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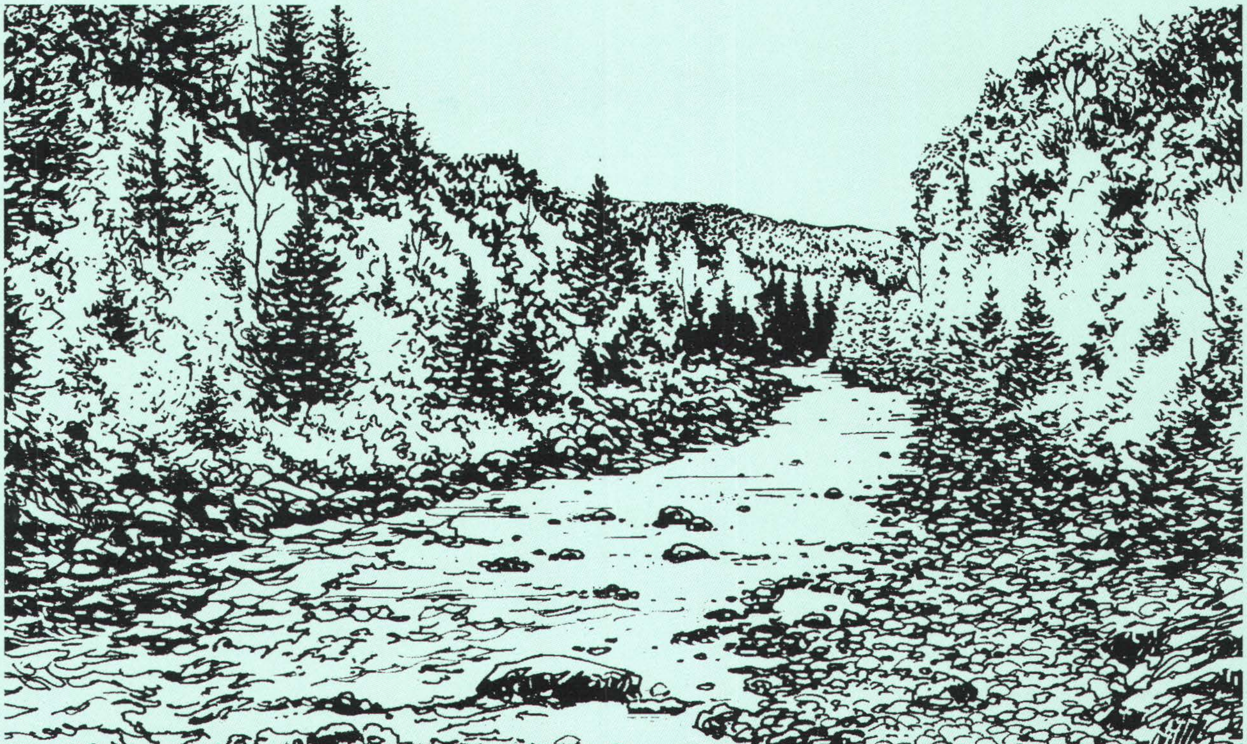
Environmental Characteristics and Water Quality of Hydrologic Benchmark Network Stations in the Midwestern United States, 1963–95



U.S. Geological Survey Circular 1173–B

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

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

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U.S. DEPARTMENT OF THE INTERIOR
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FOREWORD

In 1962, Luna Leopold, Chief of the U.S. Geological Survey's Water Resources Division from 1957–66, 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," consists of a series of four individual circulars that include stations in (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 is intended to provide information that will aid researchers and others in the application and interpretation of historical data collected as part of the Hydrologic Benchmark Network Program.

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
square kilometer (km^2)	0.386	square mile
microequivalent per liter alkalinity (µeq/L)	0.0500	milligram per liter alkalinity (as $CaCO_3$)
microequivalent per liter ammonium (µeq/L)	0.0140	milligram per liter ammonium (as nitrogen)
microequivalent per liter calcium (µeq/L)	0.0200	milligram per liter calcium
microequivalent per liter chloride (µeq/L)	0.0355	milligram per liter chloride
microequivalent per liter magnesium (µeq/L)	0.0122	milligram per liter magnesium
microequivalent per liter nitrite plus nitrate (µeq/L)	0.0140	milligram per liter nitrite plus nitrate (as nitrogen)
microequivalent per liter potassium (µeq/L)	0.0391	milligram per liter potassium
micromole per liter silica (µmol/L)	0.0602	milligram per liter silica
microequivalent per liter sodium (µeq/L)	0.0230	milligram per liter sodium
microequivalent per liter sulfate (µeq/L)	0.0480	milligram per liter sulfate

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

$$°F = 9/5\ (°C) + 32$$

Additional abbreviations used in this report:

cubic meter per second per year ($(m^3/s)/yr$)
milliequivalent per 100 grams (meq/100 g)
milligram per liter (mg/L)
microequivalent per liter per year ((µeq/L)/yr)
micrometer (µm)
micromole per liter per year ((µmol/L)/yr)
microsiemens per centimeter at 25 degrees Celsius (µS/cm)

Environmental Characteristics and Water Quality of Hydrologic Benchmark Network Stations in the Midwestern 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 14 benchmark basins in the Midwestern United States. The stations discussed in this report and their physiographic provinces are as follows: Cossatot River, Arkansas, and Kiamichi River, Oklahoma, in the Ozark Plateaus; North Sylamore Creek, Arkansas, in the Ouachita Province; South Hogan Creek, Indiana, Elk Creek, Iowa, North Fork Whitewater River, Minnesota, and Blue Beaver Creek, Oklahoma, in the Central Lowland; Big Creek, Louisiana, in the Coastal Plain; Washington Creek, Michigan, Kawishiwi River, Minnesota, and Popple River, Wisconsin, in the Superior Upland; Upper Twin Creek, Ohio, in the Interior Low Plateaus; and Devils River, Texas, and South Fork Rocky Creek, Texas, in the Great Plains. The information in this report was compiled to aid in the application and interpretation of historical water-quality data collected by the U.S. Geological Survey Hydrologic Benchmark Network program.

The Hydrologic Benchmark Network streams discussed in this report drain either forested areas or grasslands with a variety of land-use activities that range from recreational use, timber harvesting, and military training on publicly owned land to agriculture and residential development on privately owned land. In most of the basins, stream-water chemistry appeared to be controlled by the interaction of dilute precipitation with the underlying soils and bedrock. Land use had a minimal effect on stream-water chemistry at the Hydrologic Benchmark Network stations, except for South Hogan Creek, Indiana, Elk Creek, Iowa, and North Fork Whitewater River, Minnesota, which were influenced by upstream agricultural activities, road salting, or wastewater discharge. Temporal trends in water-quality constituents were observed at a number of stations and were attributed to environmental and method-related factors. Upward trends in major solutes and nutrients in the North Fork Whitewater River, Minnesota, were probably caused by agricultural activities in the basin, particularly dairy operations. Trends in base cations, alkalinity, and sulfate concentrations in Upper Twin Creek, Ohio, and Blue Beaver Creek, Oklahoma, were attributed to landscape disturbance and runoff from roads rather than changes in atmospheric deposition. Trends in stream chemistry at most of the remaining stations were attributed to method-related factors rather than environmental change.

INTRODUCTION

In 1962, L.B. Leopold, then Chief Hydrologist of the U.S. Geological Survey (USGS), proposed the establishment of a network of hydrologic benchmarks for making 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 human-related 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 human-related 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-gaging stations and one lake-stage station in 39 States (fig. 1).

As a result of an evaluation of the HBN program in the early 1990's, eight stations were discontinued and two stations were replaced for the following reasons: (1) The sites were operated as discharge-only stations during the period of record (Tallulah River,

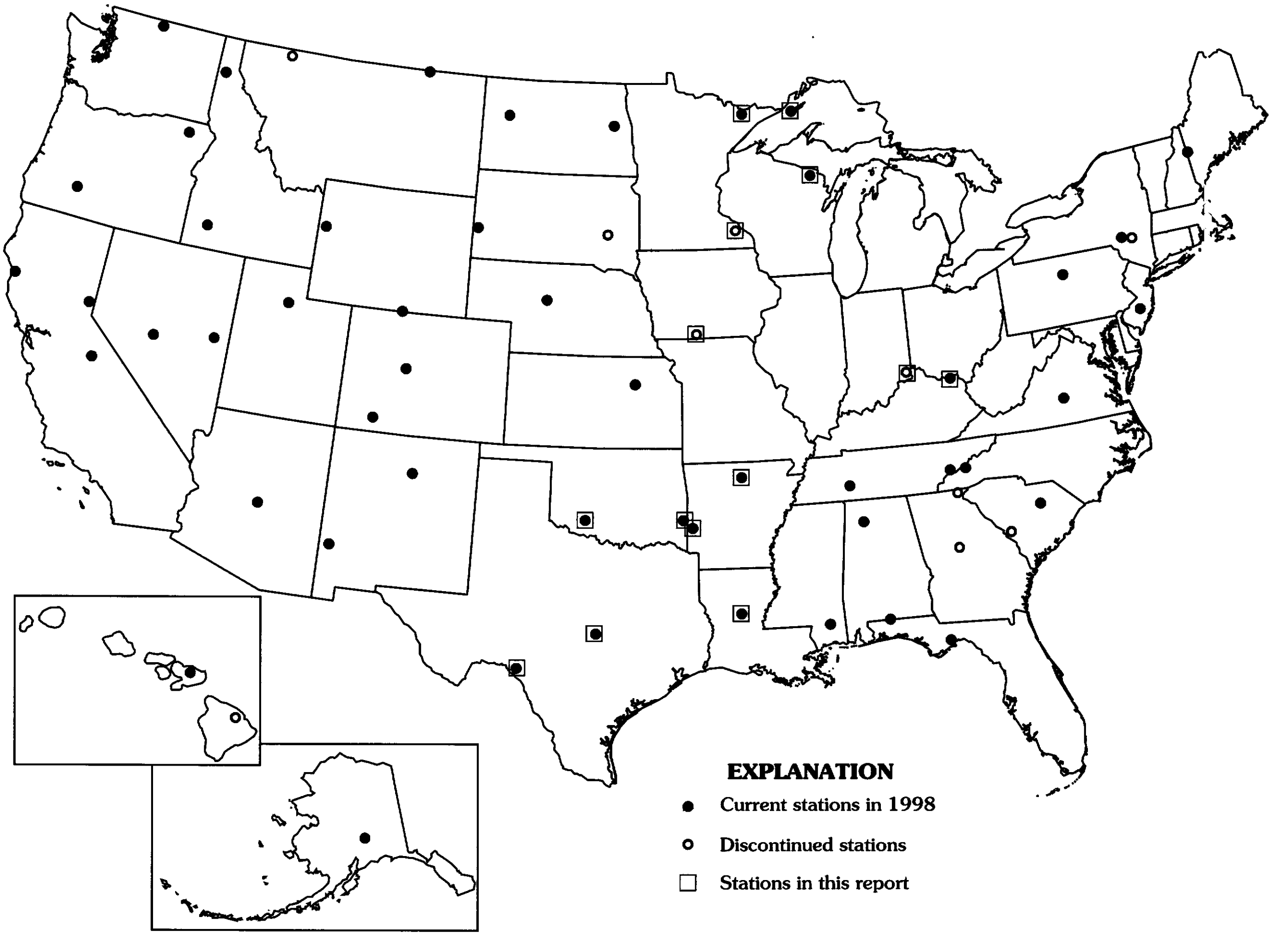


Figure 1. Map showing locations of streamflow-gaging stations in the Hydrologic Benchmark Network.

