitrate	<.7	3.6	7.1	7.1	16	101	13[c]
Silica	2.0	84	110	120	140	162	--

[a] Values are volume-weighted mean concentrations for 1980–94.

[b] Laboratory pH.

[c] Nitrate only.

station are presented in table 22. Precipitation chemistry at the NADP station, which is about 30 km south of the basin, is dilute and acidic with a VWM pH of 4.6 for 15 years of record. The dominant cations in precipitation were hydrogen and ammonium, which contributed 57 and 15 percent of the total cation charge, respectively. The dominant anions were sulfate, which accounted for 61 percent of the total anions, and nitrate, which accounted for 30 percent. The low pH and predominance of strong acid anions indicates that precipitation at the NADP station probably is affected by anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain (Likens and others, 1977).

Stream water in the Wild River is dilute and weakly buffered; alkalinities were generally below 120 μeq/L, and total ionic constituents ranged from 220 to 770 μeq/L. The major cations in stream water were calcium and sodium, and the major anions were alkalinity and sulfate. The low concentrations of weathering-derived constituents, particularly alkalinity, reflect the slow weathering rates of silicate minerals in the bedrock. High rates of acidic deposition probably also contribute to the low alkalinities measured at this station. The median chloride concentration in stream water was 21 μeq/L, which was 5.4 times larger than the VWM concentration of 3.9 μeq/L in precipitation. On the basis of the difference between annual precipitation and runoff, evapotranspiration can account for no more than a twofold increase in the concentration of precipitation, indicating that a small amount of stream-water chloride may be derived from sources other than precipitation. Additional sources of stream-water chloride might include weathering of amphibole minerals in the gneiss and schist (Peters, 1991) or possibly deicing salts applied to a section of State Highway 113. The median concentration of sulfate in stream water was 99 μeq/L compared to 26 μeq/L in precipitation, indicating that sulfate is derived from sources other than wet deposition. Dry deposition is generally assumed to be the source of additional stream-water sulfate, if no other sources are present in the basin. In most parts of Maine, contributions of sulfate from dry deposition are assumed to equal those in wet deposition (Kahl and others, 1991). Therefore, atmospheric inputs can account for most or all of the sulfate in stream water. Concentrations of inorganic nitrogen species in stream water were well below the average concentration in precipitation, indicating that most atmospheric nitrogen is retained by vegetation and soils in the basin.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 23). Most weathering-derived constituents, particularly silica, had negative correlations with discharge. These results are consistent with a hydrologic system where weathering-enriched base flow is diluted by waters from shallow or surficial sources during periods of increased discharge. Among the ions, the strongest correlations were found between sodium and silica (r = 0.710) and calcium and magnesium (rho = 0.745), which indicates common mineralogic sources of these solutes. The most likely source of sodium and silica is plagioclase weathering, whereas calcium and magnesium probably are released by the weathering of hornblende and trace amounts of calcite (Stauffer and Wittchen, 1991). Chloride and sulfate were poorly correlated with other dissolved constituents with the exception of a weak positive correlation between sulfate and magnesium (rho = 0.535). This lack of correlation supports the idea that both chloride and sulfate are derived primarily from atmospheric sources. The weak correlation between sulfate and magnesium may be an indication that some stream-water cations are derived from leaching of the soil exchange complex by acidic precipitation (Johnson and Ruess, 1984).

The results of the seasonal Kendall test for trends in discharge and major dissolved constituents are shown in table 24. Statistically significant downward trends in calcium and sulfate concentrations and an upward trend in flow-adjusted silica concentrations were detected at the 0.01 confidence level. The trend in the flow-adjusted calcium concentrations was not calculated because the flow model was not statistically significant at the 0.1 confidence level. Trends in the sulfate data were similar for unadjusted and flow-adjusted concentrations, indicating that the trend was not driven by variations in stream discharge. The LOWESS curve in figure 13 shows that the decrease in sulfate concentrations was relatively constant since the late 1960's aside from the period of analytical bias in the late 1980's. Most of the decrease in calcium concentrations occurred after 1974, although the pattern probably is influenced somewhat by analytical bias in the early part of the record. A decline in stream-water sulfate in the Wild River may be linked to declining sulfur dioxide emissions in the Northeastern United States since 1970 (Husar and others, 1991) and is consistent with declines reported at other sites in the region. Smith and Alexander (1983) noted small declines in stream sulfate at a number of HBN stations in the Northeast, including the Wild River. Concentrations of sulfate in stream water at the Hubbard Brook Experimental Forest in New Hampshire have decreased at a rate of 2 (µeq/L)/yr from 1964 to 1985 (Driscoll and others, 1989). The decline in stream-water sulfate at Hubbard Brook was balanced by a decrease in base cations rather than an increase in stream-water pH, indicating that declines in stream-water concentrations of these constituents are linked to long-term decreases in the atmospheric deposition of both sulfate and base cations (Driscoll and others, 1989). The downward trend in calcium concentrations in the Wild River also may be related to declines in atmospheric deposition, although no long-term precipitation records are available to confirm such a relationship.

Table 23. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ion concentrations, Wild River, Maine, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; Si, silica]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	–0.646								
Ca	–.512	0.435							
Mg	–.503	.444	0.745						
Na	–.664	.517	.681	0.515					
K	–.168	.238	.393	.296	0.316				
Alk	–.453	.467	.413	.293	.539	0.209			
SO_4	–.182	.270	.314	.535	.258	.220	–0.044		
Cl	.015	–.038	.227	.165	.193	.004	–.013	0.293	
Si	–.826	.635	.599	.513	.710	.275	.572	.201	–0.017

Table 24. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major ion concentrations, Wild River, Maine, September 1964 through June 1995

[Trends in units of microequivalents per liter per year, except discharge in cubic meters per second per year, pH in standard units per year, and silica in micromoles per liter per year; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	0.02	0.120	--	--
pH, field	<.01	.700	< 0.01	0.313
Calcium	−1.0	.000	([a])	--
Magnesium	−.1	.042	−.1	.109
Sodium	−.2	.012	−.2	.032
Potassium	<.1	.999	<.1	.483
Alkalinity, laboratory	<.1	.249	<.1	.984
Sulfate	−.8	.000	([a])	--
Chloride	<.1	.155	−.2	.020
Nitrite plus nitrate	([b])	--	--	--
Silica	.2	.206	.4	.001

[a] Flow model not significant at $\alpha = 0.10$.

[b] Insufficient data to calculate trend.

The source of the upward trend in silica concentrations could not be determined. Because the trend was only detected in the flow-adjusted data, it probably is related to an environmental change in the basin rather than a change in analytical method (Hirsch and others, 1982). The most obvious environmental changes that have occurred during the period of record include a decrease in logging activity in the basin and a regional decline in acidic deposition. Both of these environmental changes, however, are more likely to have caused a decrease in stream-water silica than an increase, indicating that less obvious environmental factors may have contributed to the upward trend in silica.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling of October 7 and 8, 1991, are presented in table 25; locations of sampling sites are shown in figure 12. The basin was sampled during stormflow conditions following a 10-cm storm event on October 6.

Table 25. Physical properties and major ion concentrations from surface-water sampling sites in the Wild River Basin, Maine and New Hampshire, October 7–8, 1991

[Site locations shown in fig. 12; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; concentrations in microequivalents; Si, silica in micromoles per liter; <, less than; --, not measured]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria[a]	Remarks
1	01054200	3.40	17	5.8	60	26	35	9.0	15	85	12	<0.7	73		Logging downstream from site 6
2	441459071060200	--	13	5.3	36	12	30	4.1	<1.0	63	8.7	<.7	63	BG	Monzonite
3	441607071062300	--	12	5.6	37	19	22	6.1	5.1	58	8.7	<.7	53	BG	Aluminous schist, granofels
4	441647071033500	--	19	4.8	41	17	35	4.9	<1.0	69	9.6	<.7	78	BG	Quartzite, mica schist
5	441751071032600	--	22	4.7	44	19	35	3.6	<1.0	87	10	<.7	75	BG	Calc-silicate granofels
6	441758071043900	--	15	5.5	48	24	26	7.4	6.6	67	9.0	<.7	60	MT, LU	Roadless area, no logging
7	441806071045100	--	15	5.9	48	33	30	6.9	21	73	8.5	<.7	67	BG	Mixed lithology
8	442035070585100	1.43	18	6.0	80	35	39	6.9	20	90	12	<.7	78	MT, LU	Highway, logging in subbasin
9	442037070584700	.36	19	6.0	70	32	39	6.6	11	100	13	<.7	80	BG	Aluminous schist, granofels
10	442115070594100	.05	19	5.9	75	30	48	9.0	25	90	14	<.7	93	BG	Sulfidic schist
11	442213070592900	.24	22	6.4	85	40	57	9.5	34	110	14	<.7	105	BG	Sulfidic schist

[a] Criteria used in selection of sampling sites: BG = bedrock geology, MT = major tributary, LU = land use.

The daily mean discharge at the gage on October 7 and 8, 1991, was 33.7 m^3/s and 11.2 m^3/s, respectively, although the instantaneous discharge at the gage had fallen to 3.4 m^3/s at the time of sampling. Because of the storm event, solute concentrations at the gage (site 1) were below the first quartile concentrations that were measured at the gage during the entire period of record (table 22), and the alkalinity was close to the lowest concentration on record. The chemistry of the tributary streams also was extremely dilute and did not vary markedly among the sampling sites. The dominant cation was calcium, which ranged from 36 to 85 μeq/L, and the dominant anion was sulfate, which ranged from 58 to 110 μeq/L. All sites had extremely low alkalinities (less than 35 μeq/L), and two of the tributaries (sites 4 and 5) had pH values below 5.0. Nitrate concentrations in all tributaries were less than the detection limit of 0.7 μeq/L, and chloride concentrations ranged from 8.5 to 14 μeq/L. These results, particularly the low stream-water alkalinities, indicate that the tributary streams were strongly affected by the recent storm, and the data probably are not indicative of processes that control stream chemistry in the basin under base-flow conditions. A large component of stormflow would tend to mask spatial variations in stream chemistry that reflect basin characteristics, such as geology.

Cypress Creek near Janice, Mississippi (Station 02479155)

Site Characteristics and Land Use

The Cypress Creek HBN Basin is in the Southern Pine Hills section of the Coastal Plain physiographic province in southeastern Mississippi (fig. 14). The topography of the area is rolling to hilly with rounded ridges and broad, mature drainages (U.S. Department of Agriculture, 1994). Cypress Creek drains 136 km^2 of forested terrain that ranges in elevation from 34 m at the gage to 98 m along the northeast basin divide. The basin also contains some swamps along slower moving sections of the creek. The USGS gaging station is 2 km east of Janice, Miss., at latitude 31°01'30" and longitude 89°01'00". Cypress Creek is a south-flowing tributary of the Leaf River with a channel length of about 20 km upstream from the gage and an average stream gradient of 2.0 m/km. The main channel is perennial, and mean monthly discharge ranges from 1.08 m^3/s in August to 5.38 m^3/s in February and March. Average annual runoff from the basin was 70 cm from 1972 through 1995 (U.S. Geological Survey, Water Resources Data, Mississippi). Climate of the area is influenced by weather systems in the Gulf of Mexico and is characterized by persistent humidity and mild temperatures (U.S. Department of Agriculture, 1994). Average monthly air temperatures range from 9.1°C in January to 27.4°C in July, and the frost-free season averages 259 days (U.S. Department of Agriculture, 1994). Precipitation averages 152 cm annually; October is the driest month (7.6 cm) and March is the wettest (16.2 cm).

The basin lies in the Outer Coastal Plain Mixed Forest ecoregion (Bailey and others, 1994) and the dominant forest type is longleaf-slash pine. Drier sites in the basin are dominated by longleaf pine with variable amounts of turkey oak, bluejack oak, and blackjack oak (U.S. Department of Agriculture, 1985). Depending on soil moisture, understory species may include grasses, Jessamine shrubs, wax myrtle, blackberry, and prickly-pear cactus. Slash pine, the dominant species type on moist sites, grows in pure stands or stands mixed with longleaf pine, loblolly pine, and hardwoods. Wet sites along drainages are dominated by sweet bay-swamp tupelo-red maple forest communities. Most soils in the basin are classified as Ultisols (Paleudults) and are mapped in the McLaurin-Prentiss-Freestone and McLaurin-Luch-Troup soil associations (U.S. Department of Agriculture, 1994). They are found on ridges and side slopes and are generally well drained with textures that range from loamy sand to fine, sandy loam. The dominant soil minerals are quartz, kaolinite, and montmorillonite.

Bedrock in the basin includes gently dipping, nonmarine sediments of the Tertiary Hattiesburg and Citronelle Formations (Gandl and Spiers, 1980). The Hattiesburg Formation consists of greenish-gray, silty and sandy clays with interbedded sands, and the Citronelle Formation is orange-red to tan silty sand, with occasional layers of gravel and clay (Brandwein and White, 1983). Both units are composed primarily of quartz and clay and are not easily distinguished except that the heavy mineral suite of the Hattiesburg Formation contains epidote, garnet, and hornblende, which are absent in the Citronelle Formation (Brandwein and White, 1983). The Hattiesburg Formation is one of the principal aquifers used for domestic water supplies in the area (Morse, 1944).

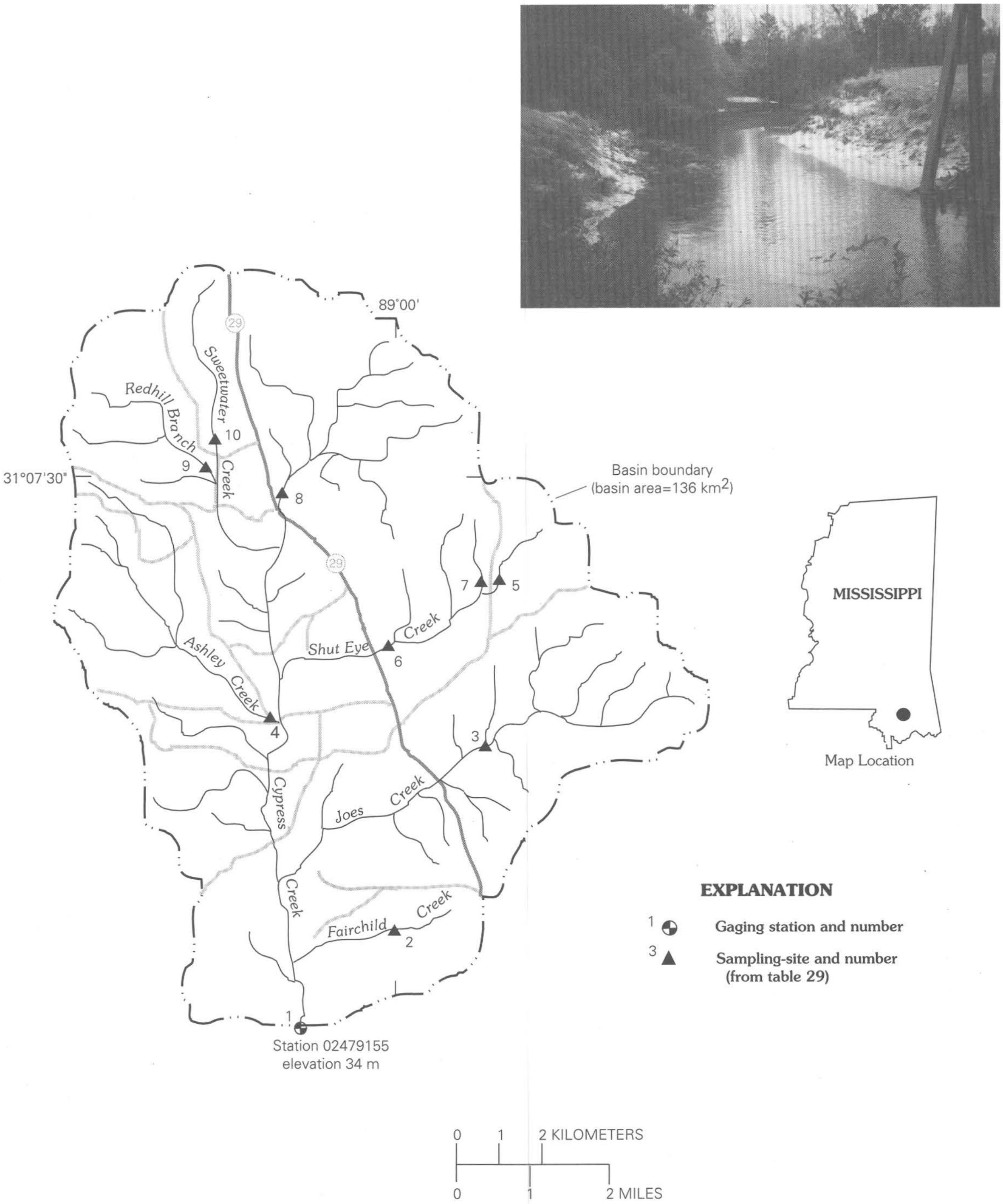

Figure 14. Map showing study area in the Cypress Creek Basin and photograph of the stream channel at the gage.

The headwaters area of Cypress Creek is underlain by the Cypress Creek Salt Dome, one of 50 such domes in the Mississippi salt-dome basin (Spiers and Gandl, 1980). In the late 1970's and early 1980's, the U.S. Department of Energy investigated the suitability of salt domes in Mississippi, including the Cypress Creek Salt Dome, as sites for nuclear waste disposal (Spiers and Gandl, 1980). A swampy area about 2.5 km^2 in extent occupies a topographic low in the headwaters of Cypress Creek directly above the salt dome. Although the dome is 460 m below the surface, this swampy area may have formed in a depression caused by dissolution of salt at depth and subsequent collapse of the overlying sediments (Spiers and Gandl, 1980).

The Cypress Creek Basin drains parts of Perry County in southeastern Mississippi and is entirely in the boundaries of the De Soto National Forest. Most land in the northern one-half of the basin is in the Camp Shelby Special Use area that is used as a military practice area by the U.S. Army National Guard. About 15 percent of land in the National Forest boundary is owned by private individuals and logging companies. More than 60 km of forest and county roads provide vehicle access to most areas of the basin. State Highway 29 bisects the basin from north to south. Public access is allowed in the Camp Shelby Special Use area except when military exercises are being conducted. Historically, land in the Cypress Creek Basin was owned by timber companies who removed most of the native longleaf pine forests in the early 1900's. Many logged areas were subsequently sold to the Federal Government, and the De Soto National Forest was established in the mid-1930's. Currently, the basin is covered by second- and third-growth pine and hardwood stands which the De Soto National Forest manages on an even-aged basis with 80-year rotations for pines and a 100-year rotation for hardwoods. The primary cutting methods used are clearcutting and seedtree and shelterwood removals of which about one-half are done by hand and one-half by mechanical means (U.S. Department of Agriculture, 1985). The forest management plan also includes provisions for improving wildlife habitat, especially for the endangered red-cockaded woodpecker and the threatened gopher tortoise (Tony Rivers, Forest Service, oral commun., 1996). A special-use permit to Camp Shelby has allowed the U.S. Department of the Army and Mississippi National Guard to use the upper one-half of the basin for military training including tank maneuvers and artillery practice since 1959. A detailed description of the Camp Shelby Training Facilities and their impacts on National Forest lands can be found in an Environmental Impact Statement prepared by the Forest Service (U.S. Department of Agriculture, 1994).

Historical Water-Quality Data and Time-Series Trends

The HBN data set analyzed for this report includes 153 water-quality samples that were collected from December 1966 through May 1995. Sampling frequency ranged from semiannual to monthly from 1967 through 1974. Sampling frequency was bimonthly from 1975 through 1982 and quarterly from 1985 through 1995. Although not documented, water-quality samples in the early part of the record probably were analyzed at one of three USGS laboratories (Raleigh, N.C.; Ocala, Fla.; Tuscaloosa, Ala.) that provided analytical services for the Southeastern Region (Durum, 1978). After establishment of the Central Laboratory System, samples were analyzed at the Central Laboratory in Atlanta, Ga., from 1973 through 1985 and at the NWQL in Arvada, Colo., from 1986 through 1995. Daily discharge records for Cypress Creek (station 02479155) are available beginning in October 1966.

Calculated ion balances for 149 samples with complete major ion analyses are shown in figure 15. Ion balances ranged from –37 to +45 percent, and 45 percent of the samples had calculated values outside the ±10 percent range. This wide range of values is not unexpected considering the difficulties in making precise analytical measurements at the low solute concentrations typical of this station. The mean charge balance was –4.7 percent, and almost 60 percent of samples had negative ion balances, indicating that the samples had a slight excess of measured anions over cations. The anion excess at this site was somewhat difficult to explain, particularly considering that organic anions may be an important component of stream water based on the tealike color of stream water. As mentioned previously, the apparent anion excess may be because of an overestimation of laboratory alkalinity by the fixed endpoint titration to pH 4.5 (Office of Water Quality Technical Memorandum No. 80.27, *New Parameter Codes for pH,*

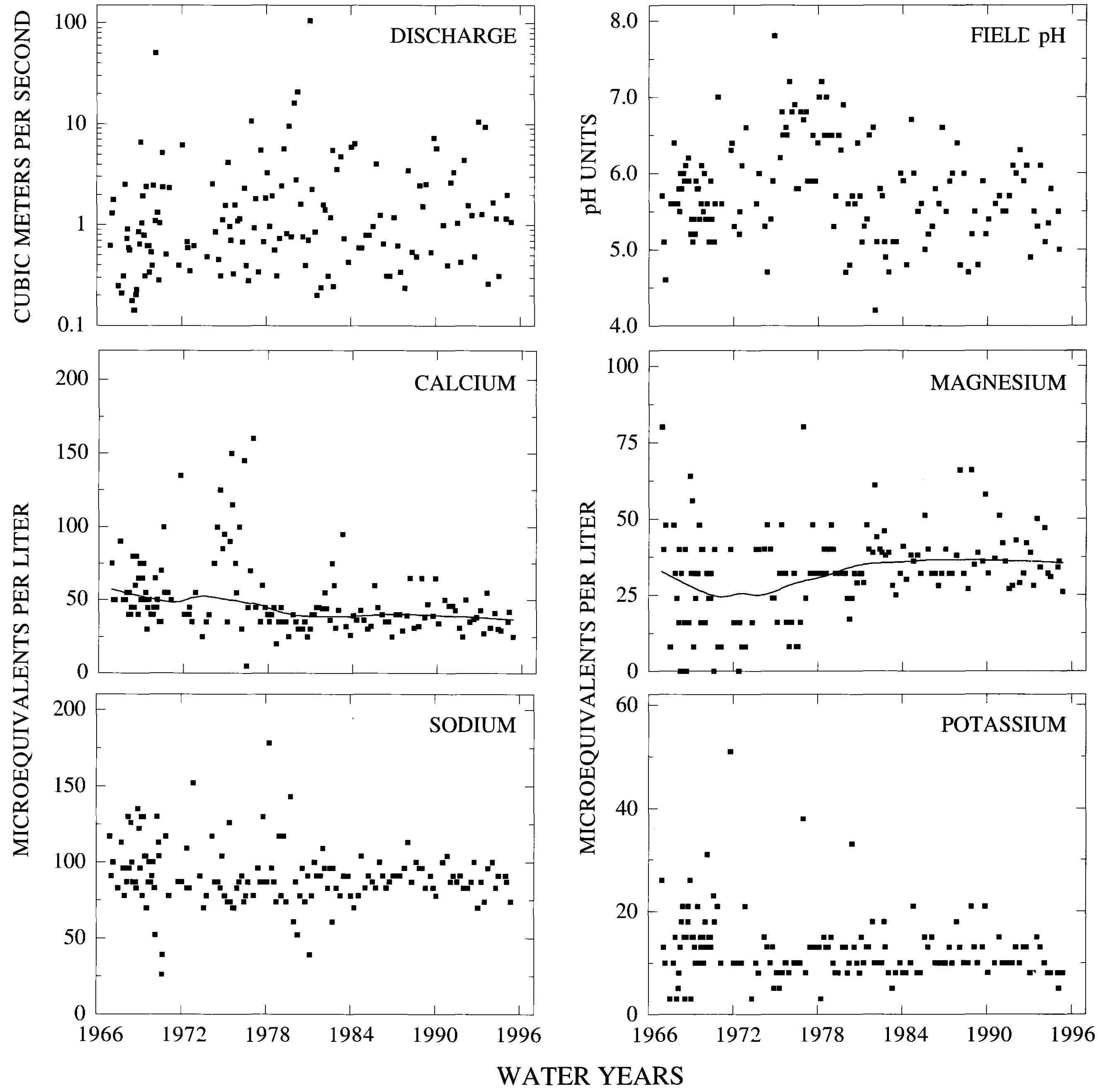

Figure 15. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Cypress Creek, Mississippi.

Alkalinity, Specific Conductance, and Carbonate/ Bicarbonate, issued September 19, 1980, at URL http://water.usgs.gov/public/admin/memo/). For waters with alkalinities below 100 µeq/L, however, the endpoint pH is closer to 5.0, and titration to pH 4.5 may overestimate alkalinity by as much as 25 µeq/L (Barnes, 1964). Because the average alkalinity and anion excesses for this station were 60 µeq/L and 27 µeq/L, respectively, a bias in the laboratory alkalinity appears to be a reasonable explanation for the negative ion balances.

Time-series plots of the major dissolved constituents were inspected for evidence of method-related effects (fig. 15). Several notable patterns were found at the Cypress Creek station, particularly for calcium, sulfate, nitrite plus nitrate, and field pH.

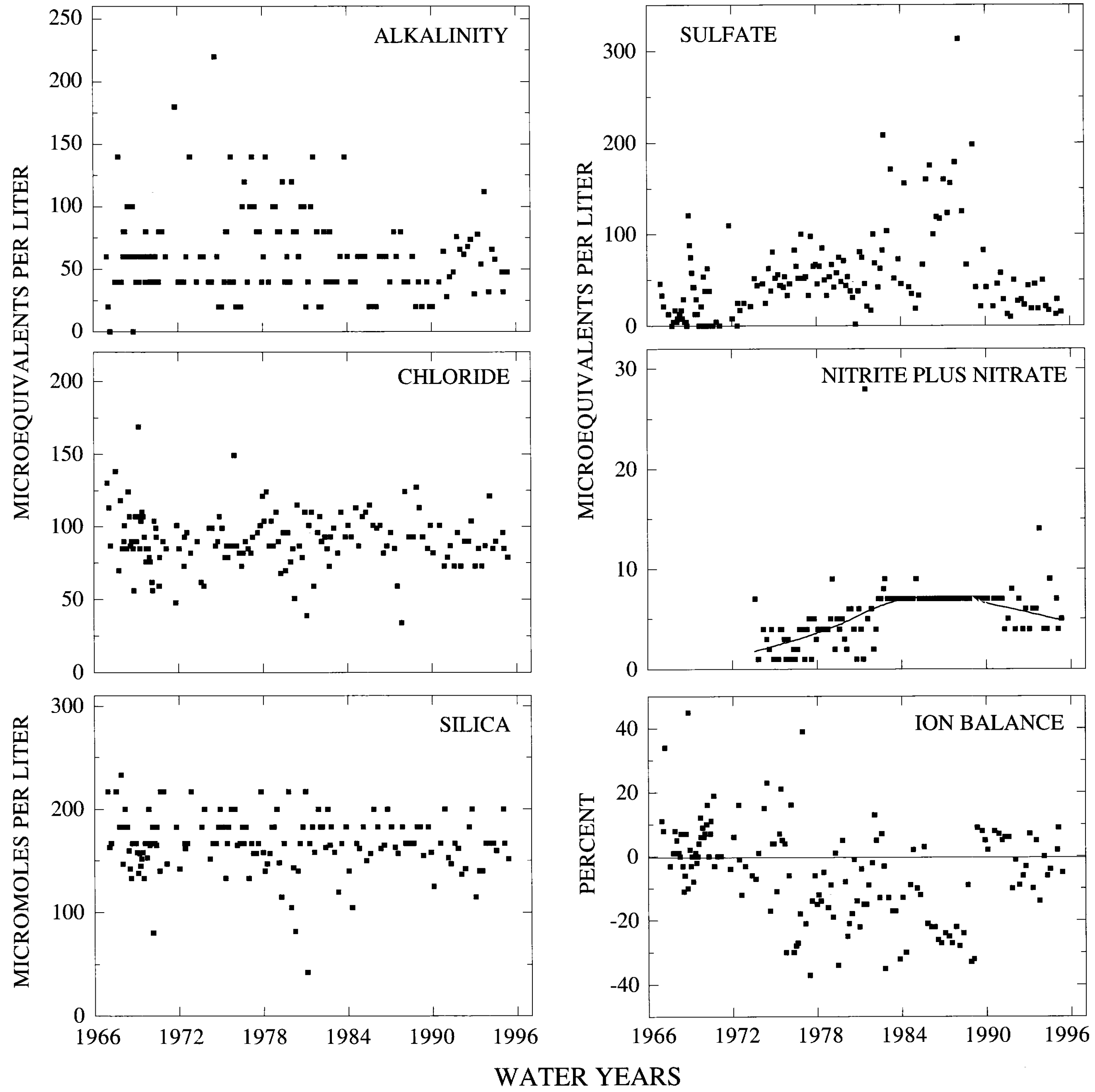

Figure 15. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Cypress Creek, Mississippi—Continued.

For example, several uncharacteristically high calcium concentrations were reported between 1974 and 1976, a pattern that has been observed at other stations in the HBN (for example, Wild River, Maine, and Scape Ore Swamp, S.C.). Because samples from these three sites were analyzed at different laboratories, it seems plausible that the high concentrations may be related to a common sampling or processing procedure. The only documented analytical or procedural change during this period was the introduction of a polypropylene churn splitter for compositing and splitting samples that was required for use at all HBN stations beginning in water year 1977 (Office of Water Quality Technical Memorandum No. 76.24–T, *Sample Splitter for Water-Sediment Samples*, issued August 16, 1976, at URL http://water.usgs.gov/public/admin/memo/).

Although problems with previous sample splitters were not documented by the OWQ, the fact that the anomalous pattern disappeared around the beginning of 1977 indicates that previous splitters or compositing devices may have been a potential source of contamination. The elevated sulfate concentrations reported between 1985 and 1989 occurred during the period when sulfate was analyzed by a turbidimetric titration method. It has been documented that sulfate concentrations can be overestimated by this technique, particularly in dilute or colored waters (Office of Water Quality Technical Memorandum No. 90.04, *Turbidimetric Sulfate Method*, issued December 21, 1989, at URL http://water.usgs.gov/public/admin/memo/). The cause of several zero sulfate concentrations reported in the early part of the record could not be identified. The pattern in nitrite plus nitrate concentrations clearly reflects several changes in the detection limit cutoffs during the period of record. The time-series plot of field pH shows two definite shifts, one upward in the early 1970's and another downward in the early 1980's. Changes in field protocols during the early part of the record are not well documented; however, the shift in the early 1980's coincides with the release of guidelines from the OWQ for obtaining accurate field pH measurements in low-conductivity waters (Office of Water Quality Technical Memorandum No. 81.08, *Electrodes for pH Measurement in Low-Conductivity Waters*, issued February 10, 1981, at URL http://water.usgs.gov/public/admin/memo/). Although these protocols were not required for pH determination at HBN stations, it is likely that many USGS offices may have changed the procedures and equipment they used shortly after this memorandum was issued.

Median concentrations and ranges of major constituents in stream water collected at the HBN gaging station and VWM concentrations in wet-only precipitation measured at the NADP Southeast Research Station in Louisiana about 80 km southwest of the basin are presented in table 26. Precipitation chemistry at the NADP station is dilute and slightly acidic, with a VWM pH of 4.8 during the 12 years of record. The dominant cations in precipitation were hydrogen, sodium, and ammonium, which contributed 34, 26, and 24 percent of the cation charge, respectively. Sulfate, the dominant anion, contributed 47 percent of the anion charge, and chloride and nitrate accounted for 29 and 24 percent, respectively. These results indicate that precipitation at the HBN station probably is affected by both anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain, and by salts derived from marine aerosols (Likens and others, 1977).

Stream water in Cypress Creek is dilute and weakly buffered; specific conductances ranged from 14 to 47 μS/cm and alkalinities generally were between 40 and 80 μeq/L. The dominant cations in stream water were sodium and calcium, and the dominant anions were chloride and alkalinity. The low concentrations of the major weathering products, particularly alkalinity, are attributed to the lack of weatherable minerals in the underlying quartz-rich sediments. The median chloride concentration in stream water was 90 μeq/L, which is about six times larger than the VWM concentration of 14 μeq/L in precipitation. On the basis of the difference between annual precipitation and runoff, evapotranspiration can account for no more than a threefold increase in the concentration of precipitation, indicating that at least one-half of stream-water chloride is derived from sources other than wet deposition. Considering the proximity of this station to the Gulf of Mexico and the predominance of both sodium and chloride in stream water, it seems plausible that dry deposition of marine aerosols is a substantial source of both these ions in surface waters. The median concentration of sulfate in stream water was 44 μeq/L compared to 23 μeq/L in precipitation. Stream-water sulfate concentrations are considerably smaller than expected, considering the concentrating effects of evapotranspiration and inputs from marine aerosols, which indicates that a substantial amount of atmospheric sulfate is retained in the basin. The most likely mechanism for retention is sulfate adsorption on clays and organic matter in the basin soils. Soil retention of sulfate is consistent with sulfate behavior in similar basins in the region and probably plays an important role in buffering stream water from the effects of acidic deposition (Cosby and others, 1991). The basin also is a substantial sink of atmospheric nitrogen, based on the low concentrations of nitrate and ammonium in stream water compared to precipitation.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 27). Most dissolved constituents were poorly correlated with discharge with the exception of weak inverse correlations with alkalinity (r = –0.555) and pH (r = –0.632). Correlations among the solutes also were weak with the exception of a positive correlation between calcium and magnesium (r = 0.728). The lack of correlations between most constituents and flow probably is related to the narrow range of solute concentrations measured at this station. The quartz-rich sediments underlying the basin are relatively unreactive and produce dilute soil and ground waters that are not significantly different in composition from that of the incoming precipitation. The result is that the chemical composition of stream water remains relatively constant over a wide range of hydrologic conditions.

Table 26. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ion concentrations measured in water-quality samples from Cypress Creek, Mississippi, December 1966 through May 1995, and volume-weighted mean concentrations in wet precipitation collected at the Southeast Research Station, Mississippi

[Concentrations in units of microequivalents per liter, discharge in cubic meters per second, specific conductance in microsiemens per centimeter at 25 degrees Celsius, pH in standard units, and silica in micromoles per liter; n, number of stream samples; VWM, volume-weighted mean; inst., instantaneous; spec. cond., specific conductance; <, less than; --, not reported]

Parameter	Stream water						Precipitation VWM[a]
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge, inst.	0.14	0.78	0.93	2.3	110	149	--
Spec. cond., field	14	20	22	25	47	151	--
pH, field	4.2	5.4	5.7	6.1	7.8	150	4.8[b]
Calcium	5.0	35	43	55	160	150	4.5
Magnesium	<8.0	24	32	40	80	150	3.1
Sodium	26	83	87	100	180	149	12
Potassium	2.6	10	10	15	79	150	.7
Ammonium	<14	19	26	36	110	62	11
Alkalinity, laboratory	<20	40	60	80	220	151	--
Sulfate	<20	20	44	67	420	152	23
Chloride	34	82	90	100	250	153	14
Nitrite plus nitrate	<.7	2.3	3.6	5.4	28	66	12[c]
Silica	40	150	160	180	820	151	--

[a] Data are volume-weighted mean concentrations for 01/83 through 12/94.

[b] Laboratory pH.

[c] Nitrate only.

Table 27. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ion concentrations, Cypress Creek, Mississippi, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; Si, silica]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	−0.632								
Ca	.406	−0.322							
Mg	.129	−.152	0.728						
Na	−.494	.169	.103	0.253					
K	−.105	.159	.353	.382	0.242				
Alk	−.555	.565	−.548	−.342	.109	0.018			
SO_4	.232	−.385	.315	.197	.046	.224	−0.366		
Cl	−.036	−.115	.088	.206	.335	−.002	−.163	0.100	
Si	−.522	.271	.011	.234	.600	.191	.106	.015	0.339

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are shown in table 28. Statistically significant upward trends were detected for magnesium and nitrite plus nitrate concentrations and a downward trend in calcium was detected at the 0.01 confidence level. The trend in magnesium was similar for unadjusted and flow-adjusted concentrations, indicating that the trend was not driven by variations in stream discharge. The trend in flow-adjusted calcium concentrations could not be calculated because the flow model was not statistically significant at the 0.1 confidence level. Visual inspection of the LOWESS curves in figure 15 indicate that most of the change in calcium and magnesium concentrations occurred in the early part of the record. Since the early 1980's, concentrations of both cations have remained relatively stable. These changes in stream chemistry may reflect environmental influences such as land-use activities or trends in precipitation chemistry. Few changes in land use have occurred during the period of record except for a slight decrease in timber harvesting (U.S. Department of Agriculture, 1985). Trends in precipitation chemistry at this site are difficult to confirm because no long-term records of precipitation chemistry are available. A method-related influence is another plausible cause of the observed trends in calcium and magnesium. At least two method-related changes were identified that might have affected calcium and magnesium concentrations prior to 1985. A switch from the USGS district laboratory to the Central laboratory occurred in 1973, and the analytical procedure was changed from AA to ICP spectroscopy in 1983 (Office of Water Quality Technical Memorandum No. 82.18). The time-series plot of nitrite plus nitrate in figure 33 demonstrates the influence of changes in reporting protocols. Prior to 1982, concentrations were reported down to a minimum of 0.7 μeq/L or 0.01 mg/L. From 1982 through 1990, the reporting limit was 7.1 μeq/L (0.1 mg/L), and from 1991 through 1995, the reporting limit was lowered to 0.05 mg/L (3.6 μeq/L). It is clear from the shape of the LOWESS curve that interpretation of the trend in nitrite plus nitrate has been greatly complicated by changes in reporting limits over the period of record.

Table 28. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major ion concentrations, Cypress Creek, Mississippi, December 1966 through May 1995

[Trends in units of microequivalents per liter per year, except discharge in cubic meters per second per year, pH in standard units per year, and silica in micromoles per liter per year; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	0.01	0.057	--	--
pH, field	–.01	.105	–0.01	0.210
Calcium	–.6	.000	(a)	--
Magnesium	.4	.005	.4	.010
Sodium	<.1	.768	.1	.335
Potassium	<.1	.421	<.1	.235
Alkalinity, laboratory	<.1	.203	–.4	.233
Sulfate	.9	.033	.6	.222
Chloride	.1	.403	.1	.564
Nitrite plus nitrate	0.4[b]	.000	--	--
Silica	<.1	.111	<–.1	.475

[a] Flow model not significant at $\alpha = 0.10$.

[b] Trend calculated using a test for censored data.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling conducted on January 17–18, 1991, are given in table 29; locations of sampling sites are shown in figure 15. Discharge at the gage was 1.02 m^3/s compared to the median daily discharge of 2.83 m^3/s for the month of January (Lawrence, 1987), indicating that the basin was sampled under low base-flow conditions for that time of year. Solute concentrations measured at the gage (site 1) during the synoptic were similar to the median values at the gage over the entire period of record except for sulfate, which was higher, and alkalinity, which was lower (table 26). Tributary streams were similar in chemical composition to stream water at the gage, and sodium and chloride were the dominant ions. All samples were slightly acidic, with pH values ranging from 4.35 to 5.38. Organic acids probably are the main source of acidity in these waters, although some acidity may be derived from strong acid inputs from precipitation. The presence of organic acids in surface waters is supported by the observation that all samples had positive ion balances (range 0.6 to 14 percent).

The results presented in table 29 indicate there was relatively little spatial variability in surface waters sampled during the synoptic. This uniformity in stream chemistry reflects the unreactive nature of the underlying quartz-rich sediments, which do not significantly alter the composition of the incoming precipitation. Site 8 was the one location that had noticeably higher solute concentrations than the other sites, particularly for sodium, chloride, and sulfate. For example, sodium was 140 µeq/L at site 8 compared to the range of 74 to 96 µeq/L at the other tributary sites. Sulfate was 110 µeq/L at site 8 compared to the range of 46 to 90 µeq/L at the other tributary sites. Site 8 is immediately downstream from a small wetland area that is believed to have formed from the collapse of sediments overlying the Cypress Creek Salt Dome. These chemical results may indicate that stream water at this site is partly affected by ground water associated with the salt dome (Spiers and Gandl, 1980). Several sites also were sampled to determine the effects of the Special Use Area on surface-water chemistry. Surface waters sampled downstream from military training areas (sites 6–10) were not significantly different in composition from streams draining unaffected subbasins (sites 3–5) except for site 8, which might be influenced by the salt dome. These results indicate that under low-flow conditions, the effect of the military operations on surface-water chemistry appears to be minimal. This finding, however, might be different during periods of high runoff when these areas may disproportionately contribute sediment and dissolved solutes to some streams within the basin.

McDonalds Branch in Lebanon State Forest, New Jersey (Station 01466500)

Site Characteristics and Land Use

The McDonalds Branch HBN Basin is in the New Jersey Pinelands region, an area encompassing 4,450 km^2 of gently undulating terrain in the Coastal Plain physiographic province in the southeastern part of New Jersey (Forman, 1979). The basin drains 6.1 km^2 of forested terrain that ranges in elevation from 36 m to 64 m. The HBN gage is in Lebanon

Table 29. Physical properties and major ion concentrations from surface-water sampling sites in the Cypress Creek Basin, Mississippi, collected January 17–19, 1991

[Site locations shown in fig. 14; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; concentrations in microequivalents; Si, silica in micromoles per liter; <, less than; --, not measured]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria[a]	Remarks
1	02479155	1.02	28	5.00	43	51	96	9.2	<10	75	99	3.6	170		
2	310223089000700	.28	22	5.38	43	50	74	10	<10	58	79	9.3	120	LU	Rural residences
3	310415088590100	.22	28	4.88	44	52	83	9.0	<10	85	100	1.4	160	LU	Forested subbasin
4	310501089011200	.14	26	4.98	39	46	83	9.7	<10	73	93	<.7	180	LU	Forested subbasin
5	310620088582000	.042	28	4.85	38	50	83	9.2	<10	83	100	<.7	170	LU	Forested subbasin
6	310542088595200	--	26	4.83	33	47	87	11	<10	65	96	1.4	180	LU	Drains bombing range area
7	310621088582100	.011	26	4.92	37	50	96	7.4	<10	90	93	<.7	200	LU	Drains bombing range area
8	310711089005400	.31	43	4.35	48	64	140	12	<10	110	130	<.7	160	LU	Drains bombing range area
9	310743089015000	.18	23	4.90	27	34	78	4.9	<10	54	85	.7	180	LU	Drains tank maneuver area
10	310801089014500	.071	21	4.86	26	32	83	4.4	<10	46	82	<.7	150	LU	Drains tank maneuver area

[a] Criterion used in selection of sampling sites: LU = land use

State Forest, 11 km southeast of the town of Browns Mill at latitude 39°53'05" and longitude 74°30'20" (fig. 16). McDonalds Branch is a first-order stream that eventually flows into the Rancocas Creek tributary of the Delaware River. The 4-km stream channel drains a hardwood swamp in the upper part of the basin and a cedar swamp near the gage. The basin also includes several upland swamp areas that are perched on clay layers in the underlying sediments and are separated from the main stream channel (Johnsson and Barringer, 1993). Streamflow is dominated by ground-water discharge and is fairly constant during the year, with mean monthly discharge ranging from 0.045 m^3/s in September to 0.083 m^3/s in April. Average annual runoff was 32 cm from 1954 to 1995 (U.S. Geological Survey, Water Resources Data, New Jersey). Average annual precipitation at a nearby weather station was 116 cm between 1951 and 1980 (Johnsson and Barringer, 1993). Estimates of evapotranspiration for the basin range from 45 to 59 percent of annual precipitation, and losses to the regional ground-water system account for 8 to 13 cm annually (Johnsson and Barringer, 1993).

Detailed descriptions of vegetation, soils, and geology in the basin are given in Lord and others (1990). The basin lies in the Eastern Broadleaf Forest (Oceanic) ecoregion (Bailey and others, 1994), and vegetation can be separated into upland and lowland floristic complexes that are determined largely by the position of the water table relative to the ground surface (McCormick, 1955). In the upland complex, which occupies 85 percent of the basin, the ground-water table is generally 60 cm below the ground surface. Vegetation is dominated by mixed pine and oak forests with an understory of scrub oak, black huckleberry, and lowbush blueberry. The remaining 15 percent of the basin is covered by lowland communities that grow in areas where the water table is at or near the ground surface during part of the year. Vegetation in these areas includes transitional pitch-pine forests and cedar swamp, hardwood swamp, and shrubby wetland communities. The distribution of soil types in the basin is determined largely by landscape position (Markley, 1979; Lord and others, 1990). Soils in the upland regions are well-drained Quartzipsamments and Hapludults, and the lowland soils are poorly drained Haploquods, mucks, and peats. In general, soils are sandy, acidic (pH 3.6 to 5.0), and have low cation-exchange capacities (less than 0.5 to 10.5 meq/100 g of soil) (Lord and others, 1990). The sand-silt fraction of soils is dominated by quartz with minor amounts of feldspar and muscovite. The dominant clay mineral is kaolinite, but soils also contain varying amounts of illite, vermiculite, gibbsite, and smectite.

The geology of the Pinelands region consists of a sequence of unconsolidated marine and near-shore sediments of Cretaceous and Tertiary age. The dominant sediment underlying the McDonalds Branch Basin is the Tertiary Cohansey Sand, which is believed to be of deltaic origin (Johnsson and Barringer, 1993). The Cohansey Sand consists of poorly sorted, limonitic quartz sand interbedded with irregularly shaped clay lenses. The sand also contains minor amounts of feldspar, muscovite, ilmenite, chert, and ironstone pebbles. Quaternary alluvial and eolian deposits are present along stream drainages and other undrained depressions in the basin (Lord and others, 1990). Although the Pinelands were unglaciated, continental ice sheets came within 30 km of the region, and tundra and arctic climates probably existed during the late Pleistocene (Rhodehamel, 1979).