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 gaging station 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 human-related changes in other streams, an understanding of the natural and human-related 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 on the basis of the original design criteria.

Purpose and Scope

This report describes the environmental characteristics and water quality of 14 HBN stream basins in the Midwestern United States. These stream basins, in order of presentation, are: Cossatot River and North Sylamore Creek, Ark.; South Hogan Creek, Ind.; Elk Creek, Iowa; Big Creek, La.; Washington Creek, Mich.; Kawishiwi River and North Fork Whitewater River, Minn.; Upper Twin Creek, Ohio; Blue Beaver Creek and Kiamichi River, Okla.; Devils River and South Fork Rocky Creek, Tex.; and Popple River, Wis. 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 each HBN station 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 that were sampled between January 1991 and April 1993. 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 HBN 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 streamflow for the period of record through water year 1980.

Few process-level investigations have been conducted by the USGS in the individual HBN 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., 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), Fort Sill Military Reservation, Shawnee 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 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. The following modifications were made to the data before statistical and

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] Before 1981, laboratory alkalinity was stored under parameter code 00410.

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

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 for these two nutrient species (Office of Water Quality Technical Memorandum No. 93.04, *Discontinuation of the National Water Quality Laboratory Determinations for "Total" Nitrite, "Total" Nitrite Plus Nitrate, "Total" Ammonium, and "Total" Orthophosphate*, issued December 2, 1992, at URL http://water.usgs.gov/admin/memo/, accessed 1997); (3) concentrations reported as less than were set equal to the reporting limit for the time-series plots and the 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 the 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 was calculated 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 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 memorandums available at URL http://water.usgs.gov/admin/memo/. Summary statistics of physical properties and water-quality constituents were calculated from the historical water-quality records at each HBN 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 range between –1.0 to 1.0, and a value of zero indicates 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). The program 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 analyses where a large number of detected concentrations were between multiple reporting limits, as often occurred for the concentrations of nitrite plus nitrate, 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 flow model fit by ESTREND 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. Trends were considered statistically significant at the 0.01 probability level. The ESTREND program 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). LOWESS curves are presented in the time-series plots only when trends in discharge or unadjusted solute concentrations were 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 from the NADP at URL http://nadp.sws.uiuc.edu.

In addition to the historical water-quality records and NADP data, stream samples were collected at the HBN gaging stations and from several major tributary streams in each basin between January 1991 and April 1993 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 (Fishman and Friedman, 1989). Chemical data for the synoptic samples are stored in NWIS.

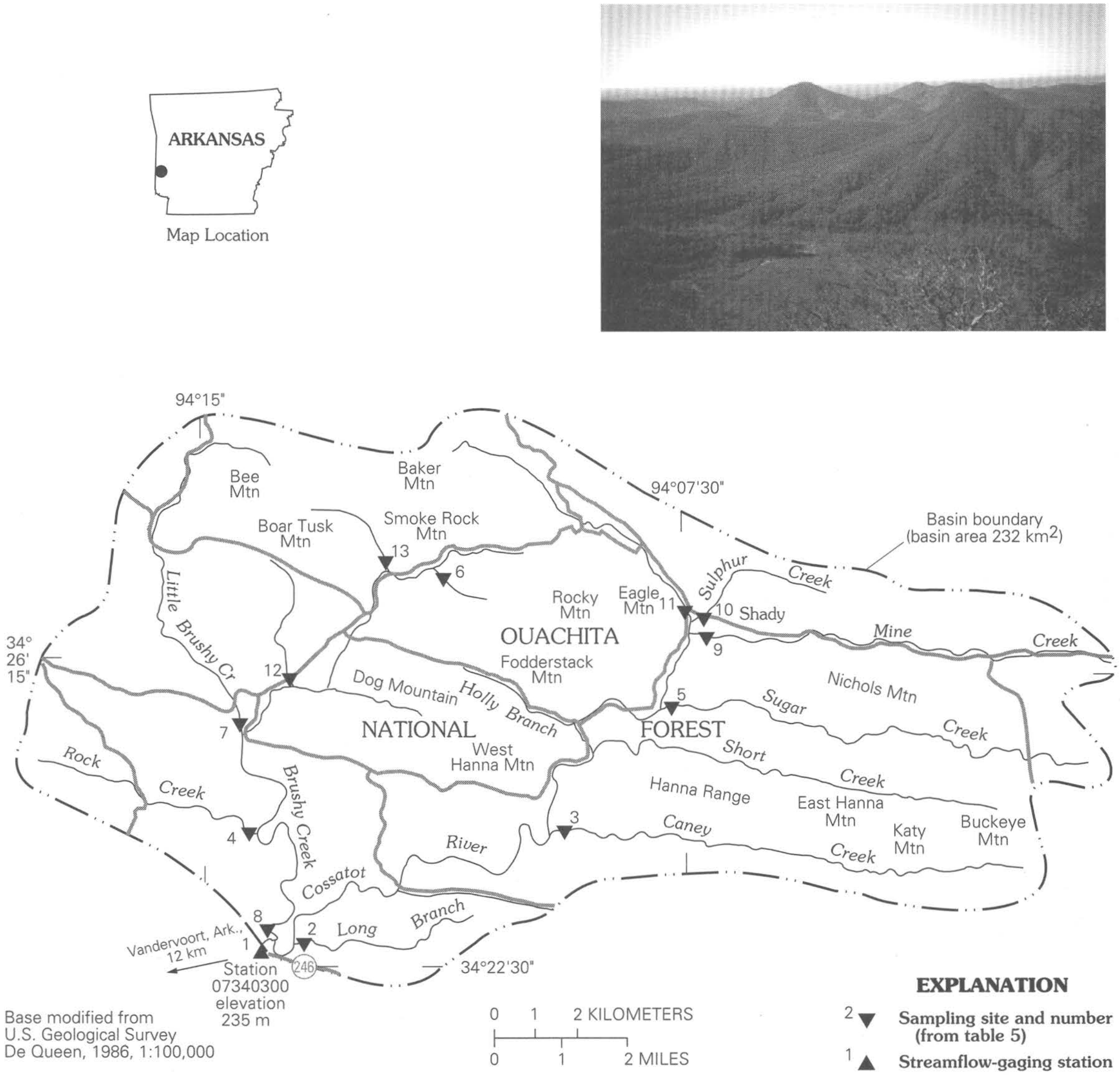
ENVIRONMENTAL CHARACTERISTICS AND WATER QUALITY OF HYDROLOGIC BENCHMARK NETWORK STATIONS

Cossatot River near Vandervoort, Arkansas (Station 07340300)

Site Characteristics and Land Use

The Cossatot River HBN Basin is in the Ouachita Mountains section of the Ouachita physiographic province in west-central Arkansas (fig. 2). The 232-km^2 basin ranges in elevation from 235 to 680 m and drains a landscape of long east-west-trending even-crested ridges separated by narrow flat-bottomed stream valleys. The USGS gaging station is located 12 km east of the town of Vandervoort, Ark., at latitude 34°22'46" and longitude 94°14'08". The Cossatot River flows south into the Little River, a tributary of the Red River, and has a channel length of about 30 km upstream from the gaging station and an average stream gradient of 5.6 m/km. Mean monthly discharge varies from 0.84 m^3/s in August to 10.5 m^3/s in March, and average annual runoff from the basin was 78 cm from 1967 through 1995 (Porter and others, 1996). Streamflow is highly variable during storms because of surface runoff from steep hillslopes in the basin but is well sustained by springs during periods of low rainfall. The climate is characterized as subtropical with hot, humid summers and mild winters (U.S. Department of Agriculture, 1990a). Average daily air temperatures range from 5.0°C in January to 27.2°C in July. Average annual precipitation is about 130 cm with rainfall in March, April, and May accounting for 40 percent of the annual precipitation (Freiwald, 1985).

The basin is located in the Southeastern Mixed Forest ecoregion (Bailey and others, 1994), and vegetation is dominated by second growth (50 to 70 years old) pine and oak vegetation types (U.S. Department of Agriculture, 1990c). Drier south- and west-facing slopes are dominated by shortleaf pine and minor amounts of loblolly pine. Pines and hardwoods grow together on wetter north- and east-facing slopes. The predominant hardwood species are white oak, black oak, post oak, blackjack oak, black hickory, pignut hickory, and mockernut hickory. Stunted scrubby pines and hardwoods, which are interspersed with mosses and lichens, cover large



Base modified from
U.S. Geological Survey
De Queen, 1986, 1:100,000

Figure 2. Map showing study area in the Cossatot River Basin and photograph of the landscape of the basin.

expanses of exposed novaculite bedrock on the ridgetops. Vegetation along the flood plain includes alder, sycamore, sweetgum, and river birch. Soils in the basin are classified as Ultisols and Inceptisols and are mapped in the Sherwood-Pickens-Rock Land soil association (Hoelscher and others, 1975). The Sherwood series is mapped along the ridgetops and includes well-drained soils developed in interbedded sandstone and shale. A typical soil profile has a surface layer of yellowish-brown fine sandy loam that is 20 cm thick overlying a subsoil of yellowish-red sandy clay loam that extends to a depth of 70 cm. These soils have low base saturation (9 to 19 percent), low soil pH (4.8 to 4.9), and low organic-matter content (0.3 to 2.3 percent) (Hoelscher and others, 1975). The Pickens series includes shallow, well-drained soils on hillslopes. A typical profile has a surface layer of dark grayish-brown shaly sandy loam that is 15 cm thick overlying a subsoil of yellowish-brown shaly sandy loam that extends to a depth of 30 cm. The Rock Land series includes shallow (2 to 10 cm), acidic loams directly overlying sandstone and novaculite on the crests and sideslopes of steep ridges.

The Ouachita Mountains are formed by sedimentary rocks of Paleozoic age that have been intensely deformed into a series of east-west-trending, tightly folded anticlines and synclines that strongly control the local topography (Miser and Purdue, 1929; Ericksen and others, 1983). The Paleozoic units in the basin include, from oldest to youngest, the Bigfork Chert, Polk Creek Shale, Blaylock Sandstone, Missouri Mountain Shale, Arkansas Novaculite, and Stanley Shale. The Bigfork Chert, which crops out in the eastern part of the Sugar Creek subbasin, consists of gray to black chert with finely disseminated grains of calcite. The Blaylock Sandstone and Stanley Shale are the most common units along the valley floors. The Stanley Shale is a black shale with sandstone interbeds and the Blaylock Sandstone is a gray quartzitic sandstone. The Arkansas Novaculite is a highly fractured, thermally metamorphosed chert that forms most of the topographic ridges because of its resistance to weathering. The Arkansas Novaculite and Bigfork Chert are important sources of water to springs in the area, which contribute locally to the base flow of streams (Ludwig, 1992). Some rocks in the area contain small deposits of metallic and industrial minerals. For example, the Arkansas Novaculite contains deposits of manganese oxide and veins of barite, and the Bigfork Chert, Missouri Mountain Shale, and Stanley Shale locally contain sulfide-bearing veins. Many inactive manganese mines are in the basin, some of which were operated until the late 1950's (Cole and Morris, 1986).

The Cossatot River drains the southern part of Polk County of Arkansas and is entirely in the boundaries of the Mena Ranger District of the Ouachita National Forest. About 40 km^2, or 17 percent, of National Forest land in the Caney Creek and Short Creek drainages also is in the boundaries of the Caney Creek Wilderness. Privately owned lands, which are concentrated along the main channel of the Cossatot River and the Sugar Creek tributary, account for 13 percent of land in the basin (J.A. Clingenpeel, U.S. Department of Agriculture Forest Service, written commun., 1997). More than 200 km of National Forest and county roads traverse the basin, paralleling the upper two-thirds of the main Cossatot River channel as well as most of the major tributaries. Because of infrequent snow or ice, there is no salting or plowing of roads in the basin (J.A. Clingenpeel, written commun., 1997). The Caney Creek Wilderness is accessible from a well-maintained foot trail along Caney Creek and an unmaintained foot trail that follows an abandoned road along Short Creek.

Land cover in the Cossatot River Basin is 99.5 percent forest and 0.5 percent pasture and residential land (J.A. Clingenpeel, written commun., 1997). The major land-use activities on National Forest land are timber harvesting and recreation. Through the 1980's, the U.S. Department of Agriculture Forest Service (Forest Service) used clearcutting as the primary harvest method (J.A. Clingenpeel, written commun., 1997). Since 1990, forests have been managed by using a combination of even-aged and uneven-aged silvicultural systems. Thinning, single-tree selection, and shelter woods are the main harvesting techniques. Privately and commercially owned lands continue to be harvested by clearcutting. Other human-related features in the basin include rural residences, hunting cabins, the community of Shady (population 100), and strips of pasture land bordering the streams, as along many streams in the Ouachita Mountains. The only major change in land use in the basin during the past 30 years was the designation of the Caney Creek Wilderness in 1975. Two segments of the Cossatot River, totaling 30 km, are currently being studied for possible designation as components of the National Wild and Scenic Rivers System (U.S. Department of Agriculture, 1990c). In the early 1990's, the Forest Service conducted a number of studies in the Brushy Creek and Caney Creek subbasins to evaluate the cumulative effect of forest management practices on physical, chemical, and biological characteristics of streams in the Ouachita National Forest. Preliminary results of these studies are summarized in Clingenpeel (1994).

Historical Water-Quality Data and Time-Series Trends

The data set for the Cossatot River HBN Station analyzed for this report includes 59 water-quality samples that were collected from November 1985 through October 1995 on a bimonthly schedule. Water-quality records also are available for an additional nine samples that were collected in 1967, 1968, and 1984 before the inclusion of the station in the HBN. All water-quality samples that were collected after 1985 were analyzed at the NWQL in Arvada, Colo. Daily discharge records are available for the Cossatot River (station 07340300) beginning in June 1967.

Calculated ion balances for 59 samples with complete major-ion analyses are shown in figure 3. Ion balances ranged from −16 to 8 percent, and 85 percent of samples had values in the ±10 percent range, indicating that the analytical measurements were of good quality. Almost 85 percent of samples had negative ion balances, indicating an excess of measured anions over cations in solution. Because stream water at this station generally has low alkalinity, 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/admin/memo/, accessed 1997). In low ionic-strength water, the actual stoichiometric endpoint of the bicarbonate part of the titration is often closer to pH 5.0 (Barnes, 1964), so that titration to pH 4.5 tends to overestimate the alkalinity of the sample. Alkalinity also was determined in the field beginning in 1988 by incremental titration. Comparison of the two alkalinity determinations revealed that the fixed-endpoint alkalinities were, on average, 30 μeq/L greater than the incremental alkalinities. This difference was similar to the average anion excess for all samples of 33 μeq/L, indicating that the alkalinity determination is a reasonable explanation of the negative bias in the ion balance. Time-series plots of major dissolved constituents were inspected for evidence of other method-related effects (fig. 3). No unusual patterns were apparent, except for the slightly elevated sulfate concentrations during the late 1980's. This pattern coincides with a period when sulfate was analyzed by a turbidimetric method. This method was documented as often producing a positive bias in sulfate concentrations, 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/admin/memo/, accessed 1997). A positive bias in sulfate concentrations during this period of record also was observed at several HBN stations in the Eastern United States (Mast and Turk, 1999).

Median concentrations and ranges of major constituents in stream water at the Cossatot River Station and VWM concentrations in wet-only deposition measured at the Caddo Valley NADP Station are listed in table 2. Precipitation chemistry at the NADP station, which is located about 110 km southeast of the HBN station, was dilute and slightly acidic with a VWM pH of 4.7 for 13 years of record. The predominant cations were hydrogen, which composed 44 percent of the total cation charge, and ammonium, which accounted for 22 percent. Sulfate accounted for 56 percent of the total anions, whereas nitrate contributed 30 percent and chloride contributed 14 percent. These results indicate 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 Cossatot River is dilute and weakly buffered; specific conductance ranged from 20 to 73 μS/cm, and alkalinity was between 100 and 560 μeq/L (table 2). The major ions in stream water were calcium, magnesium, and bicarbonate, which are attributed to the dissolution of carbonate minerals in the underlying sedimentary rocks. The median concentration of chloride in stream water was 48 μeq/L, which is about seven times greater than the VWM concentration of 6.6 μeq/L in precipitation. On the basis of the difference between annual precipitation and runoff, evapotranspiration can account for roughly a threefold increase in the concentration of precipitation, indicating that stream-water chloride is derived from sources other than precipitation. Additional sources of stream-water chloride might include salts in the marine sedimentary rocks or, perhaps, septic drainfields or runoff from pasture land along the drainages. The median concentration of sulfate in stream water was 73 μeq/L compared to 26 μeq/L in precipitation. This difference in concentration can be largely accounted for by evapotranspiration, indicating that stream-water sulfate is derived primarily from precipitation and behaves fairly conservatively in the basin. Conservative sulfate behavior also was reported by Nix and others (1988) who studied chemical budgets in two small, forested basins in southwestern Arkansas. The low concentrations of nitrate and of ammonium in stream water compared to precipitation indicate that nitrogen is strongly retained by soils and vegetation in the basin. In addition, the low stream-water nitrogen concentrations indicate that strips of grazing land bordering the streams do not seem to greatly affect the nutrient composition of stream water at the HBN station.

The solute composition of stream water was further evaluated by analyzing correlations between dissolved constituents and stream discharge

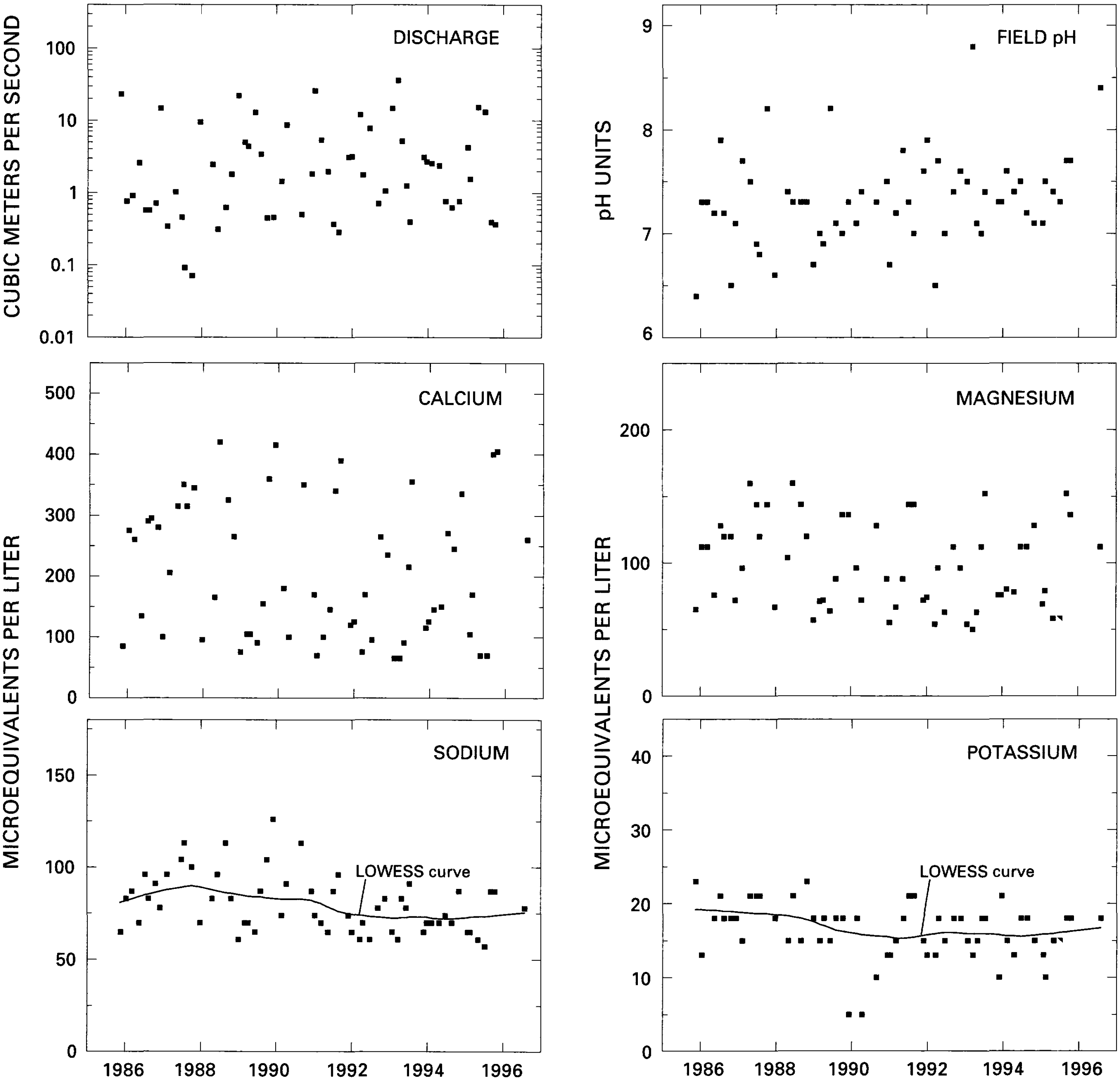


Figure 3. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at the Cossatot River, Arkansas.