The McDonalds Branch Basin is in the east part of Burlington County and is entirely in the boundaries of the Lebanon State Forest. The basin also is in the area referred to as the New Jersey Pinelands, which was designated as a National Reserve in 1978. Land use in the Pinelands is regulated by the Pinelands Commission, which was established by the State legislature in 1979 to balance protection and development interests within the region (Good and Good, 1984). The basin is accessible by way of several public roads that are maintained by the Lebanon State Forest. The Butterworth Road, the only paved road in the basin, enters the basin near the gage and traverses the entire length of the basin roughly parallel to the main drainage. Several gravel roads cross the basin perpendicular to the main drainage. Deicing salts are not used on roads in winter, but Butterworth Road is occasionally plowed.

A detailed description of the history of land use and fire in the McDonalds Branch Basin is in McCormick (1955), from which the following summary of events was taken. The upland forests of the basin were cut at least twice to support the local bog-iron industry in the mid-1800's, and most cedar stands in the basin were cut between 1865 and 1890.

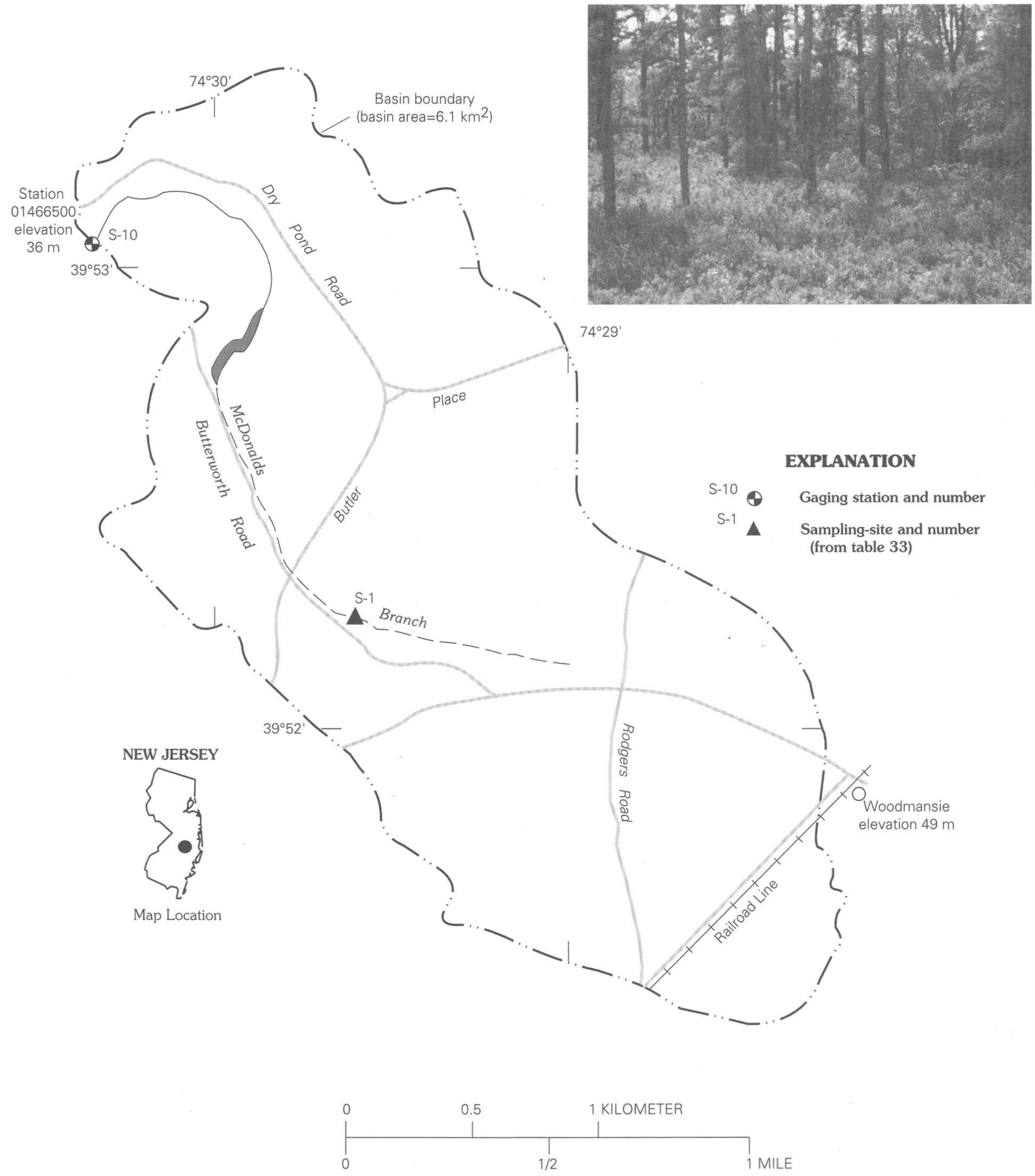

Figure 16. Map showing study area in the McDonalds Branch Basin and photograph of a typical wooded area in the basin.

At least eight wildfires burned portions of the basin between 1850 and the early 1900's, and the entire basin was burned by a large fire in 1922. Land in the basin was purchased from the Federal Government sometime between 1912 and 1930 and eventually designated as State Forest. During the 1930's, the Civilian Conservation Corps built roads, undertook various forest-stand improvement measures, and planted native and exotic tree species and experimental wildlife food patches in the basin. Between 1930 and 1955, more than one-half of the basin was treated by prescribed burning techniques.

Land use in the basin since the establishment of the HBN station has been limited to recreation (hunting, mountain biking, dog sledding) and prescribed burning. Prescribed burning is used by the State Forest to protect property and maintain forest diversity. Burning in the Lebanon State Forest occurs annually in blocks that range from 20 to 200 ha in size, and portions of the basin are burned at least once every 3 years (Christian Bethman, Lebanon State Forest, oral commun., 1994). The only logging activity is in the southeast corner of the basin near an abandoned railroad line. The McDonalds Branch Basin also has been the site of numerous scientific investigations during the past 40 years and is arguably the most intensively studied area in the Pinelands region (R.A. Zampella, Pinelands Commission, written commun., 1994). The USGS conducted an intensive study in the basin from 1984 to 1988 to improve understanding of hydrogeochemical processes and the effects of acidic deposition on surface-water quality (Lord and others, 1990; Johnsson and Barringer, 1993). Other notable studies in McDonalds Branch include hydrologic studies by Rhodehamel (1970); biogeochemical investigations by Johnson (1979), Swanson and Johnson (1980), Turner and others (1985), Madsen and others (1986), Ryan and Gschwend (1990), and Zampella (1994); and vegetation studies by Wang (1984) and McCormick (1955). A compendium of New Jersey Pinelands literature has been compiled by Gemmell and others (1989).

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for this report includes 247 water-quality samples that were collected from June 1963 through September 1995. Sampling frequency ranged from semiannually to monthly from 1963 through 1975 and bimonthly from 1976 through 1995. As many as 12 additional samples were collected each year during a USGS acidic deposition study in the basin from 1984 through 1989 (Lord and others, 1990). Samples in the early part of the record were analyzed at a USGS laboratory in Philadelphia, Pa., from 1963 through 1967 and a laboratory in Harrisburg, Pa., from 1967 through 1972. After establishment of the Central Laboratory System, samples were analyzed in Atlanta, Ga., from 1973 through 1985 and at the NWQL in Arvada, Colo., from 1986 through 1995. Daily discharge records for McDonalds Branch (station 01545600) are available beginning in October 1953. Daily water temperature and specific conductance were measured at the gage from 1961 through 1992 and 1969 through 1992, respectively. Daily measurements of dissolved oxygen and pH were made with a minimonitor from 1985 through 1992.

Calculated ion balances for 240 samples with complete major ion analyses are shown in figure 17. Ion balance ranged from –40 to +40 percent, and only 60 percent of samples had values within the ±10 percent range. This large range of values is not unexpected considering the difficulty in making precise analytical measurements at the low solute concentrations typical of this station. The average charge balance for all samples was 1.4 percent, which agrees with the data of Johnsson and Barringer (1993), who reported a charge balance of 3 percent in monthly samples that were collected at the gage from 1984 through 1988.

Time-series plots were inspected for evidence of method-related effects (fig. 17). Calcium, magnesium, and sodium all had a similar pattern of high data scatter in the first one-half of the record and low scatter in the later one-half of the record. For example, the standard deviation of calcium concentrations was 32 μeq/L for the period 1963–83 compared to 12 μeq/L for the period 1983–95. This pattern is coincident with a change in the HBN operational protocols documented in OWQ Technical Memorandum No. 82.18 (Office of Water Quality Technical Memorandum No. 82.18, *National Water-Quality Networks*, issued September 28, 1982, at URL http://water.usgs.gov/public/admin/memo/). Beginning in water year 1983, the analytical method for major cations and trace inorganic constituents was changed from AA spectroscopy to ICP spectroscopy. Based on this information, it seems plausible that the temporal patterns in these cations reflect a difference in the precision of these two analytical methods rather than a real change in stream-water chemistry. A similar pattern was observed in the sulfate concentrations, which showed a noticeable reduction in data scatter beginning in 1990. This pattern is coincident with a change in the analytical method to ion chromatography in 1990. At least three different methods were used to analyze sulfate prior to 1990. The turbidimetric technique, used at the NWQL between March 1986 and December 1989, was known to overestimate sulfate concentrations in dilute waters, and the effect was commonly most pronounced in colored waters (Office of Water Quality Technical Memorandum No. 90.04, *Turbidimetric Sulfate Method*, issued December 21, 1989, at URL http://water.usgs.gov/public/admin/memo/). A positive bias also was noted by Johnsson and Barringer (1993), who observed that sulfate concentrations in samples analyzed by this technique were more likely to be overestimated in samples with high concentrations of DOC. Assuming the ion chromatographic determinations are unbiased, these results indicate that the analytical methods used prior to 1982 may have introduced a positive bias as well.

Median concentrations and ranges of major constituents in stream water collected at the HBN gaging station and VWM concentrations in wet precipitation collected in the basin from 1985 to 1987 (Johnsson and Barringer, 1993) are listed in table 30. Precipitation chemistry in the basin was dilute and acidic with a VWM pH of 4.3 for 3 years of record. The dominant cations in precipitation were hydrogen, sodium, and ammonium, which contributed 53, 20, and 15 percent, respectively, of the total cation charge. Sulfate was the dominant anion, accounting for 48 percent of the anion charge, and chloride and nitrate each accounted for 26 percent. The results indicate that precipitation at McDonalds Branch probably is a mixture of both strong acids derived from anthropogenic emissions of sulfur and nitrogen compounds and salt derived from marine aerosols.

Stream water in McDonalds Branch is very dilute and acidic. The median pH of stream water was 4.2, which was slightly lower than the pH of precipitation. The major cations in stream water were sodium and hydrogen, and the major anions were sulfate and chloride. Low concentrations of weathering-derived constituents, particularly calcium, magnesium, and alkalinity, reflect the lack of carbonates and other weatherable minerals in the quartz-rich soils and sediments. The relatively high stream-water concentrations of sodium and chloride relative to precipitation probably are because of dry deposition of marine-derived aerosols because inputs from road salt and bedrock weathering are negligible. The high sulfate concentrations and low pH values suggest that stream acidity is at least partially derived from strong acids in precipitation. Stream waters also may be naturally acidic because of the presence of organic acids. Johnsson and Barringer (1993) reported dissolved organic carbon (DOC) concentrations between 3.8 and 12 mg/L in McDonalds Branch. The relatively high concentrations of dissolved aluminum and iron in stream water probably also are related to the high concentrations of DOC.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 31). Discharge was strongly correlated with silica (rho = –0.741) and positively correlated with aluminum (rho = 0.672), iron (rho = 0.502), and DOC (rho = 0.762). Among the ions, the strongest correlations were found between aluminum and DOC (rho = 0.820) and iron and DOC (rho = 0.716). Johnsson and others (1993) found similar relationships and suggested that variations in stream chemistry were controlled largely by hydrology. During low flow, streamflow is primarily derived from groundwater discharge that is rich in dissolved silica because of weathering in the subsurface. With increasing flows, a larger percentage of streamflow is derived from shallow subsurface flow that is enriched in aluminum, iron, and DOC because of the interactions with wetland vegetation and soils.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are shown in table 32. A statistically significant downward trend was detected in calcium concentrations at the 0.01 probability level, which was similar for the unadjusted and flow-adjusted concentrations. The LOWESS curve in figure 17 reveals that most of the decline in calcium concentrations occurred prior to 1983, and concentrations have remained relatively constant since then. The downward trend in calcium may be attributed to the change in analytical method discussed previously. Statistically significant trends were not detected when the trend test was applied separately to the periods before [–1.5 (μeq/L)/yr, p = 0.101] and after [<0.1 (μeq/L)/yr, p = 0.947] 1983, inferring that the

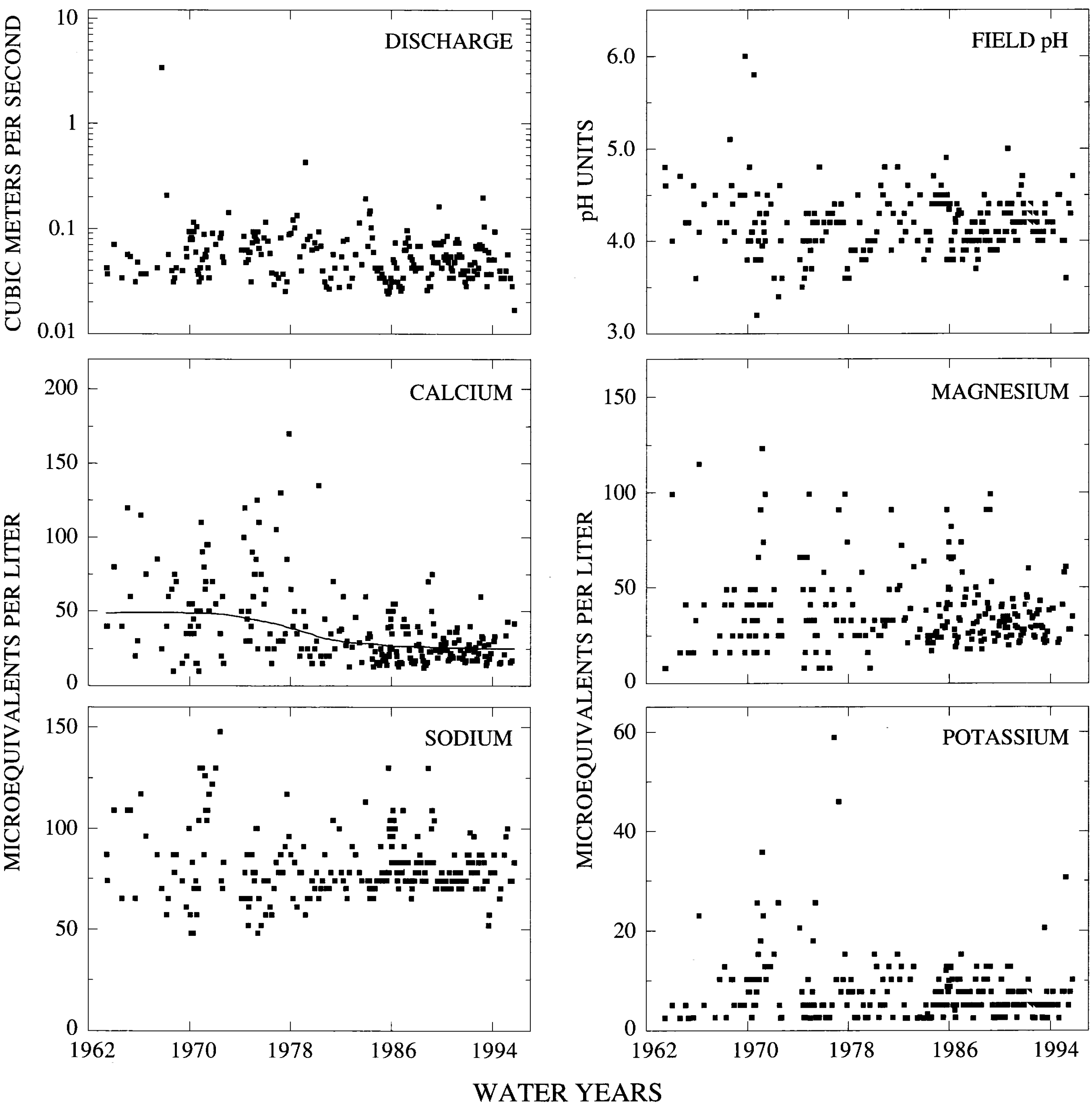

Figure 17. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at McDonalds Branch, New Jersey.

trend is an analytical artifact. In contrast to this study, trends in stream-water pH at McDonalds Branch have been reported in earlier investigations. Johnson (1979) reported a downward trend in pH of 0.02 pH units per year ($p = 0.05$) from 1963 through 1978. Although Johnson (1979) attributed the trend to atmospheric deposition of strong acids, the increase in hydrogen ion was not balanced by a corresponding increase in stream-water sulfate or nitrate. Morgan (1984) conducted a followup study of pH trends at McDonalds Branch and found no significant long-term decline in pH at the site. However, Morgan (1984) did observe several short-term trends that were attributed to natural causes other than acidic deposition.

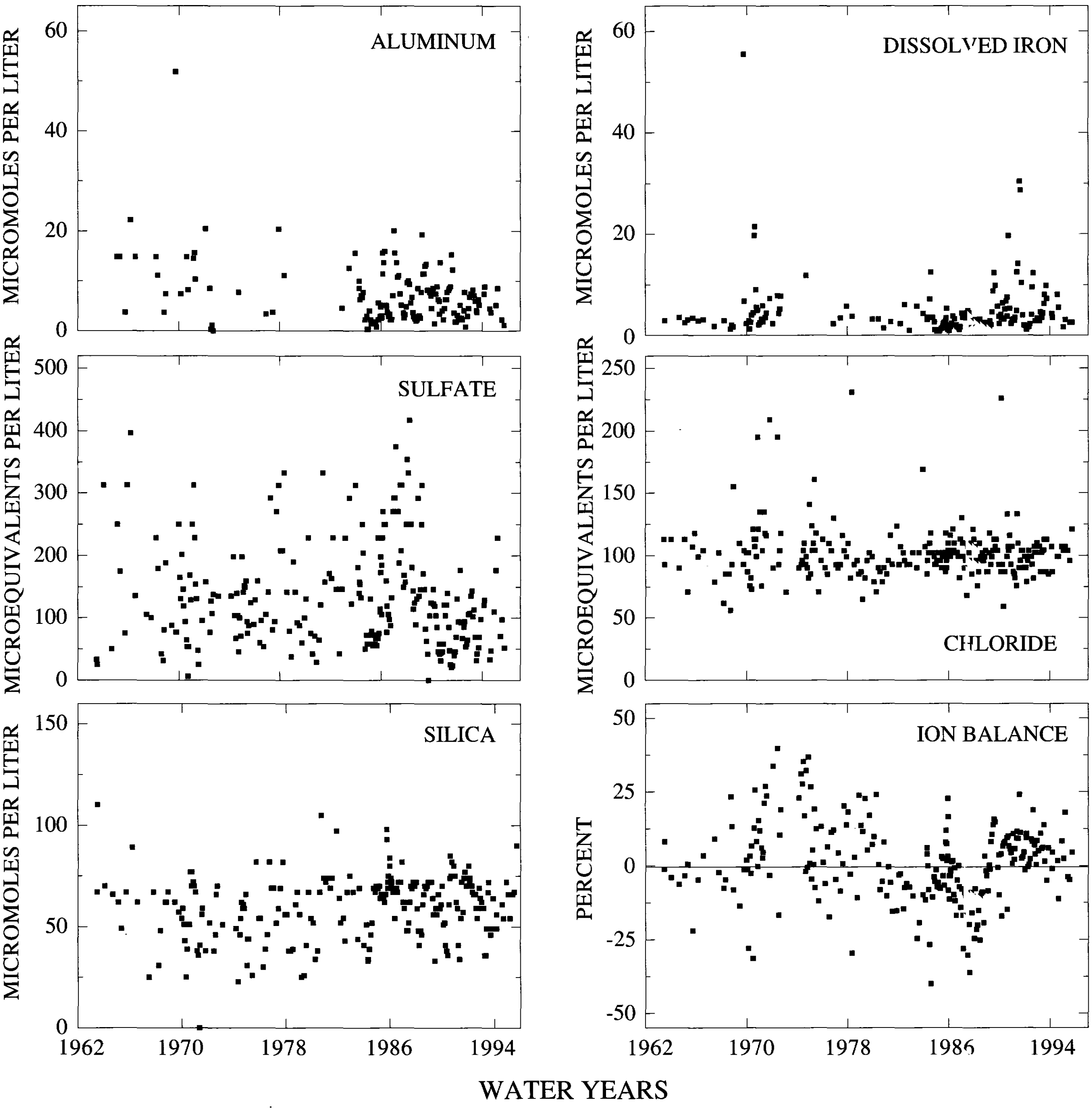

Figure 17. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at McDonalds Branch, New Jersey—Continued.

Synoptic Water-Quality Data

Synoptic samples were not collected in the McDonalds Branch Basin as part of this study because surface-water samples were collected at 10 sites in the basin during an intensive USGS acidic deposition study in the late 1980's (Johnsson and Barringer, 1993). Locations and results of chemical analyses of all 10 sites can be found in Lord and others (1990). Table 33 lists the chemistry data from two sites along the main channel; S–10, located in a cedar swamp at the gage, and S–1, an upstream site located in a hardwood swamp (fig. 16). In general, the concentrations of the major dissolved constituents calcium, sodium, magnesium, sulfate, chloride, and silica at the downstream site are similar to or slightly larger than

Table 30. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ion concentrations measured in water-quality samples from McDonalds Branch, New Jersey, June 1963 through September 1995, and volume-weighted mean concentrations in precipitation collected in the McDonalds Branch Basin

[Concentrations in units of microequivalents per liter, discharge in cubic meters per second, specific conductance in microsiemens per centimeter at 25 degrees Celsius, aluminum, iron, and silica in micromoles per liter, and dissolved organic carbon in milligrams per liter; n, number of stream samples; VWM, volume-weighted mean; inst., instantaneous; spec. cond., specific conductance at 25 degrees Celsius; <, less than: --, not reported]

Parameter	Stream water						Precipitation VWM[a]
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge, inst.	0.02	0.04	0.05	0.07	3.4	235	--
Spec. cond., field	20	34	45	60	120	242	--
pH, field	3.2	4.0	4.2	4.4	6.0	242	4.3
Calcium	10	20	30	45	170	245	5.0
Magnesium	8.0	25	33	42	120	244	4.8
Sodium	48	70	78	87	150	242	19
Potassium	<2.0	5.1	5.1	10	46	238	1.3
Aluminum, dissolved	<.4	3.0	5.9	8.9	22	153	--
Iron, dissolved	.8	2.0	3.0	4.7	30	176	--
Sulfate	6.0	73	120	170	420	246	46
Chloride	56	90	99	110	230	244	25
Nitrite plus nitrate	<.7	<3.6	<7.1	<7.1	13	200	26[b]
Silica	23	51	62	70	110	238	--
Dissolved organic carbon	.5	2.9	5.6	8.0	20	139	--

[a] Values are volume-weighted mean concentrations for 01/85–03/86 and 12/86–11/87 (Lord and others, 1990).

[b] Nitrate only.

Table 31. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ion concentrations, McDonalds Branch, New Jersey, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Al, Aluminum; Fe, Iron; SO_4, sulfate; Cl, chloride; Si, silica; DOC, dissolved organic carbon]

	Q	pH	Ca	Mg	Na	K	Al	Fe	Cl	SO_4	Si
pH	–0.608										
Ca	.398	–0.489									
Mg	–.004	–.301	0.739								
Na	–.243	–.173	.495	0.734							
K	–.364	.072	.323	.488	0.472						
Al	.672	–.661	.554	.169	.088	–0.104					
Fe	.502	–.215	.003	–.389	–.460	–.413	0.492				
Cl	–.035	–.144	.068	.135	.216	.032	.169	0.129			
SO_4	.317	–.634	.568	.532	.435	.228	.444	–.242	0.118		
Si	–.741	.499	–.159	.157	.351	.493	–.481	–.446	.187	–0.211	
DOC	.762	–.576	.285	–.118	–.261	–.355	.820	.716	.103	.189	–0.620

concentrations at the upstream sampling site. In contrast, concentrations of DOC, aluminum, and iron were 4 to 10 times larger at the upstream site than at the downstream site. In addition, monthly samples from the upstream site had an average cation excess of 20 percent compared to only 3 percent at the gage (S–10). Johnsson and Barringer (1993) suggested that the chemical differences in waters collected at these two sites are due largely to differences in hydrology between the upper and lower areas of the basin. Stream water in the upland areas is derived primarily from a shallow, subsurface reservoir perched on layers of clay within the sand, whereas flow at the gage is derived from a deeper ground-water system that is recharged by precipitation in the upland areas of the basin.

Table 32. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major ion concentrations, McDonalds Branch, New Jersey, October 1967 through September 1995

[Trends in units of microequivalents per liter per year, except discharge in cubic meters per second per year, pH in standard units per year, aluminum, iron, and silica in micromoles per liter per year; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	<–0.01	0.029	--	--
pH, field	<.01	.944	<0.01	0.191
Calcium	–1.3	.000	–1.1	.000
Magnesium	<.1	.781	(b)	--
Sodium	<.1	.831	–.1	.622
Potassium	<.1	.909	(b)	--
Aluminum, dissolved	–.1[a]	.469	–.1[a]	.057
Iron, dissolved	<.1[a]	.218	<.1[a]	.042
Sulfate	–1.1	.101	–.1	.784
Chloride	<.1	.789	(b)	--
Silica	.2	.045	<–.1	.750

[a] Trend calculated for 1982–95.

[b] Flow model not significant at $\alpha = 0.10$.

Table 33. Physical properties and major ion concentrations at two surface-water sampling sites in McDonalds Branch Basin, New Jersey, November 25, 1986, through June 28, 1988[1]

[Site locations shown in fig. 16; µS/cm, microsiemens per centimeter at 25 degrees Celsius; µeq/L, microequivalents per liter; µmol/L, micromoles per liter; mg/L, milligrams per liter]

Parameter	Cedar swamp (S–10)	Hardwood swamp (S–1)
Number of samples	12	12
pH, field	4.1	3.9
Specific conductance (µS/cm)	62	91
Calcium (µeq/L)	31	24
Magnesium (µeq/L)	40	22
Sodium (µeq/L)	83	87
Potassium (µeq/L)	7.7	3.3
Aluminum (µmol/L)	9.6	37
Iron (µmol/L)	3.0	30
Sulfate (µeq/L)	250	200
Chloride (µeq/L)	100	110
Silica (µmol/L)	60	63
Dissolved organic carbon (mg/L)	7.7	32

[1] Data from table 9 in Johnsson and Barringer (1993).

Esopus Creek at Shandaken, New York (Station 01362198)

Site Characteristics and Land Use

The Esopus Creek HBN Basin is in the Catskill Mountains in southeastern New York in the Appalachian Plateaus physiographic province (fig. 18). The basin drains 165 km^2 of steep, mountainous terrain that ranges in elevation from 304 m at the gage to 1,145 m at the summit of Panther Mountain. The USGS gaging station is 0.8 km west of the town of Allaben, N.Y., at latitude 42°07'01" and longitude 74°22'50". The channel length of Esopus Creek upstream from the gage is about 20 km, and stream gradients range from 10 m/km near the gage to 220 m/km in the headwater tributaries. Esopus Creek flows southeast into Ashokan Reservoir, 21 km downstream from the gage, which provides drinking water for the city of New York. The main channel is perennial, and mean monthly discharge ranges from 0.86 m^3/s in August to 9.5 m^3/s in April. Average annual runoff was 74 cm from 1964 through 1995 (U.S. Geological Survey, Water Resources Data, New York). Climate of the area is characterized by cold winters and moderately warm summers with average daily air temperatures that range from –4.2°C in January to 21.5°C in July (Tornes, 1979). Annual precipitation rates in the headwaters of Esopus Creek are among the highest in the Northeast (Kudish, 1979). A National Weather Service station near Winnisook Lake (elevation 808 m) receives an average of 157 cm/yr of precipitation, of which 18 percent falls as snow (Murdoch, 1991). Annual precipitation decreases with elevation in the Catskill Mountains at a rate of about 6.5 cm per 100 m (Kudish, 1979). Therefore, average annual precipitation at the gage was estimated to be 125 cm.

The basin lies in the Adirondack-New England Mixed Forest ecoregion (Bailey and others, 1994); the forest can be separated into two major zones—the Northern Hardwood forest type at altitudes below 1,000 m and the Spruce-Fir type above 1,000 m. The dominant hardwood species are American beech, sugar maple, yellow birch, black cherry, red maple, white ash, and red oak. Spruce-fir forests are dominated by red spruce and balsam fir with mountain ash and occasionally paper birch. A more complete description of forests in the Catskill Mountains can be found in Kudish (1971).

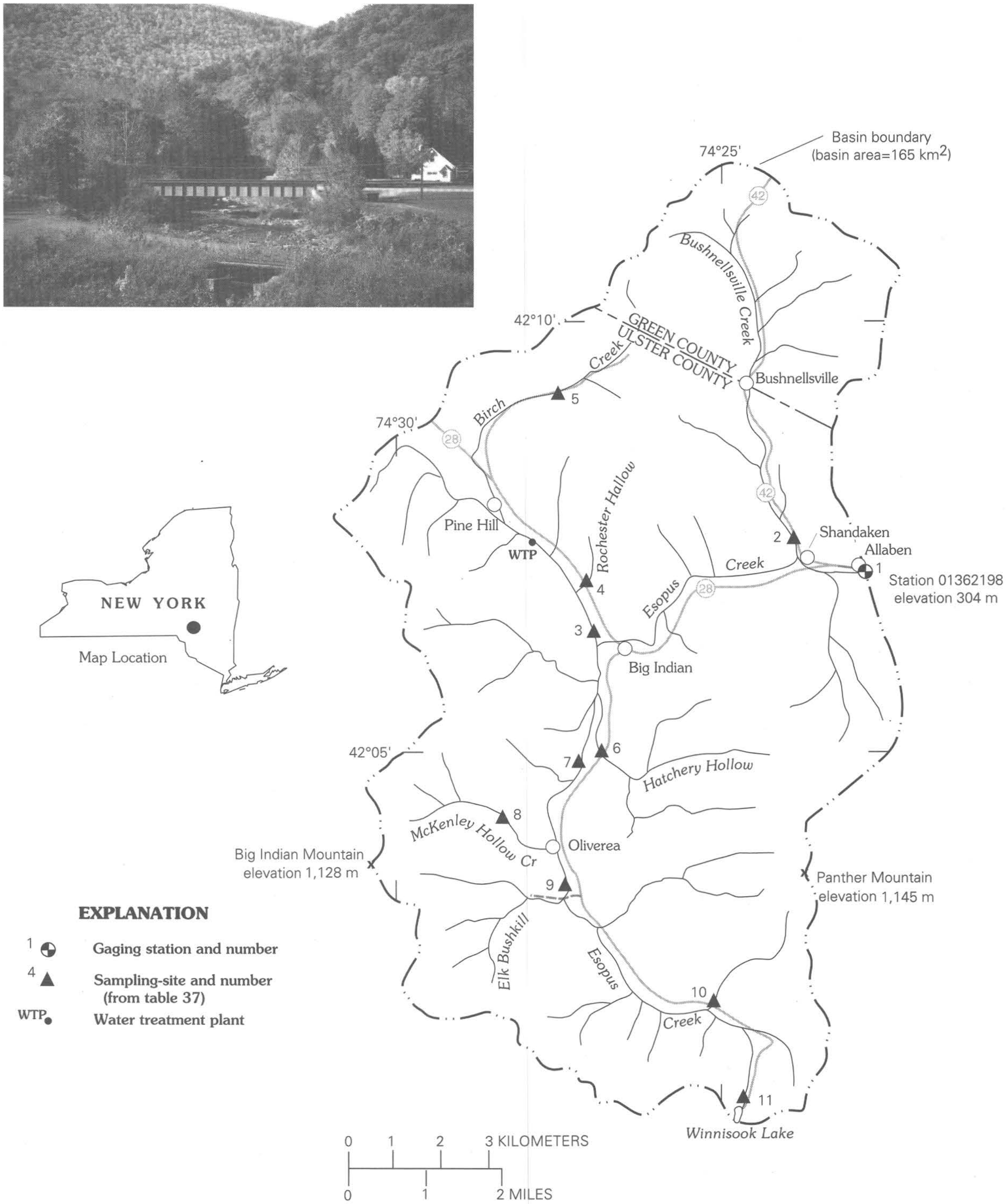

Figure 18. Map showing study area in the Esopus Creek Basin and photograph of the stream channel near the town of Big Indian, New York.

Soils in the basin are classified as Inseptisols and are mapped in the Arnot-Oquaga-Lackawanna soil association (Tornes, 1979). They are well-drained, bouldery, silt loams developed in till derived from reddish sandstone and shale. Soils in the Lackawanna series have a dense fragipan 50 cm or more below the surface that restricts rooting and slows the infiltration of water. Chemically, the soils are acidic (mean pH of 4.4), have low cation-exchange capacities (5.7 meq/100 g of soil), and low sulfate-adsorption capacities (Murdoch and Stoddard, 1993).

Bedrock that underlies the basin consists of gently sloping to flat-lying shales, sandstones, and conglomerates of Devonian age. The sediments were uplifted as a broad plateau and subsequently dissected into steep-walled valleys by the action of streams and glaciers. Mineralogic differences among the sedimentary rocks in the Catskill Mountains are minor, and most sediments are composed of detrital quartz (70 percent), fine-grained metamorphic rock fragments (16 percent), and minor amounts of mica and feldspar (Ethridge, 1977). Trace amounts of calcite and hematite also are present as cement materials in the sandstones. The glacial history of the Catskill Mountains is complex owing to the presence of both a continental ice sheet and local alpine-type glaciers (Rich, 1935). Till in the Esopus Creek drainage is derived predominantly from Catskill rocks to the north and consists of an unsorted mixture of clay, sand, and boulders that range in thickness from a few centimeters on the summits to more than 40 m along the valley bottoms (Kudish, 1979).

The Esopus Creek Basin drains parts of Green and Ulster Counties and is in the boundaries of the Catskill Park. The Catskill Park is a State Forest Preserve that is interspersed with private holdings. The preserve is administered by the New York State Department of Environmental Conservation under the guidelines of the Catskill Park State Land Plan (McAllister and Ochman, 1992). The basin also is in the 1,479-km^2 Catskill Reservoir District, which together with the Schoharie Basin provides 40 percent of New York City's drinking water (Perry, 1971; Freud, 1991). Access into the basin is by way of State Highways 28 and 42, which are paved roads that traverse the basin along the Birch Creek and Bushnellsville Creek drainages, respectively. Both highways are open year-round and are salted and plowed in winter. A gravel road parallels the main Esopus Creek drainage between Big Indian and Winnisook Lake. Earthen roads follow many of the smaller tributary streams to access residential areas. Access to the upper slopes and ridges is limited to foot trails.

Details of the settlement and land-use history of the Catskill region can be found in Kudish (1979) and McIntosh (1972). Extensive settlement and disturbance by Europeans began in the early 1800's when the Catskill Mountains became the center of a large tanning industry that harvested the native hemlock forests for tanbark. Sawmills also were operated in the area, cutting hardwoods and pines for barrels and other wood products. By the end of the 19th century, most of the Catskill forests had been cut at least once, and only forests above 850 m in altitude remained undisturbed (McIntosh, 1972).The Catskill Mountains gained increasing popularity as a resort and recreation area in the mid-1800's (Francis, 1983), and the upper slopes and summits were designated a State Forest Preserve in 1870.

Current (1997) land cover in the basin is about 94 percent forest, 5 percent residential, and less than 1 percent agricultural and commercial. Most State-owned lands in the basin are designated as wilderness and are protected from future development. Most land-use activities in the basin are related to the road network and residential population. More than 3,000 full- and part-time residents live in six small communities and in scattered residential areas that are localized along the main drainage and major tributaries. The basin also contains several impoundments and a wastewater-treatment plant that was constructed in 1925 downstream from the community of Pine Hill. Three sand and salt piles for winter highway maintenance are currently stored at public garages in the communities of Allaben and Big Indian (James Mayfield, New York City Department of Environmental Protection, written commun., 1993). The most significant land-use change since the gage was established has been an increase in residential population. Census data are not available specifically for the HBN basin; however, the population of the Esopus Creek Basin upstream from the Ashokan Reservoir increased 147 percent between 1940 and 1980. During the same period, residential land use in the basin increased 230 percent, whereas commercial and agricultural land use decreased 80 percent (Freud, 1991).

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for this report includes 233 water-quality samples that were collected from August 1963 through August 1992 when the station was removed from the HBN. Sampling frequency progressively increased from 2 samplings per year in 1963 to 12 samplings per year in 1968. Sampling frequency was monthly from 1968 through 1982, then quarterly from 1983 through 1992. Water-quality samples were analyzed at a USGS laboratory in Albany, N.Y., from 1964 through 1977, the USGS Central Laboratory in Atlanta, Ga., from 1978 through 1985, and at the NWQL in Arvada, Colo., from 1986 through 1992. Daily discharge records for Esopus Creek (station 01362198) are available beginning in October 1963. Daily water temperature at the gage was measured from July 1963 through July 1968, January 1970 through May 1994, and after January 1995. In October 1988, the gage was moved 0.8 km downstream owing to the increasing popularity of a swimming hole near the former gage site (A.J. Ranalli, U.S. Geological Survey, oral commun., 1994). Records after 1988 for the relocated station are published as Esopus Creek at Allaben (station 01362200).

Calculated ion balances for 228 samples with complete major ion analyses are shown in figure 19. Ion balances ranged from –26 to +36 percent, and 90 percent of samples had values within the ±10 percent range, indicating the analytical results were of good quality. The average charge balance for all samples was –0.9 percent, indicating that unmeasured constituents, such as organic anions, do not contribute substantially to the ionic composition of stream water at this station. Time-series plots of major dissolved constituents were inspected for evidence of analytical-related influences (fig. 19). At least two patterns are evident at the Esopus Creek station in the middle part of the record. For example, field pH values decreased somewhat abruptly around 1976, remained low for the next several years, then increased again around 1980. This pattern coincides with a period when pH was determined in the field by using a water-quality analyzer produced by the Hydrolab Corporation (N.E. Peters, U.S. Geological Survey, oral commun., 1994). It has been documented that, in low ionic-strength water, the Hydrolab can produce errors as large as one pH unit when used with a standard reference electrode (Hydrolab, 1992). The usual result of this combination is a lower than expected pH, which is consistent with the low values reported at this site in the late 1970's. A somewhat sudden change also occurred in the calculated ion balance around the beginning of 1975, but the cause of the shift could not be identified. A similar pattern was not observed in the major ionic constituents, indicating the shift was not caused by a bias in any individual constituent. In addition, the pattern did not coincide with any documented changes in analytical methods or field-related activities.

Median concentrations and ranges of major constituents in stream water collected at the HBN gaging station and VWM concentrations in wet-only precipitation measured at the Biscuit Brook NADP station are listed in table 34. Precipitation chemistry at Biscuit Brook, which is about 5 km west of Winnisook Lake, is dilute and acidic with a VWM pH of 4.3 for 10 years of record. The dominant cations in precipitation were hydrogen, which contributed 74 percent of the total cation charge, and ammonium, which contributed 15 percent. Sulfate and nitrate were the dominant anions, accounting for 61 and 33 percent of the anion charge, respectively. The low pH and predominance of strong acid anions indicates that precipitation at the NADP station probably is affected by anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain.

Stream water in Esopus Creek is dilute and weakly buffered; total ionic constituents ranged from 220 to 780 μeq/L, and alkalinities were generally between 160 and 300 μeq/L. The major cations in stream water were calcium and magnesium, and the dominant anions were alkalinity and sulfate. The low concentrations of weathering-derived constituents, particularly alkalinity, reflect the slow weathering rates of the sandstone bedrock. High rates of acidic deposition probably also contribute to the low stream-water alkalinities at this station. The median chloride concentration in stream water was 96 μeq/L, compared to the VWM concentration of 4.5 μeq/L in precipitation, indicating that a substantial fraction of stream-water chloride is derived from sources in the basin. Because the bedrock contains only minor amounts of halite (Murdoch, 1991), it is likely that human activities such as application of deicing salts and discharge of sewage effluent are the primary sources of chloride in stream water. The median sulfate concentration of 160 μeq/L in stream water was 3.6 times larger than the VWM concentration, 44 μeq/L, in wet precipitation. Based on the difference between average annual precipitation and runoff, evapotranspiration can account for no more than a twofold increase in the concentration of precipitation, indicating that a substantial amount of stream-water sulfate is derived from sources other than wet deposition. Dry deposition is generally assumed to be the source of additional stream-water sulfate if no other sources are present in the basin. Some sulfate may be released from weathering of trace amounts of pyrite in the sandstones; however, this source is believed to be minor relative to atmospheric sulfate in Catskills streams (Murdoch, 1991). Nitrate concentrations in stream water were slightly smaller than in precipitation and had the same range of concentrations that was measured in pristine headwater streams throughout the Catskill Mountains (Murdoch and Stoddard, 1993).

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 35). Base cations and alkalinity were inversely correlated with discharge. These results are consistent with a hydrologic system where weathering-enriched base flow is diluted by waters from shallow or surficial sources during periods of increased discharge. Among the solutes, the strongest correlations were found between calcium and magnesium (rho = 0.900) and sodium and chloride (rho = 0.876). Silica was not correlated with the other dissolved constituents or with discharge. The positive correlations between calcium, magnesium, and alkalinity and lack of correlation with silica are consistent with the weathering stoichiometry of carbonate minerals. Trace amounts of carbonates are present as cements in the sedimentary rocks and possibly as limestone fragments in the glacial till (Murdoch and Barnes, 1991). The influence of human activities on stream chemistry is further supported by the strong positive correlation between sodium and chloride. The processes that control silica in stream water are not clear, particularly since concentrations varied relatively little over a wide range of streamflows. Weathering of silicate minerals and metamorphic rock fragments in the sandstone and till is the most likely source of silica in ground water and to the stream during base-flow conditions. Under high-flow conditions, however, dissolution of amorphous silica minerals, biological activity, and sorption reactions in shallow ground water or soil environments may be the dominant processes that control silica concentrations in the stream (Stoddard and Murdoch, 1991).

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents from 1963 through 1992 are presented in table 36. Statistically significant trends were detected in sodium, chloride, nitrate, and sulfate at the 0.01 confidence level. Trends in the flow-adjusted concentrations were similar to the unadjusted concentrations, indicating that trends were not driven by changes in stream discharge. The LOWESS curves in figure 19 show that the trends in sodium and chloride were of similar magnitude and timing, and most of the increase occurred between 1972 and 1984. Increasing use of deicing salts and discharge from the wastewater-treatment plant in the basin are the most likely causes of the upward trends in these constituents. This result is consistent with trends in chloride of 1 to 3 (μeq/L)/yr that were observed in other Catskill rivers from 1964 through 1990 (Freud, 1991). Freud attributed the trends to increases in population and residential land use in the region from 1950 to 1980. The upward trends in stream-water calcium and nitrate and downward trend in sulfate in Esopus Creek are consistent with trends in the chemistry of other Catskill streams (Peters and others, 1982; Stoddard, 1991; Murdoch and Stoddard, 1993). Stoddard (1991) reported significant upward trends in calcium plus magnesium concentrations in 19 Catskill streams from 1945 to 1990; he attributed the increases to landscape disturbance, which is consistent with the increase in residential population that was observed in the basin during the past 30 years. Declines in stream-water sulfate are consistent with the observed decreases in atmospheric sulfur emissions in the Northeast since 1970 (Husar and others, 1991). Unlike sulfate, the patterns in stream-water nitrate do not mimic regional trends in nitrogen deposition, which have remained stable since 1970 (Stoddard, 1991). Murdoch and Stoddard (1993) have suggested that Catskill forests are no longer able to retain incoming atmospheric nitrogen and may be approaching nitrogen saturation owing to the cumulative effects of acidic deposition.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling of October 9 and 10, 1991, are presented in table 37; locations of sampling sites are shown in figure 18. Discharge at the gage was 0.40 m^3/s compared to the median daily discharge of 1.00 m^3/s for October, indicating that low base-flow conditions existed for that time of year. Concentrations measured at the gage (site 1) during the synoptic sampling were generally above the third-quartile concentrations that were measured at the gage during the entire period of record (table 34). The upstream sites spanned a wide range of concentrations that bracketed the concentrations

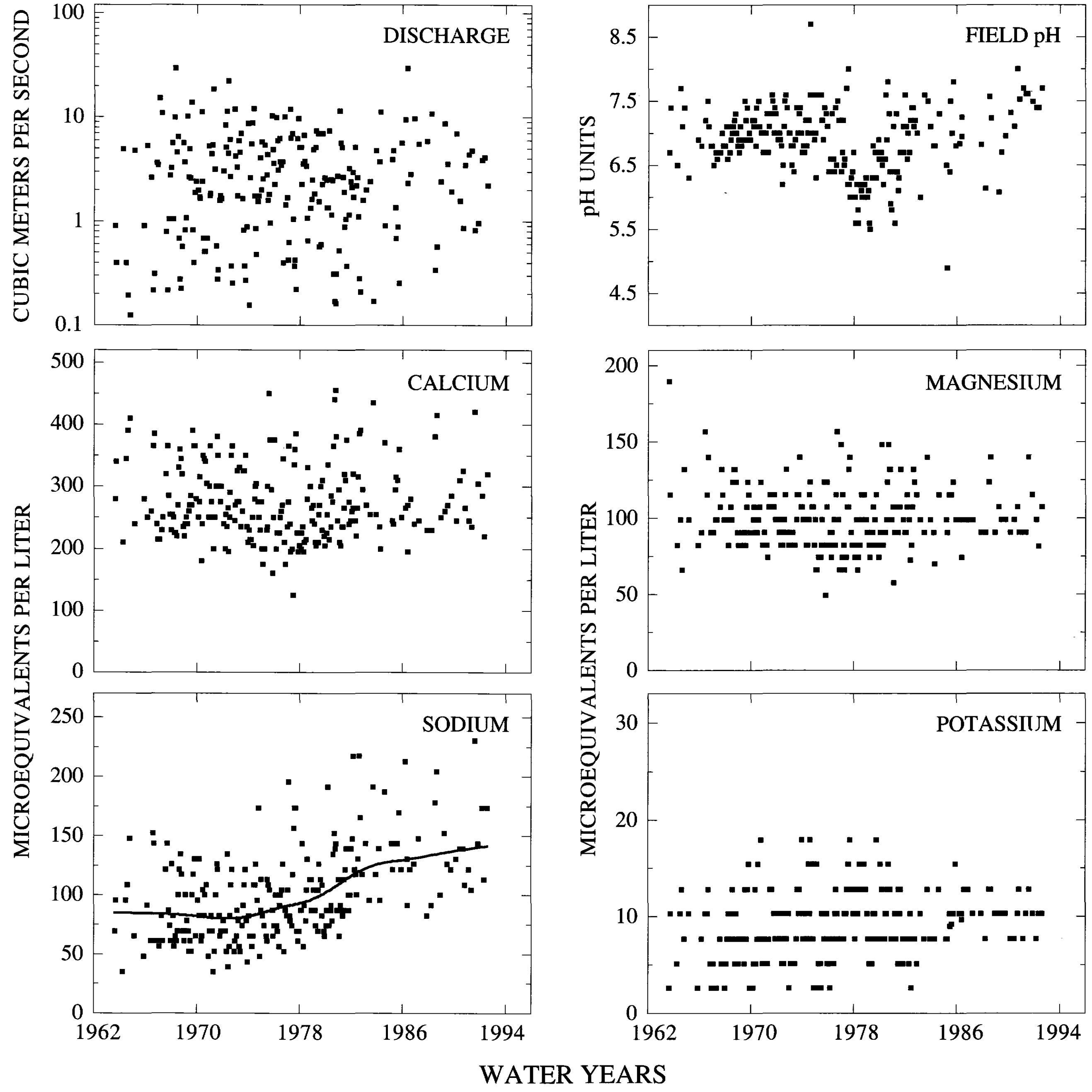

Figure 19. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Esopus Creek, New York.

measured at the gage. Ion balances of the synoptic samples ranged from –2.8 to 4.2 percent, indicating that organic anions did not contribute substantially to the ionic content of stream water during the sampling period.