(table 3). Most dissolved constituents were inversely correlated with discharge, particularly calcium (rho = –0.945), magnesium (rho = –0.920), and alkalinity (rho = –0.940). The exception was silica, which had a strong positive correlation with discharge (rho = 0.642). The distribution of different sedimentary units in the basin may provide a possible explanation for the opposite behavior of silica and the other major weathering products. In general, the stream valleys tend to be cut into the less resistant shale units, whereas the hillslopes and ridges are formed by the resistant novaculite. Limestone layers, which are in most of the shale units, are the most likely source of calcium, magnesium, and alkalinity in stream water. In contrast, the novaculite is depleted in carbonate minerals but is rich in microcrystalline quartz, which probably is a substantial source of stream-water silica. One possible result of this topographic distribution

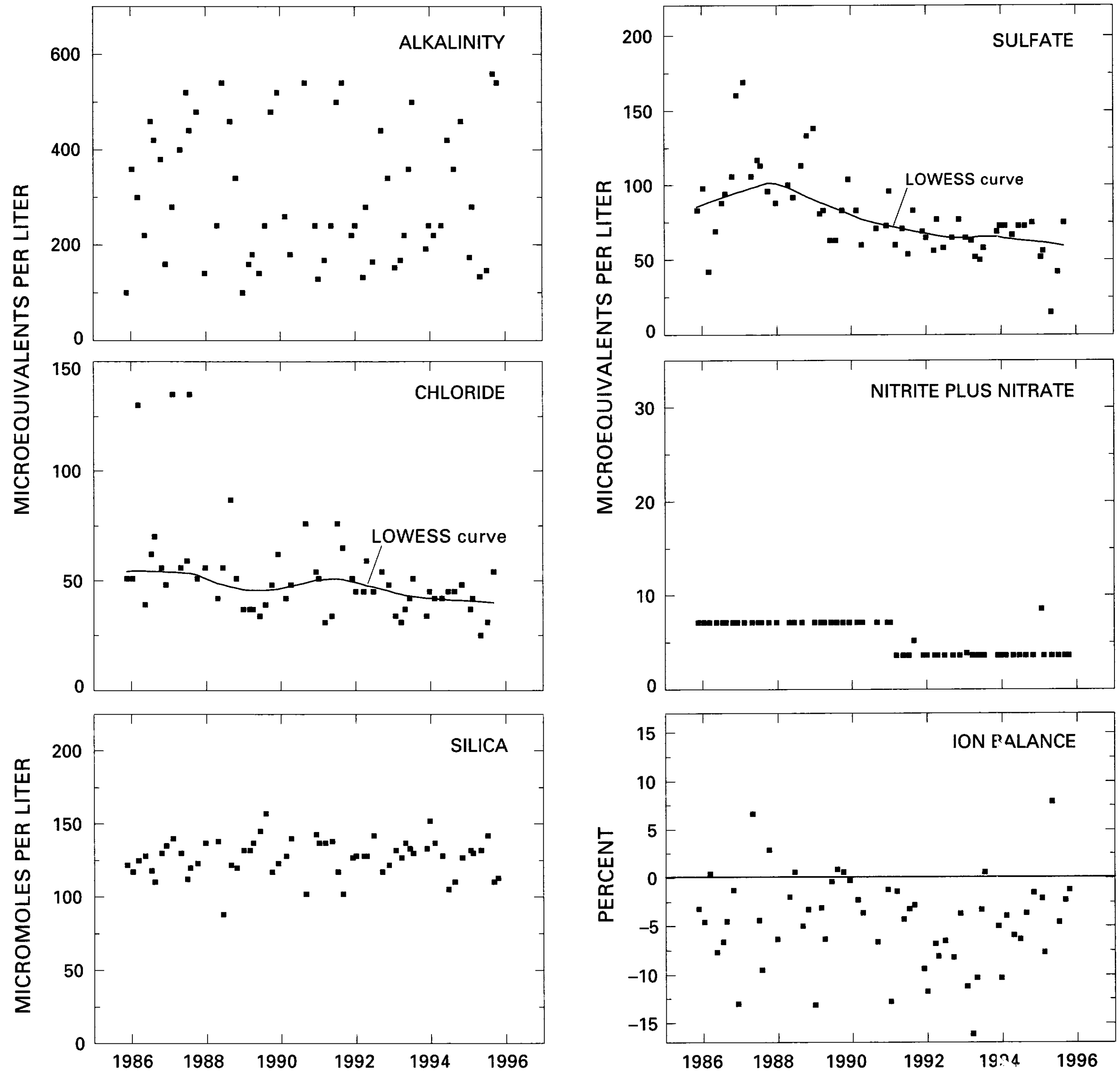


Figure 3. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at the Cossatot River, Arkansas—Continued.

of rock types is that during low-flow conditions, discharge is primarily supplied by carbonate-rich water from the underlying shales. During high-flow conditions, however, there probably is a larger contribution of runoff from the hillslopes and ridges, which may produce water enriched in dissolved silica.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents from 1986 through 1995 are listed in table 4. Trends were calculated for only 10 years because the station was not added to the HBN until 1986. Statistically significant downward trends were observed in the unadjusted sodium, potassium, sulfate, and chloride concentrations at the 0.01 probability level. Results were similar for unadjusted and flow-adjusted sodium, sulfate, and chloride concentrations, indicating that these trends were not caused by variations in stream discharge. After flow adjustment, a statistically

Table 2. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major dissolved constituents measured in water-quality samples from the Cossatot River, Arkansas, November 1985 through October 1995, and volume-weighted mean concentrations in wet precipitation collected at the Caddo Valley Station, Arkansas

[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.	0.071	0.62	1.8	5.1	35.7	59	--
Spec. cond., field	20	30	38	69	73	59	13
pH, field	6.4	7.0	7.3	7.5	8.8	59	4.7[b]
Calcium	65	100	170	320	420	59	5.9
Magnesium	50	72	96	130	160	59	2.1
Sodium	57	70	78	91	130	58	6.4
Potassium	5.1	15	18	18	23	57	.8
Ammonium	<.7	<.7	2.1	2.7	14	34	10
Alkalinity, laboratory	100	170	260	440	560	59	--
Sulfate	15	63	73	96	170	59	26
Chloride	25	39	48	56	140	59	6.6
Nitrite plus nitrate	<3.6	<3.6	<7.1	<7.1	8.6	58	14[c]
Silica	88	120	130	140	160	59	--

[a] Data are volume-weighted mean concentrations for 1984–95.

[b] Laboratory pH.

[c] Nitrate only.

Table 3. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major dissolved constituents, Cossatot River, Arkansas, 1986–95

[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	−0.166								
Ca	−.945	0.132							
Mg	−.920	.154	0.977						
Na	−.776	.020	.805	0.817					
K	−.395	−.120	.407	.482	0.318				
Alk	−.940	.205	.976	.953	.781	0.376			
SO_4	−.324	−.149	.383	.404	.462	.342	0.290		
Cl	−.696	−.017	.700	.692	.747	.384	.665	0.496	
Si	.642	−.035	−.690	−.640	−.421	−.367	−.707	−.283	−0.550

significant downward trend also was detected in the magnesium concentrations. The LOWESS curves in figure 3 show that the sulfate trend was primarily caused by elevated sulfate concentrations in the late 1980's. In contrast, the declines in sodium, potassium, and chloride concentrations have been more gradual during the period of record. Trends in stream chemistry at this station may reflect changes in environmental factors, such as precipitation chemistry or land-use activities. Lynch and others (1995) reported significant declines in calcium, magnesium, and sulfate concentrations in precipitation at a nearby NADP station in Arkansas from 1982 through 1990. Although the downward trends in stream-water sulfate and magnesium were consistent with trends in atmospheric deposition, the trend in flow-adjusted sulfate concentrations [–4.5 (µeq/L)/yr] was significantly larger than the decrease in flow-adjusted magnesium [–1.2 (µeq/L)/yr] and, in addition, no significant trend was detected in stream-water calcium. Declines in stream-water chloride, sodium, and potassium probably cannot be attributed to changes in atmospheric deposition on the basis of results from Lynch and others (1995), but may reflect human activities upstream from the gaging station. Although the basin is primarily forested, there is pasture land and a number of rural residential areas along the main river channel and major tributaries that may affect the concentrations of these ions. Method-related factors also may be responsible for the stream-water trends, particularly for sulfate. Elevated sulfate concentrations before 1990 were coincident with a period when sulfate was determined by turbidimetric titration method, which often introduced a positive bias in sulfate concentrations, particularly in dilute water. Although how much the method elevated sulfate concentrations before 1990 is not known, the sulfate trend at this station probably is at least partly an artifact of this analytical bias.

Table 4. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major dissolved constituents, Cossatot River, Arkansas, November 1985 through October 1995

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

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge, inst.	0.12	0.228	--	--
pH, field	.02	.211	([a])	--
Calcium	–7.2	.254	–2.6	0.036
Magnesium	–2.5	.130	–1.2	.006
Sodium	–2.2	.004	–1.2	.011
Potassium	–.5	.002	([a])	--
Alkalinity, laboratory	–8.0	.336	.8	.649
Sulfate	–5.5	.000	–4.5	.000
Chloride	–2.2	.001	–2.1	.001
Nitrite plus nitrate	([b])	--	--	--
Silica	<.1	.748	–.2	.927

[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 in the Cossatot River Basin on January 29 and 30, 1991, are listed in table 5, and the locations of sampling sites are shown in figure 2. During the sampling period, discharge at the gaging station was about 2.4 m^3/s compared to the median daily discharge of about 2.8 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 site 1 during the synoptic sampling were generally between the first-quartile and median concentrations reported for the HBN station during the entire period of record (table 2). The concentrations of solutes in the tributary streams bracketed the composition of stream water collected at the gaging station (site 1), except for calcium and alkalinity, which were lower than at site 1, except for site 5. Ion balances for all samples ranged from –3.9 to 5.5 percent, indicating that organic anions did not seem to be an important component of stream water during the sampling period.

Most of the variability in stream chemistry in the Cossatot River Basin was measured in the weathering-derived constituents calcium and alkalinity. For example, calcium ranged from a minimum of 27 µeq/L at site 13 to a maximum of 260 µeq/L in Sugar Creek (site 5) (table 5). A similar pattern was measured in the concentration of alkalinity, which ranged from 30 µeq/L at site 13 to 260 µeq/L in Sugar Creek (site 5). This range in calcium and alkalinity concentrations among the tributary streams may reflect differences in the mineralogy of the sedimentary units. For example, the highest concentrations were measured in Sugar Creek (site 5), which drains an area underlain by the Bigfork Chert, and the lowest concentrations were at sites 3 and 13, which primarily drain the Arkansas Novaculite. Although both sedimentary units consist mostly of quartz, the Bigfork Chert contains interbedded limestones and disseminated grains of calcite, whereas the Arkansas Novaculite is nearly carbonate free (Ericksen and others, 1983). These results also reveal that the concentrations of calcium and alkalinity at the HBN station were not representative of most of the tributary streams sampled during the synoptic sampling. In contrast to calcium and alkalinity, concentrations of the remaining solutes varied by less than a factor of two. For example, sulfate concentrations ranged from 58 to 79 µeq/L and silica ranged

Table 5. Physical properties and major dissolved constituents from surface-water sampling sites in the Cossatot River Basin, Arkansas, collected January 29–30, 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; Si, silica; concentrations in microequivalents per liter, except silica in micromoles per liter; <, less than; criteria used in selection of sampling sites: BG = bedrock geology, LU = land use, MT = major tributary]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria	Remarks
1	07340300	2.4	31	7.3	140	79	74	13	180	67	42	0.7	120	--	Gaging station
2	342249094133300	.046	25	7.0	60	42	100	16	110	63	42	1.4	170	BG	Stanley Shale
3	342408094083200	.18	17	6.7	28	58	43	12	34	69	37	1.4	120	BG, LU	Arkansas Novaculite, wilderness
4	342440094155700	.017	21	6.9	46	38	78	14	74	71	39	<.7	150	BG	Stanley Shale
5	342549094075000	.25	44	7.5	260	96	52	12	260	69	39	5.7	100	BG, LU	Bigfork Chert, rural development
6	342551094080000	.039	25	6.9	60	96	52	13	97	79	42	1.4	95	BG, LU	Blaylock Sandstone, mines
7	342615094144200	.020	23	6.9	55	44	96	16	85	69	42	<.7	180	BG	Stanley Shale
8	342615094144300	.099	29	7.3	120	79	65	14	150	67	42	<.7	140	BG, MT	Mixed lithology
9	342643094060300	.23	21	6.9	50	61	65	11	84	58	39	1.4	150	BG	Stanley Shale
10	342659094071000	.070	25	6.8	75	76	65	11	110	65	48	2.1	140	LU	Rural development
11	342704094072200	.088	26	7.1	95	67	70	12	130	60	39	2.1	140	BG, LU	Stanley Shale, rural development
12	342737094120500	.042	25	6.6	65	88	39	11	110	71	42	<.7	110	BG, LU	Mixed lithology, mines
13	342739094111700	.017	16	6.3	27	57	43	10	30	71	37	1.4	110	BG	Arkansas Novaculite

from 95 to 180 µmol/L. The similarity in sulfate concentrations among the sites supports the assumption that sulfate is primarily derived from atmospheric deposition. Internal sources of sulfate, such as weathering of pyrite from mineralized areas, might be expected to produce a wider range of sulfate concentrations among the tributary streams. Chloride and nitrate, which are often indicators of human activities, had uniformly low concentrations throughout the basin. For example, nitrate concentrations at all sites were less than 6 µeq/L, and chloride varied only from 37 to 48 µeq/L. These data indicate that the effect of pasture land and rural residential areas on water quality during the sampling period was minimal.

North Sylamore Creek near Fifty Six, Arkansas (Station 07060710)

Site Characteristics and Land Use

The North Sylamore Creek HBN Basin is located in the Springfield-Salem Plateaus section of the Ozark Plateaus physiographic province in north-central Arkansas (fig. 4). The 150-km^2 basin ranges in elevation from 133 to 415 m and drains an area characterized by steep V-shaped valleys separated by long, narrow winding ridges. The USGS gaging station is located 4.4 km north of Fifty Six, Ark., at latitude 35°59'30" and longitude 92°12'50". North Sylamore Creek flows southeast into the White River, a tributary of the Mississippi River, and has a channel length of about 25 km upstream from the gaging station and an average stream gradient of 2.9 m/km. Mean monthly discharge varies seasonally from a minimum of 0.18 m^3/s in August to 3.1 m^3/s in April, and streamflow is highly variable during storms because of rapid runoff from the steep hillslopes. Average annual runoff from the basin was 28 cm from 1966 through 1995 (Porter and others, 1996). The climate is temperate with hot summers and moderately cool winters (Ward, 1983). Average daily air temperatures range from 1.9°C in January to 26.2°C in July. Precipitation averages 112 cm annually and is greatest in spring and least in the late fall and winter (Freiwald, 1985; Adamski and others, 1995). Annual snowfall is about 15 cm, although snow cover generally lasts only a few days at a time. Estimated mean annual evapotranspiration in the region is between 75 and 90 cm annually (Hanson, 1991).

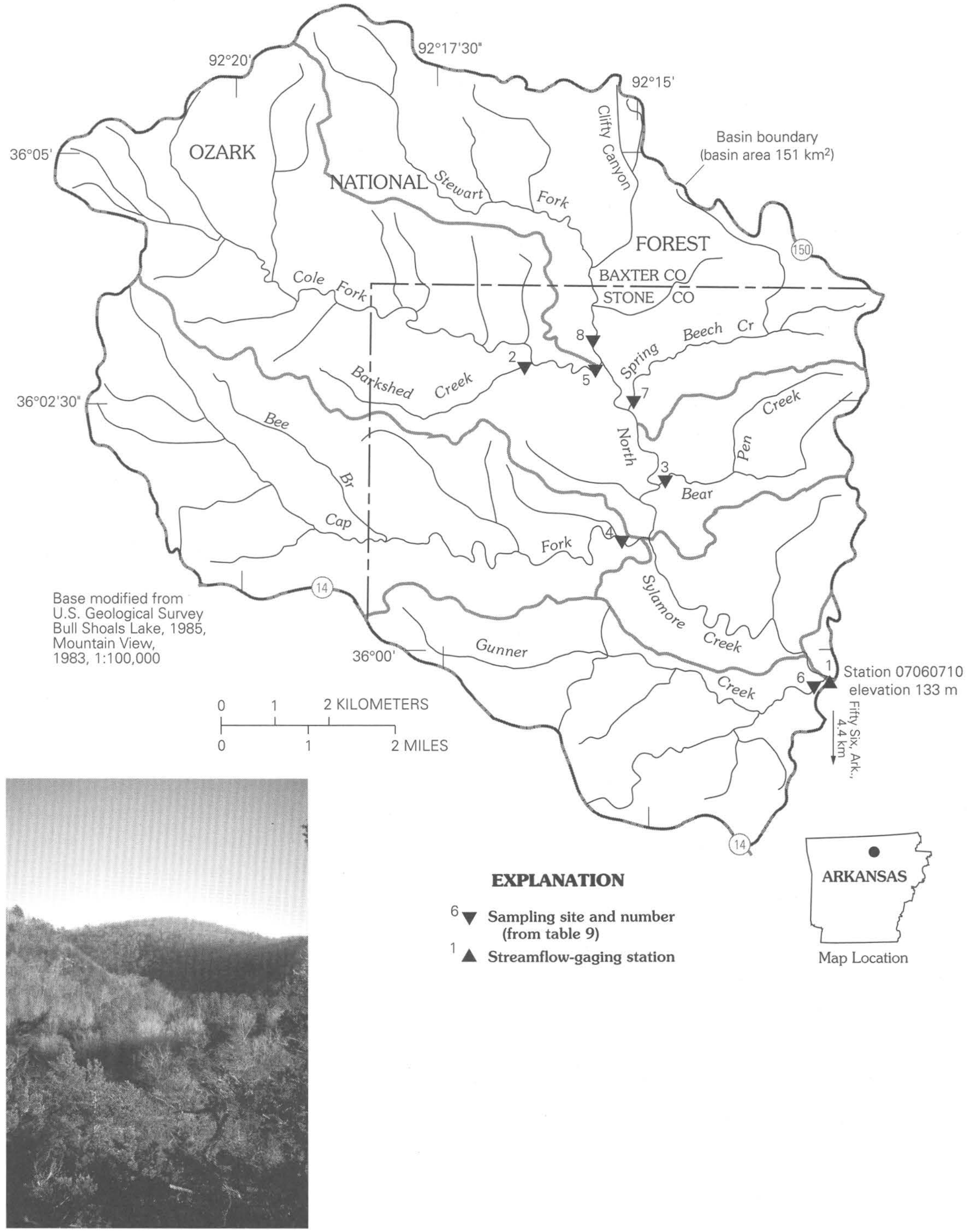


Figure 4. Map showing study area in the North Sylamore Creek Basin and photograph of the landscape of the basin.

The North Sylamore Creek Basin is in the Eastern Broadleaf Forest (Continental) ecoregion (Bailey and others, 1994), and vegetation consists of 65 percent hardwoods and 35 percent pines. The most common forest community is the oak-hickory association, which grows on south-facing slopes, hilltops, and upper northern exposures (Dale and others, 1978). Common species include post oak, white oak, blackjack oak, black oak, mockernut hickory, and dogwood. Pine and pine-oak forest types most commonly grow on soils derived from sandstone and shale. The predominant species include shortleaf pine and upland oak species. Cedar glades grow almost exclusively on soil derived from limestone and dolomite. The predominant glade species are red cedar and white cedar with a ground cover of prairie grasses and forbs (Dale and others, 1978). Most soils in the basin are classified as Ultisols (Typic Paleudults) and are mapped in the Norak and Clarksville soil series, which includes well-drained cherty soils developed in residuum of cherty limestone (Ward, 1983). The Norak soils are on gently sloping hillslopes and ridges and generally have a grayish-brown surface layer of cherty silt loam up to 30 cm thick overlying a yellowish-red cherty silt clay subsoil that extends to a depth of 200 cm. Clarksville soils are similar to Norak soils, except they form on steeper hillslopes and ridges and have a slightly higher clay content. Soils in both series contain between 35 to 80 percent chert fragments, are strongly acidic (pH 4.5 to 5.5), and depleted in organic matter (Ward, 1983). The predominant clay minerals in these soils are kaolinite, illite, and iron and aluminum oxides (Adamski and others, 1995).

Bedrock in the basin consists of flat-lying sedimentary rocks of Ordovician and Mississippian age. The oldest formation, the St. Peter Sandstone of Ordovician age, primarily crops out along the streambeds and contains massive layers of well-rounded sandstone interbedded with greenish-gray shale and layers of dolomite (McFarland and others, 1979). The valley walls are formed by limestones and dolomites of the Joachim Dolomite, Plattin Limestone, Kimmswick Limestone, and Fernvale Limestone of Ordovician age. Rocks of the younger Boone Formation of Mississippian age cap the uplands and ridges and consist of light-gray limestone interbedded with chert. The limestones and dolomites provide water for a large number of springs and, as a result, many streams in the region have a well-sustained base flow (Ludwig, 1992).

North Sylamore Creek drains parts of Baxter and Stone Counties in Arkansas and is entirely in the Sylamore Ranger District of the Ozark-St. Francis National Forest. About 14 percent of National Forest land that is adjacent to the main stream corridor and to segments of the Clifty Canyon, Cole Fork, Cap Fork, and Stewart Fork tributaries has special protection in the Clifty Canyon Botanical Area. Privately owned parcels account for less than 5 percent of land in the National Forest boundary; most of the parcels are concentrated in the Gunner Creek subbasin. The basin is accessible by a few gravel roads and several jeep trails, except for the Clifty Canyon Botanical Area, which is primarily roadless. Because of the steep, canyonlike topography along the drainages, most roads and trails follow the ridgelines. Access to the main stream channel, upstream from the gaging station, is limited to two road crossings and several unmaintained hiking trails that follow abandoned logging roads.

Land cover in the North Sylamore Creek Basin is 99 percent forest and 1 percent cleared land, including maintained wildlife openings and a few private fields and residences (Joseph Dabney, U.S. Department of Agriculture Forest Service, written commun., 1996). Land-use activities in the basin include timber harvesting, recreation, and a small amount of cattle grazing. National Forest land in the basin is divided into two management areas, special interest areas, and general forest (U.S. Department of Agriculture, 1985b). The Clifty Canyon Botanical Area includes 125 km^2 of forest land that is managed to protect, study, and enhance sensitive plants that have been identified by the Forest Service and the Arkansas Natural Heritage Commission. In this area, motorized travel is restricted to designated routes, livestock grazing is prohibited, and the area is considered unavailable for timber harvest, except where necessary to improve conditions for sensitive plants. The remainder of the basin is classified as general forest, of which about 70 percent is suitable for timber production (U.S. Department of Agriculture, 1985b). Second growth pines and hardwoods are managed on a 80-year rotation, and old growth forests are cut on a 200-year rotation. Timber harvesting in the basin for the past 7 years has affected about 165 ha annually with thinning, group selection, and shelterwood being the most common methods of harvest (Joseph Dabney, written commun., 1996). The Forest Service also maintains a small reservoir and recreational site at the mouth of Gunner Creek and a picnic area near the mouth of Barkshed Creek. The only substantial change in land use since the establishment of the HBN station has been a decrease in land available for timber management owing to the expansion of the Clifty Canyon Botanical Area in 1984. A more complete history of land use in the Ozark-St. Francis National Forest is described in Bass (1981).