Considerable spatial variability in stream chemistry was measured in the basin, particularly for calcium, sodium, chloride, and alkalinity. This variability appears to reflect the density of residential areas in the basin rather than variations in natural basin characteristics, such as geology or vegetation. For example, chloride and sodium concentrations in tributaries that drain undeveloped areas, such as site 10 and site 8, were 3 to 15 times smaller than concentrations at site 3 and site 2, which drain areas with sections of highway and large residential areas.

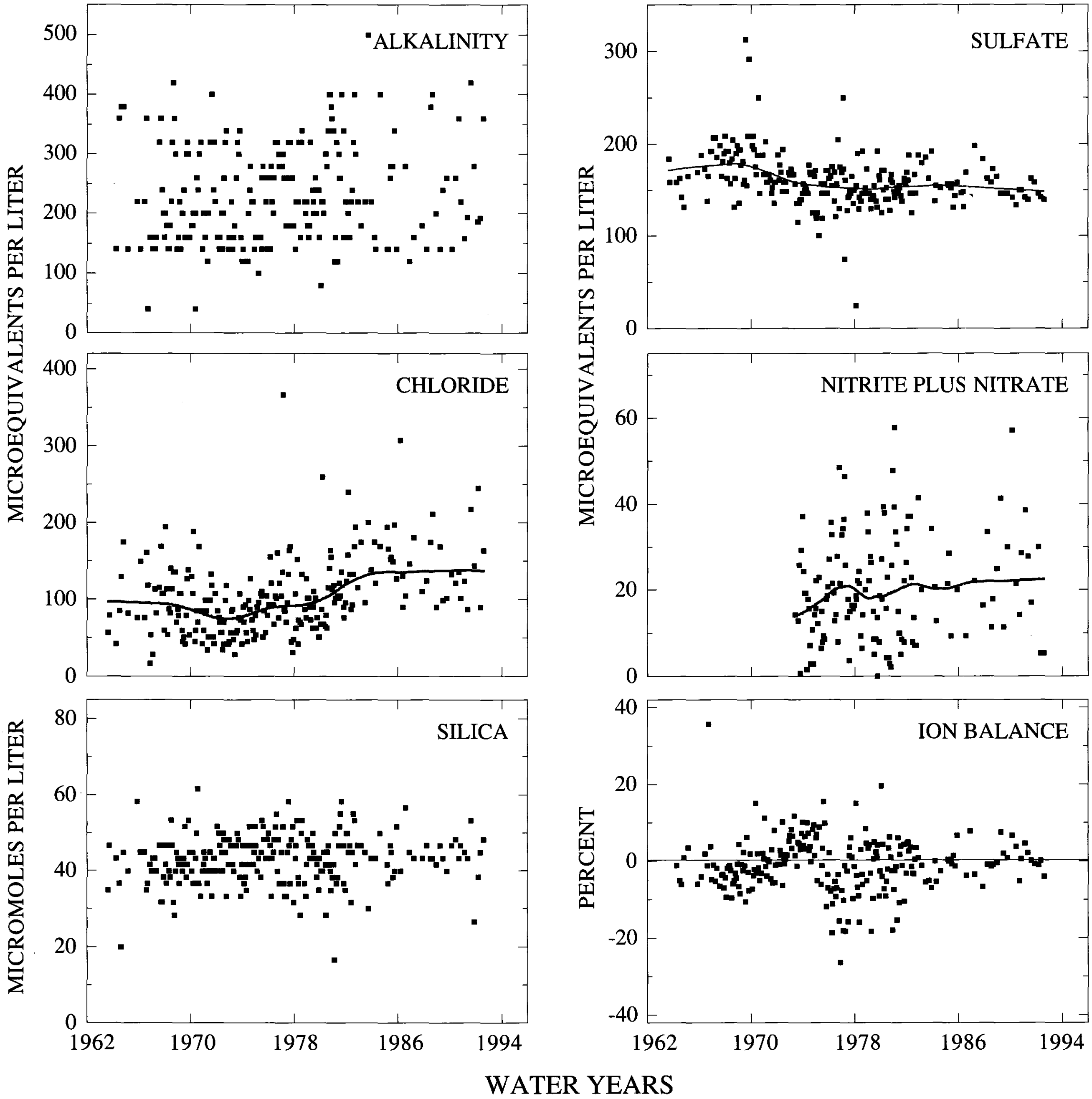

Figure 19. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Esopus Creek, New York—Continued.

The low sodium and chloride concentration in Birch Creek at site 5 compared with those of Birch Creek at site 3 demonstrates the effect of the wastewater-treatment plant on water quality in the basin. Effluent from the wastewater-treatment plant apparently also contributes calcium, magnesium, and alkalinity to stream water, as indicated by the elevated concentrations of these constituents at site 3. These data also show that stream-water chemistry at the gage was affected by human activities in the basin. In contrast, silica and sulfate showed little variability among the sampling sites. Silica concentrations in the synoptic samples ranged from 11 to 75 μeq/L, and sulfate ranged from 100 to 170 μeq/L. The similarity between silica and sulfate concentrations in Birch Creek upstream and downstream from the community of

Table 34. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ion concentrations measured in water-quality samples from Esopus Creek, New York, August 1963 through August 1992, and volume-weighted mean concentrations in wet precipitation collected at the Biscuit Brook Station, New York

[Concentrations in units of microequivalents per liter, discharge in cubic meters per second, specific conductance in microsiemens per centimeter at 25 degrees Celsius, pH in standard units, and silica in micromoles per liter; n, number of stream samples; VMW, volume-weighted mean; inst., instantaneous; spec. cond., specific conductance at 25 degrees Celsius; pH in standard units; <, less than; --, not reported]

Parameter	Stream water						Precipitation VWM[a]
	Minimum	First quartile	Median	Second quartile	Maximum	n	
Discharge, inst.	0.12	0.91	2.5	5.1	29	232	--
Spec. cond., field	31	45	51	61	82	230	--
pH, field	4.9	6.6	6.9	7.3	8.7	229	4.3[b]
Calcium	130	240	260	310	460	233	3.0
Magnesium	50	92	100	110	190	233	1.4
Sodium	35	70	93	120	230	232	3.3
Potassium	<2.5	8.0	8.0	10	18	232	.4
Ammonium	<.7	<.7	2.1	3.6	18	91	11
Alkalinity, laboratory	39	160	210	300	500	228	--
Sulfate	25	150	160	170	310	230	44
Chloride	17	70	96	130	370	230	4.5
Nitrite plus nitrate	<.7	11	19	28	58	139	24[c]
Silica	17	40	43	47	61	231	--

[a] Values are volume-weighted mean concentrations for 1983–94.

[b] Laboratory pH.

[c] Nitrate only.

Table 35. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ion concentrations, Esopus Creek, New York, 1980 through 1992

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; N, nitrite plus nitrate; Si, silica]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	N
pH	−0.306									
Ca	−.786	0.368								
Mg	−.667	.209	0.900							
Na	−.500	.355	.741	0.768						
K	−.329	.126	.453	.467	0.329					
Alk	−.693	.335	.678	.553	.302	0.270				
SO_4	−.012	−.091	.143	.226	.105	−.060	0.005			
Cl	−.320	.172	.594	.676	.876	.211	.134	0.223		
N	.438	−.152	−.312	−.172	−.062	−.288	−.433	.069	0.136	
Si	−.015	−.015	.180	.208	.243	.000	−.030	.004	.189	−0.072

Pine Hill and the wastewater-treatment plant (sites 3 and 5) demonstrates that these constituents are only minimally affected by human activities. Although elevated nitrate concentrations were expected downstream from the wastewater-treatment plant, concentrations were consistently larger in streams that drain undeveloped areas of the basin. The tributaries with the highest nitrate concentrations, site 8 and site 10, were sampled immediately downstream from ground-water discharge zones or springs. Burns (1993) noted larger nitrate concentrations in Catskill streams fed by springs and hypothesized that ground water discharging from the springs was enriched in nitrate because ground water was recharged predominantly during the nongrowing season when plant demand for nitrogen is minimal.

Table 36. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major ion concentrations, Esopus Creek, New York, August 1963 through August 1992

[Trends in units of microequivalents per liter per year, except discharge in cubic meters per second per year, pH in standard units per year, and silica in micromoles per liter per year; <, less than; --, not calculated

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	0.02	0.207	--	--
pH, field	<.01	.259	0.01	0.055
Calcium	<.1	.684	.8	.007
Magnesium	<.1	.577	.2	.257
Sodium	2.6	.000	2.9	.000
Potassium	<.1	.033	<.1	.009
Alkalinity, laboratory	<.1	.721	1.0	.035
Sulfate	−1.0	.001	(b)	--
Chloride	2.5	.000	2.9	.000
Nitrite plus nitrate	.6[a]	.009	.4[a]	.151
Silica	.1	.184	.1	.268

[a] Trend calculated for 1973–92.

[b] Flow model not significant at $\alpha = 0.10$.

Cataloochee Creek near Cataloochee, North Carolina (Station 03460000)

Site Characteristics and Land Use

The Cataloochee Creek HBN Basin is in the eastern one-half of Great Smoky Mountains National Park (GSMNP) in the Blue Ridge physiographic province in western North Carolina (fig. 20). The basin drains 127 km^2 of steep, mountainous terrain that ranges in elevation from 749 m at the gage to 1,876 m at the summit of Big Cataloochee Mountain. The USGS gaging station is 2.9 km upstream from the National Park boundary at latitude 35°40'02" and longitude 83°04'22". Cataloochee Creek flows northeast and eventually discharges into the Waterville Reservoir on the Pigeon River, 4.3 km downstream from the gage. The channel length upstream from the gage is about 16 km, and stream gradients range from 16 m/km along the valley floor to as much as 130 m/km in the steep headwater streams.

Table 37. Physical properties and major ion concentrations from surface-water sampling sites in the Esopus Creek Basin, New York, October 9–10, 1991

[Site locations shown in fig. 18; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; concentrations in microequivalents per liter; Si, silica in micromoles per liter; WTP, wastewater-treatment plant; <, less than; --, not measured]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria[a]	Remarks
1	01362198	0.40	86	7.4	420	150	170	12	350	160	270	6.4	43		
2	420723074240200	.051	97	7.6	550	13	270	13	550	170	200	9.3	58	MT, LU	Residential areas
3	420618074265400	.035	130	8.0	600	210	350	18	650	170	420	2.0	42	MT, LU	Downstream from Pine Hill WTP
4	420656074271200	--	55	7.0	310	140	78	11	340	150	26	<.7	75	LU	Undeveloped subbasin
5	420912074274400	.006	45	7.2	250	110	78	11	240	130	51	7.9	53	LU	Upstream from Pine Hill WTP
6	420459074265600	--	44	6.3	230	120	43	8.2	200	150	31	14	48	LU	Undeveloped subbasin
7	420551074265800	.19	49	7.0	240	120	83	9.5	190	150	85	1.4	25	LU	Downstream from town of Oliverea
8	420414074282900	.006	50	6.8	290	110	43	10	200	140	28	79	48	LU	Undeveloped subbasin
9	420317074272700	.14	46	7.0	220	99	83	8.4	150	140	76	21	22	LU	Upstream from town of Oliverea
10	420200074251400	.001	48	7.1	300	99	87	9.5	210	170	39	54	40	LU	Undeveloped subbasin
11	420057074244600	--	30	6.6	130	62	56	9.0	85	100	48	<.7	11	LU	Undeveloped subbasin

[a] Criteria used in selection of sampling sites: BG = bedrock geology, MT = major tributary, LU = land use.

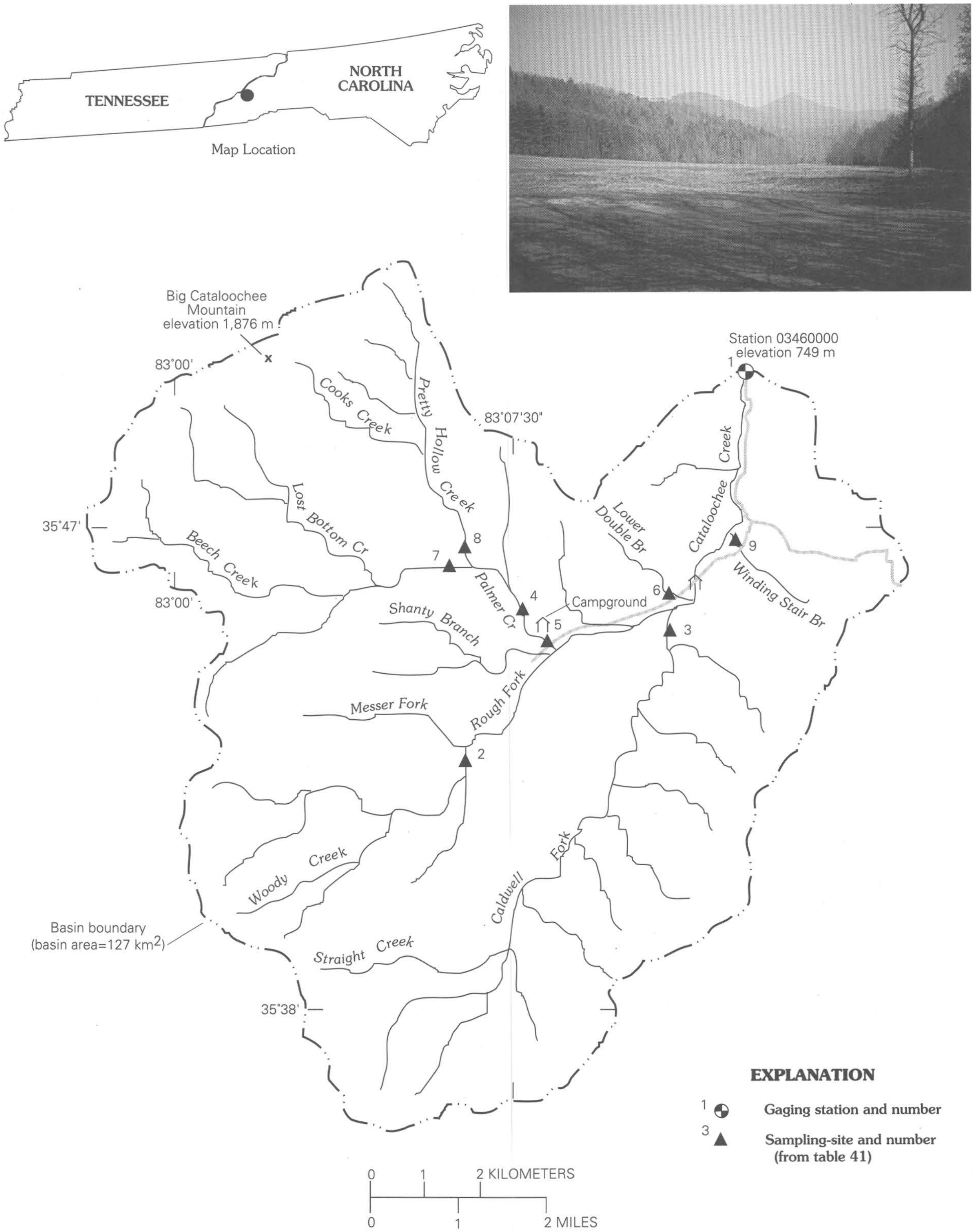

Figure 20. Map showing study area in the Cataloochee Creek Basin and photograph of a maintained opening along the valley floor.

The main channel is perennial, and mean monthly discharge varies from 1.5 m^3/s during low flow in September and October to 5.7 m^3/s in March when spring rains combine with snowmelt. Average annual runoff from the basin was 78 cm from 1934 through 1995 (U.S. Geological Survey, Water Resources Data, North Carolina). Climate of the area is characterized by abundant precipitation and moderate temperatures, and both vary considerably with elevation (Elwood and others, 1991). For example, average annual precipitation in GSMNP increases from 147 cm at an elevation of 445 m to 231 cm at an elevation of 1,920 m (Shanks, 1954). Snowfall is common at higher elevations during winter months; however, a seasonal snowpack seldom lasts through the winter. Mean monthly air temperatures also vary with elevation and range from 4°C in December to 23°C in July at an elevation of 445 m and 0°C in March to 16°C in July at an elevation of 1,920 m (Shanks, 1954).

Detailed descriptions of forest vegetation in GSMNP can be found in Arends (1981) and MacKenzie (1993). The basin lies in the Central Appalachian Broadleaf Forest ecoregion (Bailey and others, 1994) and is covered by hardwood-hemlock forest types at elevations below 1,450 m. The most common tree species are red maple, yellow poplar, black locust, white oak, black oak, sweet birch, and hemlock with lesser amounts of white pine, shortleaf pine, pitchpine, dogwood, and sumac. Rosebay rhododendron and mountain laurel are locally abundant as a dense understory. Although most hardwoods represent second-growth forests, Pyle (1985) has mapped large virgin hardwood stands in the Caldwell Fork and Woody Creek subdrainages. Above 1,450 m, vegetation is dominated by red spruce and Fraser fir forests that are locally interrupted by beech stands and open areas covered by mountain laurel and blueberries. Recently there has been widespread dieback of the Fraser fir owing to the attack of the wooly aphid (Eagar, 1984). Most soils in the basin are classified as Inseptisols and are described as fairly deep, well-drained soils developed in residuum weathered from the underlying bedrock (Feldman and others, 1991). Chemically, the soils are acidic (pH 4.1 to 5.8) and have a low organic content and low cation-exchange capacity (Daniels and others, 1987). Aluminum generally dominates the exchange complex, which is almost entirely derived from the organic matter. The mineralogy of the sand and silt fraction is dominated by quartz, mica, and feldspar, and the clay fraction is dominated by regularly interstratified mica/vermiculite, smectite, kaolinite, and gibbsite.

Bedrock in the eastern part of GSMNP consists of a thick mass of variably metamorphosed sedimentary rocks of late Precambrian age. At higher elevations, the Cataloochee Creek Basin is underlain primarily by the Thunderhead Sandstone, which consists of a thick-bedded feldspathic sandstone that forms extensive cliffs and numerous waterfalls. At lower elevations, the Roaring Fork Sandstone and Longarm Quartzite are the dominant bedrock units. The Roaring Fork Sandstone is described as a highly feldspathic sandstone interbedded with dark siltstones. The Longarm Quartzite consists of a clean, coarse-grained, feldspathic quartzite and arkose. All bedrock units in the basin are mineralogically similar and are composed primarily of detrital quartz, potassium feldspar, and plagioclase and metamorphic biotite, muscovite, and chlorite. Carbonate minerals are found only in trace amounts in most rocks with the exception of occasional carbonate layers in the Roaring Fork Sandstone. Pyrite is present in trace amounts in the Roaring Fork Sandstone but is absent in the Thunderhead Sandstone. Bedrock in many areas of the basin is covered by saprolite locally as much as 30 m thick. Complete descriptions of GSMNP geology can be found in King (1968) and Hadley and Goldsmith (1963).

The Cataloochee Creek Basin drains the western part of Haywood County, N.C., and is entirely in the boundaries of GSMNP. The basin is in the eastern one-half of GSMNP and is accessible by two low-speed gravel roads that enter the basin from the northeast. Road access in the basin is limited primarily to the valley floor. Foot and equestrian trails allow access to headwater areas of the basin. Several trailheads along the western basin divide are accessible from roads outside the basin boundary.

Although most land in GSMNP is currently protected, substantial landscape disturbance owing to logging, farming, and fire occurred in the park prior to its establishment (Pyle, 1985; Lambert, 1957; Lambert, 1960). The Cataloochee Creek Basin was settled by Europeans in the 1830's, and disturbance was limited primarily to farming activities and selective logging along the valley floor. The early 1900's was the most intense period of human disturbance when large stands of timber were harvested by corporate logging companies. Although logging companies penetrated much of the park, forests in many areas of the Cataloochee Creek Basin were never cut and represent some of the largest remaining virgin timber stands in the Eastern United States (Pyle, 1985). Almost 700 residents lived in the Cataloochee Valley when GSMNP was established in 1934, but they were no longer allowed to farm or raise animals. The last residents left the valley by the early 1940's, and most of the structures were burned in order to return the valley to a wilderness state (Powers, 1974).

The current management objectives of GSMNP are to restore and preserve the natural environment and are described in detail in the park's general management plan (U.S. Department of the Interior, 1988). The Cataloochee Creek Basin is in a relatively isolated region and receives considerably less tourist traffic than other road-accessible areas of the park. The valley bottom is currently designated as a historic district, and several pioneer structures, rustic wooden fences, and large open meadows that are maintained to reproduce the early pioneer setting. Permits are occasionally granted to local farmers to harvest hay in the open meadows; however, grazing is not allowed (Wayne Williams, National Park Service, oral commun., 1996). The Cataloochee Creek Basin is most popular as a base camp for equestrian backcountry trips. A 35-site campground with a septic system and well is along the main channel just downstream from the confluence with Caldwell Fork, and a horse camp containing stables and a shelter is near the confluence with Palmer Creek. The park also maintains a ranger station, bunk house, and small maintenance building in the valley.

Owing to the wide diversity of natural resources in GSMNP, the park has become an important research area for studying environmental impacts on terrestrial and aquatic ecosystems (Nodvin and others, 1993). A complete bibliography of scientific research in the park has been compiled by Nodvin and others (1993) and is available in digital form at URL http://funnelweb.utcc.utk.edu/%7Enodvin/smokyhtml.html. Air pollution is currently one of the biggest problems facing both natural resources and visitors in the park, and consequently, GSMNP has one of the most comprehensive air-quality-monitoring programs in the National Park system. The current monitoring system includes nine weather stations, three atmospheric deposition sites, and seven air-quality-monitoring stations (Jim Renfro, National Park Service, oral commun., 1996). The National Park Service also monitors the water quality of several streams in the park, including an intensively monitored site at the headwaters of Noland Creek, about 25 km west of the Cataloochee Creek Basin (Jim Renfro, oral commun., 1996).

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for this report includes 161 water-quality samples that were collected from October 1967 through August 1995. Sampling frequency ranged from monthly to bimonthly from 1968 through 1982 and quarterly from 1983 through 1995. Eleven samples were collected in 1963, before the site was added to the HBN. Although not documented, water-quality samples in the early part of the record probably were analyzed at a USGS laboratory in Raleigh, N.C., which was operated until 1973 (Durum, 1978). After the establishment of the USGS Central Laboratory System, samples were analyzed at the Atlanta laboratory from 1973 through 1985 and at the NWQL in Arvada, Colo., from 1986 though 1995. Daily discharge records for Cataloochee Creek (station 03460000) are available from October 1933 through September 1952 and after October 1962. Daily water temperature and specific conductance were measured at the gage from October 1962 through September 1986 and May 1974 through September 1986, respectively. Daily precipitation amount was measured at the gage from November 1990 through February 1996.

Calculated ion balances for 164 samples with complete major ion analyses are shown in figure 21. Ion balances ranged from –30 to +34 percent, and about 55 percent of samples had values outside of the ±10 percent range. This large range of values reflects the difficulty in making precise analytical measurements at the low solute concentrations typical of this station. The average charge balance for all samples was –7.0, and 77 percent had negative ion balances, indicating an excess of measured anions over cations in solution. As mentioned previously, the apparent anion excess may be due to an overestimation of laboratory alkalinity by the fixed endpoint titration to pH 4.5 (Office of Water Quality Technical Memorandum No. 80.27, *New Parameter Codes for pH,* *Alkalinity, Specific Conductance, and Carbonate/Bicarbonate*, issued September 19, 1980, at URL http://water.usgs.gov/public/admin/memo/). For waters with low alkalinities, the endpoint pH is closer to 5.0, and titration to pH 4.5 may overestimate alkalinity by as much as 25 µeq/L (Barnes, 1964). Alkalinities also were measured by incremental titration in the field beginning in 1987. A comparison of the two alkalinity determinations shows that the fixed endpoint concentrations were, on average, 20 µeq/L larger than the incremental titration concentrations, indicating that the alkalinity is a reasonable explanation for the negative ion balances.

Time-series plots of the major dissolved constituents were inspected for evidence of method-related effects (fig. 21). Several notable patterns were found at the Cataloochee Creek gaging station. For example, uncharacteristically high calcium concentrations were evident during the period 1974 through 1976. The only documented analytical or procedural change during this period was the introduction of a polypropylene churn splitter for compositing and splitting samples that was required for use at all HBN stations beginning in water year 1977 (Office of Water Quality Technical Memorandum No. 76.24–T, *Sample Splitter for Water-Sediment Samples*, issued August 16, 1976, at URL http://water.usgs.gov/public/admin/memo/). Although problems with previous sample splitters were not documented by the Office of Water Quality (OWQ), the fact that the anomalous pattern disappeared around the beginning of 1977 indicates that previous splitters or compositing devices may have been a potential source of contamination. Figure 21 also reveals a period of elevated sulfate concentrations during the late 1980's. This pattern coincides with the use of a turbidimetric titration for sulfate analysis at the NWQL between March 1986 and December 1989 (Fishman and others, 1994). In 1989, the NWQL determined that sulfate concentrations can be overestimated by this technique and changed the method to ion chromatography in 1990 (Office of Water Quality Technical Memorandum No. 90.04, *Turbidimetric Sulfate Method*, issued December 21, 1989, at URL http://water.usgs.gov/public/admin/memo/). The bias was most pronounced in dilute waters, although it was not consistent among samples and appeared to be affected by factors such as color and turbidity (Schertz and others, 1994).

The time-series plot of field pH reveals a sudden increase in pH at the beginning of 1975 followed by a steady decrease through the 1980's and another sudden increase near the beginning of 1993. These patterns may, in part, be explained by changes in instrumentation used by field personnel. Some instrument-electrode systems are known to give erroneous readings, particularly when measuring pH in low-conductivity waters (Office of Water Quality Technical Memorandum No. 81.08, *Electrodes for pH Measurement in Low-Conductivity Waters*, issued February 10, 1981, at URL http://water.usgs.gov/public/admin/memo/). Unfortunately, changes in field methods were not well documented, which complicates verification of analytical bias, particularly in the earlier records. Beginning in 1981, laboratory pH is available for comparison. Poor agreement between the two pH measurements during this period of record indicates that the decline in pH in the late 1980's probably is because of analytical error in the field. The sudden increase in pH in 1993 is coincident with a change in the pH electrode type (refillable to gel-filled) used by the field personnel at this station (Gene Barker, U.S. Geological Survey, oral commun., 1996).

Median concentrations and ranges of major constituents in stream water collected at the HBN gaging station and VWM concentrations in wet-only deposition measured at the Elkmont NADP station about 35 km east of the basin are presented in table 38. Atmospheric deposition of sulfate, nitrate, and hydrogen in the Southern Blue Ridge is among the highest reported in the Eastern United States (Elwood and others, 1991). The VWM pH of wet precipitation measured at the Elkmont NADP station was 4.5 for 15 years of record. The dominant cations in precipitation were hydrogen, which contributed 63 percent of the total cation charge, and ammonium, which contributed 20 percent. The dominant anions were sulfate and nitrate, which accounted for 65 and 29 percent of the total anions, respectively.

Stream water in Cataloochee Creek is dilute and weakly buffered: specific conductances ranged from 10 to 25 µS/cm and alkalinities generally were below 140 µeq/L. The major cations in stream water were calcium and sodium, and alkalinity was the dominant anion. The low concentrations of the weathering-derived solutes, particularly alkalinity, reflect the slow-weathering sandstones and quartzites

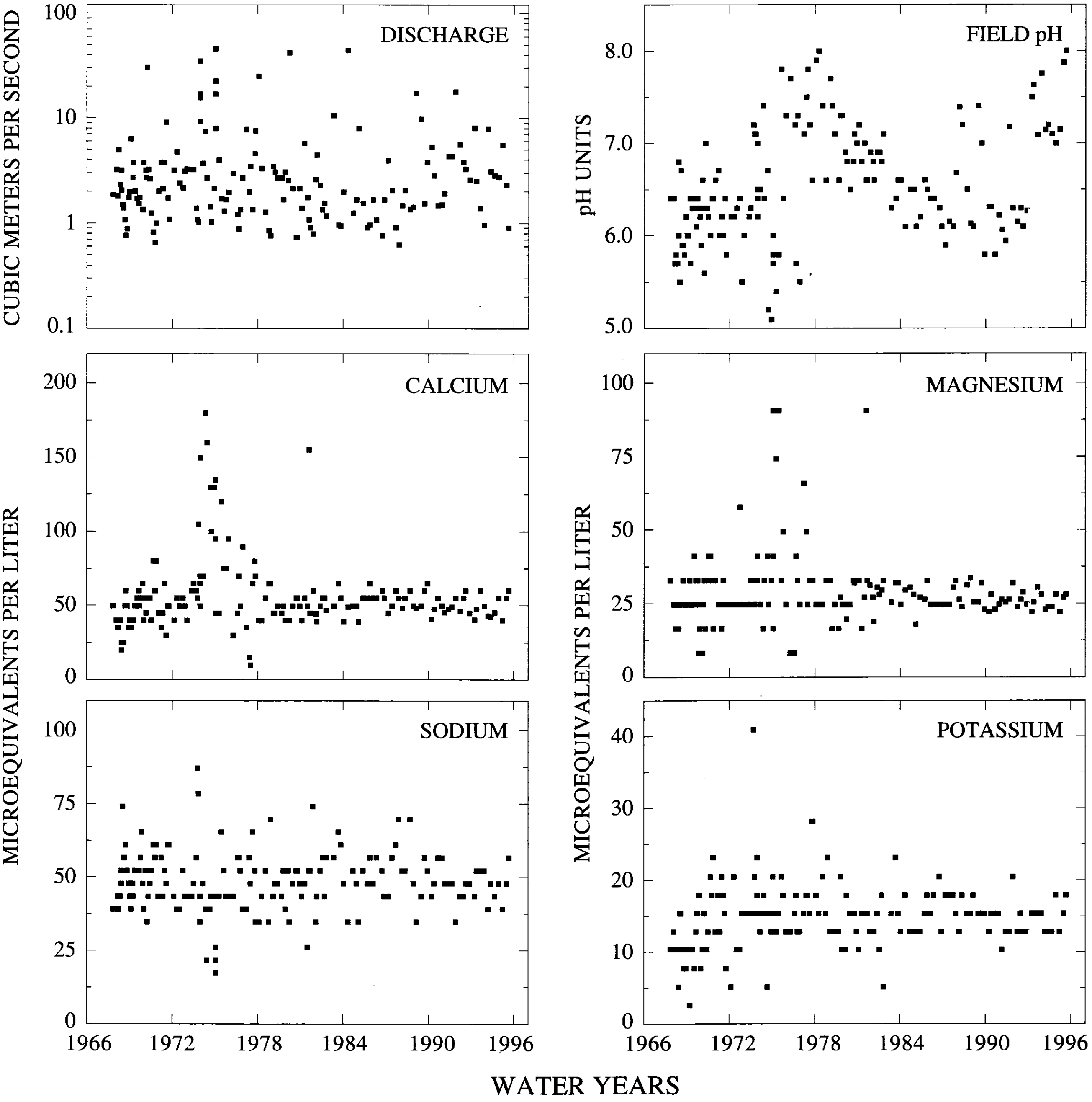

Figure 21. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Cataloochee Creek, North Carolina.

in the underlying bedrock. The median chloride concentration in stream water was 17 µeq/L, which is about 5.5 times larger than the VWM concentrations of chloride in precipitation. Based on the difference between average annual runoff and precipitation, evapotranspiration can account for about a twofold increase in the concentration of precipitation, indicating that as much as one-half of stream-water chloride may be derived from sources other than wet deposition. Measurements at a high-elevation site in GSMNP indicate that total annual chloride deposition may be twice that of wet deposition owing to additional inputs from dry deposition and cloud interception (Elwood and others, 1991). Estimates of total sulfate and nitrate deposition at the high-elevation site were two to five times greater than wet deposition.

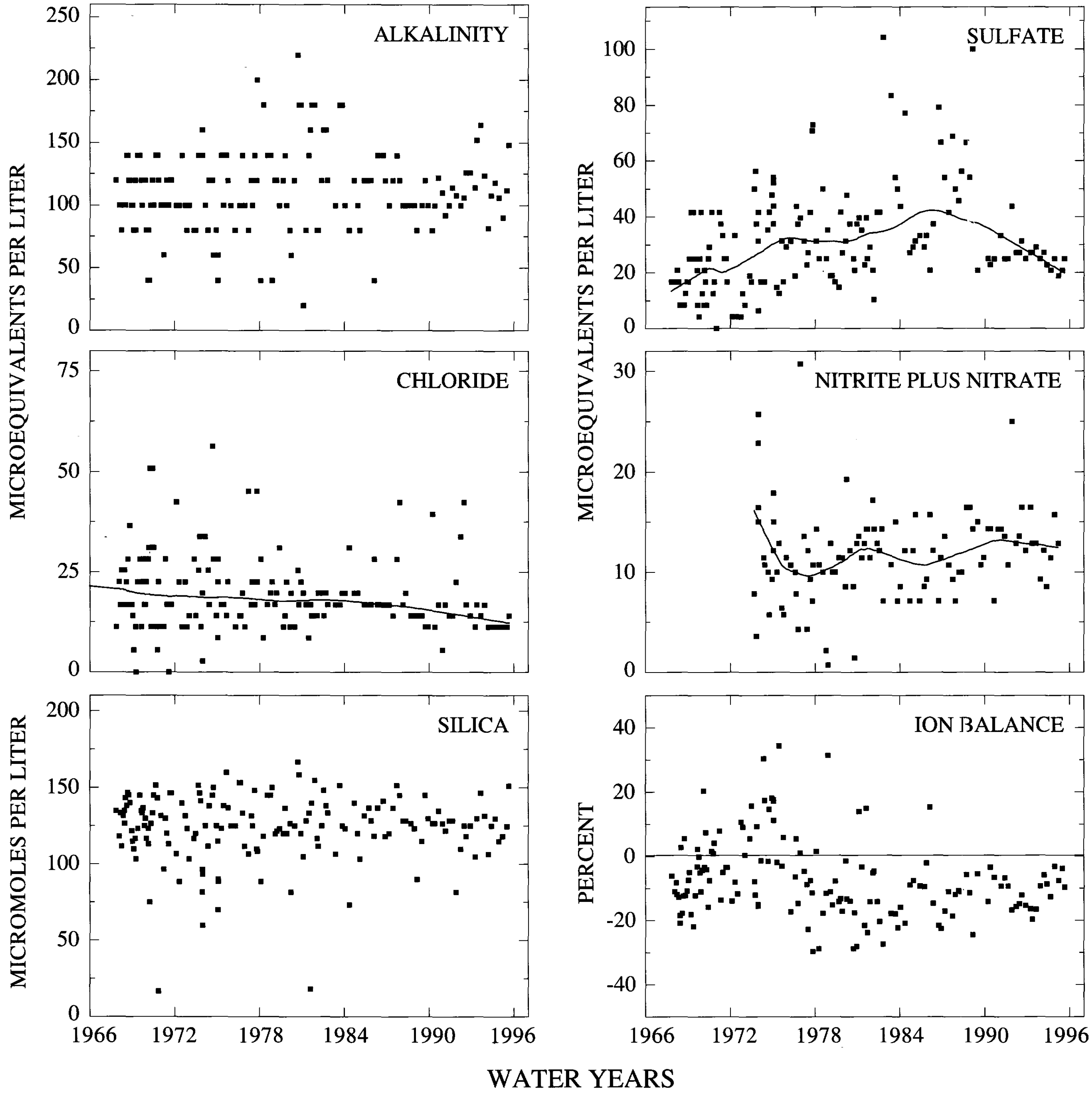

Figure 21. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Cataloochee Creek, North Carolina—Continued.

The median concentration of sulfate in Cataloochee Creek was actually smaller than the VWM concentration in wet precipitation. Considering the high levels of dry deposition measured elsewhere in GSMNP, these results suggest that a substantial portion of atmospherically deposited sulfate is retained in the basin. The most likely mechanism for sulfate retention is adsorption on clays and organic matter in the basin soils. The basin also appears to be an important sink for nitrogen species, based on the smaller concentrations of both nitrate and ammonium in stream water compared to precipitation. By contrast, many higher elevation streams in GSMNP have been found to have nitrate concentrations similar to those that are measured in precipitation (Nodvin and others, 1995). Because of the slow-weathering bedrock, basin retention of sulfate and nitrate probably is the dominant process buffering stream water from the effects of acidic deposition (Cosby and others, 1991).

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 39). Most weathering-derived constituents, particularly silica, had negative correlations with discharge. These correlations are consistent with a hydrologic system where weathering-enriched base flow is diluted by waters from shallow or surficial sources during periods of increased discharge. Among the ions, the strongest correlations were found between sodium and silica (r = 0.634) and calcium and alkalinity (rho = 0.539). These correlations suggest that weathering of carbonate cements and detrital feldspars

Table 38. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ion concentrations measured in water-quality samples from Cataloochee Creek, North Carolina, October 1962 through August 1995, and volume-weighted mean concentrations in wet precipitation collected at the Elkmont Station, Tennessee

[Concentrations in units of microequivalents per liter, discharge in cubic meters per second, specific conductance in microsiemens per centimeter at 25 degrees Celsius, pH in standard units, and silica in micromoles per liter; n, number of stream samples; VWM, volume-weighted mean; inst., instantaneous; spec. cond., specific conductance; <, less than; --, not reported]

Parameter	Stream water						Precipitation VWM[a]
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge, inst.	0.62	1.4	2.1	3.7	46	159	--
Spec. cond., field	10	14	15	16	25	161	--
pH, field	5.1	6.1	6.4	6.9	8.0	159	4.5[b]
Calcium	10	45	50	60	180	161	4.5
Magnesium	8.2	25	26	33	91	161	1.4
Sodium	17	44	48	52	87	161	2.7
Potassium	2.6	13	15	18	41	161	.9
Ammonium	<.7	<.7	<.7	2.1	11	101	10
Alkalinity, laboratory	20	100	110	140	220	161	--
Sulfate	4.2	18	26	42	100	155	34
Chloride	<2.8	14	17	23	56	155	3.1
Nitrite plus nitrate	<7.1	9.3	11	14	26	111	15[c]
Silica	17	115	125	140	170	161	--

[a]Values are volume-weighted mean concentrations for 1980–94.
[b]Laboratory pH.
[c]Nitrate only.

Table 39. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ion concentrations, Cataloochee Creek, North Carolina, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; N, nitrite plus nitrate; Si, silica]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	N
pH	–0.028									
Ca	–.559	–0.258								
Mg	–.561	.003	0.453							
Na	–.658	–.018	.510	0.328						
K	–.109	–.239	.470	.109	0.160					
Alk	–.636	.105	.539	.444	.518	0.203				
SO_4	–.159	–.333	.299	.245	.332	.370	–0.001			
Cl	–.066	–.142	.152	.133	–.013	.065	–.096	0.153		
N	.402	–.165	–.190	.052	–.382	.056	–.313	–.019	–0.073	
Si	–.712	.079	.454	.264	.634	.155	.627	–.012	–.106	–0.525

in the sandstones and quartzites is an important process that controls the composition of surface waters. The atmospherically derived solutes—sulfate, chloride, and nitrite plus nitrate—were poorly correlated with the weathering-derived constituents except for a weak inverse correlation between nitrate and silica (rho = –0.525). This correlation may indicate that stream-water silica is controlled by weathering processes in the deeper ground-water system, whereas stream-water nitrogen is controlled by biological processes in the shallow soil environment.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents from 1967 through 1995 are presented in table 40. Statistically significant trends were detected in sulfate, chloride, and nitrite plus nitrate at the 0.01 confidence level. Results for the flow-adjusted concentrations were similar to the unadjusted concentrations, indicating that variations in discharge were not driving the observed trends in stream chemistry. The LOWESS curves in figure 21 show that most of the increase in sulfate concentrations occurred prior to 1990, although the pattern probably is influenced somewhat by analytical bias during the late 1980's. The nitrite plus nitrate record begins in 1974 and shows a pattern of gradually increasing concentrations between 1978 and 1995. The upward trend in stream-water sulfate may be linked to increases in atmospheric sulfate deposition in the Southeast since the 1960's (Husar and others, 1991) and is consistent with the observed increases in stream-water sulfate concentrations at the nearby Coweeta Hydrologic Laboratory in North Carolina (Swank and Waide, 1988). The Coweeta streams also had downward trends in alkalinity and base cations, whereas no trends were detected for these constituents in Cataloochee Creek. The upward trend in nitrite plus nitrate is consistent with the hypothesis that many high-elevation streams in GSMNP are reaching an advanced stage of nitrogen saturation owing to the cumulative effects of atmospheric nitrogen deposition (Flum and Nodvin, 1995). Although the increase in nitrite plus nitrate in Cataloochee Creek has been relatively small [0.2 (μeq/L)/yr], with continued high rates of nitrogen deposition, the area of nitrogen saturation may begin to move downslope and have an increasing effect on nitrogen concentrations at the gage (Flum and Nodvin, 1995).

Table 40. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major ion concentrations, Cataloochee Creek, North Carolina, October 1967 through August 1995

[Trends in units of microequivalents per liter per year, except discharge in cubic meters per second per year, pH in standard units per year, and silica in micromoles per liter per year; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	<0.01	0.726	--	--
pH, field	.01	.218	0.01	0.237
Calcium	<.1	.803	<.1	.859
Magnesium	<.1	.759	<–.1	.824
Sodium	<.1	.363	.1	.022
Potassium	<.1	.134	<.1	.174
Alkalinity, laboratory	<.1	.486	–.1	.637
Sulfate	.6	.002	.7	.002
Chloride	–.2	.009	–.2	.006
Nitrite plus nitrate	.2[a]	.007	.2	.009
Silica	–.1	.422	–.1	.379

[a] Trend calculated for 1973–95.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling of October 31, 1991, are presented in table 41; locations of sampling sites are shown in figure 20. Discharge at the gage was 1.16 m^3/s compared to the median daily discharge of 1.50 m^3/s for October (Lawrence, 1987), indicating that the basin was sampled during base-flow conditions for that time of year. Solute concentrations measured at the gage (site 1) during the synoptic sampling were generally between the median and third-quartile concentrations reported for the gage during the entire period of record (table 38). All tributary streams were similar in composition to the gage, with calcium and sodium the dominant cations and alkalinity the dominant anion. Ion balances ranged from 1.7 to 14 percent, indicating that unmeasured organic anions may have been an important component of stream water during the sampling period.