Historical Water-Quality Data and Time-Series Trends

The data set for the North Sylamore Creek HBN Station analyzed for this report includes 267 water-quality samples that were collected from June 1966 through August 1995. Sampling frequency was monthly from 1968 through 1982 and bimonthly from 1983 through 1995. Monthly samples were collected from 1993 through 1995 as part of the National Water-Quality Assessment Program in the Ozark Plateaus study unit (Davis and others, 1995). Water-quality samples from the early part of the record were analyzed at a USGS laboratory in Little Rock, Ark., that operated until 1973 (Durum, 1978). After establishment of the central laboratory system, samples were analyzed at a laboratory in Atlanta, Ga., from 1973 through 1985 and at the NWQL in Arvada, Colo., from 1986 through 1995. Daily discharge records are available for North Sylamore Creek (station 07060710) beginning in December 1965.

Calculated ion balances for 255 samples with complete major-ion analyses are shown in figure 5. Ion balances ranged from –14 to 19 percent, and 99 percent of samples had values within the ±5 percent range, indicating that the analytical measurements were of high quality. The average ion balance for all samples was –0.4 percent, indicating that unmeasured constituents, such as organic anions, do not seem to contribute substantially to the ion balance of stream water at this site. Time-series plots of major dissolved constituents were inspected for evidence of method-related effects. No unusual patterns were apparent, except perhaps in the sodium, potassium, and chloride concentrations. Sodium and potassium had slightly different concentration patterns in the late 1980's; the potassium concentrations were somewhat lower than average, and the sodium concentrations were somewhat higher. Although there are no documented changes in field or laboratory methods for these constituents during this period of record, the possibility of analytical bias cannot be completely ruled out. Chloride concentrations seemed to increase near the beginning of record then level off after the early 1970's. The cause of this apparent increase could not be identified, although it may be related to the change in analytical laboratory that occurred in 1973.

Median concentrations and ranges of major constituents in stream water at the North Sylamore Creek Station and VWM concentrations in wet-only deposition measured at the Buffalo National River NADP Station are listed in table 6. Precipitation chemistry at the NADP station, which is located about 36 km west of the HBN station, was dilute and slightly acidic and had a VWM pH of 4.8 for 13 years of record. The predominant cations were hydrogen, which accounted for 40 percent of the total cation charge, and ammonium, which accounted for 25 percent. Sulfate composed 57 percent of the total anions, whereas nitrate contributed 30 percent and chloride contributed 13 percent. These results indicate that precipitation at the nearby NADP station may be affected by anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain.

Stream water in North Sylamore Creek is fairly concentrated and strongly buffered; specific conductance ranged from 100 to 320 µS/cm, and alkalinity was between 940 and 3,400 µeq/L (table 6). The major ions in stream water were calcium, magnesium, and bicarbonate, which accounted for more than 90 percent of the total ionic charge. The predominance of these ions in stream water is attributed to the dissolution of carbonate minerals in the underlying limestone and dolomite bedrock. The median chloride concentration in stream water was 51 µeq/L, which is about 10 times greater than the VWM chloride concentration of 5.0 µeq/L in precipitation. On the basis of the difference between average annual precipitation and runoff, evapotranspiration can account for about a fourfold increase in the chloride concentration in precipitation, indicating that stream-water chloride is derived from sources other than precipitation. Human-related sources of chloride are probably minimal because roads are not salted in winter,

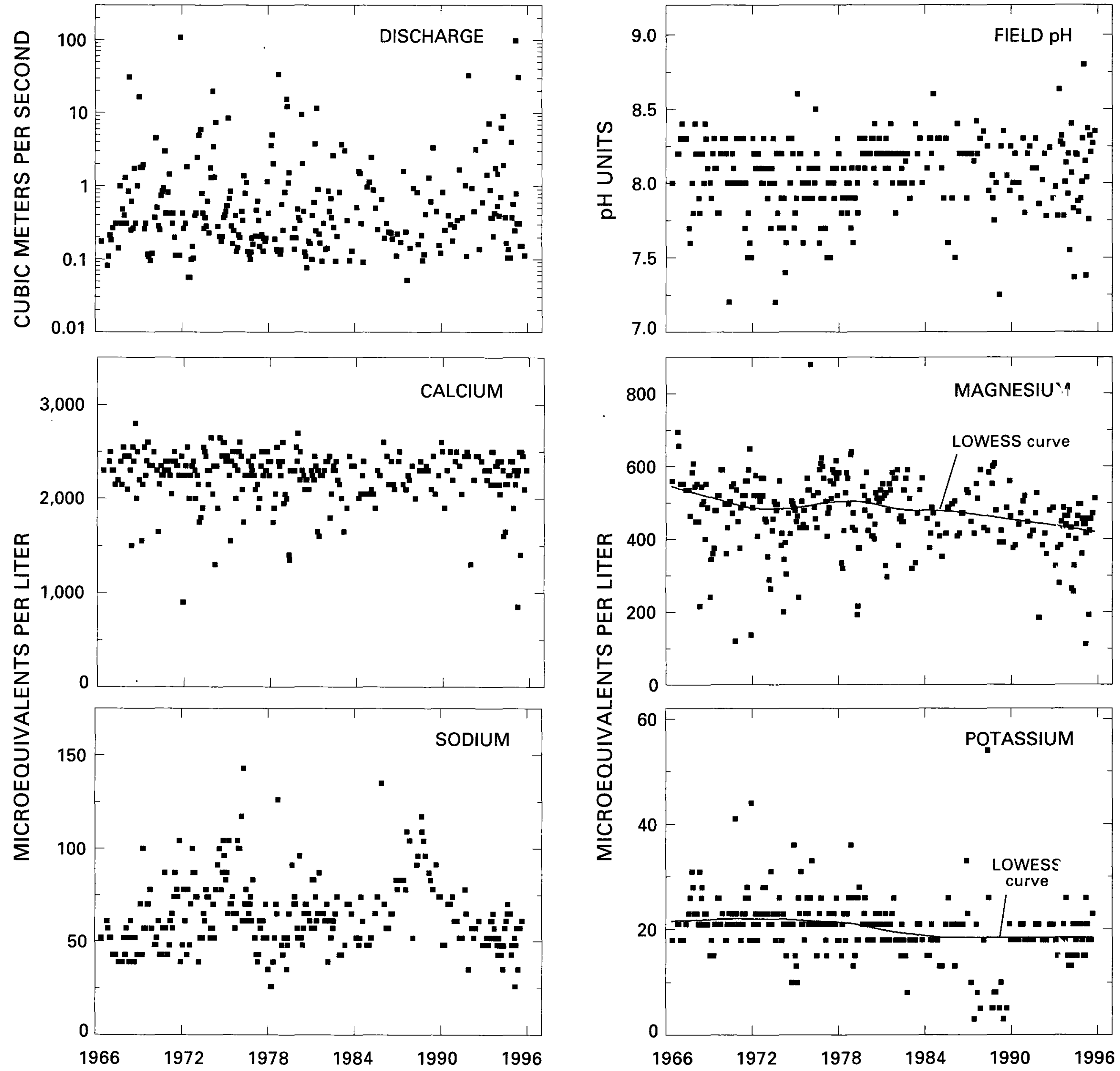


Figure 5. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at North Sylamore Creek, Arkansas.

and there are only a few residences and campsites upstream from the gaging station. The excess stream-water chloride, therefore, probably is derived from natural sources, such as trace amounts of halite in the underlying marine sediments (Craig and others, 1984). The median concentration of sulfate in stream water was 120 µeq/L, which is about five times greater than the VWM concentration of 25 µeq/L in precipitation. This difference in concentration can largely be accounted for by evapotranspiration, indicating that stream-water sulfate is derived primarily from precipitation and behaves fairly conservatively in the basin. Inorganic nitrogen species seem to be strongly retained in the basin, based on the low concentrations of nitrate and of ammonium in stream water compared to precipitation. Stream-water

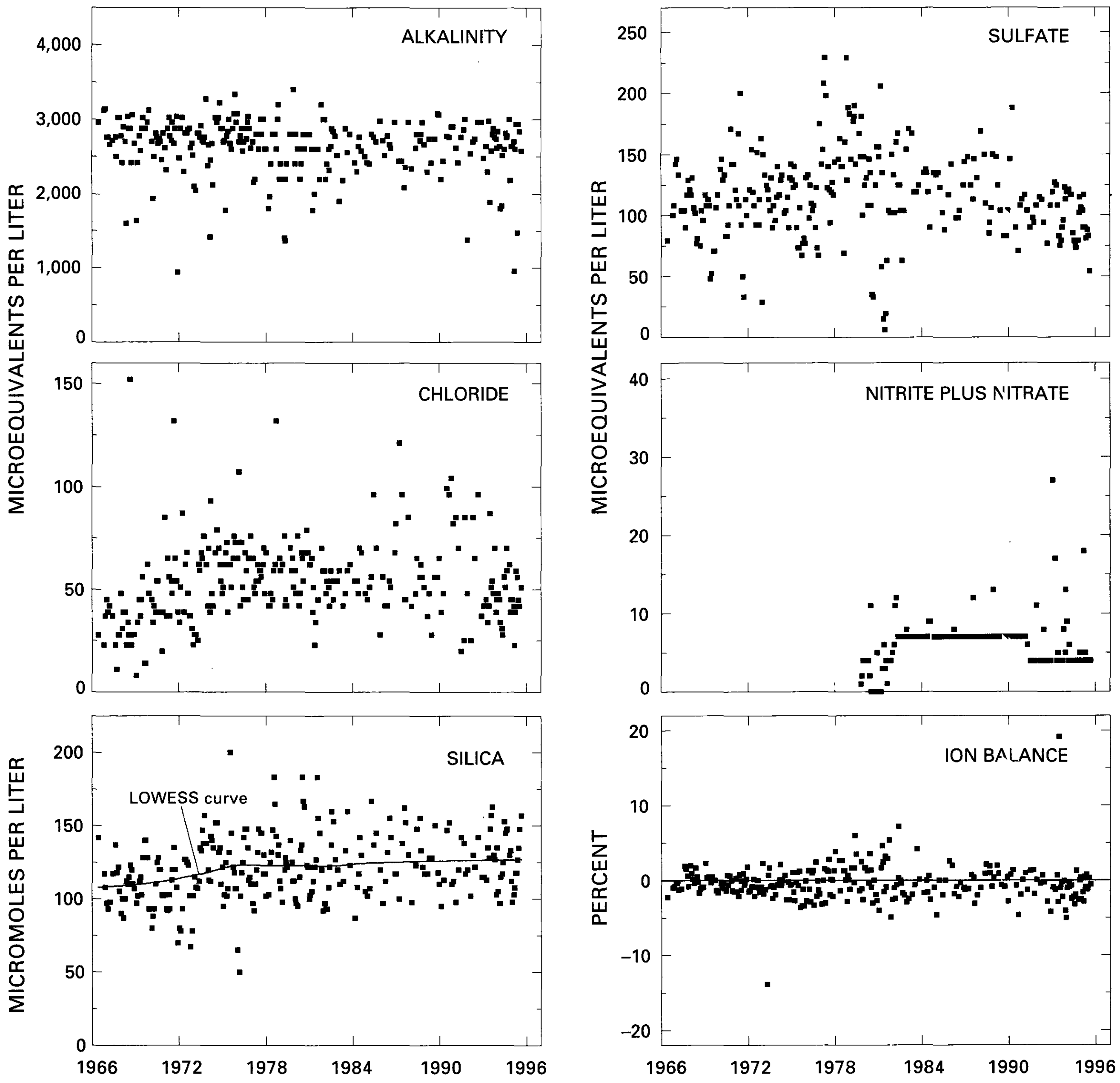


Figure 5. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at North Sylamore Creek, Arkansas—Continued.

concentrations of nitrate and of ammonium were similar to concentrations reported for other undisturbed streams draining forested areas in the Ozark Plateaus Province (Smart and others, 1985).

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 7). The major weathering products had moderately strong inverse correlations with discharge (–0.411 > rho > –0.789), except for silica (rho = –0.335). Inverse correlations between weathering products and discharge are consistent with a hydrologic system where weathering-enriched base flow is diluted by waters from shallow sources during periods of increased discharge. Chloride also had an inverse correlation with flow (rho = –0.497), supporting the assumption

Table 6. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major dissolved constituents measured in water-quality samples from North Sylamore Creek, Arkansas, June 1966 through August 1995, and volume-weighted mean concentrations in precipitation collected at the Buffalo National River Station, Arkansas

[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	0.051	0.18	0.37	0.91	110	267	--
Spec. cond., field	100	250	270	280	320	264	12
pH, field	7.2	7.9	8.1	8.2	8.8	264	4.8[b]
Calcium	850	2,150	2,300	2,400	2,800	267	6.9
Magnesium	110	420	480	540	880	265	2.0
Sodium	26	52	61	74	140	264	4.7
Potassium	<2.6	18	21	23	54	265	1.2
Ammonium	<.7	<.7	1.4	2.1	24	119	11
Alkalinity, laboratory	940	2,500	2,720	2,880	3,400	265	--
Sulfate	6.3	94	120	140	270	264	25
Chloride	8.5	42	51	65	150	262	5.0
Nitrite plus nitrate	<3.6	<7.1	<7.1	7.1	27	198	13[c]
Silica	50	110	120	140	200	266	--

[a] Data are volume-weighted mean concentrations for 1982–95.

[b] Laboratory pH.

[c] Nitrate only.

Table 7. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major dissolved constituents, North Sylamore Creek, Arkansas, 1966–95

[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	–0.043								
Ca	–.412	–0.023							
Mg	–.788	–.059	0.471						
Na	–.570	–.018	.409	0.653					
K	–.173	.015	.146	.137	0.073				
Alk	–.548	–.096	.757	.608	.404	0.105			
SO_4	.243	.092	–.136	–.146	–.155	–.266	–0.262		
Cl	–.497	.008	.292	.457	.427	.152	.300	–0.086	
Si	–.335	.065	.137	.265	.401	.230	.140	–.561	0.192

that stream-water chloride may be derived from dissolution of salt in the underlying limestone and dolomite. Among the solutes, the strongest correlations were between calcium and alkalinity (rho = 0.757) and magnesium and alkalinity (rho = 0.608). Silica had little correlation with other weathering-derived solutes, except for a weak positive correlation with sodium (rho = 0.401). The strong correlations among calcium, magnesium, and alkalinity and the lack of correlations with silica are consistent with the weathering stoichiometry of carbonate minerals. The processes that control silica in stream water are not clear, particularly because silica concentrations varied minimally for a wide range of streamflows. Weathering of quartz, chert, and clay minerals in the sedimentary rocks is the most likely source of silica in stream water during low-flow conditions. During high-flow conditions, however, silica may be regulated largely by processes occurring in soil and shallow ground-water environments. These processes may include dissolution of amorphous silica minerals, biological activity, and sorption reactions.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are listed in table 8. Statistically significant trends were observed in magnesium, potassium, and silica concentrations at the 0.01 probability level. Trends in all three constituents were similar for unadjusted and flow-adjusted concentrations, indicating that trends were not caused by variations in stream discharge. The LOWESS curves in figure 5 indicate slightly different trend patterns for all three constituents. For example, the upward trend in silica is primarily caused by a period of low concentrations in the early part of the period of record. Since 1973, silica concentrations have remained nearly constant. By contrast, the greatest change in magnesium and potassium concentrations occurred in the later one-half of the period of record. The decline in potassium occurred during a short period in the early 1980's, whereas the decline in magnesium was more gradual.

Table 8. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major dissolved constituents, North Sylamore Creek, Arkansas, June 1966 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; inst., instantaneous; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge, inst.	0.002	0.294	--	--
pH, field	.01	.027	0.01	0.030
Calcium	–2.2	.124	–2.7	.157
Magnesium	–2.9	.000	–2.0	.000
Sodium	<.1	.568	.2	.257
Potassium	–.1	.000	–.2	.000
Alkalinity, laboratory	–5.0	.013	–4.2	.050
Sulfate	–.3	.211	–.5	.077
Chloride	.4	.097	.4	.042
Nitrite plus nitrate	(a)	--	--	--
Silica	.3	.003	.4	.003

[a] Insufficient data to calculate trend.

Trends in stream chemistry at this HBN station may reflect changes in environmental factors, such as land-use activities or precipitation chemistry. The effect of land use on stream chemistry at this station probably is minimal because the basin is primarily forested and, except for a small amount of logging, has been used little by humans during the period of record. Trends in precipitation chemistry at this site are difficult to confirm because no long-term records are available for the entire period of record. Lynch and others (1995) did report significant declines in calcium, magnesium, and sulfate concentrations at a nearby NADP station in Arkansas from 1982 through 1990. Although the trend in magnesium is consistent with the downward trend in stream-water magnesium, it is unlikely that changes in atmospheric deposition would have a measurable effect on stream-water chemistry at this station, given the dilute concentration of precipitation compared to the stream. Method-related factors may provide an alternative explanation for trends in some constituents at this station. For example, the low silica concentrations in the early part of the period of record are coincident with a period when samples were analyzed at a USGS laboratory in Arkansas from 1966 through 1972 (Durum, 1978). Procedural changes that may have affected magnesium and potassium concentrations include a change in the analytical method for cations and trace metals 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/admin/memo/, accessed 1997) and a switch to the NWQL in Arvada, Colo., in 1985.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling in the North Sylamore Creek Basin on November 28 and 29, 1990, are listed in table 9, and the locations of sampling sites are shown in figure 4. During the sampling period, discharge at the gaging station was about 1.1 m^3/s compared to the median discharge of 0.3 m^3/s for November (Lawrence, 1987), indicating that the basin was sampled during high-flow conditions for that time of year. Solute concentrations measured at site 1 during the synoptic sampling were between the first- and third-quartile concentrations reported for the HBN station during the entire period of record, except for chloride (table 6). The tributary

Table 9. Physical properties and major dissolved constituents from surface-water sampling sites in the North Sylamore Creek Basin, Arkansas, collected November 28–29, 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; Si, silica; concentrations in microequivalents per liter, except silica in micromoles per liter; <, less than; criteria used in selection of sampling sites: BG = bedrock geology, MT = major tributary, LU = land use]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria	Remarks
1	7060710	1.1	260	8.3	2,400	460	52	21	2,840	120	93	<7.1	120	--	Gaging station
2	360254092162200	.16	240	8.4	2,300	240	61	20	2,860	81	93	<7.1	130	BG	Limestone and shale
3	360146092144200	.060	270	7.8	2,600	380	57	22	2,900	140	99	<7.1	130	BG	Limestone and shale
4	360107092150400	.077	280	8.3	2,700	240	48	20	2,960	120	85	<7.1	120	BG, MT	Limestone and shale
5	360256092162100	.47	190	8.3	1,850	390	43	21	2,160	79	45	<7.1	110	BG, MT	Sandstone along streambed
6	355943092124700	.045	290	8.2	2,900	200	57	22	3,060	140	96	29	130	LU	Some development
7	360228092151000	.0020	300	7.6	2,800	500	48	22	3,220	130	87	<7.1	130	BG	Limestone and shale
8	360256092153100	.27	290	8.2	2,550	620	52	23	3,180	130	100	<7.1	130	BG, MT	Sandstone along streambed

streams were similar in composition to stream water collected at the gaging station (site 1), with calcium and bicarbonate the predominant ions. Ion balances for all samples but one were slightly negative and ranged from −1.0 to −7.4 percent. An anion excess was somewhat unexpected because of the high ionic content of the water and may indicate a slight bias in one of the analytical determinations.

In general, concentrations of the major solutes did not vary markedly among the tributary sites. For example, alkalinity ranged from a minimum of 2,160 μeq/L in Cole Fork (site 5) to a maximum of 3,220 μeq/L in Spring Beech Creek (site 7) (table 9). Calcium concentrations ranged from 1,850 to 2,900 μeq/L, and magnesium concentrations ranged from 200 to 620 μeq/L. The presence of limestone and dolomite in the bedrock throughout most of the basin and the rapid weathering rate of carbonate minerals are the most likely reasons for the lack of substantial spatial variation in the concentrations of these solutes. The noncarbonate solutes also had a narrow range of concentrations during the synoptic sampling. For example, sodium ranged from 43 to 61 μeq/L, and silica varied only from 110 to 130 μmol/L. Sulfate and chloride concentrations were similar among the sampling sites, except for slightly lower sulfate concentrations in Barkshed Creek (site 2) and Cole Fork (site 5) and a lower chloride concentration in Cole Fork (site 5). Cole Fork not only had the lowest chloride and sulfate concentrations of the sampled tributaries, but had the lowest alkalinity and calcium concentrations as well. The lower concentrations at this site may be because this site had the largest discharge of the seven sampled tributaries. Nitrate was less than the reporting limit at all sites, except for Gunner Creek (site 6), which had a concentration of 29 μeq/L. This slightly elevated nitrate concentration may reflect upstream human activities because this sampling site is immediately downstream from a small impoundment and a developed recreational area, which includes picnic and camping facilities.