Most spatial variability in water chemistry in the basin was measured in the weathering-derived constituents, particularly alkalinity and silica. Since the basin is underlain by similar rock types, these spatial patterns may reflect local variations in the mineralogic composition of the different sedimentary units. For example, the somewhat elevated concentrations of calcium, magnesium, and alkalinity at site 9 probably reflects the presence of limestone and

Table 41. Physical properties and major ion concentrations from surface-water sampling sites in the Cataloochee Creek Basin, North Carolina, October 31, 1991

[Site locations shown in fig. 20; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO$_4$, sulfate; Cl, chloride; NO$_3$, nitrate; concentrations in microequivalents; Si, silica in micromoles per liter; <, less than; --, not measured]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO$_4$	Cl	NO$_3$	Si	Criteria[a]	Remarks
1	03460000	1.16	17	6.95	55	26	65	17	110	21	12	<0.7	140		
2	353623083074400	.12	18	6.83	60	32	65	15	93	27	14	17	130	MT	Virgin hardwood forest
3	353744083051900	.45	16	6.93	48	25	61	16	97	21	14	<.7	140	MT	Virgin hardwood forest
4	353746083070100	.34	14	6.89	45	21	57	15	89	21	12	<.7	120	LU	Upstream from horse camp
5	353752083051800	.62	17	7.02	55	27	65	15	110	21	12	<.7	130	LU	Downstream from horse camp
6	353802083050600	.017	18	6.90	43	21	78	26	130	13	10	<.7	210	BG	Roaring Fork Sandstone
7	353820083075100	.23	13	6.82	40	21	52	14	76	19	14	<.7	110	BG	Thunderhead Sandstone
8	353831083074400	.091	13	6.72	39	20	52	14	64	19	13	9.0	100	BG	Thunderhead Sandstone
9	353844083043100	.025	22	6.97	75	46	74	24	140	29	15	<.7	180	BG	Walden Creek Group

[a] Criteria used in selection of sampling sites: BG = bedrock geology, MT = major tributary, LU = land use.

dolomite layers in the Walden Creek Group, which crops out in this subbasin. Spatial patterns in stream chemistry also may reflect basin characteristics other than geology. Silsbee and Larson (1982; 1983) analyzed stream chemistry throughout GSMNP and found substantial gradients in concentration with elevation with smaller concentrations of alkalinity, sodium, potassium, and silica at higher elevations. This pattern was attributed to higher flushing rates because of greater precipitation, and slower chemical weathering rates because of lower temperatures at higher elevations (Silsbee and Larson, 1982). Similar inverse relations with elevation were found for the same constituents in this study ($r = -0.511$ to -0.728), suggesting that elevation explains most of the spatial variation in weathering-derived constituents. By contrast, variability in the atmospherically derived components was relatively small. For example, chloride concentrations ranged from 12 to 15 μeq/L and sulfate ranged from 13 to 29 μeq/L. Nitrate concentrations were below the detection limit of 0.7 μeq/L at 9 of the 11 sites sampled. These nitrate concentrations were lower than the long-term median concentration at the gage (table 38), which may reflect the time of year the samples were collected. Silsbee and Larson (1982) observed that stream-water nitrate concentrations in GSMNP varied seasonally, with the highest concentrations in winter and spring and the lowest concentrations in autumn. The authors suggested that low autumn concentrations result from uptake of nitrogen by microorganisms during the initial stages of leaf fall.

Young Womans Creek near Renovo, Pennsylvania (Station 01545600)

Site Characteristics and Land Use

The Young Womans Creek HBN Basin is in the Appalachian Plateaus physiographic province in north-central Pennsylvania in an area characterized by high, flat-topped uplands dissected by steep-sided stream valleys. The basin drains 120 km^2 of forested terrain that ranges in elevation from 238 m at the gage to 665 m on the gently sloping upland surface. The HBN gage is in Sproul State Forest, about 8 km northeast of Renovo, Pa., at latitude 41°23'22" and longitude 77°41'28" (fig. 22). Young Womans Creek is a southwest-flowing tributary of the West Branch of the Susquehanna River with a channel length of about 17 km upstream from the gage.

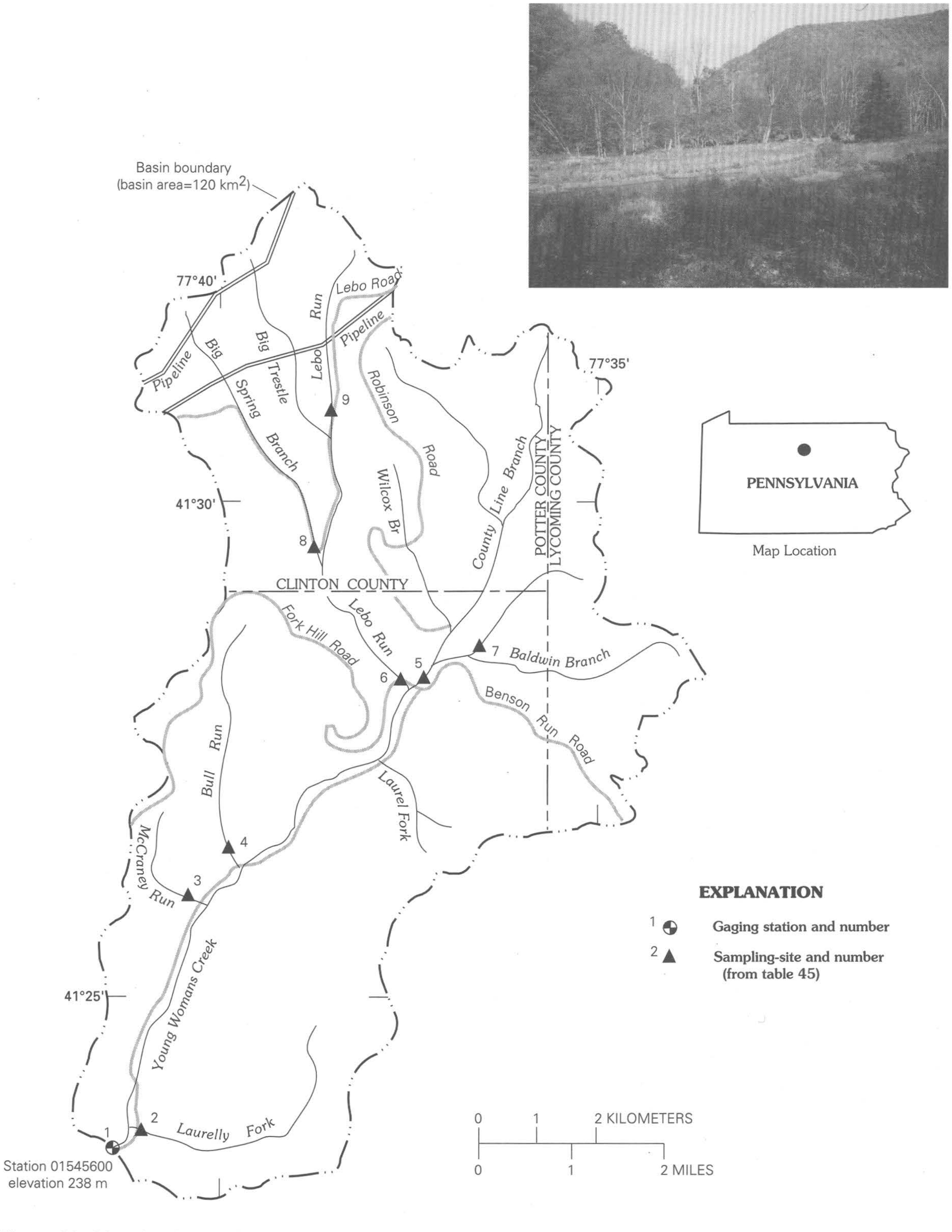

Figure 22. Map showing study area in the Young Womans Creek Basin and photograph of the landscape of the basin.

Stream gradients range from 11 m/km in the lower one-half of the basin to as much as 35 m/km in the headwater tributaries. Mean monthly discharge at the gage ranges from 0.66 m^3/s in September to 4.62 m^3/s in April. Average annual runoff from the basin was 56 cm from 1965 through 1995 (U.S. Geological Survey, Water Resources Data, Pennsylvania). Climate of the area is characterized as a humid continental type with cold winters and warm summers. Average daily air temperatures range from −3.3°C in January to 22.5°C in July (Kohler, 1986). Precipitation averages 105 cm annually and is fairly evenly distributed throughout the year (Kohler, 1986). Frontal storms are the most common source of precipitation, although thundershowers are prevalent in summer. Average seasonal snowfall is 120 cm; however, a seasonal snowpack rarely persists through the winter.

The basin lies in the Laurentian Mixed Forest ecoregion (Bailey and others, 1994) and is covered by second and third growth oak-hickory and maple-beech-birch forest types. The dominant species are white oak, red oak, pignut hickory, shagbark hickory, sugar maple, red maple, beech, and yellow birch (Kohler, 1986). Several stands of eastern hemlock also are scattered throughout the basin (Overdorff, 1987). The dominant understory species is flowering dogwood; blueberry, mountain laurel, sweet-fern, and sassafras comprise most of the ground cover (Goodlett, 1955). Pine forest types account for less than 10 percent of the forest cover; the dominant pine species are white pine, Virginia pine, and pitch pine. Soils in the basin are classified as Ultisols and Inseptisols and are mapped in the Dekalb-Clymer-Cookport soil association (Kohler, 1986). These are acidic, well-drained soils on hillslopes and ridges and are formed in material weathered from sandstone, siltstone, and shale. A typical profile has a thin organic horizon (5 cm) and a brown loam surface layer down to 25 cm overlying a yellowish-brown, sandy clay loam down to a depth of 100 cm. Most soils are extremely rocky and contain between 15 and 60 percent thin fragments of sandstone and shale.

Bedrock that underlies the basin includes Late Devonian to Pennsylvanian sedimentary rocks that have been deformed into low-amplitude, northeast-trending folds that plunge to the southwest (Colton and Stanley, 1965). The lower one-half of Young Womans Creek runs roughly parallel to the axis of a large syncline, and the upper tributaries in the Lebo Run subbasin drain perpendicular to the northwest limb of the fold. The rock units exposed in the basin are, from oldest to youngest, the Catskill Formation, Pocono Group, and Pottsville Group (Colton and Stanley, 1965). The Pocono Group, the most common formation in the basin, is a massive gray sandstone with layers of conglomerate and shale. The sandstone is highly permeable and is a common source of spring water in the region (Dinicola, 1982). Rocks of the Pottsville Group crop out along the eastern edge of the basin and include sandstones and conglomerates separated by discontinuous beds of shale and coal. The Lebo Run subbasin is underlain by rocks of the Catskill Formation, which includes sandstones, siltstones, and shales with lenses of calcareous conglomerate and limestone (Colton and Stanley, 1965). The basin is unglaciated and lies about 12 km southeast of the lower limit of Wisconsinan glacial deposits (Denny, 1956).

Young Womans Creek Basin drains parts of Potter and Clinton Counties, and more than 95 percent is State forest land administered by the Pennsylvania Bureau of Forestry. The southern one-half of the basin is in the boundaries of the Sproul State Forest and the northern one-half is in the boundaries of the Susquehannock State Forest. A 3-km strip of land adjacent to Young Womans Creek downstream from Bull Run is privately owned (fig. 22). Several private cabins are situated along Lebo Run and Big Spring Branch in the upper part of the basin. Access into the basin is by way of an improved road that parallels the main stem of Young Womans Creek from the gage to the confluence with Bull Run. This road was earthen until the early 1980's when it was resurfaced with limestone chips (Robert Davey, Sproul State Forest, oral commun., 1994). Secondary roads or foot trails parallel almost every major tributary in the basin, and several roads traverse the upper plateau area. Roads in the basin are not plowed in winter, although many are used as snowmobile trails.

The history of logging and settlement in the Young Womans Creek Basin and surrounding areas can be found in Goodlett (1955) and Beebe (1934). During the 1800's, most forests in the area were harvested for white pine, hardwoods, and hemlock. Owing to concerns about the impact of logging and associated fires on the water quality of streams, the State of Pennsylvania began purchasing land as tax sales from the County Commissioners. The first such purchase, in 1898, was a parcel of land near Bull Run in the Young Womans Creek Basin and marks the beginning of the Pennsylvania State Forest system. Since the establishment of the HBN station in 1967, land in the basin has been managed for timber production, recreation, and wildlife habitat. The most intensive period of logging occurred during the late 1970's when 150 ha of timber were clearcut on the upland plateau (J.D. Thomas, Susquehannock State Forest, written commun., 1993). In the mid-1980's, 40 ha were cut in the upland area at the head of Laurelly Fork, and in the early 1990's, a 7.2-ha parcel was clearcut in the upland area north of Wilcox Branch (Robert Davey, oral commun., 1994). All roads built by logging companies are gated and reseeded with grasses after completion of the timber sale (Robert Davey, oral commun., 1994). The basin overlies the Leidy gas field, which is situated 1,500 m below the surface in the Devonian Ridgeley Formation (Harper, 1989). Natural gas was first discovered in the Leidy field in 1950, but the field was quickly exhausted and was converted to a gas storage field around 1961 (Harper, 1989). Although most gas wells in the basin were drilled in the 1950's, two storage wells and an observation well were drilled in the late 1980's at the upper end of Big Spring Branch. Several shallow exploratory wells (1,525 m) were drilled along the southeast basin divide in the early 1990's (J.D. Thomas, written commun., 1993). There are currently two gas pipelines that access several gas storage wells in the headwaters of Lebo Run and Big Spring Branch. Gas wells have yielded salty water to surface-water systems in the area, but there is no evidence that surface waters are contaminated in the Young Womans Creek Basin (R.E. Hughey, Pennsylvania Department of Environmental Resources, oral commun., 1993). Coal mine drainage presents another major water-quality problem in the region (Hainly and others, 1989); however, no active or abandoned coal mines are present upstream from the Young Womans Creek gage. In 1994, intense rainfall from tropical storm Beryl washed out several roads and bridges in the basin. Limestone quarry waste was used to reconstruct the main channel just downstream from Laurel Fork, and a limestone ford was added where Fork Hill Road crosses Young Womans Creek (Robert Davey, oral commun., 1994). There are no campgrounds in the basin, and camping along waterways on State forest land is prohibited. Several small cabins scattered throughout the basin are used primarily during hunting season.

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for this report includes 213 water-quality samples that were collected from October 1967 through August 1995. Sampling frequency was monthly from 1967 to 1982 and quarterly from 1983 through 1995. Although not documented, water-quality samples in the early part of the record probably were analyzed at a USGS laboratory in Harrisburg, Pa., which was operated until 1973 (Durum, 1978). Following establishment of the Central Laboratory System, samples were analyzed at the Central Laboratory in Atlanta, Ga., from 1973 to 1985 and at the NWQL in Arvada, Colo., from 1986 through 1995. Daily discharge records for Young Womans Creek (station 01545600) are available beginning in December 1964.

Calculated ion balances for 211 samples with complete major ion analyses are shown in figure 23. Ion balances ranged from –35 to +21 percent, and 62 percent of the samples were in the ±10 percent range. This large range of concentrations was not unexpected considering the difficulty of making precise analytical measurements at the solute concentrations typical of this station. The mean charge balance of all samples was –3.8 percent, and 68 percent of the samples had a slight excess of measured anions over cations in solution. Laboratory alkalinity in HBN samples was determined by a fixed-endpoint titration to pH 4.5. For waters with low alkalinities, however, the endpoint pH is closer to 5.0, and titration to pH 4.5 may overestimate alkalinity by as much as 25 µeq/L (Barnes, 1964). Because the average alkalinity and anion excess for this station were 160 µeq/L and 13 µeq/L, respectively, a positive bias in the laboratory alkalinity appears to be a reasonable explanation for the negative ion balances.

Median concentrations and ranges of major dissolved constituents in stream water collected at the HBN gaging station and VWM concentrations in wet-only deposition measured at the Jasper NADP station are presented in table 42. Precipitation chemistry at the NADP station, which is about 80 km northeast of the basin, is dilute and acidic, with a VWM pH of 4.3 during 16 years of record. The major cations were hydrogen ion, which contributed 66 percent of the cation charge, and ammonium, which contributed 17 percent. Sulfate accounted for 65 percent of the total anion charge and nitrate accounted for 31 percent. The low pH and predominance of strong

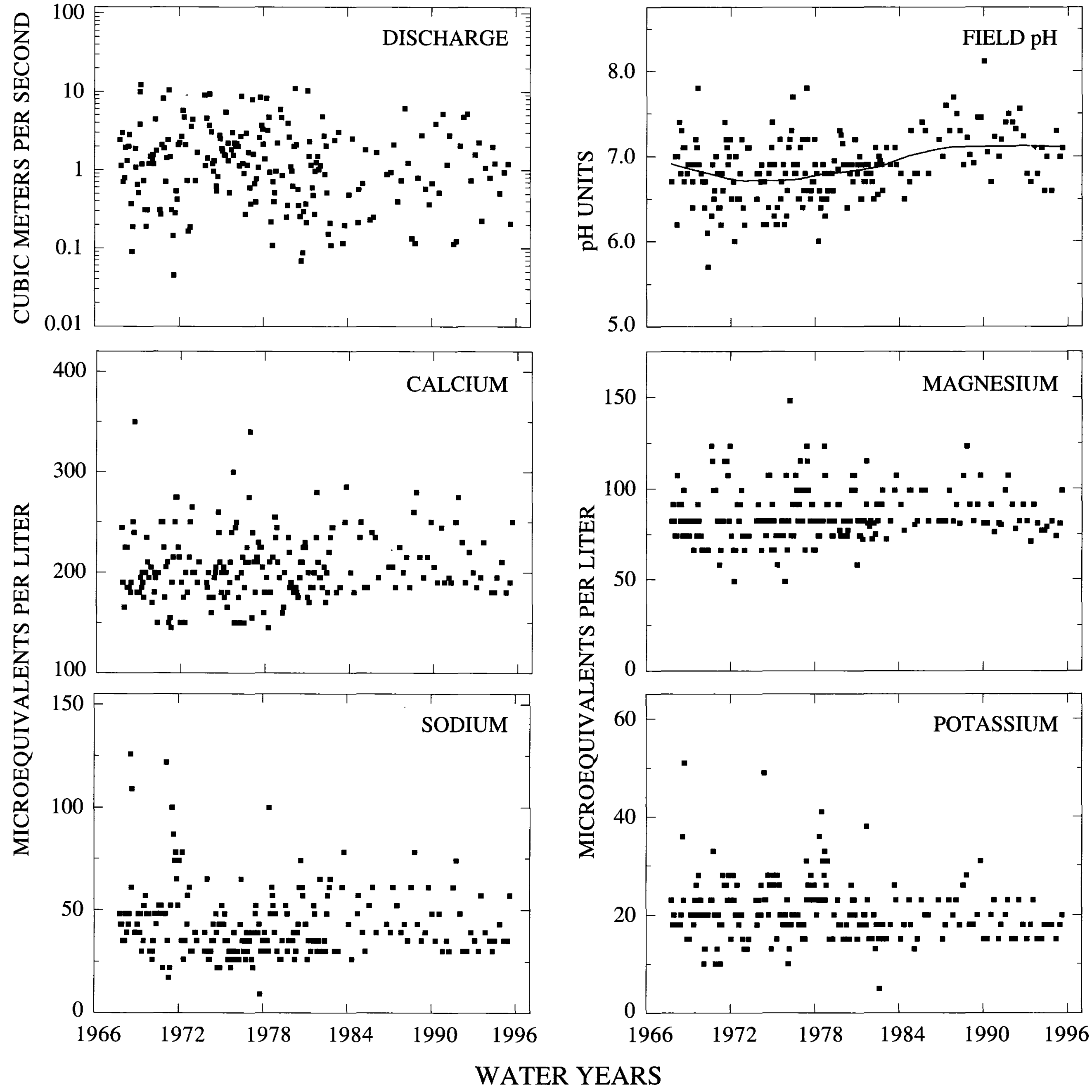

Figure 23. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Young Womans Creek, Pennsylvania.

acid anions indicates that precipitation at the NADP site probably is affected by anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain (Lynch and others, 1988).

Stream water in Young Womans Creek is dilute and weakly buffered; total ionic constituents ranged from 470 to 1,120 µeq/L, and alkalinities generally were between 120 and 220 µeq/L. The major cation in stream water was calcium and the major anions were sulfate and bicarbonate. The low concentrations of weathering-derived constituents, particularly alkalinity, are attributed to the lack of weatherable minerals in the underlying sandstones. High rates of acidic deposition probably also contribute to the low stream-water alkalinities at this station. The median chloride concentration in stream water was 37 µeq/L

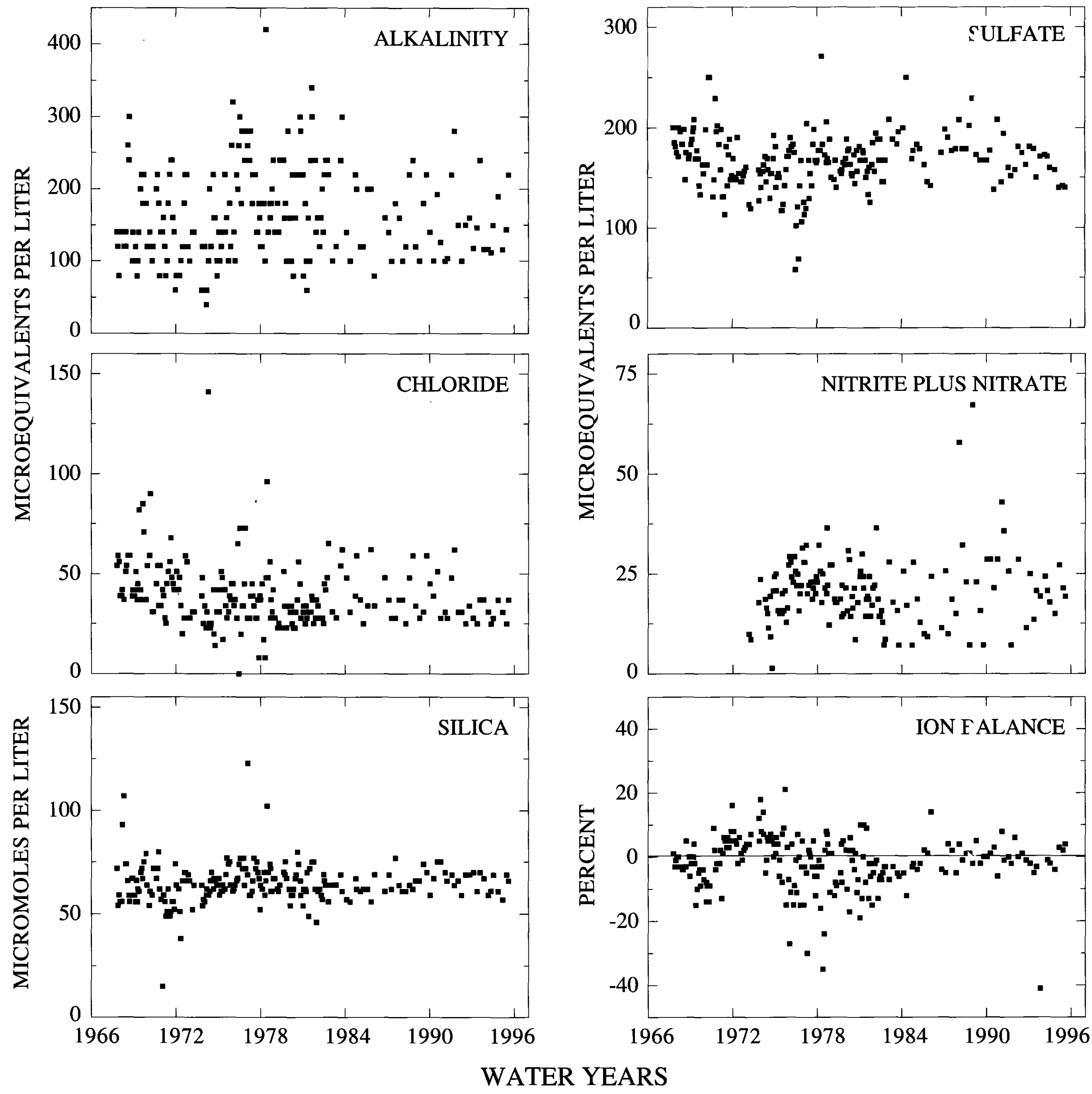

Figure 23. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Young Womans Creek, Pennsylvania—Continued.

compared to the VWM concentration of 3.2 in precipitation. Based on the difference between annual precipitation and runoff, evapotranspiration can account for about a twofold increase in the concentration of precipitation, indicating that some stream-water chloride is derived from sources other than precipitation. Because deicing salts are not used in the basin, the most likely additional sources of chloride are dissolution of trace amounts of halite in the underlying sedimentary rocks or possibly leakage of brine from the gas storage wells in the upper part of the basin. The median sulfate concentration in stream water was 170 μeq/L, which was about three times larger than the VWM concentration of 53 μeq/L in precipitation, indicating sulfate is derived from sources other than wet deposition. Assuming bedrock sources of sulfate are minor, dry deposition can account for most of the additional stream-water sulfate. Lynch and Corbett (1989) estimated that dry deposition accounted for as much as 30 percent of stream-water sulfate in a forested basin in central Pennsylvania. Concentrations of nitrate and ammonium in stream water were well below the VWM concentrations in precipitation, indicating that most atmospheric nitrogen was retained by vegetation and soils in the basin.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 43). Discharge was inversely correlated with the weathering-derived constituents with the exception of silica. These results are consistent with a hydrologic system where weathering-enriched base flow is diluted by waters from shallow or surficial sources during periods of increased discharge. In contrast, sulfate and nitrate

Table 42. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ion concentrations measured in water-quality samples from Young Womans Creek, Pennsylvania, October 1967 through August 1995, and volume-weighted mean concentrations in wet precipitation collected at the Jasper Station, New York

[Concentrations in units of microequivalents per liter, discharge in cubic meters per second, specific conductance in microsiemens per centimeter at 25 degrees Celsius, pH in standard units, and silica in micromoles per liter; n, number of stream samples; VWM, volume-weighted mean; inst., instantaneous; spec. cond., specific conductance at 25 degrees Celsius; <, less than; --, not reported]

Parameter	Stream water						Precipitation VWM[a]
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge, inst.	0.05	0.51	1.2	2.3	12	214	--
Spec. cond., field	25	37	39	42	56	213	--
pH, field	5.7	6.6	6.9	7.1	8.1	212	4.3[b]
Calcium	150	190	200	230	350	210	5.1
Magnesium	50	74	82	91	150	211	1.7
Sodium	9.0	30	39	48	130	212	2.4
Potassium	5.0	18	21	23	51	211	.4
Ammonium	<.7	<.7	.7	1.4	14	68	14
Alkalinity, laboratory	40	120	150	220	420	213	--
Sulfate	58	150	170	180	270	213	53
Chloride	8.0	28	37	45	140	212	3.2
Nitrite plus nitrate	1.4	16	20	25	67	147	26[c]
Silica	15	61	64	69	120	212	--

[a]Values are volume-weighted mean concentrations for 1980–95.

[b]Laboratory pH.

[c]Nitrate only.

Table 43. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ion concentrations, Young Womans Creek, Pennsylvania, 1980 through 1995

[Q, discharge; Ca, calcium, Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; N, nitrite plus nitrate; Si, silica]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	N
pH	–0.149									
Ca	–.742	0.294								
Mg	–.723	.277	0.840							
Na	–.799	.390	.816	0.835						
K	–.390	.308	.662	.591	0.534					
Alk	–.848	.200	.796	.679	.678	0.579				
SO_4	.491	–.069	–.430	–.315	–.383	–.224	–0.414			
Cl	–.631	.169	.698	.589	.713	.291	.542	–0.293		
N	.371	.004	–.175	–.289	–.283	–.329	–.464	.328	–0.095	
Si	–.095	-.029	.229	.203	.058	.284	.165	–.225	–.125	0.123

had positive correlations with discharge, implying that these solutes are controlled by processes in the soil environment. Atmospherically deposited sulfate probably is stored in soils during low-flow conditions and subsequently exported to the stream during periods of high flow (Lynch and Corbett, 1989). Overdorff (1987) observed a similar relationship between nitrate and discharge in a tributary of Young Womans Creek and determined that increases in stream-water nitrate during high-flow conditions in winter and spring were the result of nitrate influx from the snowpack and soils. Among the ions, the strongest correlations were found between base cations, alkalinity, and chloride; the weakest correlations were with silica. The strong correlations between calcium, magnesium, and alkalinity and the lack of correlation with silica are consistent with the weathering stoichiometry of carbonate minerals. The strong correlations between chloride and base cations, particularly sodium, provide additional evidence that stream-water chloride is derived from bedrock sources. The processes that control silica concentrations in stream water are not clear, particularly since concentrations varied relatively little over a wide range of streamflows. Weathering of silicate minerals in the sandstones and shales is the most likely source of silica in base flow. During high-flow periods, however, dissolution of amorphous silica minerals, biological activity, and sorption reactions along shallow flow paths may be the dominant processes that control stream-water concentrations of silica.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are shown in table 44. Statistically significant upward trends were detected in field pH and magnesium at the 0.01 confidence level. The trend in pH was similar for unadjusted and flow-adjusted values. The trend in magnesium, however, was not significant for the flow-adjusted concentrations, indicating that the trend in magnesium probably was related to variations in stream discharge. The LOWESS curve in figure 23 shows that most of the increase in pH occurred between the late 1970's and early 1980's. Hainly and others (1989) studied trends in water-quality parameters for 12 tributary basins of the West Branch of the Susquehanna River from 1972 to 1982. Significant upward trends in pH at seven of the stations, including Young Womans Creek, were attributed to improvement in the treatment of acidic mine drainage from coal mines. However, this is not a reasonable explanation for the pH trend in Young Womans Creek because no active or abandoned coal mines are present upstream from the gage. Smith and Alexander (1983) reported increases in stream-water alkalinity and sulfate concentrations at this station from 1967 through 1981 that they attributed to regional declines in acidic deposition. Although the increase in pH detected in this study is consistent with the acidic deposition hypothesis, trends in alkalinity and sulfate were not detected from 1967 through 1995. The extensive network of roads also might be considered a likely mechanism for producing upward trends in stream-water pH. The Bureau of Forestry has increasingly used limestone gravel to resurface unpaved roads in the State Forests not only for its physical properties but also for its buffering effect on acidic precipitation (Robert Davey, oral commun., 1994).

Table 44. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major ion concentrations, Young Womans Creek, Pennsylvania, October 1967 through August 1995

[Trends in units of microequivalents per liter per year, except discharge in cubic meters per second per year, pH in standard units per year, and silica in micromoles per liter per year; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	–0.01	0.056	--	--
pH, field	.02	.000	0.02	0.000
Calcium	.4	.056	<.1	.974
Magnesium	.2	.010	.2	.102
Sodium	<.1	.663	<–.1	.494
Potassium	<.1	.192	<–.1	.098
Alkalinity, laboratory	<.1	.646	.2	.746
Sulfate	–.1	.716	<–.1	.889
Chloride	<–.1	.132	–.2	.035
Nitrite plus nitrate	<.1	.673	.2	.065
Silica	<.1	.690	<–.1	.889

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling of October 22, 1991, are presented in table 45; locations of sampling sites are shown in figure 22. Discharge at the gage was 0.093 m^3/s compared to the median daily discharge of 0.45 m^3/s for October (Lawrence, 1987), indicating that low-flow conditions existed for that time of year. Concentrations measured at the gage (site 1) during the synoptic sampling were generally above the third-quartile concentrations that were measured at the gage during the entire period of record (table 42). The tributary sites were generally similar in composition to the gage, with calcium the dominant cation and alkalinity and sulfate the dominant anions. Ion balances of the synoptic samples ranged from –2.5 to 4.5 percent, inferring that organic anions did not contribute significantly to the ionic content of stream water during the sampling period.

Stream chemistry during the sampling period varied markedly over the basin, particularly the concentrations of calcium, magnesium, and alkalinity. For example, alkalinities ranged from a minimum of 22 μeq/L in North Baldwin Branch (site 7) to a maximum of 470 μeq/L in the upper reaches of Lebo Run (site 9). A similar pattern was measured in pH, which ranged from 6.0 at site 7 to 7.5 at site 9. These differences in stream-water chemistry can be explained by the distribution of major rock types in the basin. The three tributaries with the highest alkalinity and pH values (sites 6, 8, and 9) drain areas underlain by rocks of the Catskill Formation, whereas the tributary with the lowest alkalinity and pH, North Baldwin Branch, drains rocks belonging to the Pottsville Group. Tributaries with intermediate compositions drain rocks of the Pocono Group. Base-cation concentrations showed the same relation with rock type. Streams that drain rocks of the Catskill Formation had substantially larger concentrations than tributaries that drain the other two bedrock units. A similar relation between stream chemistry and rock type was observed by Dinicola (1982) and DeWalle and others (1987) for streams that drain areas underlain by rocks of the Pottsville and Pocono Groups in southwestern Pennsylvania. The authors attributed the pattern to differences in the amounts of limestone and carbonate cements in the sedimentary units.

In contrast to alkalinity, sulfate concentrations did not vary markedly among the sampling sites. This consistency in stream-water concentrations probably reflects the fact the sulfate is derived from atmospheric sources and behaves relatively conservatively in the basin. Chloride concentrations also were fairly uniform (23 to 62 μeq/L) with the exception of Lebo Run above Big Trestle (site 9) that had a concentration of 160 μeq/L. This subbasin has a high density of cabins and gas storage wells, both of which are potential sources of chloride. Nitrate concentrations in the tributary streams ranged from less than 0.7 μeq/L to 93 μeq/L. The highest nitrate concentrations were measured in McCraney Run (site 3) and Bull Run (site 4), both of which were sampled downstream from ground-water discharge zones. Hainly and Ritter (1986) also reported elevated nitrate concentrations for three small tributaries in the basin including Bull Run. Relatively high nitrate concentrations were measured in ground-water-fed streams in the Catskill Mountains of New York (Burns, 1993). Burns hypothesized that ground water discharging from springs was enriched in nitrate because it was recharged predominantly during the nongrowing season when plant demand for nitrogen is minimal.

Table 45. Physical properties and major ion concentrations from surface-water sampling sites in the Young Womans Creek Basin, Pennsylvania, October 22, 1991

[Site locations shown in fig. 22; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; concentrations in microequivalents per liter; Si, silica in micromoles per liter; Fm, Formation; <, less than; --, not measured]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria[a]	Remarks
1	01545600	0.093	56	7.1	270	110	74	22	200	160	62	10	62		
2	412335077410700	.009	43	6.8	180	99	65	24	130	190	27	25	73	BG	Pocono Group
3	412554077401600	<.001	61	6.9	290	120	74	24	170	250	31	93	87	BG	Pocono Group
4	412607077395100	--	57	6.9	250	110	61	21	170	200	23	71	63	BG	Pocono Group
5	412748077374600	.040	44	7.1	210	91	61	19	160	160	42	14	65	MT, BG	Pocono and Pottsville Group
6	412753077374800	.017	63	7.2	350	120	78	21	310	190	60	16	70	MT, BG	Pocono and Catskill Group
7	412812077365600	--	40	6.0	170	82	30	23	22	230	23	36	65	BG	Pottsville Group
8	412919077385600	.002	59	7.3	320	110	78	20	300	170	54	8.6	82	LU, BG	Gas wells, Catskill Group
9	413021077385000	.004	88	7.5	460	140	170	20	470	190	160	<0.7	78	BG	Catskill Fm

[a] Criteria used in selection of sampling sites: BG = bedrock geology, MT = major tributary, LU = land use.

Scape Ore Swamp near Bishopville, South Carolina (Station 02135300)

Site Characteristics and Land Use

The Scape Ore Swamp HBN Basin is in the Congaree Sand Hills region of the Coastal Plain physiographic province of South Carolina (fig. 24). The 249-km^2 basin drains an area characterized by small hills with long, gentle slopes and broad summits that ranges in elevation from 50 to 120 m. The USGS gaging station is 8 km southwest of the town of Bishopville, S.C., at latitude 34°09'02" and longitude 80°18'18". Scape Ore Swamp is a southeast-flowing tributary of the Pee Dee River with a channel length of about 28 km upstream from the gage and an average stream gradient of 1.4 m/km. The main channel is perennial, and mean monthly discharge varies over a relatively narrow range from a minimum of 1.66 m^3/s in July to 4.87 m^3/s in March. Average annual runoff from the basin was 38 cm from 1968 through 1995 (U.S. Geological Survey, Water Resources Data, South Carolina). Climate of the area is relatively temperate with warm, humid summers and mild winters. Average daily summer and winter temperatures are 25.5°C and 5.5°C, respectively (Mitchell, 1990). Winter ground frost is common, but snowfall is rare. Precipitation averages 115 cm annually and is fairly evenly distributed throughout the year (Mitchell, 1990).

The basin lies in the Outer Coastal Plain Mixed Forest ecoregion, which is characterized by temperate evergreen forests (Bailey and others, 1994). Forests on hillslopes and upland areas are dominated by southern pine and upland hardwood communities; the dominant species are loblolly pine, longleaf pine, slash pine, shortleaf pine, oak, and hickory. The flood plains are covered by lowland hardwood forests of water tupelo, swamp tupelo, water oak, and bald cypress. Most soils in the basin are classified as Ultisols and mapped in the Alpin and Blanton soil series (Mitchell, 1990). These soils are formed in sandy marine sediments and are generally found on broad ridgetops and side slopes of sand hills. A typical profile has a sandy surface layer, 10 to 30 cm thick, overlying a sandy to loamy subsoil down to a depth of 200 cm. Because of the high sand content, these soils are highly permeable and acidic (pH 4.5 to 6.0) and have a low nutrient-holding capacity. Poorly drained soils in relatively narrow strips along the flood plains are mapped in the Johnson Series (Mitchell, 1990). A typical Johnson soil has a black loam surface layer about 75 cm thick overlying a grayish sandy loam sublayer. The dominant minerals in all soils are quartz and kaolinite (Mitchell, 1990).

The basin is underlain by Upper Cretaceous sediments of the Tuscaloosa Formation (Cooke, 1936). The Tuscaloosa Formation consists of fluvial and marine sediments assumed to be derived from weathered crystalline rocks of the Piedmont. Cooke (1936) described the sediments as light-colored arkosic sands composed of quartz, feldspar, and muscovite, interlayered with lenses of light-colored clay. Argillaceous sands of the Eocene Black Mingo Formation underlie the basin near the gage but are covered by sandy Pleistocene terrace deposits.

The Scape Ore Swamp Basin drains parts of Lee and Kersaw Counties. Land ownership in the basin is 96 percent private and 4 percent Federal, State, and county (Mike Newman, Natural Resources Conservation Service, written commun., 1996). More than 200 km of primary and secondary roads provide access to most areas of the basin. Because of swampy conditions along most of the stream channels, roads tend to follow the sand hills summits rather than parallel the drainages. A 13-km segment of Interstate 20 crosses the center of the basin in the east-west direction. Land use in the basin is 60 percent forest and 40 percent crop and pasture land. Farmland is more commonly situated on the hillslopes and broad summits of the sand hills, whereas forested areas are concentrated along the drainages. Most farms in the basin are relatively small (average size 70 ha) and generally produce soybeans, corn, peanuts, and cotton; pasture lands are covered by a mixture of Coastal Bermuda, Common Bermuda, annuals, and native grasses (Mike Newman, written commun., 1996). About 30 small impoundments located in the basin are primarily used for irrigation and recreational fishing. Residents in the basin use ground water as their primary domestic water supply. A major resource problem in the basin is soil loss from highly erodible cropland, which results in damage to streams, roads, and property (Lynn Newton, Natural Resources Conservation Service, written commun., 1996). The U.S. Department of Agriculture instituted the Conservation Reserve Program (CRP) in 1985 as a means of reducing soil erosion by paying farmers to plant permanent vegetation types, such as grasses and pines. About 20 percent of agricultural land in the basin is currently managed under the CRP (Wayde Ross, Natural Resources Conservation Service, written commun., 1996).

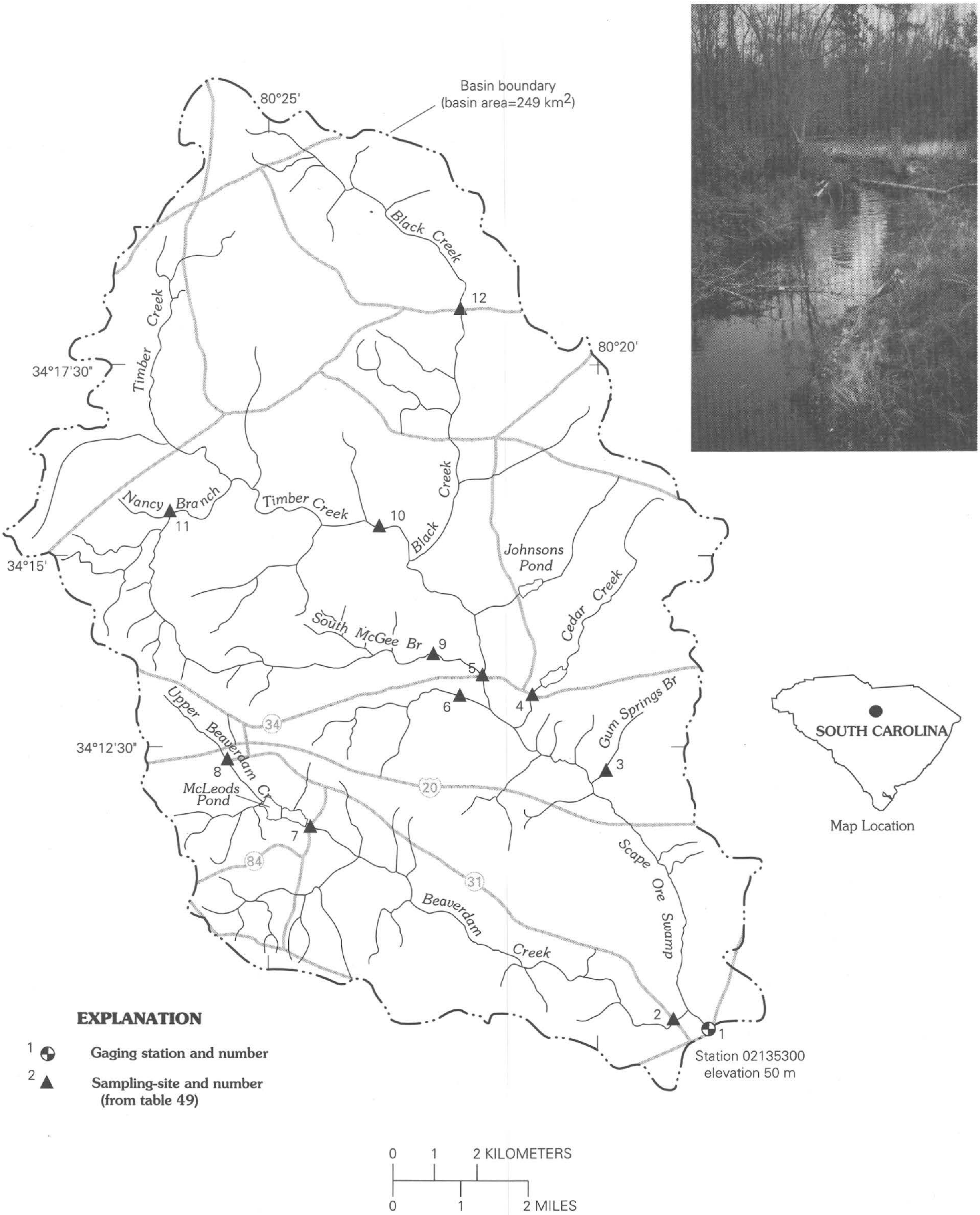

Figure 24. Map showing study area in the Scape Ore Swamp Basin and photograph of a typical tributary stream.

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for this report includes 212 water-quality samples that were collected from August 1970 through September 1995. Sampling frequency was monthly from 1971 through 1982 and bimonthly from 1983 through 1995. Although not documented, water-quality samples in the early part of the record probably were analyzed at USGS laboratory in Raleigh, N.C., which was operated until 1973 (Durum, 1978). After establishment of the USGS Central Laboratory System, samples were analyzed at the Atlanta laboratory from 1973 through 1985 and at the NWQL in Arvada, Colo., from 1986 through 1995. Daily discharge records for Scape Ore Swamp (station 02135300) are available beginning in July 1978.

Calculated ion balances for 205 samples with complete major ion analyses are shown in figure 25. Ion balances ranged from −45 to +31 percent and more than 65 percent of samples had values within the ±10 percent range, indicating that the analytical measurements were generally of good quality. The average charge balance for all samples was 1.1 percent, indicating measured cations and anions were close to balanced. Time-series plots of the major dissolved constituents were inspected for evidence of method-related effects (fig. 25). Several patterns are evident at the Scape Ore station. For example, elevated sulfate concentrations were reported for most samples during the late 1980's. This pattern coincides with the use of a turbidimetric titration for sulfate analyses at the NWQL between March 1986 and December 1989 (Fishman and others, 1994). In 1989, the NWQL determined that sulfate concentrations can be overestimated by this technique and changed the method to ion chromatography in 1990 (Office of Water Quality Technical Memorandum No. 90.04, *Turbidimetric Sulfate Method*, issued December 21, 1989, at URL http://water.usgs.gov/public/admin/memo/). Uncharacteristically high calcium concentrations also were evident during the period 1974 through 1976. Interestingly, a similar pattern of high calcium concentrations also was observed at the Wild River station in Maine during the same period of record. Because samples from these two sites were analyzed at different laboratories during this period, it seems likely that high calcium concentrations may be related to collection or processing procedures common to both stations. The only documented procedural change during this period was the introduction of a polypropylene churn splitter for compositing and splitting samples that was required for use at all HBN stations beginning in water year 1977 (Office of Water Quality Technical Memorandum No. 76.24–T, *Sample Splitter for Water-Sediment Samples*, issued August 16, 1976, at URL http://water.usgs.gov/public/admin/memo/). Although problems with previous sample splitters were not documented by the Office of Water Quality (OWQ), the fact that the anomalous pattern disappeared around the beginning of 1977 indicates that previous splitters or compositing devices may have been a potential source of contamination. Temporal patterns in pH also reveal potential bias in the field determinations. Between 1983 and 1985, field pH values were 0.5 to 1 pH unit smaller than values typically reported for this station. A possible cause of this shift was the gel-filled pH probe used by field personnel in the USGS office in South Carolina during this period of record (John Barton, USGS, oral commun., 1996). Some instrument-electrode systems are known to give erroneous readings when measuring pH in low-conductivity waters, and the electrode commonly is the critical component (Office of Water Quality Technical Memorandum No. 81.08, *Electrodes for pH Measurement in Low-Conductivity Waters*, issued February 10, 1981, at URL http://water.usgs.gov/public/admin/memo/).

Median concentrations and ranges of major constituents in stream water collected at the HBN gaging station and VWM concentrations in wet-only deposition measured at the Santee National Wildlife Refuge NADP station about 60 km south of the basin are presented in table 46. Precipitation chemistry at the NADP station was dilute and acidic with a VWM pH of 4.6 for 10 years of record. The dominant cations were hydrogen, which contributed 45 percent of the cation charge, and sodium, which contributed 18 percent. Sulfate accounted for 54 percent of the total anions, and nitrate and chloride each accounted for 23 percent. These results suggest that precipitation at the NADP station probably is a mixture of both anthropogenic emissions of sulfate and nitrogen compounds and salt derived from marine aerosols.

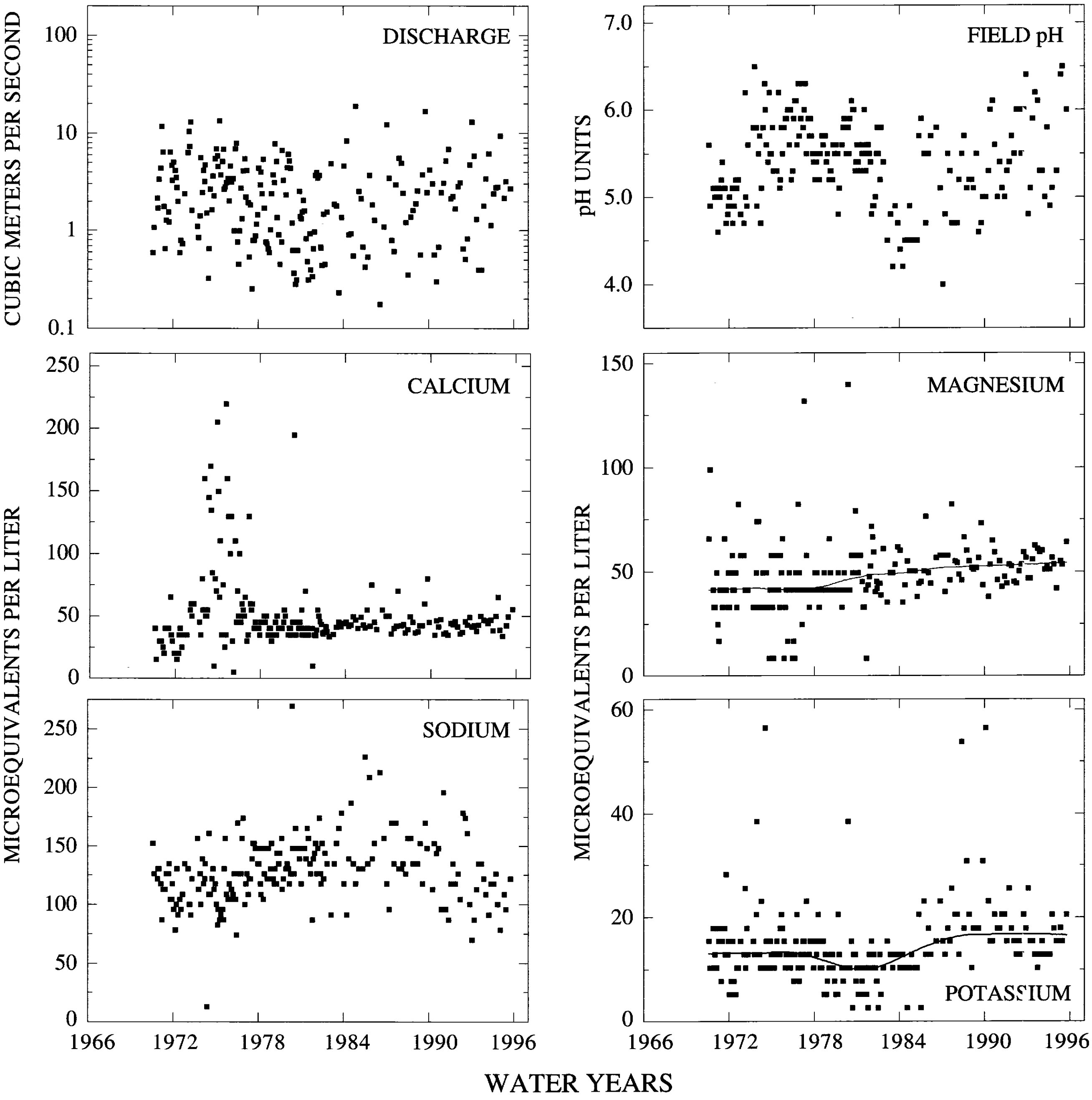

Figure 25. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Scape Ore Swamp, South Carolina.

Stream water in the Scape Ore Swamp is dilute and weakly buffered; total ionic constituents ranged from 210 to 860 μeq/L, and alkalinities were generally below 70 μeq/L. The major cation in stream water was sodium, and the dominant anion was chloride. The low concentrations of the major weathering products, particularly alkalinity, are attributed to the slow weathering rates of the quartz-rich soils and sediments in the basin. The median chloride concentration in stream water was 120 μeq/L, which was about 10 times larger than the VWM concentration of chloride in precipitation. Based on the difference between annual precipitation and runoff, evapotranspiration can account for no more than a threefold increase in the chloride concentration of precipitation, indicating that a substantial amount of stream-water chloride

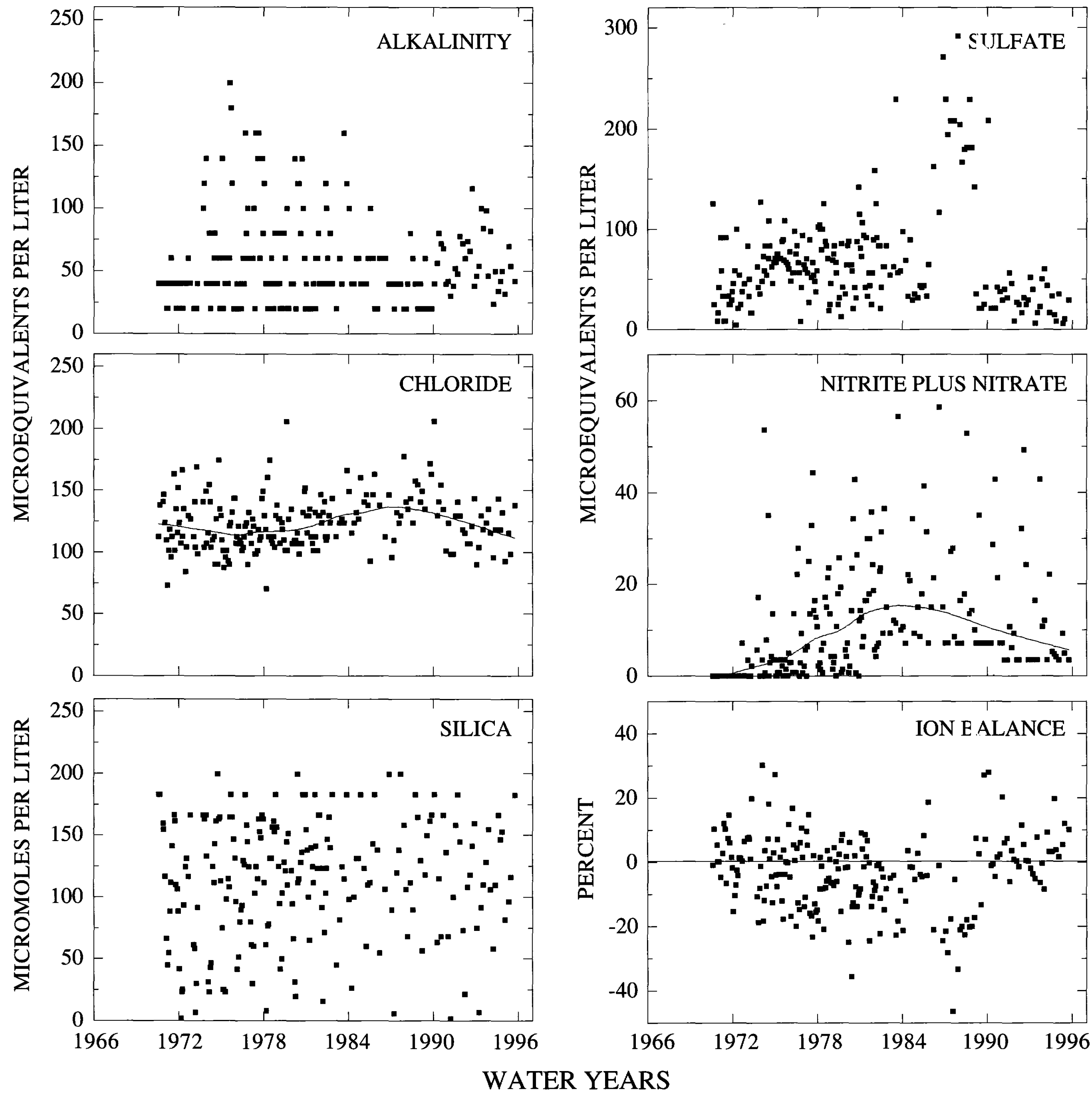

Figure 25. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Scape Ore Swamp, South Carolina—Continued.

is derived from sources other than precipitation. Considering the proximity of this site to the coast, dry deposition of marine aerosols probably is the dominant source of chloride (and sodium) in stream water. Chloride also may be derived from manmade sources, such as runoff from agricultural areas or discharge from domestic wastewater systems. The median concentration of sulfate in stream water was twice the VWM concentration in precipitation, which was somewhat less than expected considering the effects of evapotranspiration and additional inputs of sulfate in dry deposition. This difference indicates that a substantial portion of atmospherically deposited sulfate is retained in the basin. Possible mechanisms of sulfate retention include adsorption on basin soils or sulfate reduction in wetland areas along the stream channel. The basin also is apparently an important sink of atmospherically deposited nitrogen based on the smaller concentrations of both nitrate and ammonium in stream water compared to precipitation. The low stream-water nitrate concentrations also indicate that agricultural areas in the basin do not significantly affect stream-water nutrient concentrations at the gage. Because weathering supplies only minor amounts of base cations and alkalinity to surface waters in the basin, basin retention of sulfate and nitrate probably is the dominant process buffering surface waters from acidic deposition (Elwood and others, 1991).

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 47). Discharge was poorly correlated with most dissolved constituents with the exception of weak inverse correlations with pH (rho = –0.588), sodium (rho = –0.0462), and alkalinity (rho = –0.536). Solutes in stream water also

Table 46. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ion concentrations measured in water-quality samples from Scape Ore Swamp, South Carolina, August 1970 through September 1995, and volume-weighted mean concentrations in wet precipitation collected at Santee National Wildlife Refuge, South Carolina

[Concentrations in units of microequivalents per liter, discharge in cubic meters per second, specific conductance in microsiemens per centimeter at 25 degrees Celsius, pH in standard units, and silica in micromoles per liter; n, number of stream samples; VWM, volume-weighted mean; inst., instantaneous; spec. cond., specific conductance; <, less than; --, not reported]

Parameter	Stream water						Precipitation VWM[a]
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge, inst.	0.18	0.85	2.0	4.0	19	212	--
Spec. cond., field	20	25	26	29	43	209	--
pH, field	4.0	5.1	5.4	5.7	6.5	211	4.6[b]
Calcium	5.0	36	43	50	220	211	4.5
Magnesium	<8.2	41	46	55	140	211	3.0
Sodium	13	110	130	150	270	211	10
Potassium	<2.6	10	13	17	56	211	2.3
Ammonium	<.7	1.4	2.1	3.6	13	96	5.6
Alkalinity, laboratory	<20	37	40	71	200	211	--
Sulfate	4.2	33	56	83	290	210	29
Chloride	69	110	120	140	200	210	12
Nitrite plus nitrate	<.7	4.3	8.6	18	59	181	12[c]
Silica	1.7	80	120	160	220	211	--

[a] Values are volume-weighted mean concentrations for 1984–94.

[b] Laboratory pH.

[c] Nitrate only.

Table 47. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ion concentrations, Scape Ore Swamp, South Carolina, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; Si, silica]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	–0.588								
Ca	.149	–0.235							
Mg	.047	–.083	0.551						
Na	–.462	.165	.294	0.294					
K	.311	–.193	.350	.409	–0.052				
Alk	–.536	.504	–.089	.043	.159	–0.157			
SO_4	.243	–.357	.102	.204	.199	.044	–0.321		
Cl	.114	–.28	.198	.390	.264	259	–203	0.171	
Si	-.251	–.005	.156	.291	.301	071	014	–003	0.426

were poorly correlated with each other with the exception of a weak positive correlation between calcium and magnesium (rho = 0.551). The lack of strong correlations among these constituents probably is related both to hydrologic and geochemical factors. The highly permeable soils and sediments on the hillslopes and upland surfaces allow precipitation to infiltrate quickly into the ground-water system. In turn, streamflow is supplied by ground-water discharge, which maintains a relatively constant flow rate and stream composition throughout the year. Additionally, the quartz-rich soils and sediments contain few weatherable minerals and, as a consequence, produce soil and ground waters that are not significantly different in composition from that of the incoming precipitation.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents from 1970 through 1995 are shown in table 48. Statistically significant upward trends were observed for unadjusted magnesium, potassium, and chloride concentrations at the 0.01 confidence level. The flow-adjusted concentrations of magnesium were not tested for trends because the flow model was not statistically significant at $\alpha = 0.1$. The unadjusted and flow-adjusted trends were similar for potassium and chloride, indicating that the trends were not driven by variations in stream discharge. The LOWESS curve in figure 25 shows a pattern of increasing chloride concentrations between 1972 and 1986 and decreasing concentrations after 1986. A similar pattern also was observed for sodium, although a trend was not detected during the entire period of record. Land-use changes may be a likely mechanism for producing the similar patterns in chloride and sodium because both ions are commonly indicators of manmade effects. The most substantial land-use change in the basin was the conversion of about 20 percent of cropland to permanent vegetation as a result of the Conservation Reserve Program (CRP). Interestingly, chloride and sodium concentrations began to decrease shortly after the CRP was instituted in 1985. In contrast to chloride, potassium concentrations declined through the early part of the record, then increased somewhat abruptly in 1986. Most of the increase in magnesium concentrations occurred in the early 1980's. It is unlikely that the sudden increase in potassium is associated with the CRP. A decrease in agricultural land use is more likely to cause a decline in stream-water potassium concentrations, particularly since potassium is a common component of fertilizer. It is perhaps more likely that the sudden increase in potassium was caused by a analytical-related factor. The increase in potassium, for example, occurred at the same time that the analytical determinations were switched from the Central Laboratory in Atlanta to the NWQL in Arvada, Colo. A method change also may provide a plausible explanation for the upward trend in magnesium. For example, the analytical method for the determination of several constituents, including magnesium, was changed from AA spectroscopy to ICP spectroscopy in 1983 (Office of Water Quality Technical Memorandum No. 82.18, *National Water-Quality Networks*, issued September 28, 1982, at URL http://water.usgs.gov/public/admin/memo/), which correlates with the increase in magnesium concentrations in the early 1980's.

Table 48. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major ion concentrations, Scape Ore Swamp, South Carolina, August 1970 through September 1995

[Trends in units of microequivalents per liter per year, except discharge in cubic meters per second per year, pH in standard units per year, and silica in micromoles per liter per year; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	−0.01	0.554	--	--
pH, field	<.01	.849	<−0.01	0.906
Calcium	.1	.214	(a)	--
Magnesium	.7	.000	(a)	--
Sodium	<.1	.914	−.2	.509
Potassium	.1	.008	.2	.007
Alkalinity, laboratory	<.1	.318	.2	.485
Sulfate	−.7	.132	−.9	.093
Chloride	.8	.002	.9	.001
Nitrite plus nitrate	<.1[b]	.601	--	--
Silica	.6	.103	.5	.093

[a] Flow model not significant at $\alpha = 0.10$.

[b] Trend calculated for 1973–95, using a trend test for censored data.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling of January 10 and 11, 1991, are presented in table 49; locations of sampling sites are shown in figure 24. Discharge at the gage was 2.27 m^3/s compared to the median daily discharge of 3.68 m^3/s for January (Lawrence, 1987), indicating that the basin was sampled during base-flow conditions for that time of year. Solute concentrations measured at the gage (site 1) during the synoptic sampling were generally below the first-quartile concentrations reported for the gage during the entire period of record (table 46). The tributary streams were extremely dilute, and sodium and chloride were the dominant ions. Measured alkalinities were below the detection limit at 9 of the 12 sites, and pH ranged from 4.92 to 6.54, indicating that most surface waters were slightly acidic. The source of most stream-water acidity probably is organic acids, although some may be derived from strong acids in precipitation. Although DOC was not measured in this study, all samples had positive ion balances (range 3.8 to 14 percent), inferring that organic anions were an important component of stream water during the sampling period.

In general, stream chemistry did not vary markedly among the sampling sites. For example, specific conductance ranged from 18 to 34 µS/cm, and most dissolved constituents did not vary by more than a factor of three. This result primarily reflects the uniform composition and slow weathering rate of soils and sediments in the basin. Some subtle variations in stream chemistry are evident, however, which may reflect the influence of factors other than geology. For example, samples that were collected in the Beaverdam Creek subbasin (sites 2, 7, and 8) had elevated concentrations of calcium, alkalinity, and nitrate. These solutes are common components of fertilizer and sewage, and their elevated concentrations may be indicative of human disturbance in this subbasin. Substantial differences also were observed in Beaverdam Creek upstream from (site 8) and downstream from (site 7) McLeods Pond. For example, alkalinity concentrations almost tripled downstream from the pond, whereas nitrate concentrations decreased by a factor of 10. This change in stream chemistry indicates that the impoundment may have a strong influence on stream-water chemistry in this tributary. Chloride, which is commonly used as an indicator of human activities, was remarkably uniform over the basin and ranged from 110 to 140 µeq/L. In contrast, sodium concentrations varied by more than a factor of two. Interestingly, streams in the northern one-half of the basin (sites 4, 5, 9, 10, 11, and 12) had an average sodium-to-chloride ratio of 0.6, whereas sites in the southern one-half of the basin (sites 2, 3, 6, 7, and 8) had an average ratio of 1.0. Sulfate also differed slightly between tributaries

Table 49. Physical properties and major ion concentrations from surface-water sampling sites in the Scape Ore Swamp Basin, South Carolina, January 9–10, 1991

[Site locations shown in fig. 24; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; concentrations in microequivalents; Si, silica in micromoles per liter; <, less than, --, not measured]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria[a]	Remarks
1	02135300	2.27	26	4.98	32	40	96	15	<10	31	130	6.4	63		
2	340910080184900	.62	27	5.88	35	42	140	19	39	17	140	19	87	MT, LU	Significant development
3	341230080195100	.042	22	5.45	19	30	120	13	<10	21	120	2.9	120	BG	Black Mingo Shale
4	341321080210300	.093	18	5.81	22	34	78	9.7	<10	23	110	2.9	90	MT, LU	Reservoir in subbasin
5	341335080214900	--	25	4.90	33	45	83	15	<10	38	130	2.9	87	MT, LU	Upstream from most development
6	341322080221300	--	23	5.28	21	30	110	14	<10	20	120	1.4	130	LU	I–20 crosses subbasin
7	341141080241800	.062	29	6.54	60	55	130	28	110	15	130	2.9	38	LU	Downstream from large impoundment
8	341232080253400	.006	34	5.89	60	67	160	13	43	25	140	30	92	LU	Upstream from large impoundment
9	341354080223200	.15	25	5.14	31	40	96	18	<10	38	140	5.0	130	LU	No I–20 influence
10	341528080231900	.71	26	4.92	40	47	87	18	<10	42	130	2.1	110	MT, LU	Forested, little development
11	341539080263100	.13	27	5.13	45	48	74	26	<10	58	120	4.3	100	MT, LU	Forested, little development
12	341812080221000	.27	25	4.99	36	54	65	21	<10	40	120	7.9	67	LU	Primarily forested

[a] Criteria used in selection of sampling sites: BG = bedrock geology, MT = major tributary, LU = land use.

that drain the upper and lower parts of the basin. For example, sulfate averaged 40 µeq/L in the northern tributaries compared to 20 µeq/L in the southern tributaries. These differences in stream chemistry may be related, in part, to land-use patterns in the basin. Subbasins in the northern one-half of the basin are primarily forested, whereas those in the southern one-half have a greater percentage of agricultural land.

Upper Three Runs near New Ellenton, South Carolina (Station 02197300)

Site Characteristics and Land Use

The Upper Three Runs HBN Basin is in the Aiken Plateau region of the Coastal Plain physiographic province in southern South Carolina (fig. 26). The 255-km^2 basin drains an area characterized by broad upland ridges separated by narrow, steep-sided stream valleys that range in elevation from 50 to 155 m. The USGS gaging station is 7.2 km southeast of New Ellenton, S.C., in the boundaries of the Savannah River Site (SRS) at latitude 33°22'14" and longitude 81°37'43". Upper Three Runs is a southwest-flowing tributary of the Savannah River with a channel length of about 18 km upstream from the gage and an average stream gradient of 3.9 m/km. Streamflow is strongly controlled by ground-water discharge, and mean monthly discharge varies over a narrow range from 2.74 in October to 3.25 m^3/s in March. Average annual runoff from the basin was 36 cm from 1966 through 1994 (U.S. Geological Survey, Water Resources Data, South Carolina). Meteorological data have been collected at the SRS since the early 1960's (Hunter, 1990). Climate of the area is characterized by warm, humid summers and mild winters. Average daily temperatures range from 7.5°C in January to 27.1°C in July. Precipitation averages 120 cm annually and is generally largest in March and least in November (Hunter, 1990). At a nearby study area in the SRS, evapotranspiration returned 70 percent of incoming precipitation to the atmosphere (Dennehy and others, 1988).

The basin lies along the margin of the Outer Coastal Plain Mixed Forest ecoregion (Bailey and others, 1994) and is covered by both hardwood and pine forest types. Hardwoods in upland areas are dominated by turkey oak, blackjack oak, and white oak; the lowland hardwood communities are dominated by bald cypress, sweet gum, water gum, yellow poplar, and laurel. Most of the pine forests are plantations that were planted in previously farmed or logged areas. The major pine species are loblolly pine, longleaf pine, and slash pine. A detailed description of the forest community types in the SRS can be found in Jones and others (1981). Most soils in the basin are classified as Ultisols and are mapped in the Blanton-Lakeland soil association (Rogers, 1990). These soils are developed in sandy and loamy marine sediments and are found on broad ridgetops and side slopes of the plateau surface. Because of their high sand content, the soils are well drained, acidic (pH 3.5 to 4.5), and have low base saturation capacities (9 to 27 percent) (Ruhe and Matney, 1980). Soils along the flood plains are subject to frequent flooding during the wet season and are mapped in the Pickney Series (Rogers, 1990). These soils are poorly drained, acidic (pH 3.6 to 5.5), and have a high organic content. A typical soil profile contains a surface layer of black sand as much as 90 cm thick overlying a gray to brown sandy subsoil down to 150 cm (Rogers, 1990). The dominant minerals in both the upland and lowland soil types are quartz, feldspar, kaolinite, and interlayered chlorite-vermiculite (Ruhe and Matney, 1980).

The basin is underlain by flat-lying sediments of the Cretaceous Tuscaloosa Formation and Tertiary Huber, Congaree, McBean, and Barnwell Formations (Siple, 1967; Prowell, 1994). The Tuscaloosa Formation, which crops out along the stream channels, consists of fluvial and estuarine sediments assumed to be derived from weathered crystalline rocks of the Piedmont. The sediments are described as light-colored, arkosic sands, composed primarily of quartz, feldspar, and muscovite, interlayered with lenses of light-colored clay and kaolin (Cooke, 1936). Tertiary sediments cover most of the upland areas of the basin. These sediments were deposited in an open-marine environment and are composed of poorly sorted quartz sand with beds of calcareous clay, sandy limestone, and marl (Prowell, 1994). The Tuscaloosa Formation forms the principal aquifer in the area and is recharged through the overlying rocks of Tertiary age in the upland areas around Aiken (Langley and Marter, 1973).

The Upper Three Runs Basin drains the southern part of Aiken County. Ninety percent of land in the basin is privately owned and 10 percent is in the boundaries of the SRS. The SRS is currently operated by the Westinghouse Corporation for the U.S. Department of Energy as a natural environmental research park that constitutes the largest protected natural area in the Eastern United States (Cohn, 1984).

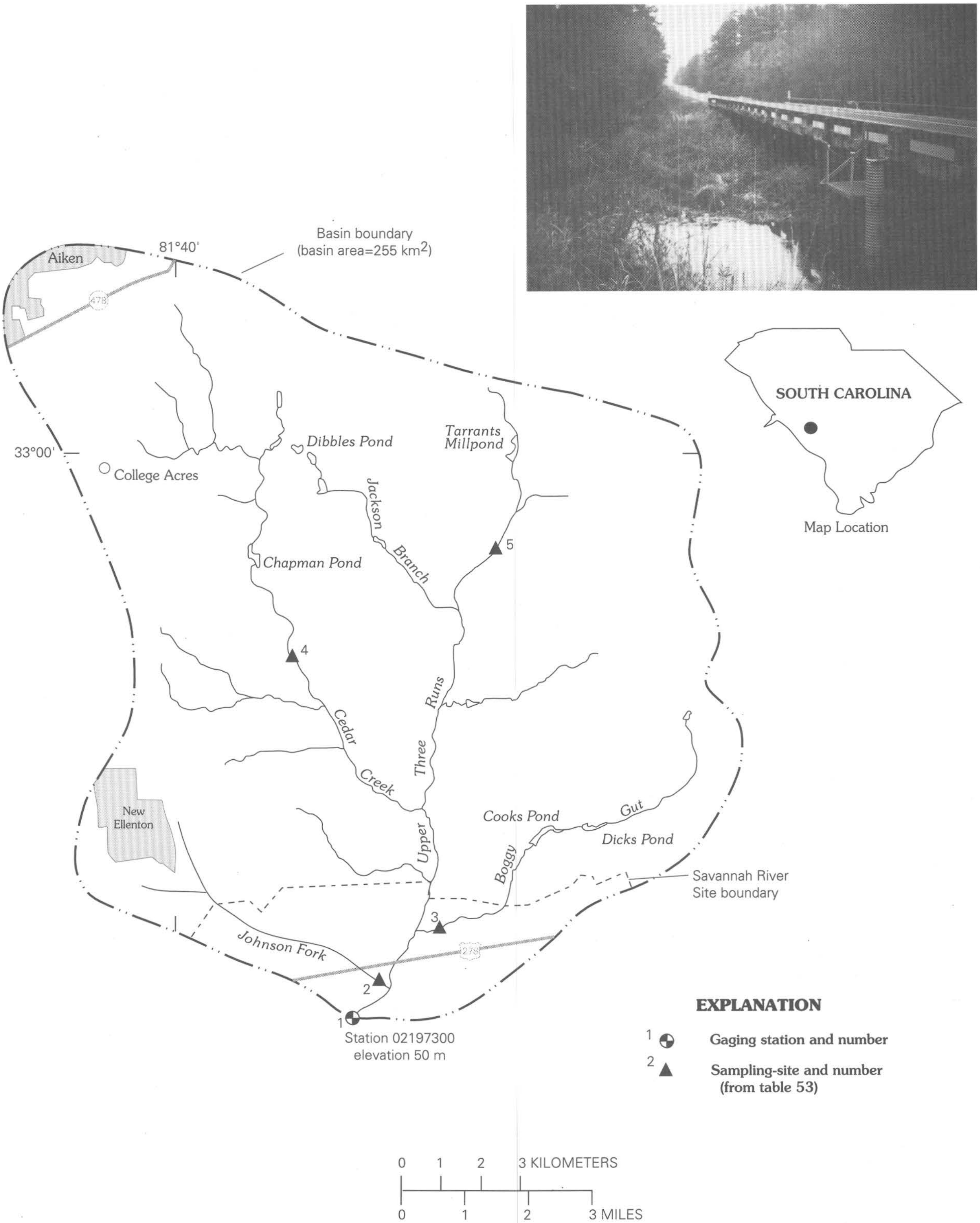

Figure 26. Map showing study area in the Upper Three Runs Basin and photograph of the stream channel at the gage.

Several primary and secondary roads provide access to most areas in the basin. Access to the main channel is limited to bridge crossings because of swampy conditions along the flood plain. Security clearance is necessary to access the gage and areas of the basin in the SRS.

Current (1997) land use in the basin is 78 percent forest, 12 percent agriculture, and 10 percent residential (David Howe, Natural Resources Conservation Service, oral commun., 1996). Past disturbance and years of poor management have resulted in poor timber quality throughout the area (Jones and others, 1981). About two-thirds of the agricultural land is used for pasture and one-third is planted in corn and soybeans. Most of the residential communities are in and around the communities of New Ellenton (population 2,520) and Aiken (population 19,870), which is only partly in the basin. A substantial land-use change in the basin has been the recent growth in suburban residential communities. Although the basin is currently only 10 percent residential, this could increase to 30 percent during the next 5 years if the current rate of growth is sustained (David Howe, oral commun., 1996). Other manmade features in the basin include 3 sewage-treatment facilities, a fiberglass plant and waste pond, several large equestrian farms, and more than 20 livestock ponds. Residents in the basin use ground water from the Tuscaloosa Formation as their primary domestic water supply. The southernmost 10 percent of the basin is in the boundaries of the SRS and is protected from future development.

Historical Water-Quality Data and Time-Series Trends

The HBN data set analyzed for this report includes 153 water-quality samples that were collected from November 1967 through September 1993, when the site was removed from the HBN. Sampling frequency ranged from bimonthly to monthly from 1968 through 1982 and quarterly from 1983 through 1993. Although not documented, water-quality samples in the early part of the record probably were analyzed at a USGS laboratory in Raleigh, N.C., which was operated until 1973 (Durum, 1978). After establishment of the USGS Central Laboratory System, samples were analyzed at the Central Laboratory in Atlanta, Ga., from 1973 through 1985 and at the NWQL in Arvada, Colo., from 1986 though 1993. Daily discharge records for Upper Three Runs (station 02197300) are available beginning in June 1966. The gage was situated along Highway 278 until September 1989, when it was moved 1.6 km downstream primarily for safety reasons (Frank Melendez, U.S. Geological Survey, oral commun., 1996). Water-quality samples continued to be collected at the old gage site until sampling was suspended in 1993. Daily precipitation amount was measured at the gage from April 1992 through February 1996.

Calculated ion balances for 147 samples with complete major ion analyses are shown in figure 27. Ion balances ranged from –29 to +29 percent, and almost 50 percent of samples had values outside the ±10 percent range. This wide range of values reflects the difficulty in making precise analytical measurements at the low solute concentrations typical of this station. The average charge balance for all samples was –6.2 percent, and 70 percent had negative ion balances, indicating an excess of measured anions over cations in solution. Laboratory alkalinity was determined by a fixed-endpoint titration to pH 4.5. For waters with alkalinities below 100 µeq/L, however, the endpoint pH is closer to 5.0, and titration to pH 4.5 may overestimate alkalinity by as much as 25 µeq/L (Barnes, 1964). Alkalinity was determined by incremental titration in the field beginning in 1987. A comparison of the incremental alkalinity concentrations with the fixed-endpoint laboratory concentrations shows that the field alkalinities were, on average, 17 µeq/L smaller than the laboratory alkalinities. This discrepancy is similar to the average anion excess of 18 µeq/L, indicating that the laboratory alkalinity is a probable cause of the negative ion balances.

Time-series plots of the major dissolved constituents were inspected for evidence of analytical-related influences (fig. 27). For example, several uncharacteristically high calcium concentrations were noted from 1974 through 1976. Interestingly, a similar pattern of high calcium concentrations also was observed at the Wild River station in Maine during the same period of record. Because samples from these two sites were analyzed at different laboratories during this period, it seems likely that high calcium concentrations may be related to collection or processing procedures common to both stations. The only documented procedural change during this period was the introduction of a polypropylene churn splitter for compositing and splitting samples that was

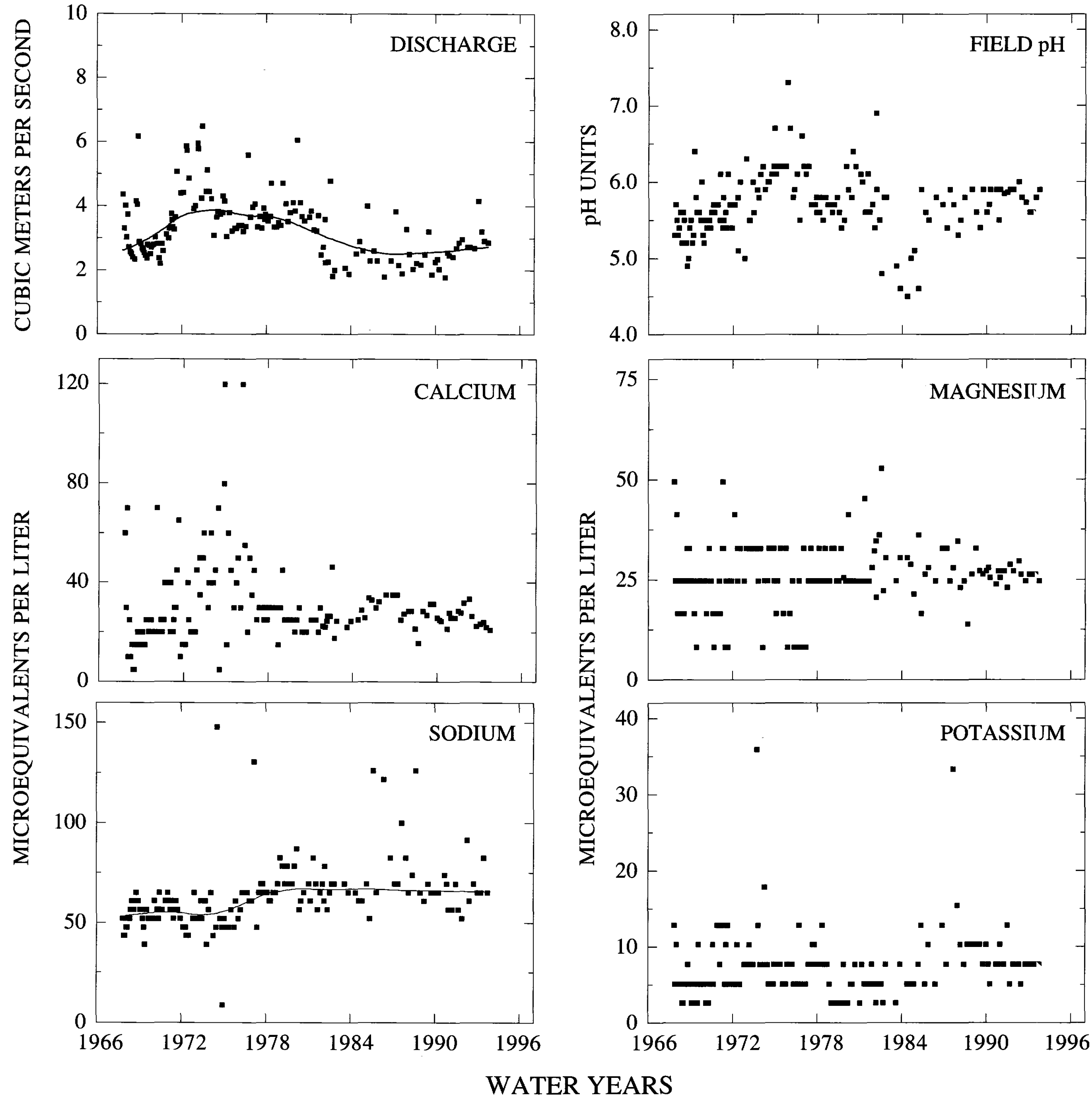

Figure 27. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Upper Three Runs, South Carolina.

required for use at all HBN stations beginning in water year 1977 (Office of Water Quality Technical Memorandum No. 76.24–T, *Sample Splitter for Water-Sediment Samples*, issued August 16, 1976, at URL http://water.usgs.gov/public/admin/memo/). Although problems with previous sample splitters were not documented by the Office of Water Quality (OWQ), the fact that the anomalous pattern disappeared around the beginning of 1977 indicates that previous splitters or compositing devices may have been a potential source of contamination. Figure 27 also shows a period of elevated sulfate concentrations during the late 1980's. This pattern coincides with the use of a turbidimetric titration for sulfate analyses at

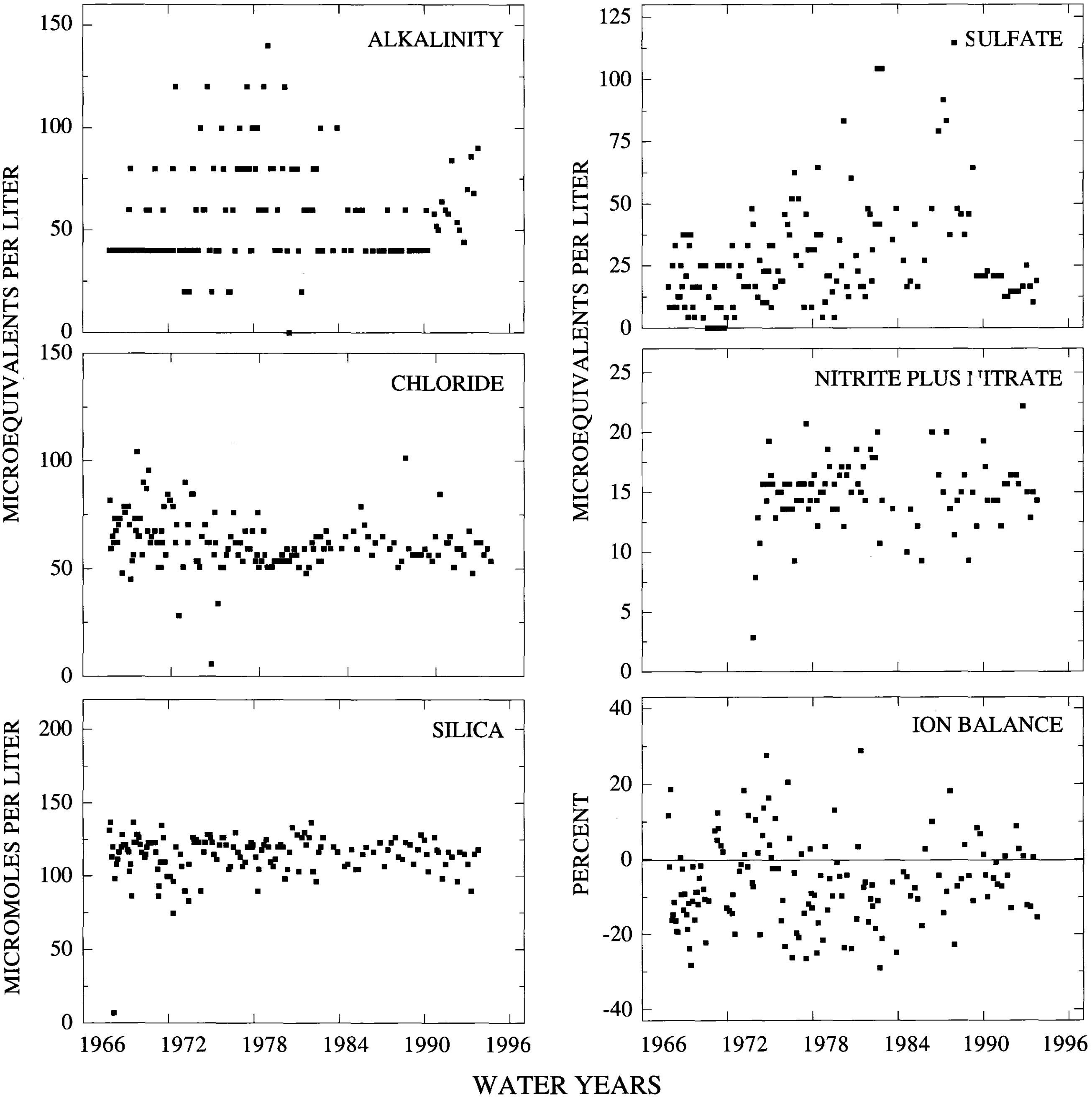

Figure 27. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Upper Three Runs, South Carolina—Continued.

the NWQL between March 1986 and December 1989 (Fishman and others, 1994). In 1989, the NWQL determined that sulfate concentrations could be overestimated by this technique and changed the method to ion chromatography in 1990 (Office of Water Quality Technical Memorandum No. 90.04, *Turbidimetric Sulfate Method*, issued December 21, 1989, at URL http://water.usgs.gov/public/admin/memo/). The time-series plots in figure 27 also reveal potential bias in the field pH measurements. Between 1983 and 1985, field pH values were 0.5 to 1 pH unit smaller than values typically reported for this station. Interestingly, a similar shift in field pH also was observed at the other South Carolina HBN station, Scape

Ore Swamp, during the same period of record. As suggested for the Scape Ore Swamp Station, a probable cause of this shift was the gel-filled pH probe used by field personnel to make pH measurements at these two stations (John Barton, U.S. Geological Survey, oral commun., 1996). Some instrument-electrode systems are known to give erroneous readings when measuring pH in low-conductivity waters, and the electrode is commonly the critical component (Office of Water Quality Technical Memorandum No. 81.08, *Electrodes for pH Measurement in Low-Conductivity Waters*, issued February 10, 1981, at URL http://water.usgs.gov/public/admin/memo/).

Median concentrations and ranges of major constituents in stream water collected at the HBN gaging station and VWM concentrations in wet-only deposition measured at the Santee National Wildlife Refuge NADP station about 100 km east of the basin are presented in table 50. Precipitation chemistry at the NADP station was dilute and acidic and had a VWM pH of 4.6 during the 10 years of record. The dominant cations in precipitation were hydrogen, which contributed 45 percent of the total cation charge, and sodium, which contributed 18 percent. Sulfate accounted for 54 percent of the total anions, and nitrate and chloride each accounted for 23 percent. These results indicate that precipitation at the NADP station probably is a mixture both of anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain, and salt derived from marine aerosols.

Stream water in Upper Three Runs is extremely dilute and weakly buffered; total ionic constituents ranged from 185 to 457 μeq/L, and alkalinities were generally below 60 μeq/L. The major ions in stream water were sodium and chloride, which accounted for almost one-half of the total ionic charge. The low concentrations of the major weathering products, particularly alkalinity, are attributed to the slow weathering rates of the underlying quartz-rich soils and sedimentary rocks. The median chloride concentration in stream water was 62 μeq/L, which is about five times larger than the VWM concentration of chloride in precipitation. Based on the difference between annual precipitation and runoff, evapotranspiration can account for about a threefold increase in the concentration of precipitation, suggesting that some stream-water chloride may be derived from sources other than precipitation. Both natural and manmade sources may contribute chloride to stream water, including dry deposition of marine aerosols, leaching of salt from the Tertiary marine sediments, or possible discharge from wastewater-treatment facilities in the basin. The median concentration of sulfate in stream water was slightly smaller than the concentration in precipitation despite the fact that evapotranspiration and dry deposition would be expected to increase sulfate concentrations in stream water. This indicates that a substantial portion of atmospherically deposited sulfate is retained in the basin. Possible mechanisms of retention include sulfate adsorption on clays and organic matter in soils or sulfate reduction in swampy areas along the flood plains. The basin also appears to be an important sink of atmospheric nitrogen based on the significantly smaller concentrations of both nitrate and ammonium in stream water compared to precipitation. Because weathering supplies only minor amounts of base cations and alkalinity to surface waters in the basin, basin retention of sulfate and nitrate probably is the dominant process buffering surface waters from acidic deposition (Elwood and others, 1991).

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 51). Discharge was poorly correlated with all the major dissolved constituents. Solutes in stream water also were poorly correlated with each other. The lack of correlation among these parameters probably is related to both hydrologic and geochemical factors. The highly permeable soils and sediments on the hillslopes and upland surfaces allow precipitation to infiltrate quickly into the ground-water system. In turn, streamflow is supplied by ground-water discharge, which maintains a relatively constant flow rate and stream composition throughout the year. Additionally, the quartz-rich soils and sediments contain few weatherable minerals and, as a consequence, produce soil and ground waters that are not significantly different in composition from that of the incoming precipitation.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents from 1968 through 1993 are shown in table 52. Statistically significant trends were observed for discharge and sodium concentrations at the 0.01 confidence level. The upward trend in sodium was similar for the unadjusted and flow-adjusted concentrations, indicating that the trend was not driven by the downward trend in stream discharge. The LOWESS curve in figure 27 shows that most of the sodium increase occurred in the late 1970's, and concentrations have remained fairly constant since then. The cause of the trend in sodium is not known. Although human activities might be a likely cause, most of the increase in residential development occurred since 1990 during which time sodium concentrations remained relatively constant. The relatively constant chloride concentrations provide additional evidence that land use was not the cause of the sodium trend because it is unlikely that human activities would affect sodium concentrations without affecting chloride concentrations as well. It is perhaps more likely that the increase in sodium was caused by an analytical-related factor, although there were no documented changes in the analytical procedure for sodium during this period of record.

Table 50. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ion concentrations measured in water-quality samples from Upper Three Runs, South Carolina, November 1967 through September 1993, and volume-weighted mean concentrations in precipitation collected at Santee National Wildlife Refuge Station, South Carolina

Concentrations in units of microequivalents per liter, discharge in cubic meters per second, specific conductance in microsiemens per centimeter at 25 degrees Celsius, pH in standard units, and silica in micromoles per liter; n, number of stream samples; VWM, volume-weighted mean; inst., instantaneous; spec. cond., specific conductance; <, less than; --, not reported]

Parameter	Stream water						Precipitation VWM[a]
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge, inst.	1.8	2.6	3.4	4.0	6.5	151	--
Spec. cond., field	10	13	14	15	22	152	--
pH, field	4.5	5.5	5.7	5.9	7.3	152	4.6[b]
Calcium	5.0	20	25	33	120	152	4.5
Magnesium	<8.2	25	25	33	53	153	3.0
Sodium	8.7	52	61	70	150	153	10
Potassium	<2.6	5.1	7.7	7.7	33	151	2.3
Ammonium	<.7	<.7	1.4	2.8	9.3	54	5.6
Alkalinity, laboratory	<20	40	40	61	140	152	--
Sulfate	<4.2	16	21	36	110	147	29
Chloride	5.6	56	62	68	100	153	12
Nitrite plus nitrate	<7.1	13	15	16	22	92	12[c]
Silica	6.7	110	120	120	140	153	--

[a] Values are volume-weighted mean concentrations for 1984–94.

[b] Laboratory pH.

[c] Nitrate only.

Table 51. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ion concentrations, Upper Three Runs, South Carolina, 1980 through 1993

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; Si, silica]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	–0.106								
Ca	.026	–0.201							
Mg	.227	–.389	0.346						
Na	–.019	–.025	.054	0.138					
K	–.344	.037	.152	.026	–0.167				
Alk	.224	.336	–.108	–.094	–.032	–0.359			
SO_4	–.221	–.147	.074	.244	.248	.173	–0.201		
Cl	–.210	–.174	.129	–.044	–.085	.189	–.310	0.088	
Si	–.078	–.069	–.186	.004	.239	.038	–.165	.161	–0.042

Table 52. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major ion concentrations, Upper Three Runs, South Carolina, November 1967 through September 1993

[Trends in units of microequivalents per liter per year, except discharge in cubic meters per second per year, pH in standard units per year, and silica in micromoles per liter per year; <, less than; --, not reported]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	–0.05	0.000	--	--
pH, field	.00	.273	(a)	--
Calcium	<.1	.860	(a)	--
Magnesium	<.1	.298	0.2	0.069
Sodium	.9	.000	.5	.000
Potassium	<.1	.349	(a)	--
Chloride	–.2	.021	(a)	--
Sulfate	.4	.095	(a)	--
Nitrite plus nitrate	<.1[b]	.934	--	--
Alkalinity, laboratory	<.1	.065	(a)	--
Silica	–.2	.048	(a)	--

[a] Flow model not significant at $\alpha = 0.10$.

[b] Trend calculated for 1974–93, using a trend test for censored data.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling of January 9, 1991, are shown in table 53; locations of sampling sites are shown in figure 26. Discharge at the gage was 2.46 m^3/s compared to the median daily discharge of 3.12 m^3/s for January (Lawrence, 1987), indicating that the basin was sampled during base-flow conditions for that time of year. Solute concentrations measured at the gage (site 1) were similar to the median concentrations reported at the gage during the entire period of record, with the exception of alkalinity (table 50). All tributary streams were similar in chemical composition to the gage; specific conductances were low, and sodium and chloride were the dominant ions. Measured alkalinities were below the reporting limit at three of the five sampling sites, and pH ranged from 4.42 to 6.04, indicating that most surface waters were slightly acidic. The source of most stream-water acidity probably was organic acids, although some may have been derived from strong acids in precipitation. Although DOC was not measured in this study, all samples had positive ion balances (range 1.7 to 14 percent), indicating that organic anions were an important component of stream water during the sampling period.

In general, stream-water chemistry did not vary markedly among the sampling sites in the basin. For example, chloride ranged from 54 to 70 μeq/L and sodium varied from 52 to 61 μeq/L. In addition, sodium and chloride concentrations were not elevated at sites 2 and 4, which are downstream from large residential areas. This indicates that these two solutes are derived primarily from atmospheric sources and behave relatively conservatively in the basin. Slightly elevated concentrations of calcium, magnesium, and alkalinity were measured in Boggy Gut (site 3) compared to the other sites. These elevated concentrations may be because of the presence of limestone layers and calcareous sands in the Tertiary McBean Formation that crops out along the stream channel in the lower reach of this tributary (Prowell, 1994). Nitrate concentrations ranged from less than 0.7 to 19 μeq/L and were not elevated in subbasins with residential development (sites 2 and 4)

Table 53. Physical properties and major ion concentrations from surface-water sampling sites in the Upper Three Runs Basin, South Carolina, January 8, 1991

[Site locations shown in fig. 26; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; concentrations in microequivalents; Si, silica in micromoles per liter; <, less than; --, not measured]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria[a]	Remarks
1	02197300	2.46	14	5.59	25	26	52	7.4	<10	19	59	15	110		
2	332304081370600	.003	24	4.42	12	18	52	1.8	<10	27	62	<0.7	110	LU	Small town in headwaters
3	332330081361500	.23	21	6.04	65	41	61	12	39	46	70	13	110	LU, BG	Ponds, McBean Formation
4	332629081380100	.34	14	5.76	19	22	61	7.4	16	10	65	15	130	LU	Residential development
5	332838081351700	.40	12	5.57	14	26	52	6.9	<10	7.9	54	19	100	LU	Primarily forested

[a] Criteria used in selection of sampling sites: BG = bedrock geology, LU = land use.

compared to the undeveloped subbasins (sites 3 and 5). Sulfate concentrations, which showed slightly more variability than chloride and nitrate, ranged from 7.9 μeq/L near the headwaters of the main drainage (site 5) to 46 μeq/L in Boggy Gut (site 3). As noted previously, sulfate is primarily derived from atmospheric sources but is strongly retained in the basin. One explanation for the variability in sulfate concentrations is that it reflects basin characteristics that control sulfate retention—for example, variations in soil mineralogy or, perhaps, the distribution of wetlands in the basin.

Buffalo River near Flat Woods, Tennessee (Station 03604000)

Site Characteristics and Land Use

The Buffalo River HBN Basin is in the Western Highland Rim section of the Interior Low Plateaus physiographic province in central Tennessee (fig. 28). The Highland Rim is a broad peneplain that has been highly dissected by streams, resulting in a landscape of irregular flat-topped ridges separated by steep-sided slopes and flat-bottomed drainages (Smalley, 1981). The Buffalo River drains 1,158 km^2 of hilly terrain that ranges in elevation from 157 to 305 m. The USGS gaging station is 2.1 km north of Flat Woods, Tenn., at latitude 35°29'45" and longitude 87°49'58". The Buffalo River has a channel length of about 108 km upstream from the gage and is one of the longest free-flowing rivers remaining in Tennessee. Stream gradients in the main channel range from 0.6 to 0.9 m/km, and the flood plain reaches more than 1.5 km in width just upstream from the gage. Discharge is perennial, and mean monthly discharge ranges from 7.6 m^3/s in September to 41.6 m^3/s in March. Average annual runoff from the basin was 59 cm from 1920 to 1995 (U.S. Geological Survey, Water Resources Data, Tennessee). Climate of the area is characterized by long, moderately hot summers and short, mild winters (Smalley, 1991). Average daily air temperatures range from 3.3°C in January to 25°C in July. Winter temperatures often fall below freezing at night and soils typically freeze several times during the average winter season. Precipitation averages 127 cm annually and is greatest from December through March and least from August through October.

The basin lies along the southern margin of the Eastern Broadleaf Forest ecoregion, which is characterized by broadleaf deciduous forests (Bailey and others, 1994). Upland areas are covered by a mixture of oak and oak-hickory forest types, and the dominant species are white oak, southern red oak, and hickories with an understory of dogwood, sourwood, sassafras, persimmon, and huckleberry. Many previously logged or farmed areas have been replanted in a mixture of loblolly and shortleaf pines (Smalley, 1991). Vegetation along the broad alluvial valley is dominated by lowland hardwood forest communities. The dominant species are sweet gum, elm, black gum, red maple, sycamore, and white oak, and the common understory species include cane, honeysuckle, ferns, and mosses. Because little forest land in the basin is under timber management, past cutting practices have contributed to a gradual decline in the amount of high-quality timber in the basin (Smalley, 1991).

Most soils in the basin are highly leached Ultisols of the siliceous thermic families (Smalley, 1981; Francis and Loftus, 1977). Upland areas of the basin are typically covered by the Montview silt loam, a well-drained soil developed in loess, which tends to be relatively free of large chert fragments in the upper 50 cm (Overton, 1959). The ridges and hillslopes are covered by the Bodine chert silt loam, which is a well-drained soil that has developed in cherty limestone. These soils tend to be cherty throughout with chert fragments accounting for 35 to 80 percent of the soil. The Captina silt loams have developed in alluvium along the river bottoms and are moderately well-drained, fertile soils that contain 15 to 35 percent chert fragments (Overton, 1959). These soils are subject to flooding, and the water table is generally within 50 cm of the surface during wet periods of the year.

Bedrock in the basin includes flat-lying marine sediments of Silurian and Mississippian age. The Silurian rocks, which primarily occupy the valley floor, are limestones that form vertical bluffs along the river and in places have flutings, cavities, and small caves near the water level. The Mississippian rocks are the most extensively outcropping units in the basin and include siliceous limestones, cherty siltstones, and shales of the Fort Payne and Warsaw Formations. These rocks are composed of 60 percent quartz and chalcedony, 37 percent calcite and dolomite, and the remainder pyrite and glauconite (Stearns and Wilson, 1971). Most upland slopes are underlain by a highly siliceous limestone or chert residuum that is formed in place by leaching and silica replacement of the Mississippian bedrock (Stearns and Wilson, 1971).

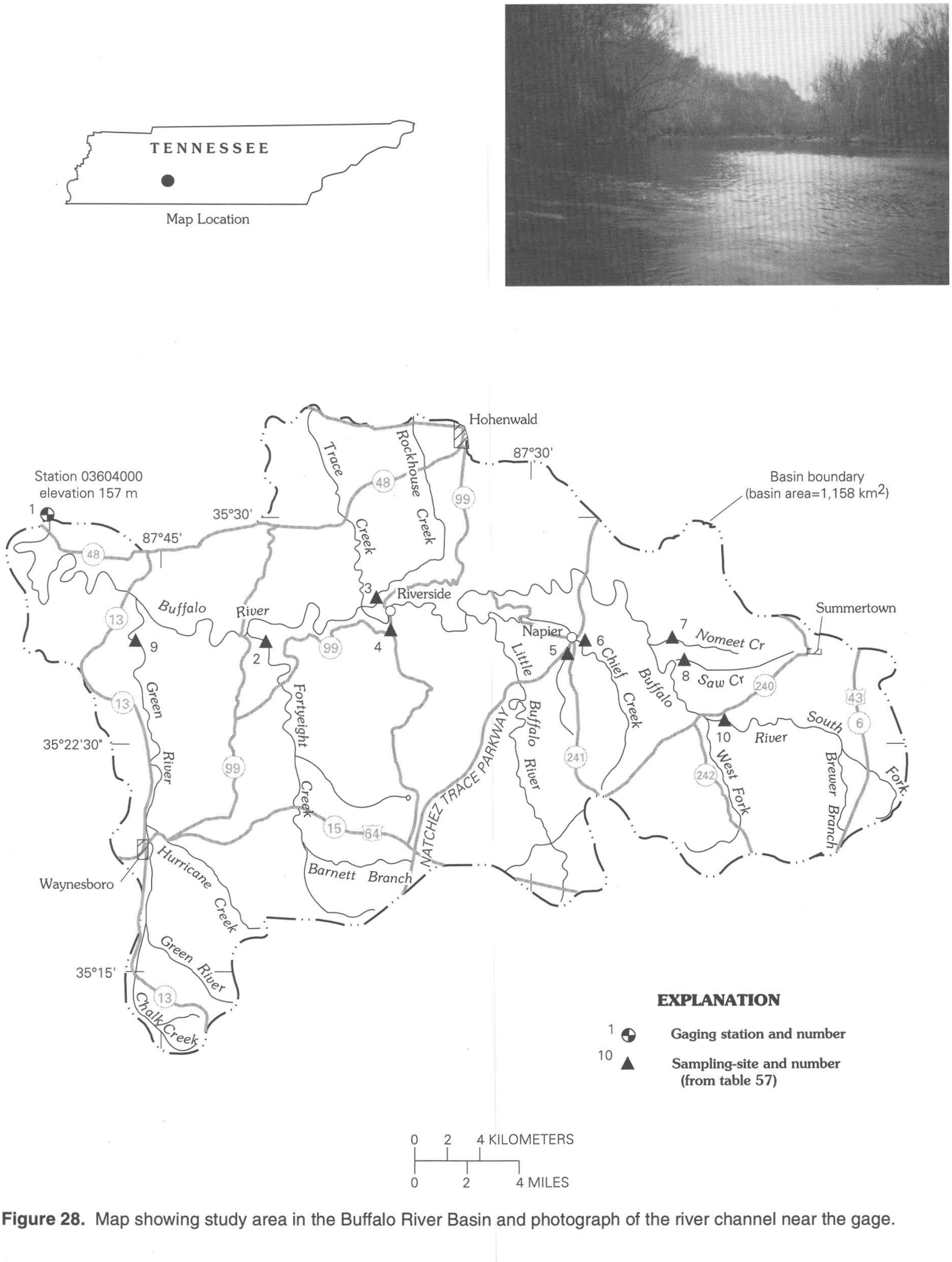

Figure 28. Map showing study area in the Buffalo River Basin and photograph of the river channel near the gage.

This moderately to highly permeable layer of residuum or saprolith reaches to 30 m in depth and forms an excellent shallow aquifer that releases water from many springs into the Buffalo River and its tributaries. The saprolith also contains deposits of limonite that were extensively mined during the 19th century in areas near Napier and south of Riverside.

The Buffalo River Basin drains parts of Lawrence, Lewis, Wayne, and Perry Counties, and land ownership is predominantly private. Private individuals own most of the land along the river, and timber companies hold most of the land on the upper slopes and ridges. Less than 7 percent of the basin is publicly owned, including 70 km^2 in the Laurel Hill Wildlife Management area in the Little Buffalo River subbasin and 5 km^2 in the Lewis State Forest southwest of the town of Hohenwald. In 1968, the State of Tennessee established a scenic river system which eventually included a short headwater section of the Buffalo River in Lawrence County (Tennessee Department of Public Health, 1974). In 1974, the Buffalo River was recommended for inclusion in the National Wild and Scenic Rivers System (Heritage Conservation and Recreation Service, 1979); however, because of opposition by owners of riparian land, the Buffalo River never received official designation as Wild and Scenic. A 28-km segment of the Natchez Trace Parkway and National Scenic Trail runs through the basin from north to south and crosses the river at Napier. The parkway right-of-way, which ranges in width from 100 to 300 m, includes scenic, historic, and recreational features and is administered by the National Park Service. Hundreds of kilometers of primary and secondary roads provide access to most areas of the basin. Public access to the river is limited to seven bridge crossings on Tennessee Department of Transportation rights-of-way and at the Natchez Trace crossing. During most periods of the year, the river is navigable by small boat or canoe downstream from Henryville, Tenn.

Land use in the basin is about 74 percent forest, 10 percent pasture, 15 percent cropland, and less than 1 percent urban and residential. The western one-half of the basin has more relief and tends to be predominantly forested; the eastern one-half of the basin is more suitable for farming. Most agricultural activities are concentrated along the drainages. The most substantial land-use change in the basin during the past 15 years has been a decrease in the amount of cropland and an increase in clearcutting activity by both large timber companies and private landowners (Mike Tatum, Natural Resources Conservation Service, oral commun., 1996). The major use of the river and its tributaries is as a local water supply for domestic, commercial, and industrial purposes (Heritage Conservation and Recreation Service, 1979). The basin contains several small communities, including Waynesboro (population 2,100) in the Green River Basin and Hohenwald (population 3,920) at the head of Rockhouse Creek. The largest potential source of pollution to the river is discharge of domestic and industrial wastewater. Municipal wastewater-treatment plants at Waynesboro, Hohenwald, and Summertown School discharge treated wastewater into the headwaters of the Green River, Rockhouse Creek, and Saw Creek, respectively (Heritage Conservation and Recreation Service, 1979). In addition, there are several sources of untreated industrial wastewater from the community of Waynesboro, including industrial cooling waters, discharge from a car-washing operation, and runoff from a log saturation process (Tennessee Department of Public Health, 1974).

Historical Water-Quality Data and Time-Series Trends

The HBN data set analyzed for this report includes 166 water-quality samples that were collected from April 1963 through December 1995. Sampling frequency ranged from 8 to 12 samplings per year from 1967 through 1971. Sampling frequency was reduced to bimonthly from 1972 through 1982 and again to quarterly from 1983 through 1995. Although not documented, water-quality samples in the early part of the record probably were analyzed at one of three laboratories (Raleigh, N.C.; Ocala, Fla.; and Tuscaloosa, Ala.) that provided analytical services for the Southeastern Region (Durum, 1978). After establishment of the USGS Central Laboratory System, samples were analyzed at the Atlanta laboratory from 1973 through 1985 and at the NWQL in Arvada, Colo., from 1986 through 1995. Daily discharge records for the Buffalo River (station 03604000) are available beginning in May 1920. Records of daily water temperature at the gage are available for July 1963 through January 1978. Daily precipitation amount was measured at the gage from December 1994 through February 1996.

Calculated ion balances for 163 samples with complete major ion analyses are shown in figure 29. Ion balances ranged from –7.1 to +9.0 percent, and more than 85 percent of samples had values within the ±5.0 percent range, indicating the analyses are of high quality. The mean charge balance of all samples was 0.1 percent, indicating that unmeasured constituents, such as organic anions, do not contribute significantly to the ion balance of stream water at this station. Time-series plots of the major dissolved constituents were inspected for evidence of method-related effects (fig. 29). For example, sulfate concentrations were slightly higher than average during the late 1980's. This pattern coincides with the use of a turbidimetric titration for sulfate analysis at the NWQL between March 1986 and December 1989 (Fishman and

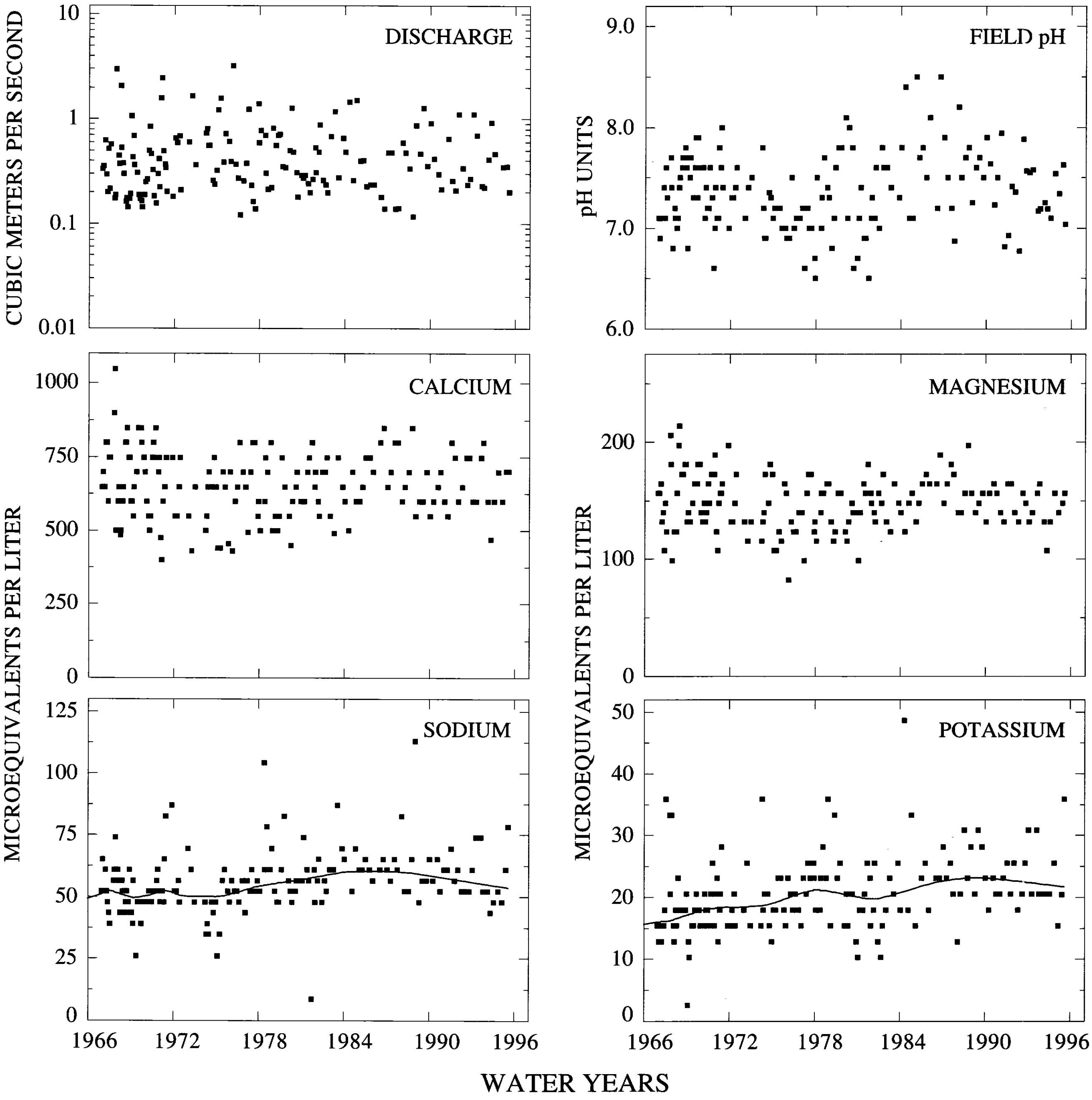

Figure 29. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Buffalo River, Tennessee.

others, 1994). In 1989, the NWQL determined that sulfate concentrations can be overestimated by this technique and changed the method to ion chromatography in 1990 (Office of Water Quality Technical Memorandum No. 90.04, *Turbidimetric Sulfate Method*, issued December 21, 1989, at URL http://water.usgs.gov/public/admin/memo/). The bias was most pronounced in dilute waters, although it was not consistent among samples and appeared to be influenced by factors such as color and turbidity (Schertz and others, 1994). The time-series plot of calculated ion balances shows a period of higher than average values in the 1970's and slightly lower than average values in the 1980's. The shift to more negative values in the 1980's correlates with the period of high sulfate values noted

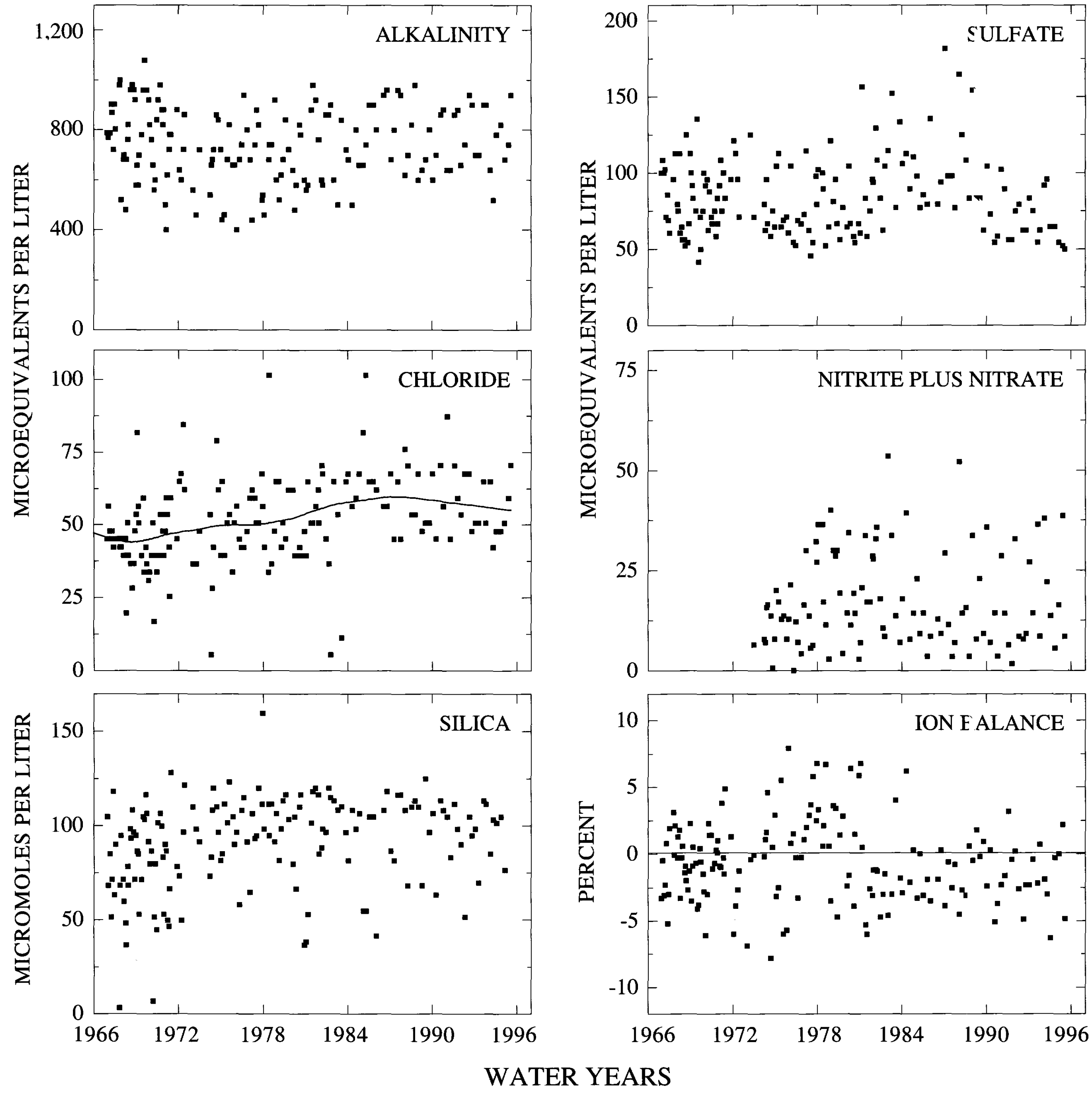

Figure 29. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Buffalo River, Tennessee—Continued.

previously. The high values in the 1970's could not be traced to a documented change in any one analytical method but are coincident with the period when samples were analyzed at the laboratory in Atlanta, Ga.

The median concentrations and ranges of major constituents in stream water collected at the gage and VWM concentrations in wet-only deposition measured at the Wilburn Chapel NADP station about 70 km southeast of the gage are presented in table 54. Precipitation chemistry at the NADP station is dilute and slightly acidic, with a VWM pH of 4.6 during the 14 years of record. The dominant cations in precipitation were hydrogen and ammonium, which contributed 55 and 24 percent of the total cation charge, respectively. Sulfate accounted for 62 percent of the total anions, and nitrate and chloride accounted for 28 and 10 percent, respectively. These results suggest that precipitation at the nearby NADP station may be affected by anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain (Likens and others, 1977).

Stream water in the Buffalo River is moderately concentrated and well buffered; specific conductances ranged from 54 to 130 μeq/L, and alkalinities generally were between 400 to 1,080 μeq/L. The major cations in stream water were calcium and magnesium, and the dominant anion was alkalinity. The relatively high concentrations of solutes in stream water indicate that dissolution of carbonate minerals in the underlying bedrock and saprolith is the primary process that controls stream chemistry at this station. The median chloride concentration in stream water was 51 μeq/L, which is about 10 times larger than the VWM concentration of 4.8 μeq/L in precipitation. Based on the difference between average annual runoff and precipitation, evapotranspiration can account for about a twofold increase in the chloride concentration of precipitation, indicating that some stream-water chloride must be derived from sources in the basin. The most likely internal source of chloride is discharge from several domestic and industrial wastewater-treatment facilities in the basin. The median concentration of sulfate in stream water was 79 μeq/L compared to 29 μeq/L in precipitation and is slightly larger than would be expected solely from the effects of evapotranspiration. Additional sources of stream-water sulfate may include dry deposition from the atmosphere and weathering of small amounts of pyrite in the bedrock and saprolith (Stearns and Wilson, 1971). Biomass appears to be an important sink for nitrogen species on the basis of smaller concentrations of both nitrate and ammonium in stream water compared to precipitation. These low concentrations of nitrate and ammonium also indicate that the wastewater-treatment facilities have a minimal effect on stream-water nitrogen concentrations at the gage.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 55). Most major weathering-derived constituents—calcium, magnesium, and alkalinity—had negative correlations with discharge. These correlations are consistent with a hydrologic system where weathering-enriched base flow is diluted by waters from shallow or surficial sources during periods of increased discharge. The positive correlation between sulfate and discharge (rho = 0.453) may provide evidence that sulfate is derived primarily from atmospheric sources. The implication is that atmospherically deposited sulfate accumulates in the unsaturated zone during dry periods and is transported to the stream when the water table rises during high-flow periods of the year (Shanley, 1992). Among the ions, the strongest correlations were found between calcium, magnesium, and alkalinity. By contrast, silica was only weakly correlated with alkalinity (rho = 0.468) and magnesium (rho = 0.454). The positive correlations between calcium, magnesium, and alkalinity and weak correlations with silica are consistent with the weathering stoichiometry of carbonate minerals. The probability that wastewater from the treatment facilities is the source of some stream-water chloride is further supported by the positive correlation between sodium and chloride (rho = 0.501).

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents from 1966 through 1995 are shown in table 56. Statistically significant upward trends in sodium, chloride, and potassium were detected in the unadjusted concentrations at the 0.01 confidence level. Results for the flow-adjusted concentrations were similar to the unadjusted concentrations, indicating that trends were not driven by changes in stream discharge. The LOWESS curves in figure 29 show that trends in sodium and chloride concentrations were of similar magnitude and timing. For example, both constituents increased by about 15 μeq/L between 1966 and 1985, then leveled off or decreased slightly between 1985 and 1995. Potassium concentrations appear to have increased steadily during the entire period of record. Because roads in the basin are not salted, the upward trends in sodium and chloride may reflect an increasing impact of domestic wastewater from septic systems and treatment facilities in the basin. Census data show that the population of Lewis, Lawrence, and Wayne Counties was relatively constant between 1950 and 1960, increased by almost 20 percent between 1970 and 1980, then stabilized again between 1980 and 1990 (data obtained from U.S. Census Bureau website at http://www.census.gov). Since the period of greatest growth coincides with the largest increase in streamwater chloride and sodium, population growth appears to be a likely cause of the upward trends in sodium and chloride concentrations at the gage. The increase in population also may be the cause of the upward trend in potassium, although activities such as fertilizer application and timber harvesting also may have contributed.

Table 54. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ion concentrations measured in water-quality samples from Buffalo River, Tennessee, April 1963 through October 1995, and volume-weighted mean concentrations in precipitation collected at the Wilburn Chapel Station, Tennessee

[Concentrations in units of microequivalents per liter, discharge in cubic meters per second, specific conductance in microsiemens per centimeter at 25 degrees Celsius, pH in standard units, and silica in micromoles per liter; n, number of stream samples; VWM, volume-weighted mean; inst., instantaneous; spec. cond., specific conductance; <, less than; --, not reported]

Parameter	Stream water						Precipitation VWM[a]
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge, inst.	4.3	8.2	12	21	110	163	--
Spec. cond., field	54	80	88	99	130	161	--
pH, field	6.5	7.1	7.3	7.6	8.5	164	4.6[b]
Calcium	400	600	650	750	1,050	165	3.5
Magnesium	82	130	150	160	250	165	1.2
Sodium	8.7	48	52	61	130	165	4.2
Potassium	2.6	15	21	23	180	165	.5
Ammonium	<.7	<.7	1.4	2.9	17	59	11
Alkalinity, laboratory	400	640	730	860	1,080	154	--
Chloride	5.6	42	51	62	100	165	4.8
Sulfate	42	656	79	100	270	165	29
Nitrite plus nitrate	<.7	7.9	14	27	54	101	13[c]
Silica	3.3	77	97	110	160	165	--

[a] Values are volume-weighted mean concentrations for 1990–94.

[b] Laboratory pH.

[c] Nitrate only.

Table 55. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ion concentrations, Buffalo River, Tennessee, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; Si, silica]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	0.153								
Ca	–.868	–0.124							
Mg	–.685	–.064	0.848						
Na	.137	.205	–.080	0.127					
K	.202	.037	.109	.242	0.410				
Alk	–.818	–.104	.942	.840	–.084	0.143			
SO_4	.453	.242	–.366	–.176	.295	.090	–0.432		
Cl	.128	.201	–.026	.063	.501	.276	–.057	0.349	
Si	–.272	–.099	.392	.454	.176	.341	.468	–.104	–0.059

Table 56. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major ion concentrations, Buffalo River, Tennessee, December 1966 through October 1995

[Trends in units of microequivalents per liter per year, except discharge in cubic meters per second per year, pH in standard units per year, and silica in micromoles per liter per year; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	0.06	0.411	--	--
pH, field	.01	.110	0.01	0.155
Calcium	<.1	.933	.4	.611
Magnesium	<.1	.951	.1	.724
Sodium	.4	.001	([a])	--
Potassium	.2	.000	.2	.000
Alkalinity, laboratory	.9	.334	1.0	.123
Sulfate	<.1	.910	.1	.833
Chloride	.6	.000	([a])	--
Nitrite plus nitrate	.1[b]	.508	.1	.272
Silica	.4	.031	.4	.032

[a] Flow model not significant at $\alpha = 0.01$.

[b] Trend calculated for 1974–95.

Synoptic Water-Quality Data

Results of the synoptic sampling event of December 1 and 2, 1990, are shown in table 57; locations of surface-water sampling sites are shown in figure 28. Discharge at the gage was 10.8 m^3/s compared to the median daily discharge of 11.3 m^3/s for December (Lawrence, 1987), indicating that the basin was sampled during base-flow conditions for that time of year. Solute concentrations measured at the gage (site 1) during the synoptic sampling were similar to the median concentrations reported for the gage during the entire period of record (table 54). The tributary streams were similar in composition to the gage, with calcium and magnesium the dominant cations and alkalinity the dominant anion. Ion balances ranged from 0.2 to 3.8 percent, suggesting that contribution from organic anions was small.

Fairly large spatial variations were measured in the concentrations of calcium, magnesium, and alkalinity among the sampled sites. For example, alkalinity ranged from a low of 250 μeq/L at site 7 to 1,280 μeq/L at site 10. Because limestone is

Table 57. Physical properties and major ion concentrations from surface-water sampling sites in the Buffalo River Basin, Tennessee, December 1–2, 1990

[Site locations shown in fig. 28; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; concentrations in microequivalents; Si, silica in micromoles per liter; WWTP, wastewater-treatment plant; <, less than; --, not measured]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria[a]	Remarks
1	03604000	10.8	89	7.78	700	160	52	17	740	67	51	<0.7	87		
2	352603087411500	1.10	95	7.74	750	150	43	14	820	81	45	<0.7	110	MT, LU	Logging in subbasin
3	352718087363100	.42	96	7.61	650	180	110	20	700	120	76	26	90	MT, LU	Hohenwald WWTP
4	353624087355500	.085	100	7.64	850	150	43	13	920	63	62	<.7	150	LU	Historic mining district
5	352620087283200	.034	63	7.43	450	140	39	12	500	52	34	5.7	94	LU	Small subbasin, forested
6	352620087283000	.28	50	7.63	370	99	35	16	420	33	31	4.9	110	LU	Reservoir and large resort
7	352620087243100	.023	36	6.98	220	91	35	9	250	44	31	5.0	120	LU	Small subbasin, forested
8	352601087231600	.27	120	7.68	950	210	48	14	1,100	23	17	14	110	LU	Summertown WWTP
9	352549087462500	1.02	93	7.75	650	170	87	22	700	100	82	13	95	MT, LU	Waynesboro WWTP
10	352355087195800	.27	130	7.74	1,150	220	52	18	1,280	71	39	21	110	MT, LU	Agriculture

[a] Criteria used in selection of sampling sites: MT = major tributary, LU = land use.

common throughout the basin, these differences in stream chemistry may reflect variable contributions of carbonate-rich ground water from the bedrock aquifer and shallow, more dilute waters from the silica-rich saprolith that mantles the upland hillslopes. The remaining ions were lower in concentration and had less spatial variability than the carbonate weathering products. For example, sodium concentrations ranged from 35 to 109 μeq/L, and chloride ranged from 17 to 76 μeq/L. The highest concentrations of sodium and chloride were measured at site 3 and site 9. Nitrogen concentrations were low at all the sampling sites and ranged from less than 0.7 μeq/L at the gage to 26 μeq/L at site 3. Sulfate ranged from 23 to 120 μeq/L and also was elevated at sites 3 and 9. The headwaters of Rockhouse Creek (site 3) and the Green River (site 9) each contain a small community and a wastewater-treatment facility, suggesting that concentrations of some dissolved constituents may be affected by human activities in these subbasins.

Little River above Townsend, Tennessee (Station 03497300)

Site Characteristics and Land Use

The Little River HBN Basin is in the western one-half of the Great Smoky Mountains National Park (GSMNP) in the Blue Ridge physiographic province in eastern Tennessee (fig. 30). The basin drains 275 km^2 of steep, mountainous terrain that ranges in elevation from 338 m at the gage to 2,025 m at the summit of Clingmans Dome, the highest point in Tennessee. The USGS gaging station is 0.7 km upstream from the National Park boundary at latitude 35°39'52" and longitude 83°42'41". The Little River is a northwest-flowing tributary of the Tennessee River with a channel length of about 36 km upstream from the gage and stream gradients that range from 16 m/km downstream from Elkmont to as much as 110 m/km in the steep headwater tributaries. The main channel is perennial, and mean monthly discharge ranges from about 3.5 m^3/s during base-flow conditions in September to 14.8 m^3/s during high flow in March. Average annual runoff from the basin was 93 cm from 1964 through 1995 (U.S. Geological Survey, Water Resources Data, Tennessee). Climate of the area is characterized by abundant precipitation and moderate temperatures, although both vary considerably with elevation. For example, average annual precipitation in GSMNP increases from 147 cm at an elevation of 445 m to 231 cm at an elevation of 1,920 m (Shanks, 1954). Snowfall is common at higher elevations during winter months; however, a seasonal snowpack seldom lasts through the winter. Mean monthly air temperatures also vary with elevation and range from 4°C in December to 23°C in July at an elevation of 445 m and 0°C in March to 16°C in July at an elevation of 1,920 m (Shanks, 1954).

Detailed descriptions of forest vegetation in GSMNP are in Arends (1981) and MacKenzie (1993). The basin lies in the Central Appalachian Broadleaf Forest ecoregion (Bailey and others, 1994) and is covered by hardwood-hemlock forest types at elevations below 1,450 m. The most common tree species are red maple, yellow poplar, black locust, white oak, black oak, sweet birch, and hemlock with lesser amounts of white pine, shortleaf pine, pitchpine, dogwood, and sumac. Rosebay rhododendron and mountain laurel are locally abundant as a dense understory. Above 1,450 m, vegetation is dominated by red spruce and Fraser fir forests that are locally interrupted by beech stands and open areas covered by mountain laurel and blueberries. Recently, there has been substantial dieback of the Fraser fir because of the attack of the wooly aphid (Eagar, 1984). Most soils in the basin are classified as Inseptisols and are described as fairly deep, well-drained soils developed in residuum weathered from the underlying bedrock (Feldman and others, 1991). Chemically, these soils tend to be acidic (pH 4.1 to 5.8) and have a low organic content and low cation-exchange capacities (Daniels and others, 1987). Aluminum generally dominates the exchange complex, which is almost entirely derived from the organic matter. The mineralogy of the sand and silt fraction is dominated by quartz, mica, and feldspar, and the dominant clays are interstratified mica/vermiculite, smectite, kaolinite, and gibbsite.

Complete descriptions of the geology of GSMNP and detailed geologic maps can be found in King (1963) and King (1968). Most bedrock in GSMNP consists of a thick mass of variably metamorphosed sedimentary rocks of late Precambrian age. The dominant units underlying the Little River Basin are the Elkmont and Thunderhead Sandstones, which are massive, thick-bedded feldspathic sandstones composed of detrital quartz, potassium feldspar, and plagioclase and metamorphic biotite, muscovite, and chlorite. The Anakeesta Formation, a dark-gray slate and phyllite, crops out in the Fish Camp Prong subbasin and the headwaters area of Middle Prong.

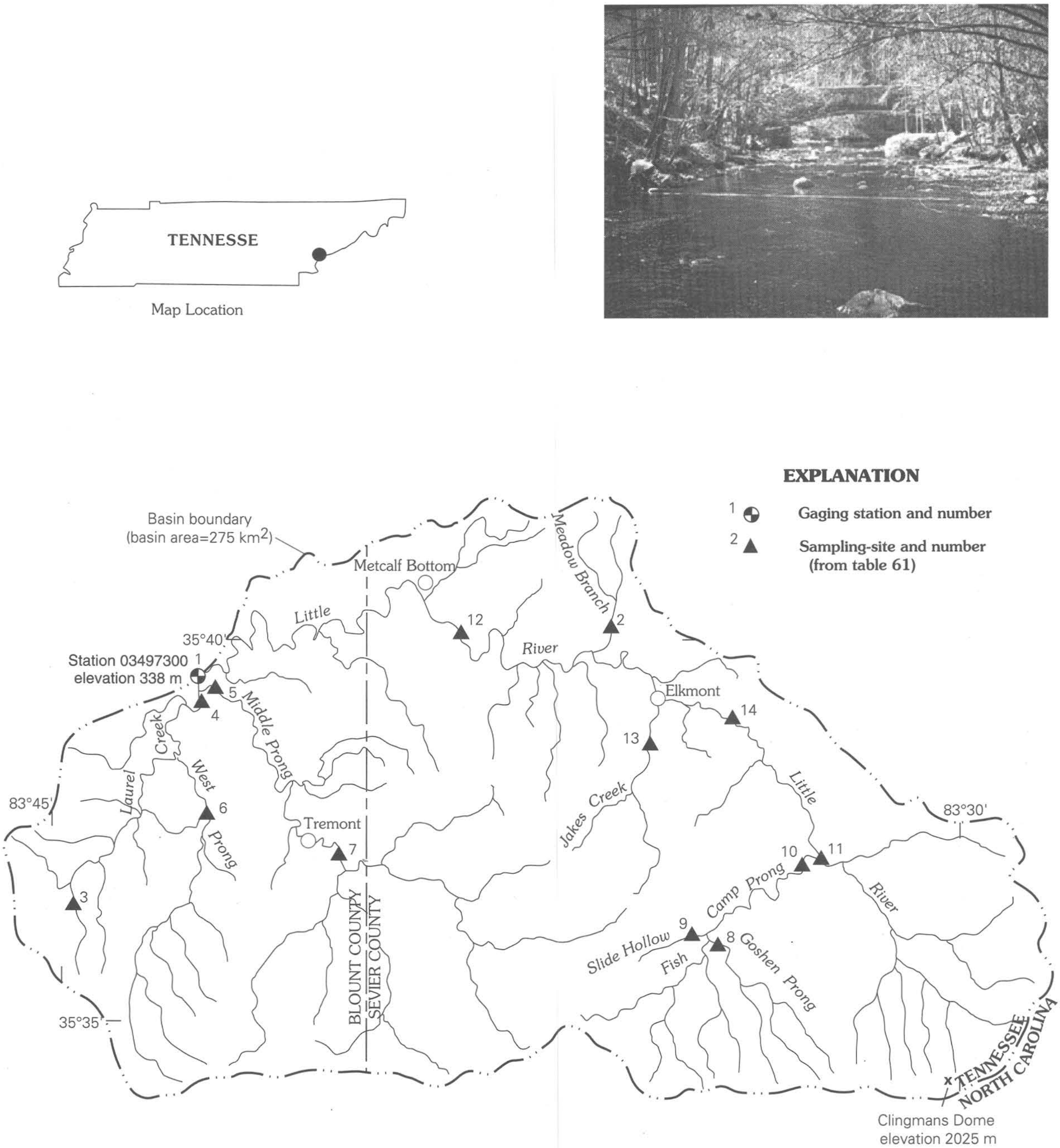

Figure 30. Map showing study area in the Little River Basin and photograph of the stream channel of the Middle Prong.

In outcrop, these rocks tend to form serrate crests and craggy pinnacles, and recent exposures are commonly heavily stained with rust owing to considerable quantities of iron sulfide minerals in the phyllite (King, 1968). Acidic leachate from roadfill materials containing rock from the Anakeesta Formation has impacted surface-water quality in some areas of GSMNP, although no problems have been identified in the Little River Basin (Mathews and Morgan, 1982). The Metcalf Phyllite is predominantly found in the northwestern part of the basin and is described as an almost homogeneous body of light-colored phyllite with minor amounts of siltstone and sandstone. About 80 percent of the phyllite consists of chlorite and sericite, and the remainder is quartz with minor amounts of feldspar and calcite. A small area near the headwaters of Laurel Creek is underlain by Ordovician limestone that is exposed by erosion of the overlying thrust sheet of Precambrian sediments. Bedrock in many areas of the basin is covered by deposits of alluvium and colluvium and saprolite that are locally as much as 30 m thick.

The Little River Basin drains parts of Sevier and Blount Counties in eastern Tennessee and is entirely in the boundaries of GSMNP. Access into the basin is by way of State Highway 73, which enters the basin at the gage and parallels the main channel as far upstream as Elkmont. Secondary roads provide access from outside the basin boundary to the Laurel Creek and Middle Fork drainages and to Clingmans Dome. State Highway 73 is occasionally plowed in winter, but deicing salts are not used on any roads in the GSMNP boundary. Foot trails provide access to most other areas in the basin, and a portion of the Appalachian Trail follows the southern basin divide.

Significant landscape disturbance because of logging, farming, and fire occurred prior to GSMNP's establishment in 1933 (Pyle, 1985; Lambert, 1957, 1960). The Little River Basin was first settled by Europeans in the 1830's, but landscape disturbance was limited primarily to farming activities and selective logging at lower elevations in the basin. The early 1900's was the most intense period of human disturbance as a result of large-scale logging operations and severe forest fires. The largest single logging operation in GSMNP was run by the Little River Lumber Company, which logged in the Little River Basin from 1904 to 1939. Most drainages in the basin were penetrated by logging railroads, many of which were eventually converted to trails and roads, including State Highway 73 through the Little River Gorge.

Since the 1940's, GSMNP has managed land in the basin primarily to restore and preserve the natural environment as outlined in the park's general management plan (U.S. Department of the Interior, 1988). The exception is the main river corridor, which is designated as a development zone allowing park facilities and roads. The largest concentration of park facilities in the corridor is at Elkmont, which contains a 120-site campground, several park residences, and a ranger station (Wayne Williams, National Park Service, oral commun., 1996). Several unoccupied structures, including 60 summer cabins and an historic hotel, still stand near the mouth of Jakes Creek. Other park structures in the basin include a picnic area and comfort station and septic system at Metcalf Bottom and an educational center and ranger station at Tremont. Elkmont and Tremont have wastewater-treatment facilities that discharge treated water into the Little River and Middle Prong, respectively, during the summer (Wayne Williams, oral commun., 1996). The Little River is in one of the most accessible areas of GSMNP and receives considerable tourist traffic during the summer.

Because of the wide diversity of natural resources in GSMNP, the park has become an important research area for studying environmental impacts on terrestrial and aquatic ecosystems (Nodvin and others, 1993). A complete bibliography of scientific research in the park has been compiled by Nodvin and others (1993) and is available in digital form at URL http://funnelweb.utcc.utk.edu/%7Enodvin/smokyhtml.htm/. Air pollution is currently one of the biggest concerns for natural resources and for visitors in the park; consequently, GSMNP has one of the most comprehensive air-quality-monitoring programs in the National Park System. The current monitoring system includes nine weather stations, three atmospheric deposition sites, and seven air-quality-monitoring stations (Jim Renfro, National Park Service, oral commun., 1996). In addition, GSMNP also monitors the water quality of several streams, including an intensively monitored site at the headwaters of Noland Creek on the south site of Clingmans Dome (Jim Renfro, oral commun., 1996).

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for this report includes 61 water-quality samples that were collected bimonthly from October 1985 through December 1995. Twenty samples were collected from August 1963 through

August 1968, prior to 1986 when the site was added to the HBN. All samples that were collected as part of the HBN were analyzed at the NWQL in Arvada, Colo. Daily discharge records for the Little River (station 03497300) are available beginning in October 1933. Records of daily water temperature at the gage are available for October 1963 through January 1982, and daily precipitation amount was measured at the gage from 1991 through 1995.

Calculated ion balance for 60 samples with complete major ion analyses is shown in figure 31. Ion balances ranged from −25 to +16 percent, and about 75 percent of samples had values within the ±10 percent range, indicating the analytical results are of good quality. The average ion balance was −7.6 percent, and 92 percent of samples had negative ion balances, indicating an excess of measured anions over cations in solution. Laboratory alkalinity in HBN

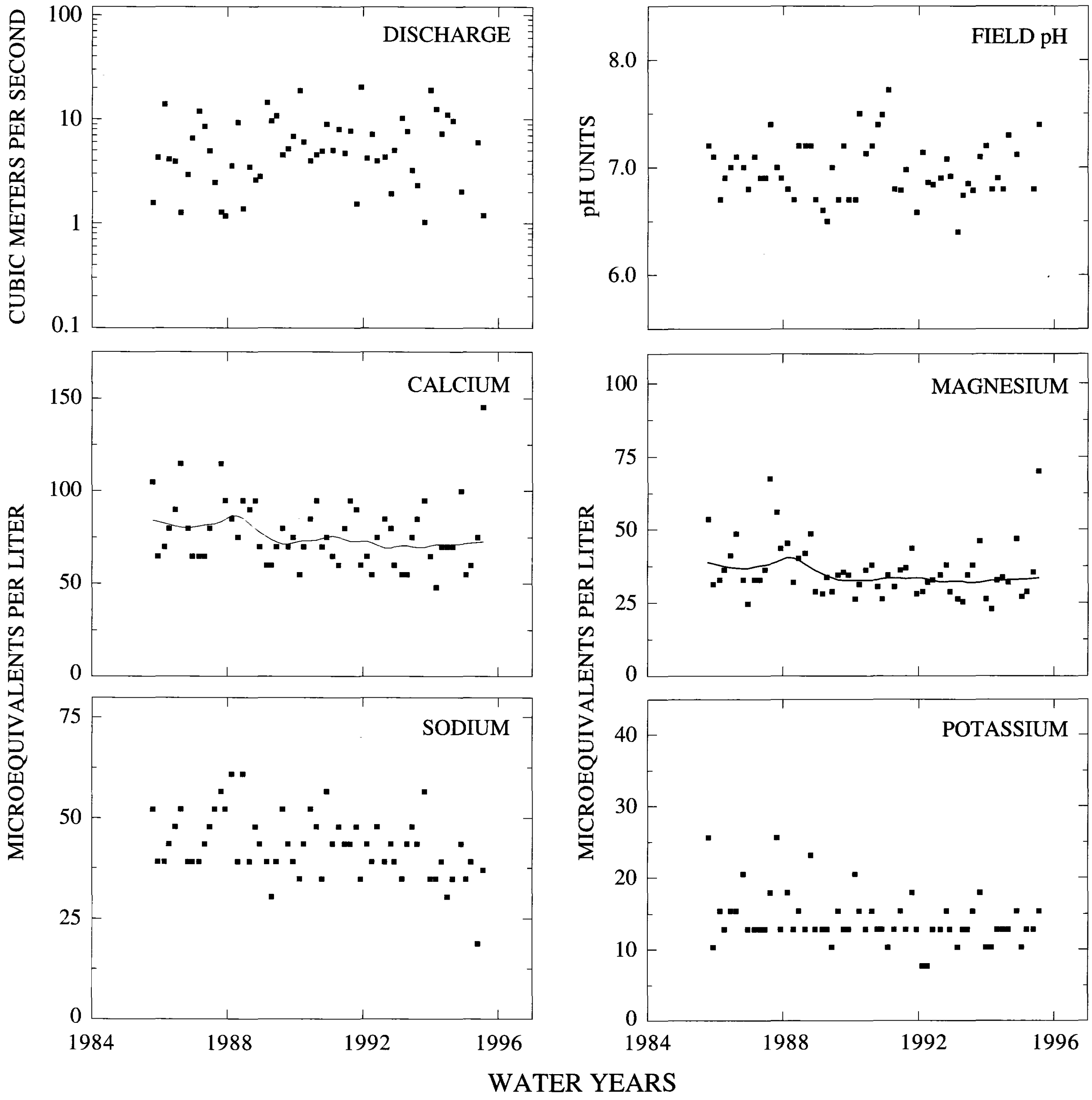

Figure 31. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Little River, Tennessee.

samples was determined by a fixed-endpoint titration to pH 4.5. For low-alkalinity waters, the endpoint pH is closer to 5.0, and titration to pH 4.5 may overestimate alkalinity by as much as 25 µeq/L (Barnes, 1964). Alkalinity also was determined by incremental titration in the field beginning in 1992. A comparison of the two alkalinity determinations shows that the fixed endpoint concentrations were, on average, 29 µeq/L larger than the incremental concentrations. This discrepancy in the two measurements is similar to the average anion excess of 30 µeq/L, suggesting that the fixed-endpoint titration is a reasonable explanation of the negative ion balances.

Time-series plots of the major dissolved constituents were inspected for evidence of method-related effects (fig. 31). The most notable pattern

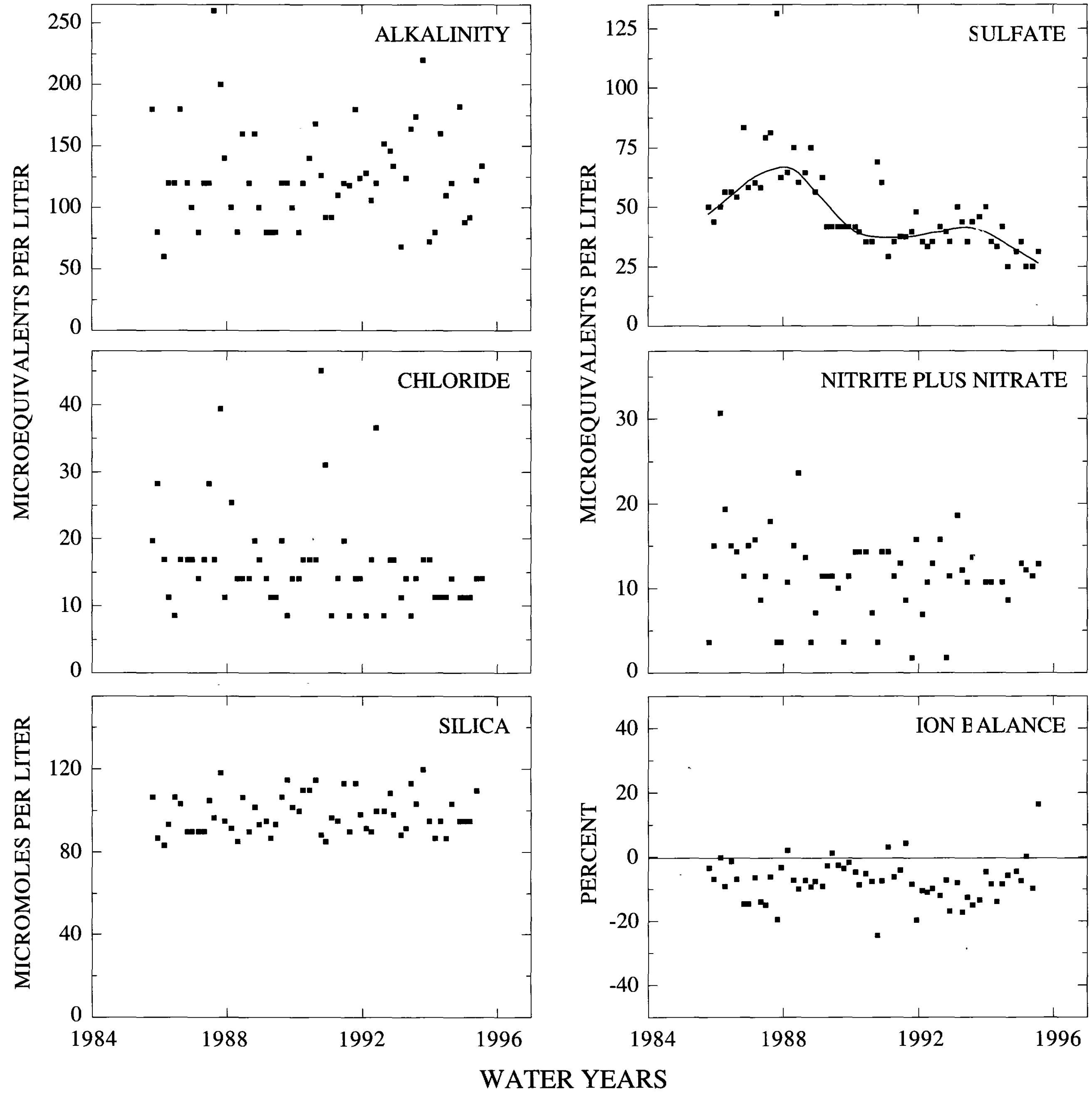

Figure 31. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Little River, Tennessee—Continued.

observed was in sulfate, which had a period of elevated concentrations during the late 1980's. This pattern coincides with the use of a turbidimetric titration for sulfate analyses at the NWQL between March 1986 and December 1989 (Fishman and others, 1994). In 1989, the NWQL determined that sulfate concentrations can be overestimated by this technique and changed the method to ion chromatography in 1990 (Office of Water Quality Technical Memorandum No. 90.04, *Turbidimetric Sulfate Method*, issued December 21, 1989, at URL http://water.usgs.gov/public/admin/memo/). The bias was most pronounced in dilute waters, although it was not consistent among samples and appeared to be affected by factors such as color and turbidity (Schertz and others, 1994).

Table 58 lists median concentrations and ranges of major constituents in stream water collected at the gage and VWM concentrations in wet-only deposition measured at the Elkmont NADP station near the Elkmont campground. Atmospheric deposition of sulfate, nitrate, and hydrogen in the Southern Blue Ridge Province is among the highest reported in the Eastern United States (Elwood and others, 1991). The VWM pH of wet precipitation measured at the Elkmont NADP station was 4.5 during the 15 years of record. The dominant cations in precipitation were hydrogen, which contributed 63 percent of the total cation charge, and ammonium, which contributed 20 percent. The dominant anions were sulfate and nitrate, which accounted for 65 and 29 percent of the total anions, respectively.

Stream water in the Little River is dilute and weakly buffered; specific conductances ranged from 10 to 61 µS/cm, and alkalinities generally were between 40 and 260 µeq/L. The major cations in stream water were calcium and sodium, and the dominant anion was alkalinity. The low concentrations of the weathering-derived solutes, particularly alkalinity, reflect the slow-weathering sandstones and quartzites of the underlying Precambrian bedrock. The median chloride concentration in stream water was 14 µeq/L, which is about four times larger than the VWM concentration of chloride in precipitation. Based on the difference between average annual runoff and precipitation, evapotranspiration can account for about a twofold increase in the concentration of precipitation, suggesting that as much as one-half of stream-water chloride may be derived from sources other than wet deposition. Measurements at a high-elevation site in GSMNP indicate that total annual chloride deposition may be twice that of wet deposition because of additional inputs from dry deposition and cloud interception (Elwood and others, 1991). Estimates of total sulfate and nitrate deposition at the high-elevation site were two to five times greater than wet deposition. The median concentration of sulfate in stream water was 42 µeq/L compared to the VWM concentration in precipitation of 34 µeq/L. Considering the combined effects of evapotranspiration and additional inputs of sulfate in dry deposition, these data suggest that a substantial portion of atmospherically deposited sulfate is retained in the basin. The most likely mechanism for retention is sulfate adsorption on clays and organic matter in the soil environment. The basin also is an important sink for nitrogen species, based on the smaller concentrations of both nitrate and ammonium in stream water compared to precipitation. By contrast, many higher elevation streams in the park have been found to have nitrate concentrations similar to those in precipitation (Nodvin and others, 1995). Retention of both sulfate and nitrate in the Little River Basin probably is an important process buffering stream water from the effects of acidic deposition (Cosby and others, 1991).

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 59). Most weathering-derived constituents, particularly calcium, magnesium, and alkalinity, had negative correlations with discharge. These results are consistent with a hydrologic system where weathering-enriched base flow is diluted by waters from shallow or surficial sources during periods of increased discharge. Among the ions, the strongest correlations were found between calcium, magnesium, and alkalinity, which indicates that weathering of carbonates is the dominant process that controls the release of base cations to surface waters. The atmospherically derived solutes, chloride and sulfate, were poorly correlated with the weathering-derived constituents with the exception of weak positive correlations with some base cations, particularly potassium. These weak correlations may be an indication that soil processes probably also are important in regulating cation concentrations stream water.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are shown in table 60. Trends at this station were calculated only during a 10-year period because the station was not added to the HBN until 1986. Statistically significant downward trends were detected in the unadjusted and flow-adjusted calcium, magnesium, and sulfate concentrations and the flow-adjusted potassium concentrations at the 0.01 confidence level. A statistically significant upward trend also was detected in the flow-adjusted alkalinity at the 0.01 confidence level. The LOWESS curve in figure 31 shows that most of the decrease in sulfate occurred around 1990 and was probably caused by the period of positive analytical bias in the 1980's. The cause of the upward trend in alkalinity is not clear but may be linked to declines in sulfate concentrations observed at many NADP stations in the Southeast from 1980 to 1992 (Lynch and others, 1995). Most NADP stations in the Southeast also had substantial declines in base cation concentrations, particularly calcium and magnesium (Lynch and

Table 58. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ion concentrations measured in water-quality samples from Little River, Tennessee, October 1985 through July 1995, and volume-weighted mean concentrations in wet precipitation collected at the Elkmont Station, Tennessee

[Concentrations in units of microequivalents per liter, discharge in cubic meters per second, specific conductance in microsiemens per centimeter at 25 degrees Celsius, pH in standard units, and silica in micromoles per liter; n, number of stream samples; VWM, volume-weighted mean; inst., instantaneous; spec. cond., specific conductance; <, less than; --, not reported]

Parameter	Stream water						Precipitation VWM[a]
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge, inst.	1.0	2.8	5.1	8.5	20	57	--
Spec. cond., field	9.6	14	17	20	61	56	--
pH, field	6.4	6.8	6.9	7.2	7.7	56	4.5[b]
Calcium	48	65	75	87	190	59	4.5
Magnesium	23	30	34	38	70	59	1.4
Sodium	19	39	44	48	61	59	2.7
Potassium	7.7	13	13	15	26	59	.9
Ammonium	<.7	<.7	<.7	1.4	3.6	59	10
Alkalinity, laboratory	60	96	120	140	260	59	--
Sulfate	25	35	42	58	130	59	34
Chloride	8.5	11	14	17	49	59	3.1
Nitrite plus nitrate	<3.6	9.7	11	14	31	56	15[c]
Silica	83	90	95	110	120	58	--

[a] Values are volume-weighted mean concentrations for 1980–94.

[b] Laboratory pH.

[c] Nitrate only.

Table 59. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ion concentrations, Little River, Tennessee, 1986 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; N, nitrite plus nitrate; Si, silica]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	N
pH	−0.341									
Ca	−.756	0.385								
Mg	−.731	.309	0.874							
Na	−.696	.311	.673	0.616						
K	−.474	.071	.619	.586	0.468					
Alk	−.742	.375	.641	.614	.560	0.485				
SO_4	−.237	.026	.355	.237	.177	.369	0.047			
Cl	−.239	.156	.211	.094	.305	.389	.146	0.321		
N	.204	−.160	−.107	−.155	−.123	−.046	−.258	−.127	−0.145	
Si	−.468	.240	.460	.492	.505	.467	.634	−.218	.086	−0.214

others, 1995), which is consistent with the downward trends in stream-water cation concentrations in the Little River. The lack of trend in stream-water nitrite plus nitrate concentrations was somewhat unexpected considering the observation that many high-elevation areas in GSMNP are reaching an advanced stage of nitrogen saturation because of the cumulative effects of atmospheric nitrogen deposition (Nodvin and others, 1995). With continued high rates of nitrogen deposition, however, the area of nitrogen saturation should begin to move downslope and eventually may cause increasing nitrate concentrations in streams at lower elevations (Nodvin and others, 1995).

Table 60. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major ion concentrations, Little River, Tennessee, October 1985 through August 1995

[Trends in units of microequivalents per liter per year, except discharge in cubic meters per second per year, pH in standard units per year, and silica in micromoles per liter per year; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	0.05	0.929	--	--
pH, field	<.01	.999	0.01	0.754
Calcium	−1.0	.008	−1.3	.001
Magnesium	−.6	.003	−.4	.005
Sodium	−.5	.060	−.5	.044
Potassium	<.1	.012	−.3	.006
Alkalinity, laboratory	1.4	.160	3.1	.008
Sulfate	−3.1	.000	−3.2	.000
Chloride	−.4	.045	−.4	.036
Nitrite plus nitrate	−.2[a]	.022	--	--
Silica	.9	.064	.9	.023

[a] Calculated using a trend test for censored data.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling of October 29 and 30, 1991, are presented in table 61; locations of sampling sites are shown in figure 30. Discharge at the gage was 1.61 m^3/s compared to the median daily discharge of 2.83 m^3/s for October (Lawrence, 1987), indicating that the basin was sampled during base-flow conditions for that time of year. Solute concentrations measured at the gage (site 1) during the sampling period were similar to the third-quartile concentrations reported for the gage during the entire period of record, except for nitrate (table 58). Most tributary streams were very dilute and similar in composition to the sample collected at the gage. All samples had ion balances close to zero (range −1.6 to 3.7 percent), indicating that organic anions did not contribute significantly to the ionic content of stream water during the sampling period.

Comparison of results in table 61 with the distribution of dominant bedrock types in the basin shows no obvious correlation between surface-water chemistry and mapped bedrock geology, with the exception of site 3. Stream-water concentrations of calcium, magnesium, and alkalinity at site 3 were significantly larger than the other sampled tributaries. For example, the calcium concentration at site 3 was 500 µeq/L compared to the average concentration of 70 µeq/L in the remaining 13 samples. Although phyllites are the dominant bedrock unit in this subbasin, Ordovician limestones are exposed in a small area along the stream channel just upstream from the sampling site. With the exception of site 3, strong inverse correlations were found between the major weathering products and elevation ($-0.603 > r > -0.793$). These results suggest that elevation accounts for most of the spatial variation in surface-water chemistry in areas of the basin without limestone bedrock. Silsbee and Larson (1982) reported similar elevational gradients in stream composition for other streams in GSMNP and suggested that smaller concentrations at higher elevations were attributed to larger flushing rates because of greater precipitation and slower chemical weathering rates because of lower temperatures.

Constituents derived primarily from atmospheric sources had much less variability than the major weathering products. For example, chloride concentrations ranged from 11 to 18 µeq/L, and nitrate concentrations were below the detection limit at all but one of the sampling sites. Neither chloride nor nitrate concentrations were elevated in stream waters downstream from Elkmont and Tremont (sites 5 and 12), indicating that the wastewater facilities do not affect water quality during periods of low visitor use in the park. Nitrate concentrations in tributary streams were lower than the long-term median concentrations at the gage (table 58), which may reflect the time of year the samples were collected. Silsbee and Larson (1982) observed that stream-water nitrate concentrations in GSMNP varied seasonally, with the highest concentrations in winter and spring and the lowest concentrations in autumn. Low autumn concentrations may result from uptake of nitrogen

Table 61. Physical properties and major ion concentrations from surface-water sampling sites in the Little River Basin, Tennessee, October 29–30, 1991

[Site locations shown in fig. 30; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; concentrations in microequivalents; Si, silica in micromoles per liter; CG, campground; SS, sandstone; <, less than; --, not measured]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria[a]	Remarks
1	03497300	1.61	22	7.16	95	42	57	18	140	38	14	<0.7	120		
2	353906083424700	--	28	7.30	95	67	83	20	190	44	16	<.7	210	BG	Metcalf Phyllite
3	353648083443600	.025	84	7.50	500	250	74	20	700	120	14	<.7	160	BG	Limestone
4	353919083423600	.19	31	6.84	140	66	65	19	220	50	18	<.7	140	MT, BG	Metcalf Phyllite
5	353926083423100	.34	19	7.07	75	36	44	15	120	33	14	<.7	110	MT, BG	Downstream from Tremont
6	353741083421900	.13	16	7.31	50	21	44	16	81	33	14	<.7	130	MT, BG	Thunderhead and Elkmont SS
7	353631083401100	.040	15	6.81	50	26	35	12	70	42	15	<.7	87	BG	Anakeesta Shale
8	353552083335500	.057	13	6.70	37	19	35	12	45	31	13	9.3	84	BG	Thunderhead SS
9	353616083334800	--	23	7.01	90	55	44	10	100	75	16	<.7	95	BG	Thunderhead and Anakeesta
10	353708083322200	--	14	6.88	45	26	35	13	69	33	13	<.7	87	BG	Thunderhead and Anakeesta
11	353709083321500	.17	16	6.96	65	23	39	13	80	42	11	<.7	92	BG	Thunderhead SS
12	353958083380500	--	18	7.07	70	29	44	17	110	35	13	<.7	110	LU	Downstream from Elkmont CG
13	353835083350800	4.3	14	6.90	48	14	39	14	76	23	12	<.7	110	BG	Elkmont SS
14	353900083334900	17	15	6.96	55	25	35	13	79	38	12	<.7	950	LU	Upstream from Elkmont CG

[a] Criteria used in selection of sampling sites: BG = bedrock geology, MT = major tributary, LU = land use.

by microorganisms during the initial stages of leaf fall (Silsbee and Larson, 1982). Sulfate concentrations also were low and fairly uniform over the basin, except for site 3 and site 9, which had concentrations of 123 μeq/L and 75 μeq/L, respectively, compared to the average concentration of 34 μeq/L for the remaining 12 sites. The slightly elevated sulfate concentrations in these tributaries indicate that weathering of pyrite in the Anakeesta Formation may contribute small amounts of sulfate to stream water in some areas of the basin.

Holiday Creek near Andersonville, Virginia (Station 02038850)

Site Characteristics and Land Use

The Holiday Creek HBN Basin is in the Piedmont physiographic province in central Virginia (fig. 32). The topography is undulating to hilly, and the landscape is dissected by numerous small streams. The Holiday Creek Basin drains 22 km^2 of forested terrain that ranges in elevation from 144 to 280 m. The HBN gage is 2 km north of Holiday Lake State Park at latitude 37°24'55" and longitude 78°38'10". Holiday Creek is a southeast-flowing tributary of the Appomattox River and has a channel length of about 8 km upstream from the gage and an average gradient of 11.5 m/km. The main channel is perennial, and mean monthly discharge varies from 0.13 m^3/s in July to 0.40 m^3/s in March. Average annual runoff was 35 cm from 1966 to 1995 (U.S. Geological Survey, Water Resources Data, Virginia). Climate is characterized by warm summers and relatively mild winters. Average daily air temperatures range from 3.0°C in January to 25.0°C in July (Bullard, 1977). Precipitation averages 105 cm annually and is fairly evenly distributed throughout the year; July and August are the wettest months and October and November are the driest (Bullard, 1977). Average annual snowfall in less than 35 cm and, on average, only 16 days per year have a snow cover of more than 2 cm.

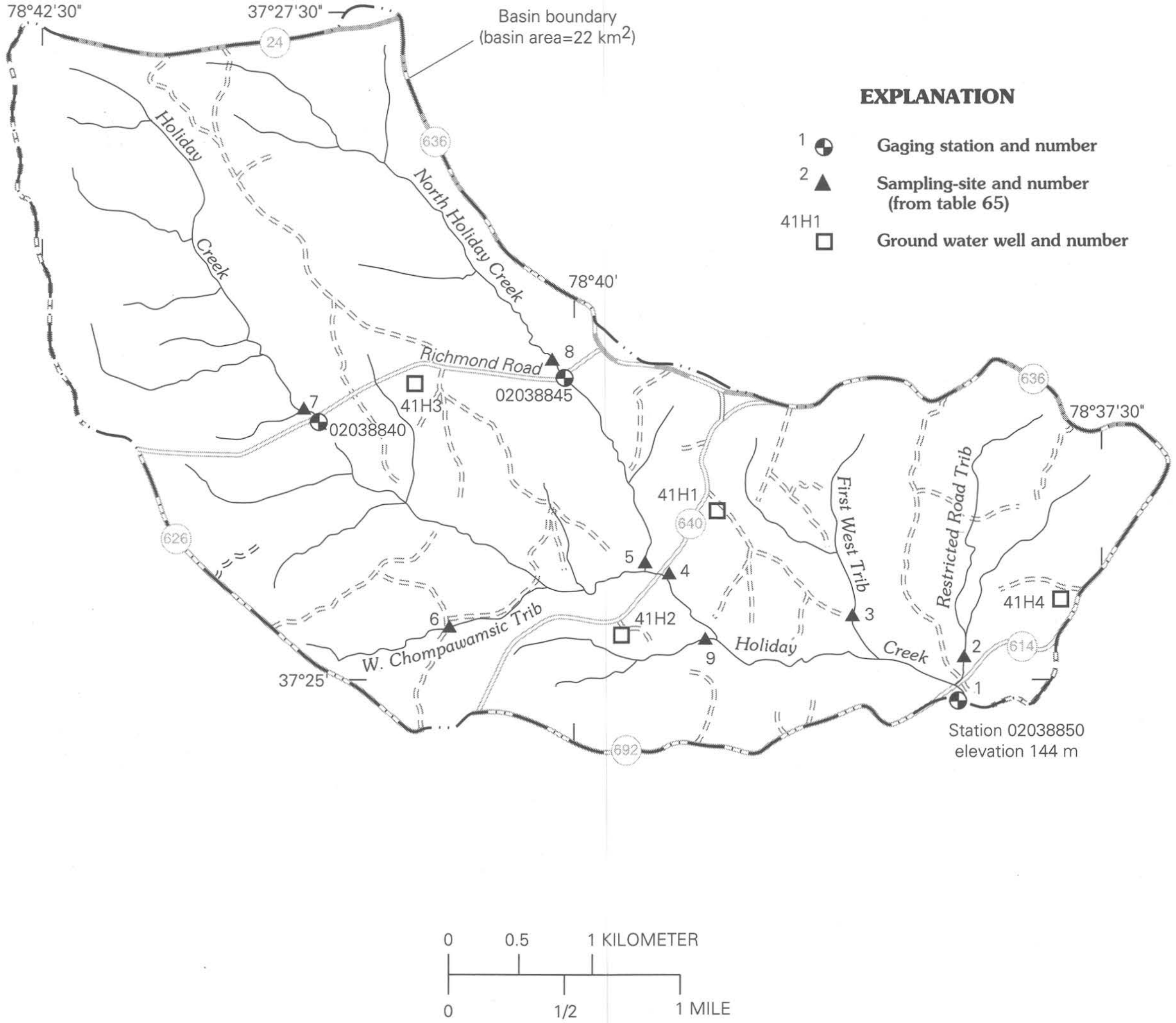

Figure 32. Map showing study area in the Holiday Creek Basin and photograph of the stream channel of North Holiday Creek.

The basin lies in the Southern Mixed Forest ecoregion (Bailey and others, 1994) and is covered by about 60 percent pine forests and 40 percent upland and lowland hardwood communities. The dominant pine species are loblolly pine, Virginia pine, and shortleaf pine; the primary hardwood species are chestnut oak, scarlet oak, red oak, white oak, and yellow poplar. Soils in the basin are mapped in the Tatum and Manteo soil series, which are representative of large areas of the southern Virginia Piedmont [Natural Resources Conservation Service (NRCS), written commun., 1994]. The Tatum series are deep, well-drained residual soils formed from the weathering of gneiss and schist. A typical profile consists of 5 cm of forest litter and 20 cm of brown loam overlying a subsoil of yellowish-red clay and clay loam that extends to a depth of 130 cm. Soils in the Manteo series are steeper and shallower than the Tatum series soils and typically contain as much as 50 percent thin, flat fragments of schist. Soils in both series are acidic and have low cation-exchange capacities. The dominant clay minerals are kaolinite and hydroxy-interlayered vermiculite (Thomas and others, 1989).

Bedrock in the basin consists of complexly folded and highly metamorphosed sedimentary and volcanic rocks of late Precambrian to early Paleozoic age (Marr, 1980). The northern two-thirds of the basin is underlain by phyllites and schists of the Candler Formation. The fine-grained, gray to green phyllites are primarily composed of muscovite, chlorite, and quartz (Ern, 1968). The schists are greenish-brown to tan and contain abundant muscovite and quartz with lesser amounts of plagioclase, chlorite, hematite, magnetite, and pyrite. Rocks of the Chopawamsic Formation underlie the lower one-third of the basin and are generally more mafic than rocks of the Candler Formation. The two dominant rock types comprising the Chopawamsic Formation are a dark-green to gray amphibole gneiss and schist and a biotite-quartz-feldspar gneiss interlayered with amphibole gneiss (Marr, 1980).

The Holiday Creek Basin drains parts of Appomattox and Buckingham Counties, and 70 percent is in the boundaries of the Appomattox-Buckingham State Forest administered by the Virginia Division of Forestry. Privately owned land, which accounts for the remaining 30 percent, is concentrated in the area of the basin north of Richmond Road (fig. 32). Primary and secondary roads trace the entire perimeter of the basin, and several gravel roads traverse the basin. Most unpaved roads in the State Forest are covered with limestone gravel. State Highway 24, which runs along the northern basin divide, is occasionally plowed and salted in winter.

Most areas of the Virginia Piedmont were logged or used for agriculture in the late 1800's and early 1900's. The State forest system was established in the 1950's on abandoned farmland that was originally acquired by the Federal Government in the 1930's. Current land cover in the basin is more than 80 percent forest, and the major land-use activities are timber harvesting and recreation. Forests on State-owned lands are currently managed on a sustained-yield basis of which about 100 ha are subject to cutting or thinning operations each year (Wayne Bowman, Appomattox-Buckingham State Forest, oral commun., 1994). Logging operations on State-owned lands are required to leave 25- to 50-m buffer strips along drainages with flowing water. Since 1990, a large percentage of forests on private land have been harvested and the land has been sold off in 10-ha parcels to real estate developers (Wayne Bowman, oral commun., 1994). Forests in the basin experienced a disproportionate amount of natural disturbance in the early 1990's because of several devastating windstorms, an ice storm, and the southern pine-beetle infestation.

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for this report includes 152 water-quality samples that were collected from October 1967 through July 1995. Nine samples were collected in 1968 and 10 in 1969 and 1970. Sampling frequency was reduced to bimonthly from 1971 through 1982 and quarterly from 1983 through 1995. Water-quality samples were analyzed at a USGS laboratory in Charlottesville, Va., from 1967 through 1972, the USGS Central Laboratory in Atlanta, Ga., from 1973 through 1985, and at the NWQL in Arvada, Colo., from 1986 through 1995. Daily discharge records for Holiday Creek (station 02038850) are available beginning in April 1966. Two partial-record gaging stations, four observation wells, two rain gages, and a number of soil-moisture tubes were installed in the basin in the early 1970's to calculate a hydrologic budget for the basin (wells and secondary gage locations shown in fig. 32). Water-level data for the four observation wells, 41H1 (station 372541078392101), 41H2 (station 372514078394301), 41H3 (station 372608078404601), and 41H4 (station 372519078374001), and maximum discharge at the two partial-record stations, Holiday Creek near Toga (station 02038840) and North Holiday Creek near Toga (station 02038845), are available from NWIS. Water-quality samples were collected from the four observation wells on August 8, 1971. Unpublished precipitation and soil-moisture data are available through the USGS office in Richmond, Va.

Calculated ion balances for 151 samples with complete major-ion analyses are shown in figure 33. Charge balance ranged from –22 to +11 percent, and almost 85 percent of samples had charge balances within the ±10 percent range, indicating the analyses are of good quality. The mean charge balance was –3.2 percent and more than 70 percent of the samples had an excess of measured anions over cations in solution. Laboratory alkalinity in HBN samples was

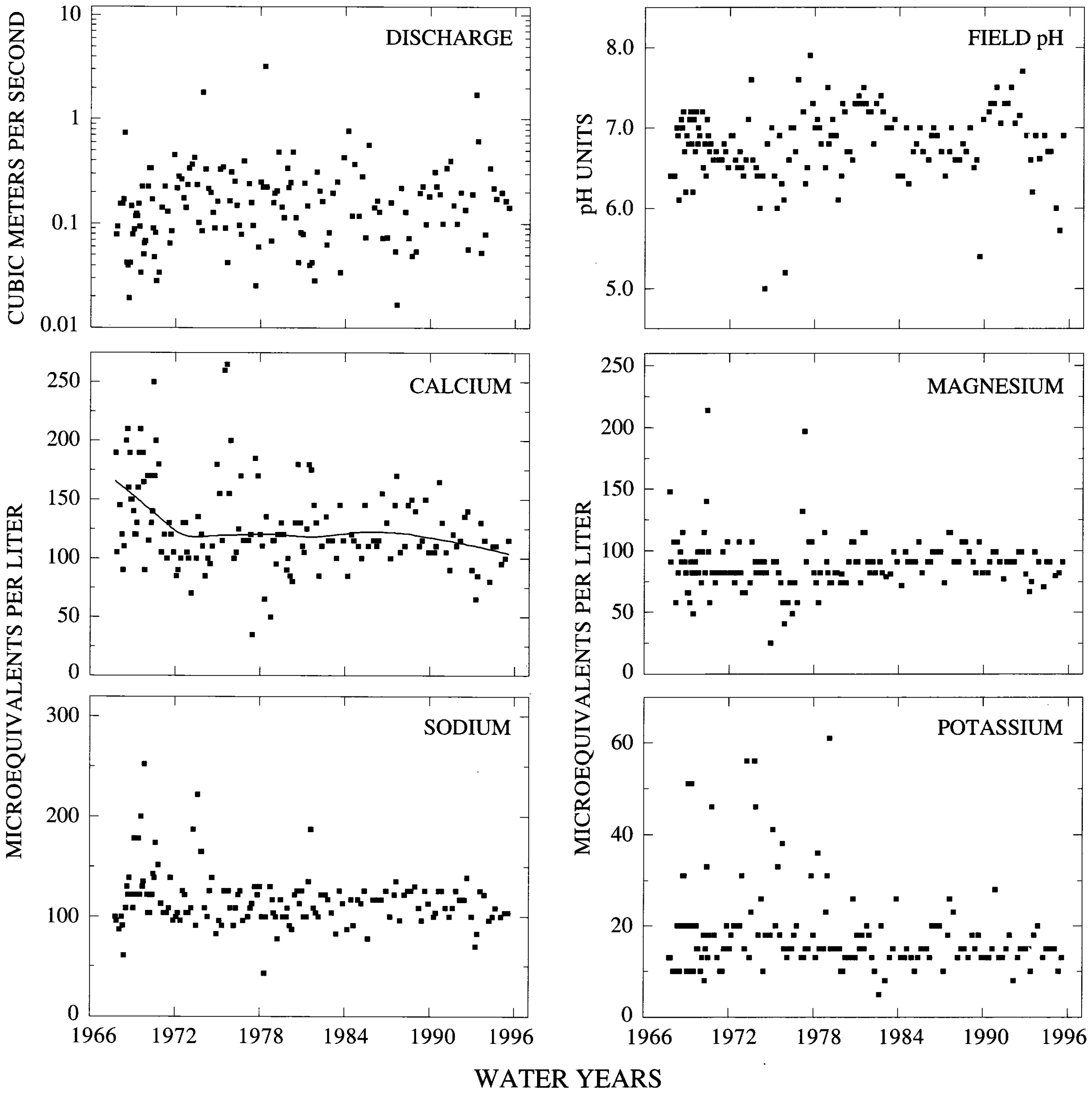

Figure 33. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Holiday Creek, Virginia.

determined by a fixed-endpoint titration to pH 4.5. For waters with low alkalinities, however, the endpoint pH is closer to 5.0, and titration to pH 4.5 may overestimate alkalinity by as much as 25 µeq/L (Barnes, 1964). Alkalinity also was determined by incremental titration in the field beginning in 1992. A comparison of the two alkalinity determinations shows that the fixed endpoint concentrations were, on average, 34 µeq/L larger than the incremental concentrations. This discrepancy in the two measurements is similar to the average anion excess of 23 µeq/L, suggesting that the fixed-endpoint titration is a reasonable explanation of the negative ion balances.

Time-series plots of the major dissolved constituents were inspected for evidence of method-related effects (fig. 33). Several uncharacteristically high sulfate concentrations were reported during the late 1980's. This pattern coincides with the use of a

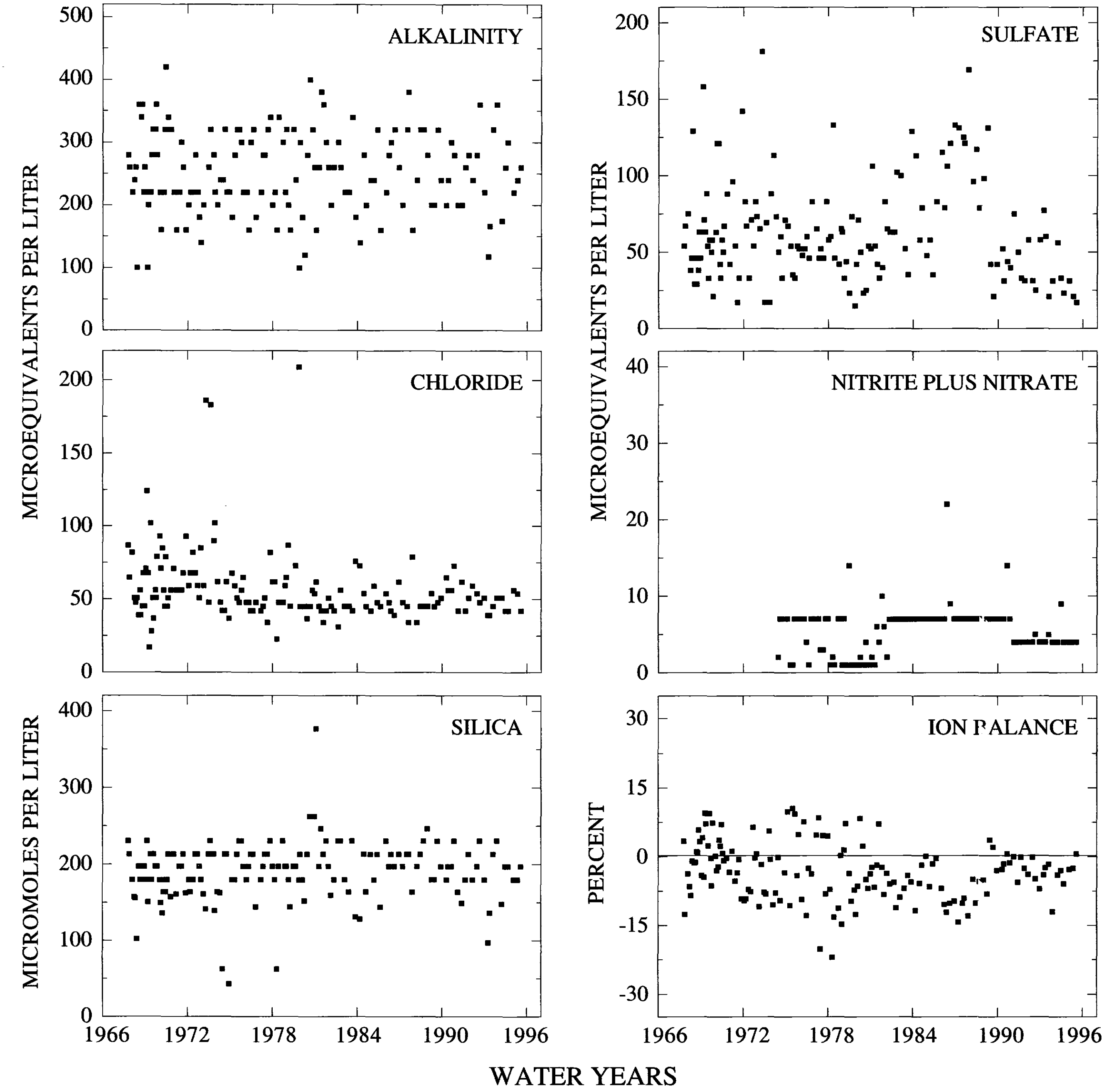

Figure 33. Temporal variation of discharge, field pH, major ion concentrations, and ion balance at Holiday Creek, Virginia—Continued.

turbidimetric titration for sulfate analyses at the NWQL between March 1986 and December 1989 (Fishman and others, 1994). In 1989, the NWQL determined that sulfate concentrations can be overestimated by this technique and changed the method to ion chromatography in 1990 (Office of Water Quality Technical Memorandum No. 90.04, *Turbidimetric Sulfate Method*, issued December 21, 1989, at URL http://water.usgs.gov/public/admin/memo/). The bias was most pronounced in dilute waters, although it was not consistent among samples and appeared to be influenced by factors such as color and turbidity (Schertz and others, 1994).

Median concentrations and ranges of major constituents in stream water collected at the HBN gaging station and VWM concentrations in wet-only deposition measured at the Charlottesville NADP station, about 75 km north of the basin, are presented in table 62. Precipitation at the NADP station was dilute and acidic with a VWM pH of 4.3 for 11 years of record. The dominant cations were hydrogen and ammonium, which contributed 68 and 18 percent, respectively, of the total cation charge. The dominant anions were sulfate, which accounted for 61 percent of the anion charge, and nitrite, which accounted for 31 percent. The low pH and predominance of strong acid anions indicates that precipitation at the NADP station probably is affected by anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain (Likens and others, 1977).

Stream water in Holiday Creek was dilute and weakly buffered; total ionic constituents ranged from 450 to 1,200 μeq/L, and alkalinities were generally between 220 to 320 μeq/L. The major cations in stream water were calcium and sodium and the major anion was alkalinity. Dissolved cations, alkalinity, and silica in stream water are most likely derived from the weathering of silicate minerals in the underlying phyllite and schist. The median chloride concentration in stream water was 51 μeq/L, which is 6.5 times larger than the VWM concentration of 6.1 μeq/L in precipitation. Based on the difference between annual precipitation and runoff, evapotranspiration can account for about a threefold increase in the concentration of precipitation, indicating that some chloride in stream water is contributed from sources other than precipitation. Additional sources of stream-water chloride might include dry deposition of marine aerosols or possibly deicing salts applied to Highway 24. In addition, the bedrock contains considerable amounts of biotite and hornblende, both of which can contribute small amounts of chloride to surface waters (Peters, 1991). Median sulfate concentration of stream water was 58 μeq/L compared to 46 μeq/L in precipitation and was somewhat smaller than expected considering the concentrating effects of evapotranspiration and additional inputs of sulfate from dry deposition, indicating some sulfate is retained in the basin. Sulfate retention probably occurs by adsorption on pedogenic iron and aluminum oxides that are common in the highly weathered soils of the Southeast (Rochelle and Church, 1987; Shanley, 1992). Concentrations of inorganic nitrogen species in stream water were well below the average concentration in precipitation at all discharge levels, indicating that most atmospheric nitrogen is retained by vegetation and soils in the basin.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 63). The weathering-derived constituents had strong negative correlations with discharge. These results are consistent with a hydrologic system where weathering-enriched base flow is diluted by waters from shallower sources during periods of high flow. Among the ions, the strongest correlations were found between the base cations, alkalinity, and silica. These associations support the idea that weathering of silicate minerals is the primary source of solutes in stream water. The lack of correlations with sulfate and chloride provides additional evidence that these ions are derived primarily from atmospheric sources.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are shown in table 64. A statistically significant downward trend was detected in both the unadjusted and flow-adjusted calcium concentrations at the 0.01 confidence level. Downward trends also were detected in the flow-adjusted potassium and chloride concentrations. The downward trend in potassium is extremely small [<–0.1 (μeq/L)/yr] and amounts to a decrease of less than 3 μeq/L during the entire period of record. The LOWESS curve in figure 33 shows that most of the decrease in calcium concentrations occurred in the late 1960's and early 1970's, and since then concentrations have remained relatively constant (fig. 33). Although not shown, the flow-adjusted chloride concentrations showed a similar pattern of slightly elevated concentrations in the early part of the record, followed by relatively constant concentrations through the remainder of the record. The cause of these trends in stream-water calcium and chloride concentrations in the early part of the record could not be identified. The only change in land use that occurred in the early 1970's was the requirement that logging companies leave buffer strips of vegetation along any drainages with flowing water (Wayne Bowman, oral commun., 1994). Changes also may have occurred in acidic deposition and road salting; however, it is unlikely that these factors

Table 62. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ion concentrations measured in water-quality samples from Holiday Creek, Virginia, October 1967 through July 1995, and volume-weighted mean concentrations in wet precipitation collected at the Charlottesville Station, Virginia

[Concentrations in units of microequivalents per liter, discharge in cubic meters per second, specific conductance in microsiemens per centimeter at 25 degrees Celsius, and silica in micromoles per liter; n, number of stream samples; VWM, volume-weighted mean; inst., instantaneous; spec. cond., specific conductance at 25 degrees Celsius; <, less than; --, not reported]

Parameter	Stream water						Precipitation VWM[a]
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge, inst.	0.02	0.08	0.16	0.24	3.1	152	--
Spec. cond., field	22	32	36	39	150	151	--
pH, field	5.0	6.6	6.8	7.1	7.9	151	4.3[b]
Calcium	35	110	120	150	270	150	3.7
Magnesium	25	81	91	99	210	150	1.8
Sodium	43	100	120	130	250	151	4.9
Potassium	5.0	13	15	21	61	150	.7
Ammonium	<.7	<.7	.7	2.1	11	62	13
Alkalinity, laboratory	100	220	260	320	420	151	--
Sulfate	15	42	58	79	180	151	46
Chloride	17	45	51	63	190	150	6.1
Nitrite plus nitrate	<.7	3.6	7.1	7.1	22	97	23[c]
Silica	43	180	200	220	380	152	--

[a] Values are volume-weighted mean concentrations for 1984–94.

[b] Laboratory pH.

[c] Nitrate only.

Table 63. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ion concentrations, Holiday Creek, Virginia, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; Si, silica]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	–0.237								
Ca	–.786	0.204							
Mg	–.756	.151	0.789						
Na	–.841	.286	.739	0.813					
K	–.278	–.029	.371	.317	0.190				
Alk	–.862	.328	.821	.769	.846	0.253			
SO_4	.143	–.295	–.150	–.043	–.197	.035	–0.304		
Cl	.283	–.050	–.240	–.182	–.161	.228	–.274	–0.015	
Si	–.832	.340	.645	.663	.755	.255	.756	–.194	–0.083

would have affected the stream-water concentrations of chloride and calcium without affecting the concentrations of other constituents as well. Alternatively, chloride and calcium concentrations may have been affected by method-related activities, the most likely being a change of analytical laboratory in 1973.

Table 64. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major ion concentrations, Holiday Creek, Virginia, October 1967 through July 1995

[Trends in units of microequivalents per liter per year, except discharge in cubic meters per second per year, pH in standard units per year, and silica in micromoles per liter per year; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	<0.01	0.315	--	--
pH, field	.01	.195	0.01	0.102
Calcium	−1.1	.002	−.8	.006
Magnesium	<.1	.466	.2	.152
Sodium	<.1	.234	<−.1	.848
Potassium	<.1	.019	<−.1	.006
Alkalinity, laboratory	<.1	.321	.1	.810
Sulfate	−.1	.692	−.5	.219
Chloride	−.3	.033	−.4	.012
Nitrite plus nitrate	([a])	--	--	--
Silica	<.1	.474	.3	.223

[a] Insufficient data to calculate trend.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling of October 24, 1991, are presented in table 65; locations of sampling sites are shown in figure 32. Discharge at the gage was 0.08 m^3/s compared to the median daily discharge of 0.09 m^3/s for October (Lawrence, 1987), indicating the basin was sampled during base-flow conditions for that time of year. Solute concentrations measured at the gage (site 1) during the synoptic sampling were generally between the first- and third-quartile concentrations reported for the gage during the entire period of record (table 62). All tributary streams were similar in composition to the gage, with calcium and sodium the dominant cations and alkalinity the dominant anion. Ion balances ranged from 1.6 to 8.3 percent, indicating unmeasured organic anions appeared to be an important component of stream water during the sampling period.

Surface-water chemistry of the tributary streams varied in a pattern that appears to reflect the underlying bedrock type. Streams that drain the Chopawamsic Formation (sites 2, 3, 6, and 9) had higher concentrations of weathering-derived solutes than streams that drain the Candler Formation (sites 4, 5, 7, and 8). For example, the average alkalinity of sites 2, 3, 6, and 9 was 400 µeq/L compared to the average alkalinity of 170 µeq/L for sites 4, 5, 7, and 8. A similar pattern was observed for calcium

Table 65. Physical properties and major ion concentrations from surface-water sampling sites in the Holiday Creek Basin, Virginia, October 24, 1991

[Site locations shown on fig. 32; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium: Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; concentrations in microequivalents per liter; Si, silica in micromoles per liter; Fm, Formation; <, less than; --, not measured]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria[a]	Remarks
1	02038850	0.093	36	7.1	130	88	120	26	260	27	45	<0.7	220		
2	372512078403500	--	32	6.6	110	64	130	26	230	27	34	<.7	250	BG	Chompawamsic Fm
3	372510078392100	.003	45	7.0	160	96	150	41	360	27	39	<.7	320	BG	Chompawamsic Fm
4	372524078393600	.048	29	6.7	90	74	100	23	190	23	42	<.7	180	BG	Candler Fm
5	372525078393900	.019	29	6.7	95	70	96	24	190	23	39	<.7	180	MT, BG	Candler Fm
6	372514078384100	.006	49	7.0	180	110	170	33	410	21	42	<.7	350	BG	Chompawamsic Fm
7	372559078411300	.019	23	6.7	55	69	87	15	140	16	45	<.7	150	BG, LU	Candler Fm, logging
8	372608078400400	.012	25	6.6	60	64	87	20	150	21	39	<.7	160	BG, LU	Candler Fm, logging
9	372501078380900	.005	72	7.3	260	210	230	49	610	42	65	<.7	380	BG	Chompawamsic Fm

[a] Criteria used in selection of sampling sites: BG = bedrock geology, MT = major tributary, LU = land use.

and silica concentrations, which were consistently higher at sites 2, 3, 6, and 9 than at sites 4, 5, 7, and 8. In addition to differences in concentrations, streams that drain the Chopawamsic Formation had higher calcium-to-sodium ratios (1.8) than streams that drain the Candler Formation, which had an average ratio of 0.8. As discussed previously, rocks in the Candler Formation are composed primarily of felsic minerals, and rocks of the Chopawamsic Formation are more mafic in composition. The larger concentrations of calcium, alkalinity, and silica at sites 2, 3, 6, and 9 probably reflect the higher weathering rates of mafic minerals in the Chopawamsic Formation compared to the more felsic plagioclase and muscovite in the Candler Formation. The differences in cation ratios among the streams also reflect this difference in bedrock mineralogy. The lower calcium-to-sodium ratios at sites 4, 5, 7, and 8 are indicative of weathering of sodium-rich plagioclase, whereas the higher ratios at sites 2, 3, 6, and 9 reflect the abundance of calcium-rich minerals, such as amphibole.

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APPENDIXES

APPENDIX A. LIST OF MAP REFERENCES

1. Blackwater River near Bradley, Alabama (Station 02369800)

a. U.S. Geological Survey topographic maps:

Bradley, Alabama (1:24,000), gaging station on this quadrangle
Carolina, Alabama (1:24,000)
Dixie, Alabama (1:24,000)
Parker Springs, Alabama (1:24,000)
Wing, Alabama (1:24,000)
Andalusia, Alabama (1:100,000)

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d. Other maps:

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2. Sipsey Fork near Grayson, Alabama (Station 02450250)

a. U.S. Geological Survey topographic map:

Bee Branch, Alabama (1:24,000), gaging station on this quadrangle
Grayson, Alabama (1:24,000)
Kinlock Spring (1:24,000)
Landersville (1:24,000)
Haleyville, Alabama (1:100,000)

b. Geologic maps:

Grosz, A.E., 1981, Geochemical survey of the Sipsey Wilderness and additions, Lawrence and Winston Counties, Alabama: U.S. Geological Survey Miscellaneous Field Studies Map MF–1288–A, scale 1:50,000.

Mory, P.C., Behum, P.T., and Ross, R.B., Jr., 1982, Maps showing mines, quarries, oil and gas activity, and sample localities in and near the Sipsey Wilderness and additions, Lawrence and Winston Counties, Alabama: U.S. Geological Survey Miscellaneous Field Studies Map MF–1288–C.

Schweinfurth, S.P., Trent, V.A., and Helton, E.D., 1981, Geologic map of the Sipsey Wilderness and additions, Lawrence and Winston Counties, Alabama: U.S. Geological Survey Miscellaneous Field Studies Map MF–1288–B, scale 1:50,000.

Schweinfurth, S.P., Mory, P.C., Ross, R.B., Jr., and Behum, P.T., 1983, Mineral resource potential map of the Sipsey Wilderness and additions, Lawrence and Winston Counties, Alabama: U.S. Geological Survey Miscellaneous Field Studies Map MF–1288–D, scale 1:50,000.

c. Soil surveys:

U.S. Department of Agriculture, 1959, Soil survey of Lawrence County, Alabama: U.S. Department of Agriculture Soil Conservation Service, 64 plates, scale 1:20,000.

———1937, Soil survey of Winston County, Alabama: U.S. Department of Agriculture Soil Conservation Service.

d. Other maps:

U.S. Department of Agriculture, 1981, Sipsey Wilderness, William B. Bankhead National Forest, Alabama: U.S. Department of Agriculture Forest Service, Southern Region, scale 1:24,000.

———1985, William B. Bankhead National Forest, Alabama: U.S. Department of Agriculture Forest Service, Southern Region, scale 1:126,720.

3. Sopchoppy River near Sopchoppy, Florida (Station 02327100)

a. U.S. Geological Survey topographic maps:

Bradwell Bay, Florida (1:24,000)
Crawfordville West, Florida (1:24,000), gaging station on this quadrangle
Lake Talquin SE, Florida (1:24,000)
Ward, Florida (1:24,000)
Tallahassee, Florida(1:100,000)

b. Geologic maps:

Cameron, C.C., and Mory, P.C., 1977, Mineral resources of the Bradwell Bay Wilderness and the Sopchoppy River Study Area, Wakulla County, Florida, scale 1:48,000.

Rupert, Frank, and Spencer, Steve, 1988, Geology of Wakulla County, Florida: Florida Geological Survey Bulletin 60, 46 p.

Schmidt, Walter, 1979, Environmental Series Tallahassee sheet: Florida Bureau of Geology Map Series 90, scale 1:250,000.

c. Soil surveys:

Allen, William J., 1991, Soil survey of Wakulla County, Florida: U.S. Department of Agriculture Soil Conservation Service, 33 soil maps, scale 1:24,000.

d. Other maps:

Tanner, G.W., Soils and vegetation of the longleaf/slash pine forest type, Apalachicola National Forest, Florida: Forest Service General Technical Report SO–68, p. 186–200, maps.

U.S. Department of Agriculture, 1986, Apalachicola National Forest: U.S. Department of Agriculture Forest Service, Southern Region, scale 1:126,720.

———1986, Apalachicola National Forest—Soil-vegetation map: U.S. Department of Agriculture Forest Service, Southern Region, Florida, scale 1:24,000.

———1990, Canoeing the national forests in Florida: U.S. Department of Agriculture Forest Service, Southern Region, Florida, 1 sheet, 68 × 41 cm.

4. Falling Creek near Julliette, Georgia (Station 02212600)

a. U.S. Geological Survey topographic maps:

Berner, Georgia (1:24,000)
Dames Ferry, Georgia (1:24,000), gaging station on this quadrangle
Gray, Georgia (1:24,000)
Hillsboro, Georgia (1:24,000)
Monticello, Georgia (1:24,000)
Milledgeville, Georgia (1:100,000)

b. Geologic maps:

Ferguson, R.B., 1978, Geologic-tectonic map of Athens 1° x 2° NTMS Area, Georgia and South Carolina: National Uranium Resource Evaluation Program, E.I. du Pont de Nemours and Company, Savannah River Laboratory, scale 1:250,000.

Georgia Department of Natural Resources, 1976, Geologic map of Georgia: Atlanta, Georgia Department of Natural Resources, Georgia Geological Survey, scale 1:500,000.

Matthews, Vincent, 1967, Geology and petrology of the pegmatite district in southwest Jasper County, Georgia: Athens, University of Georgia, M.S. thesis.

c. Soil surveys:

Payne, H.H., 1976, Soil survey of Baldwin, Jones, and Putnam Counties, Georgia: U.S. Department of Agriculture Soil Conservation Service, 86 soil maps, scale 1:20,000.

U.S. Department of Agriculture, 1982, General soil map, Jasper County, Georgia: Fort Worth, Tex., U.S. Department of Agriculture Soil Conservation Service, scale 1:20,000.

d. Other maps:

U.S. Department of Agriculture, 1989, Oconee National Forest: U.S. Department of Agriculture Forest Service, Southern Region, scale 1:126,720.

Department of the Interior, 1983, Map of Piedmont National Wildlife Refuge: Department of the Interior U.S. Fish and Wildlife Service, scale 1:126,720.

5. Tallulah River near Clayton, Georgia (Station 02178400)

a. U.S. Geological Survey topographic maps:

Dillard, Georgia-North Carolina (1:24,000)
Hightower Bald, Georgia-North Carolina (1:24,000), gaging station on this quadrangle
Rainbow Springs, North Carolina (1:24,000)
Toccoa, Georgia-South Carolina-North Carolina (1:100,000)

b. Geologic maps:

Peper, J.D., Lesure, F.G., Cox, L.J., and D'Agostino, J.P., 1991, Geology, geochemistry, and mineral resource assessment of the Southern Nantahala Wilderness and adjacent roadless areas, Rabun and Towns Counties, Georgia, and Clay and Macon Counties, North Carolina: U.S. Geological Survey Bulletin 1883, 30 p.

Hatcher, R.D., Jr., 1971, The geology of Rabun and Habersham Counties, Georgia: Geological Survey of Georgia Bulletin 83.

Hadley, J.B., and Nelson, A.E., 1971, Geologic map of the Knoxville quadrangle, North Carolina and Tennessee, and South Carolina: U.S. Geological Survey Miscellaneous Investigations Series Map I–654, scale 1:250,000.

c. Soil surveys:

Carson, W.S., and Green, T.W., 1981, Soils survey of Rabun and Towns Counties, Georgia: U.S. Department of Agriculture Soil Conservation Service, p. 97, 76 folded plates.

d. Other maps:

U.S. Department of Agriculture, 1986, Map of Chattahoochee National Forest, Georgia: U.S. Department of Agriculture Forest Service, Southern Region, scale 1:126,720.

———1986, Map of Southern Nantahala Wilderness and Standing Indian Area, Chattahoochee and Nantahala National Forests, Georgia and North Carolina: U.S. Department of Agriculture Forest Service, Southern Region, scale 1:126,720.

6. Wild River at Gilead, Maine (Station 01054200)

a. U.S. Geological Survey topographic maps:

Carter Dome, New Hampshire (1:24,000)

Chatham, New Hampshire (1:24,000)

Gilead, Maine (1:24,000), gaging station on this quadrangle

Jackson, New Hampshire (1:24,000)

Speckled Mountain, Maine (1:24,000)

Wild River, New Hampshire-Maine (1:24,000)

Mount Washington, New Hampshire-Vermont-Maine (1:100,000)

b. Geologic maps:

Bothner, W.A., Jahrling, C.E., and Kucks, R.P., 1986, Bouguer gravity and aeromagnetic maps of the wildernesses and roadless areas of the White Mountain National Forest, Coos, Carroll, and Grafton Counties, New Hampshire: U.S. Geological Survey Miscellaneous Field Studies Map MF–1594–D, scale 1:125,000.

Gazdik, G.C., Harris, L.E., Welsh, R.A., Jr., and Girol, V.P., 1988, Mines, prospects, and mineral sites, wilderness and RARE II areas, White Mountain National Forest, New Hampshire: U.S. Geological Survey Miscellaneous Field Studies Map MF–1594–E, scale 1:125,000.

Hatch, N.L., Jr., and Moench, R.H., 1984, Bedrock geologic map of the wildernesses and roadless areas of the White Mountain National Forest, Coos, Carroll, and Grafton Counties, New Hampshire: U.S. Geological Survey Miscellaneous Field Studies Map MF–1594–A, scale 1:125,000.

Moench, R.H., Canney, F.C., and Gazdik, G.C., 1984, Mineral resource potential map of the wilderness and roadless areas of the White Mountain National Forest, Coos, Grafton, and Carroll Counties, New Hampshire: U.S. Geological Survey Miscellaneous Field Studies Map MF–1594–B, scale 1:125,000.

c. Soil surveys:

Williams, B.H., Coates, W.H., and Scripture, P.N., 1948, Soil survey of Coos County, New Hampshire: U.S. Department of Agriculture Soil Conservation Service, Series 1937, no. 5, 99 p.

d. Other maps:

U.S. Department of Agriculture, 1995, White Mountain National Forest, New Hampshire and Maine: U.S. Department of Agriculture Forest Service, Eastern Region, scale 1/4 inch = 1 mile.

7. Cypress Creek near Janice, Mississippi (02479155)

a. U.S. Geological Survey topographic maps:

Beaumont, Mississippi (1:24,000)
Janice, Mississippi (1:24,000), gaging station on this quadrangle
New Augusta, Mississippi (1:24,000)
Taylor Hill, Mississippi (1:24,000)
Hattiesburg, Mississippi-Louisiana (1:100,000)

b. Geologic maps:

Bicker, A.R., 1969, Geologic Map of Mississippi: Mississippi Geological Survey, scale 1:500,000.

Brown, G.F., 1944, Geology and ground-water resources of the Camp Shelby area: Mississippi State Geological Survey Bulletin 58, scale 1:316,800.

Brandwein, S.S., and White, R.M., 1983, Surface geologic reconnaissance of Cypress Creek Dome, Perry County, Mississippi: Prepared by Law Engineering Testing Company under Contract DE-AC06-76-RLO1830–ONWI with the U.S. Department of Energy, scale 1:24,000.

c. Soil surveys:

U.S. Department of Agriculture, 1935, Soils survey of Perry County: U.S. Department of Agriculture Soil Conservation Service.

d. Other maps:

U.S. Department of Agriculture, 1993, De Soto National Forest, Mississippi, St. Stephens Meridian: U.S. Department of Agriculture Forest Service, Southern Region, scale 1:126,720.

8. McDonalds Branch in Lebanon State Forest, New Jersey (Station 01466500)

a. U.S. Geological Survey topographic maps:

Woodmansie, New Jersey (1:24,000)
Whiting, New Jersey (1:24,000)
Browns Mills, New Jersey (1:24,000), gaging station on this quadrangle
Hammonton, New Jersey (1:100,000)

b. Geologic maps:

Lord, D.G., Barringer, J.L., Johnsson, P.A., Schuster, P.A., Walker, R.L., Fairchild, J.E., Sroka, B.N., and Jacobsen, Eric, 1990, Hydrogeochemical data from an acidic deposition study at McDonalds Branch basin in the New Jersey Pinelands, 1983–1986: U.S. Geological Survey Open-File Report 88–500, geologic map of the watershed, scale 1:24,000, p. 8.

Minard, J.P., and Owens, J.P., 1963, Pre-Quaternary geology of the Browns Mills Quadrangle, New Jersey: U.S. Geological Survey Quadrangle Map GQ–264, scale 1:24,000.

Owens, J.P., and Minard, J.P., 1975, Geologic map of the surficial deposits in the Trenton area, New Jersey and Pennsylvania: U.S. Geological Survey Miscellaneous Geologic Investigations Map I–884, scale 1:24,000.

c. Soil surveys:

Lord, D.G., Barringer, J.L., Johnsson, P.A., Schuster, P.A., Walker, R.L., Fairchild, J.E., Sroka, B.N., and Jacobsen, E., 1990, Hydrogeochemical data from an acidic deposition study at McDonalds Branch basin in the New Jersey Pinelands, 1983–1986: U.S. Geological Survey Open-File Report 88–500, soils map of the watershed, scale 1:24,000, p. 11.

Markley, M.L., 1971, Soil survey of Burlington County: Somerset, New Jersey, U.S. Department of Agriculture Soil Conservation Service.

d. Other maps:

Andropogon Associates, 1981, Vegetation maps of the Pinelands, New Lisbon, N.J., prepared for New Jersey Pinelands Commission.

Lord, D.G., Barringer, J.L., Johnsson, P.A., Schuster, P.A., Walker, R.L., Fairchild, J.E., Sroka, B.N., and Jacobsen, E., 1990, Hydrogeochemical data from an acidic deposition study at McDonalds Branch basin in the New Jersey Pinelands, 1983–1986: U.S. Geological Survey Open-File Report 88–500, vegetation map of the watershed, scale 1:24,000, p. 18.

9. Esopus Creek at Shandaken, New York (Station 01362198)

a. U.S. Geological Survey topographic maps:

Seager, New York (1:24,000)
Shandaken, New York (1:24,000), gaging station on this quadrangle
West Kill, New York (1:24,000)
Pepacton Reservoir, New York (1:100,000)

b. Geologic maps:

Fisher, D.W., Isachsen,Y.W., and Richard, L.V., 1970, Geologic map of New York, Hudson-Mohawk sheet: New York State Museum and Science Service, Map and Chart Series 15, scale 1:250,000.

Rich, J.L., 1934, Glacial geology of the Catskills: New York State Museum Bulletin 299, map of the Catskill Mountains showing glacial geology, scale 1:125,000.

c. Soil surveys:

Broad, William A., 1993, Soil survey of Greene County, New York: Department of Agriculture Soil Conservation Service in cooperation with Cornell University Agricultural Experiment Station, 349 p., 48 folded plates, scale 1:15,840.

Tornes, L.A., 1979, Soil survey of Ulster County, New York: U.S. Department of Agriculture Soil Conservation Service, 273 p., 140 folded plates, scale 1:15,840.

d. Other maps:

Catskill Trails, 1987, A five-map set published by the New York-New Jersey Trails Conference.

10. Cataloochee Creek near Cataloochee, North Carolina (Station 03460000

a. U.S. Geological Survey topographic maps:

Bunches Bald, North Carolina (1:24,000)
Cove Creek Gap, North Carolina (1:24,000), gaging station on this quadrangle
Dellwood, North Carolina (1:24,000)
Knoxville, Tennessee-North Carolina (1:100,000)
Great Smoky Mountains National Park, Tennessee and North Carolina, east half (1:62,500)

b. Geologic maps:

King, P.B., 1968, Geology of the Great Smoky Mountains National Park Tennessee and North Carolina: U.S. Geological Survey Professional Paper 587, scale 1:125,000.

Hadley, J.B., and Goldsmith, R.M., 1963, Geology of the eastern Great Smoky Mountains, North Carolina and Tennessee: U.S. Geological Survey Professional Paper 349–B, scale 1:62,500.

c. Soil surveys:

Soil Conservation Service, 1997, Soil survey of Haywood County excluding Great Smoky Mountains National Park, North Carolina: U.S. Department of Agriculture Soil Conservation Service.

d. Other maps:

Earthwalk Press, 1990, Earthwalk Press hiking map and guide, Great Smoky Mountains National Park, scale 1:62,500.

MacKenzie, M.D., 1991, Vegetation map of Great Smoky Mountains National Park based on landsat thematic mapper data—Accuracy assessment and numerical description of vegetation types: Knoxville, University of Tennessee, Cooperative Park Studies Unit, 11 p.

McMaster, W.M., and Hubbard, E.F., 1970, Water resources of the Great Smoky Mountains National Park, Tennessee and North Carolina: U.S. Geological Survey Hydrologic Investigations Atlas HA–420, scale 1:125,000.

National Park Service, 1988, Great Smoky Mountains National Park trail map, North Carolina/Tennessee: U.S. Department of the Interior, National Park Service, 40 × 55 cm, scale 1:168,000.

11. Young Womans Creek near Renovo, Pennsylvania (Station 01545600)

a. U.S. Geological Survey topographic maps:

Oleona, Pennsylvania (1:24,000)
Lee Fire Tower, Pennsylvania (1:24,000)
Slate Run, Pennsylvania (1:24,000)
Young Womans Creek, Pennsylvania (1:24,000), gaging station on this quadrangle
Williamsport West, Pennsylvania (1:100,000)
Wellsboro, Pennsylvania (1:100,000)

b. Geologic maps:

Chance, H.M., 1880, Geology of Clinton County: Pennsylvania Geological Survey Report G–4, scale 1:126,72.

Sherwood, Andrew, 1880, Geology of Potter County, Pennsylvania Geological Survey Report G–3, scale 1:126,720.

Ebright, J.R., and Ingham, A.L., 1951, Geology of the Leidy gas field and adjacent areas, Clinton County: Pennsylvania Geological Survey Circular 350, scale 1:48,000.

Colton, G.W., and Stanley, J.L., 1965, Bedrock geology of the Slate Run quadrangle, Clinton, Lycoming, and Potter Counties, Pennsylvania: Pennsylvania Topographic and Geologic Survey Progress Report 167, scale 1:24,000.

c. Soil surveys:

Steputis, W.J., 1966, Soil survey of Clinton County, Pennsylvania: U.S. Department of Agriculture Soil Conservation Service, 141 p.

U.S. Department of Agriculture, 1958, Soil survey of Potter County, Pennsylvania: U.S. Department of Agriculture Soil Conservation Service.

d. Other maps:

Sproul and Susquehannock State Forest Public Use Maps: Department of Environmental Resources, Office of Resources Management, Bureau of Forestry, Commonwealth of Pennsylvania, scale 1:126,720.

Taylor, L.E., Werkheiser, W.H., and Kriz, M.L., 1983, Groundwater resources of the West Branch Susquehanna River Basin, Pennsylvania: Pennsylvania Geological Survey, Water Resource Report 56, scale 1:250,000.

U.S. Geological Survey, 1977, Land use and land cover and associated maps of Williamsport, Pennsylvania and New York: U.S. Geological Survey Open-File Report 77–0107, scale 1:250,000.

12. Scape Ore Swamp near Bishopville, South Carolina (Station 02135300)

a. U.S. Geological Survey topographic maps:

Bishopville West, South Carolina (1:24,000), gaging station on this quadrangle
Cassatt, South Carolina (1:24,000)
Lucknow, South Carolina (1:24,000)
Spring Hill, South Carolina (1:24,000)
Camden, South Carolina (1:100,000)

b. Geologic maps:

Cooke, Wythe B., 1936, Geology of the Coastal Plain of South Carolina: U.S. Geological Survey Bulletin 867, 196 p., 2 maps, scale 1:500,000.

c. Soil surveys:

Mitchell, Cleveland J., Jr., 1990, Soil survey of Kershaw County area, South Carolina: U.S. Department of Agriculture Soil Conservation Service, 165 p., 65 maps.

U.S. Department of Agriculture, 1963, Soil survey of Lee County, South Carolina: U.S. Department of Agriculture Soil Conservation Service.

d. Other maps:

U.S. Department of Agriculture, 1991, Important farmlands, Lee County, South Carolina: Columbia, S.C., U.S. Department of Agriculture Soil Conservation Service in cooperation with South Carolina Land Resources Conservation, scale 1:100,000.

13. Upper Three Runs near New Ellenton, South Carolina (Station 02197300)

a. U.S. Geological Survey topographic maps:

Aiken, South Carolina (1:24,000)
New Ellenton, South Carolina (1:24,000)
New Ellenton SW, South Carolina (1:24,000), gaging station on this quadrangle
Oakwood, South Carolina (1:24,000)
Windsor, South Carolina (1:24,000)
Barnwell, South Carolina (1:100,000)

b. Geologic maps:

Prowell, David D., 1994, Preliminary geologic map of the Barnwell 30" × 60" quadrangle: U.S. Geological Survey Open-File Report 94–673, scale 1:100,000.

———1994, Preliminary geologic map of the Savannah River site, Aiken, Allendale, and Barnwell Counties, South Carolina: U.S. Geological Survey Open-File Report 94–181, 14 p., 1 map, scale 1:48,000.

Smith, G.E., 1979, Geologic map of Aiken County, South Carolina, exclusive of Savannah River Plant: Columbia, South Carolina Geological Survey.

Siple, George E., 1967, Geology and ground water of the Savannah River Plant and vicinity, South Carolina: U.S. Geological Survey Water-Supply Paper 1841, 113 p.

c. Soil surveys:

Rogers, Vergil A., 1990, Soil survey of Savannah River Plant area and parts of Aiken, Barnwell, and Allendale Counties, South Carolina: U.S. Department of Agriculture Soil Conservation Service, 127 p., 46 soil maps, scale 1:15,840.

———1985, Soil survey of Aiken County area, South Carolina: U.S. Department of Agriculture Soil Conservation Service, 134 p., 76 soil maps, scale 1:20,000.

14. Buffalo River near Flat Woods, Tennessee (Station 03604000)

a. U.S. Geological Survey topographic maps:

Deerfield, Tennessee (1:24,000)
Ethridge, Tennessee (1:24,000)
Graves Spring, Tennessee (1:24,000)
Henerysville, Tennessee (1:24,000)
Kimmins, Tennessee (1:24,000)
Leatherwood, Tennessee (1:24,000), gaging station on this quadrangle
Negro Hollow, Tennessee (1:24,000)
Ovilla, Tennessee (1:24,000)
Riverside, Tennessee (1:24,000)
Summertown, Tennessee (1:24,000)
Topsy, Tennessee (1:24,000)
Waynseboro, Tennessee (1:24,000)
Hohenwald, Tennessee (1:100,000)
Lawrenceburg, Tennessee-Alabama (1:100,000)

b. Geologic maps:

Barnes, R.H., Lounsbury, R.E., and Moore, G.K., 1966, Geologic map of the Graves Spring quadrangle, Tennessee: Tennessee Division of Geology GM 41–SW, scale 1:24,000.

Lounsbury, R.E., and Marcher, M.V., 1964, Geologic map of the Ethridge quadrangle, Tennessee: Tennessee Division of Geology GM 51–SE, scale 1:24,000.

Marcher, M.V., 1963, Geologic map of the Ovilla quadrangle, Tennessee: Tennessee Division of Geology GM 42–SE, scale 1:24,000.

———1965, Geologic map of the Kimmins quadrangle, Tennessee: Tennessee Division of Geology GM 41–SE, scale 1:24,000.

Marcher, M.V., and Lounsbury, R.E., 1964, Geologic map of the Deerfield quadrangle, Tennessee: Tennessee Division of Geology GM 51–SW, scale 1:24,000.

———1965, Geologic map of the Henerysville quadrangle, Tennessee: Tennessee Division of Geology GM 51–NW, scale 1:24,000.

———1966, Geologic map of the Summertown quadrangle, Tennessee: Tennessee Division of Geology GM 51–NE, scale 1:24,000.

Marcher, M.V., and Wilson, C.W., 1963, Geologic map of the Negro Hollow quadrangle, Tennessee: Tennessee Division of Geology GM 42–SW, scale 1:24,000.

Wilson, C.W., Jr., 1969, Geologic map of the Leatherwood quadrangle, Tennessee: Tennessee Division of Geology GM 33–NE, scale 1:24,000.

Wilson, C.W., Jr., and Marcher, M.V., 1963, Geologic map of the Topsy quadrangle, Tennessee: Tennessee Division of Geology GM 42–NW, scale 1:24,000.

———1963, Geologic map of the Riverside quadrangle, Tennessee: Tennessee Division of Geology GM 42–NE, scale 1:24,000.

Wilson, C.W., Jr., Stearns, R.G., and Marcher, M.V., 1971, Geologic map of the Waynseboro quadrangle, Tennessee: Tennessee Division of Geology GM 33–SE, scale 1:24,000.

c. Soil surveys:

Overton, J.R., 1959, Soil survey of Lawrence County, Tennessee: Nashville, Tenn., U.S. Department of Agriculture Soil Conservation Service, 61 p., 49 soil maps.

Soil Conservation Service, 1975, General soil map, Lewis County, Tennessee: Nashville, Tenn., U.S. Department of Agriculture Soil Conservation Service, scale 1:126,720.

d. Other maps:

U.S. Department of the Interior, 1985, Natchez Trace Parkway, Mississippi, Alabama, and Tennessee—Official map and guide: Washington, D.C., U.S. Department of the Interior National Park Service.

Tennessee Valley Authority, 1981, Important farmland in Perry County, Tennessee: Tennessee Valley Authority in cooperation with the Soil Conservation Service, scale 1:100,000.

15. Little River above Townsend, Tennessee (Station 03497300)

a. U.S. Geological Survey topographic maps:

Cades Cove, Tennessee-North Carolina(1:24,000)
Clingmans Dome, North Carolina-Tennessee (1:24,000)
Gatlinburg, Tennessee (1:24,000)
Silers Bald, North Carolina-Tennessee (1:24,000)
Thunderhead Mountain, North Carolina-Tennessee (1:24,000)
Wear Cove, Tennessee (1:24,000), gaging station on this quadrangle
Knoxville, Tennessee-North Carolina (1:100,000)
Great Smoky Mountains National Park, Tennessee and North Carolina, West Half (1:62,500)

b. Geologic maps:

King, P.B., 1968, Geology of the Great Smoky Mountains National Park Tennessee and North Carolina: U.S. Geological Survey Professional Paper 587, scale 1:250,000.

———1963, Geology of the central Great Smoky Mountains, Tennessee: U.S. Geological Survey Professional Paper 349–C, scale 1:62,500.

c. Soil surveys:

Elder, J.A., 1953, Soil survey of Blount County, Tennessee: U.S. Department of Agriculture Soil Conservation Service, p. 119.

Hubbard, E.H., 1956, Soil survey of Sevier County, Tennessee: U.S. Department of Agriculture Soil Conservation Service, p. 203.

d. Other maps:

Earthwalk Press, 1990, Earthwalk Press hiking map and guide, Great Smoky Mountains National Park, scale 1:62,500.

MacKenzie, M.D., 1991, Vegetation map of Great Smoky Mountains National Park based on landsat thematic mapper data—Accuracy assessment and numerical description of vegetation types: Knoxville, University of Tennessee, Cooperative Park Studies Unit, 11 p.

McMaster, W.M., and Hubbard, E.F., 1970, Water resources of the Great Smoky Mountains National Park, Tennessee and North Carolina: U.S. Geological Survey Hydrologic Investigations Atlas HA–420, scale 1:125,000.

National Park Service, 1988, Great Smoky Mountains National Park trail map, North Carolina/Tennessee: U.S. Department of the Interior, National Park Service, 40 × 55 cm, scale 1:168,000.

16. Holiday Creek near Andersonville, Virginia (Station 02038850)

a. U.S. Geological Survey topographic maps:

Andersonville, Virginia (1:24,000)

Holiday Lake, Virginia (1:24,000), gaging station on this quadrangle

Appomattox, Virginia (1:100,000)

b. Geologic maps:

Marr, J.D., Jr., 1980, Geology of the Andersonville quadrangle, Virginia: Virginia Division of Mineral Resources, scale 1:24,000.

c. Soil surveys:

U.S. Department of Agriculture, in press, Soil survey of Appomattox County, Virginia: U.S. Department of Agriculture Soil Conservation Service.

APPENDIX B. NWIS SITE-IDENTIFICATION NUMBERS

Table B–1. NWIS site-identification numbers and site names for water-quality sampling sites in Hydrologic Benchmark Network basins discussed in this report

Site[a]	Identification number[b]	Site name
		BLACKWATER RIVER BASIN, ALABAMA
1	02369800	BLACKWATER RIVER NR BRADLEY AL
2	310159086425800	FISH TRAP BR AT BRADLEY AL
3	310337086440500	MILLER CR AT FS RD 311 NR BRADLEY AL
4	310556086431000	BEAR CR AT FS RD 305 NR DIXIE AL
5	310556086431100	BEAR HEAD CR AT FS RD 311 NR BRADLEY AL
6	310421086411800	HURRICANE CR AT COUNTY RD 68 NR BRADLEY AL
7	310423086400200	PANTHER CR AT COUNTY RD 68 NR BRADLEY AL
8	310259086382100	BLACKWATER CR NR FALCO AL
9	310533086365700	BLACKWATER CR NR POSSUM POCKET AL
		SIPSEY FORK BASIN, ALABAMA
1	02450250	SIPSEY FORK NEAR GRAYSON AL
2	341750087242300	FALL CR AT MOUTH
3	341750087242500	UPPER SIPSEY FORK
4	341754087234200	FIRST EAST TRIB
5	341826087301200	HUBBARD CR
6	341947087223700	BORDEN CR
7	341834087234000	BORDEN CR SECTION 32
8	342019087231700	FLANNAGIN CR
9	342027087281600	THOMPSON CR
10	342224087225300	UPPER FLANNAGIN CR
		SOPCHOPPY RIVER BASIN, FLORIDA
1	02327100	SOPCHOPPY RIVER NR SOPCHOPPY FL
2	300930084312200	MONKEY CREEK
3	301012084295400	SOPCHOPPY R AT S END WILDERNESS
4	301353084321900	SOPCHOPPY R AT N END WILDERNESS
5	301518084352300	EAST BR SOPCHOPPY R
6	301521084355300	WEST BR SOPCHOPPY R
		FALLING CREEK BASIN, GEORGIA
1	02212600	FALLING CREEK NR JULIETTE GA
2	330754083444500	TRIBBLE FIELDS CR
3	330755083444200	LITTLE FALLING CR
4	330739083394500	ROUND OAK CR
5	330757083401400	ALLISONS CR
6	330807083391800	TREE FARM CR
7	331032083410900	HILLSBORO CR
8	331126083411600	TOWN/FREEMAN CR
9	331112083432700	STALKING HEAD CR
10	331139083464200	GLADESVILLE CR
11	331303083413200	FALLING CREEK BELOW SWAMP
		TALLULAH RIVER BASIN, GEORGIA
1	02178400	TALLULAH RIVER NR CLAYTON GA
2	345324083314500	PERSIMMON CR BLW PERSIMMON
3	345407083305200	HIGH SHOALS CR NR PERSIMMON

Table B–1. NWIS site-identification numbers and site names for water-quality sampling sites in Hydrologic Benchmark Network basins discussed in this report—Continued

Site[a]	Identification number[b]	Site name
		TALLULAH RIVER BASIN, GEORGIA—Continued
4	345447083300300	LITTLE PERSIMMON CR NR PERSIMMON
5	345448083300700	PERSIMMON CR AB PERSIMMON
6	345509083335600	PLUMORCHARD CR NR PERSIMMON
7	345549083324600	COLEMAN R NR TATE CITY
8	345706083331300	CHARLIES CREEK NR TATE CITY
9	345739083332700	TALLULAH R BLW TATE CITY
10	345924083332500	BEECH CR NR TATE CITY
11	350043083332600	TALLULAH R AB TATE CITY
		WILD RIVER BASIN, MAINE
1	01054200	WILD RIVER AT GILEAD, ME
2	441459071060200	UNAMED TRIBUTARY TO WILD RIVER NR NORTH BALDFACE, ME
3	441607071062300	SPRUCE BROOK NR GILEAD, ME
4	441647071033500	BLUE BROOK AT BLUE BROOK SHELTER, ME
5	441751071032600	UNAMED TRIBUTARY TO BLUE BROOK NR GILEAD, ME
6	441758071043900	WILD RIVER AT WILD RIVER CAMPGROUND, ME
7	441806071045100	MORIAH BROOK NR GILEAD, ME
8	442035070585100	EVANS BROOK AB MORRISON BROOK NR GILEAD, ME
9	442037070584700	MORRISON BROOK NR GILEAD, ME
10	442115070594100	UNAMED TRIBUTARY TO WILD RIVER NR HASTINGS, ME
11	442213070592900	LITTLE LARY BROOK NR GILEAD, ME
		CYPRESS CREEK BASIN, MISSISSIPPI
1	02479155	CYPRESS CR NR JANICE MS
2	310223089000700	FAIRCHILD CR NR JANICE MS
3	310415088590100	JOES CR NR OAK GROVE MS
4	310501089011200	ASHLEY CR NR JANICE MS
5	310620088582000	SHUTEYE CR NR BOMBING RANGE NR OAK GROVE MS
6	310542088595200	SHUTEYE CR AT HWY 29 NR OAK GROVE MS
7	310621088582100	BOMBING RANGE TRIB NR OAK GROVE MS
8	310711089005400	UPPER CYPRESS CR AT HWY 29 NR NEW AUGUSTA MS
9	310743089015000	REDHILL BR NR NEW AUGUSTA MS
10	310801089014500	SWEETWATER CR NR NEW AUGUSTA MS
		MCDONALDS BRANCH BASIN, NEW JERSEY
S–10	01466500	MCDONALDS BRANCH IN LEBANON STATE FOREST NJ
S–1	395216074294000	S-1 NJ
		ESOPUS CREEK BASIN, NEW YORK
1	01362198	ESOPUS CREEK AT SHANDAKEN, NY
2	420723074240200	BUSHNELLSVILLE CREEK NEAR SHANDAKEN, NY
3	420618074265400	BIRCH CEEKR NR BIG INDIAN, NY
4	420656074271200	ROCHESTER HOLLOW CREEK NEAR BIG INDIAN, NY
5	420912074274400	BIRCH CREEK AT PINE HILL, NY
6	420459074265600	HATCHERY HOLLOW CR NR BIG INDIAN NY
7	420551074265800	ESOPUS CR BLW OLIVEREA NY
8	420414074282900	MCKENLEY HOLLOW CR NR OLIVEREA NY
9	420317074272700	ESOPUS CR AB OLIVEREA NY
10	420200074251400	GIANT LEDGE CR NR OLIVEREA NY
11	420057074244600	TRIBUTARY BLW WINNISOOK LK NR OLIVEREA NY

Table B–1. NWIS site-identification numbers and site names for water-quality sampling sites in Hydrologic Benchmark Network basins discussed in this report—Continued

Site[a]	Identification number[b]	Site name
CATALOOCHEE CREEK BASIN, NORTH CAROLINA		
1	03460000	CATALOOCHEE CREEK NEAR CATALOOCHEE NC
2	353623083074400	ROUGH FORK
3	353744083051900	CALDWELL FORK NR NELLIE
4	353746083070100	PALMER CREEK AT NELLIE
5	353752083051800	PALMER CR AT CAMPGROUND NR NELLIE
6	353802083050600	LOWER DOUBLE BRANCH NR NELLIE
7	353820083075100	PALMER CR AB PRETTY HOLLOW NR NELLIE
8	353831083074400	PRETTY HOLLOW NR NELLIE
9	353844083043100	WINDING STAIR BRANCH NR NELLIE
YOUNG WOMANS CREEK BASIN, PENNSYLVANIA		
1	01545600	YOUNG WOMANS CR NR RENOVO PA
2	412335077410700	LAURELLY FORK NR RENOVO PA
3	412554077401600	MCCRANEY RUN NR RENOVO PA
4	412607077395100	BULL RUN NR RENOVO PA
5	412748077374600	COUNTY LINE BRANCH NR RENOVO PA
6	412753077374800	LEBO RUN NR RENOVO PA
7	412812077365600	N BALDWIN BRANCH NR RENOVO PA
8	412919077385600	BIG SPRING BRANCH NR RENOVO PA
9	413021077385000	LEBO RUN AB BIG TRESTLE RUN NR RENOVO PA
SCAPE ORE SWAMP BASIN, SOUTH CAROLINA		
1	02135300	SCAPE ORE SWAMP NR BISHOPVILLE SC
2	340910080184900	BEAVERDAM CREEK AT MOUTH
3	341230080195100	GUM SPRINGS BRANCH
4	341321080210300	CEDAR CR
5	341335080214900	SCAPE ORE SWAMP ABOVE I-20
6	341322080221300	I-20 BRANCH
7	341141080241800	BEAVERDAM CREEK AT MCLEODS POND
8	341232080253400	UPPER BEAVERDAM CR
9	341354080223200	SOUTH MCGEE BRANCH
10	341528080231900	TIMBER CR
11	341539080263100	NANCY BR
12	341812080221000	BLACK CR AT COUNTY LINE
UPPER THREE RUNS BASIN, SOUTH CAROLINA		
1	02197300	UPPER THREE RUNS NR NEW ELLENTON SC
2	332304081370600	JOHNSON FORK
3	332330081361500	BOGGY GUT
4	332629081380100	CEDAR CR
5	332838081351700	UPPER THREE RUNS BELOW MILLPOND
BUFFALO RIVER BASIN, TENNESSEE		
1	03604000	BUFFALO RIVER NEAR FLAT WOODS TN
2	352603087411500	FORTYEIGHT CREEK NEAR MOUTH
3	352718087363100	ROCKHOUSE CREEK AT MOUTH
4	353624087355500	ALLENS CREEK NEAR RIVERSIDE
5	352620087283200	SQUAW BRANCH NEAR NAPIER
6	352620087283000	CHIEF CREEK BLW RESERVOIR
7	352620087243100	NOMEET CREEK NEAR BARNESVILLE

Table B–1. NWIS site-identification numbers and site names for water-quality sampling sites in Hydrologic Benchmark Network basins discussed in this report—Continued

Site[a]	Identification number[b]	Site name
		BUFFALO RIVER BASIN, TENNESSEE–Continued
8	352601087231600	SAW CREEK AT BARNESVILLE
9	352549087462500	GREEN RIVER NEAR MOUTH
10	352355087195800	BUFFALO RIVER AT BUFFALO ROAD
		LITTLE RIVER BASIN, TENNESSEE
1	03497300	LITTLE RIVER AB TOWNSEND TN
2	353906083424700	MEADOW BRANCH AB TOWNSEND
3	353648083443600	LAUREL CREEK AB TOWNSEND
4	353919083423600	WEST PRONG AB TOWNSEND
5	353926083423100	MIDDLE PRONG AB TOWNSEND
6	353741083421900	WEST PRONG AB LAUREL CREEK AB TOWNSEND
7	353631083401100	SAMS CREEK AB TOWNSEND
8	353552083335500	GOSHEN PRONG AB ELKMONT
9	353616083334800	SLIDE HOLLOW AB ELKMONT
10	353708083322200	FISH CAMP PRONG AB ELKMONT
11	353709083321500	LITTLE RIVER AB FISH CAMP PRONG AB ELKMONT
12	353958083380500	LITTLE RIVER BLW ELKMONT
13	353835083350800	JAKES CREEK NR ELKMONT
14	353900083334900	LITTLE RIVER AB ELKMONT
		HOLIDAY CREEK BASIN, VIRGINIA
1	02038850	HOLIDAY CR NR ANDERSONVILLE VA
2	372512078403500	RESTRICTED RD TRIB NR ANDERSONVILLE VA
3	372510078392100	FIRST W TRIB NR ANDERSONVILLE VA
4	372524078393600	HOLIDAY CR AT STATE RD 640 NR ANDERSONVILLE VA
5	372525078393900	N HOLIDAY CR AT MOUTH NR ANDERSONVILLE VA
6	372514078384100	WEST CHOMPAWAMSIC CR NR ANDERSONVILLE VA
7	372559078411300	HOLIDAY CR AT OLD RICHMOND RD NR ANDERSONVILLE VA
8	372608078400400	N HOLIDAY CR AT OLD RICHMOND RD NR ANDERSONVILLE VA
9	372501078380900	EAST CHOMPAWAMSIC CR NR ANDERSONVILLE VA

[a] Site numbers correspond to sampling sites shown in figures 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, and 32.

[b] Used for identification in the U.S. Geological Survey National Water Information System (NWIS).

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