South Hogan Creek near Dillsboro, Indiana (Station 03276700)

Site Characteristics and Land Use

The South Hogan Creek HBN Basin is in the Central Lowlands physiographic province in southeastern Indiana (fig. 6). The 99-km^2 basin ranges in elevation from 174 to 303 m and drains the remnants of a broad undulating plateau dissected by deeply entrenched streams forming rugged V-shaped valleys. The USGS gaging station is located 1.9 km northeast of the town of Dillsboro, Ind., at latitude 39°01'47" and longitude 85°02'17". South Hogan Creek is a southeast-flowing tributary of the Ohio River and has a channel length of about 29 km upstream from the gaging station and an average stream gradient of 4.2 m/km. The main channel is perennial, and mean monthly discharge varies from 0.23 m^3/s in September to 2.8 m^3/s in March; there are occasional periods of no flow during the late summer and fall (July through November). Streamflow is highly variable during storms as a result of rapid runoff from the deeply incised stream channel and rocky streambed. Average annual runoff from the basin was 39 cm from 1961 through 1993 (Stewart and others, 1994). The climate is characterized by cold winters and hot summers (McWilliams, 1985). Average daily air temperatures

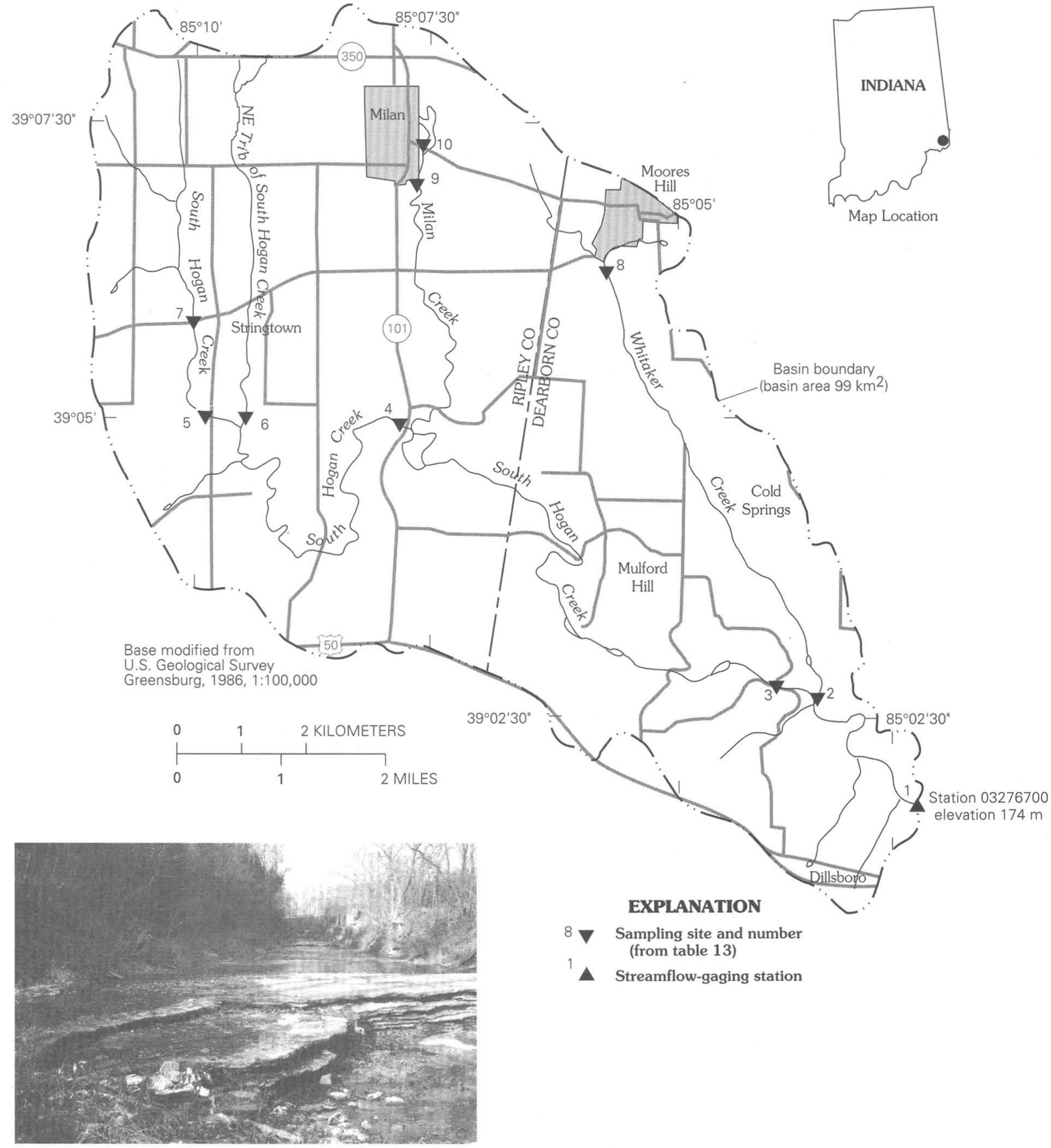


Figure 6. Map showing study area in the South Hogan Creek Basin and photograph of the Whitaker Creek tributary.

range from −1.9°C in January to 22.9°C in July. Average annual precipitation is 100 cm, of which about 50 percent falls between March and July. Average annual snowfall is 42 cm, and, on average, 11 days of the year have at least 2 cm of snow on the ground (McWilliams, 1985).

The South Hogan Creek Basin is in the Eastern Broadleaf Forest (Continental) ecoregion, and forest vegetation, which covers about 30 percent of the basin, is dominated by the oak-hickory association (Bailey and others, 1994). The predominant tree species are American beech, white ash, sugar maple, white oak, chinquapin oak, red oak, shagbark hickory, blue ash, tuliptree, Ohio buckeye, and black walnut (Homoya and others, 1985). Common understory species include flowering dogwood, sassafras, and hophornbeam. Soils in the basin are classified as Alfisols (Fragiudalfs, Ochraqualfs, and Hapludalfs) and are mapped in the Cobbsfork-Avonburg and Cincinnati-Rossmoyne-Hickory soil associations (McWilliams, 1985). The Cobbsfork-Avonburg soils are on the almost level to gently sloping upland plateau surface and are deep, poorly drained soils developed in loess and in silty glacial drift. A typical soil profile has a surface layer of dark grayish-brown silt loam as much as 25 cm thick overlying a subsoil of light-gray to yellowish-brown mottled silt loam and silty clay loam that extents to a depth of 200 cm. The Cincinnati-Rossmoyne-Hickory association includes well-drained soils on hillslopes that have developed in loess and in silty glacial drift. These soils range in thickness from 200 to 300 cm and often have a fragipan in the lower part of the subsoil. Soils in both associations have acidic surface layers (pH 5.1 to 6.0) that are sometimes limed to raise the soil pH for certain crops (McWilliams, 1985). The clay fraction of soils is dominated by smectite, which probably is derived from the underlying Peoria loess (Burras and others, 1996).

The basin is underlain by flat-lying marine sedimentary rocks of Ordovician age consisting of the Dillsboro Formation and Saluda Formation (Gray and others, 1972; Renn and Arihood, 1991). The Dillsboro Formation consists of argillaceous, rubbly limestone and calcareous shale, and the overlying Saluda Formation is a gray, silty dolomitic limestone. The Saluda Formation is more resistant to weathering than the Dillsboro Formation and tends to be the ridge-forming rock unit, whereas the Dillsboro Formation is the valley-forming rock unit (Renn and Arihood, 1991). In the upland areas, the bedrock is covered by unconsolidated glacial till of late Wisconsinan age, which has an average thickness of 6 m. The till consists of clay to gravel-size deposits and, in parts of the basin, is mantled by a thin (30- to 100-cm) layer of Peoria loess (McWilliams, 1985).

The South Hogan Creek Basin drains parts of Ripley and Dearborn Counties in southern Indiana. Land ownership in the basin is 99 percent private and 1 percent county and State (Irvin Harmeyer, U.S. Department of Agriculture Natural Resources Conservation Service, written commun., 1996). More than 80 km of paved and gravel roads provide access to most areas of the basin. Access to waterways is limited to rights-of-way at public road crossings.

Current land use in the basin is about 40 percent row crops, 30 percent pasture, and 30 percent forest (Irvin Harmeyer, written commun., 1996). Agricultural lands tend to be located on the upland plateau surface, and forested areas are concentrated along the drainages. The major row crops are corn and soybeans, which are tilled conventionally (Renn and Arihood, 1991). In addition to agricultural land, the basin contains the communities of Milan (population 1,530), Moores Hill (population 650), and part of Dillsboro (population 1,200). The town of Milan has some industrial development and a wastewater-treatment facility that discharges treated water into the headwaters of Milan Creek. Moores Hill has a wastewater-treatment facility that discharges into the headwaters of Whitaker Creek. Neither treatment facility was in operation when South Hogan Creek was selected as an HBN station (Cheryl Silcox, U.S. Geological Survey, written commun., 1997). Most residents in the basin obtain domestic water from reservoirs because the bedrock and glacial deposits are poor sources of ground water (Renn and Arihood, 1991). Other human-related activities in the basin include road salting, channel-bottom excavation for fossil exploration, several livestock yards, and an active freight-hauling railroad paralleling almost the entire length of the main channel of South Hogan Creek (Cheryl Silcox, written commun., 1997). The only change in land use since the establishment of the HBN site has been a slight increase in urban development (Irvin Harmeyer, written commun., 1996).

Historical Water-Quality Data and Time-Series Trends

The data set for the South Hogan Creek HBN Station analyzed for this report includes 189 water-quality samples that were collected from October 1968 through May 1993. Samples were collected monthly from 1969 through 1982 and quarterly from 1983 through 1993. Water-quality samples in the early part of the period of record probably were analyzed at a USGS laboratory in Columbus, Ohio, that was operated until 1973 (Durum, 1978). After establishment of the central laboratory system, samples were analyzed at a laboratory in Atlanta, Ga., from 1973 through 1985 and at the NWQL in Arvada, Colo., from 1986 through 1993. Daily discharge records are available for South Hogan Creek (station 03276700) from July 1961 through September 1993, and sediment discharge records are available from 1969 through 1993.

Calculated ion balances for 186 samples with complete major-ion analyses are shown in figure 7. Ion balances ranged from –8.2 to 12 percent, and more than 95 percent of samples had values within the ±5 percent range, indicating that the analytical measurements were of high quality. The average charge balance for all samples was 0.4 percent, indicating that unmeasured constituents, such as organic anions, do not seem to contribute substantially to the ion balance of stream water at this site. No unusual patterns were evident in the time-series plots to indicate any method-related biases in the water-quality data for this HBN station (fig. 7).

Median concentrations and ranges of major constituents in stream water at the South Hogan Creek Station and VWM concentrations in wet-only precipitation measured at the Oxford NADP Station are listed in table 10. Precipitation chemistry at the NADP station, which is located about 63 km northeast of the HBN station, was dilute and acidic with a VWM pH of 4.3 for 12 years of record. The predominant cations were hydrogen, which accounted for 63 percent of the total cation charge, and ammonium, which accounted for 20 percent. Sulfate and nitrate were the predominant anions and contributed almost 95 percent of the total anion charge. 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 South Hogan Creek is concentrated and strongly buffered; specific conductance ranged from 120 to 720 μS/cm, and alkalinity was between 700 and 5,500 μeq/L (table 10). The major ions in stream water were calcium and alkalinity, which accounted for almost 70 percent of the total ionic charge. The high concentrations of these ions in stream water are attributed to the dissolution of carbonate minerals in the limestone bedrock and glacial till. The median chloride concentration in stream water was 390 μeq/L compared to the VWM concentration of 4.2 μeq/L in precipitation. This large difference in concentration indicates that most stream-water chloride is derived from sources in the basin. Although some chloride may be derived from bedrock sources, most is probably derived from human activities. A number of point and nonpoint sources of chloride exist in the basin, including discharge from two wastewater-treatment plants and road salt and fertilizer applications. Sulfate concentrations also were considerably higher in stream water than in precipitation; the median stream-water concentration was 1,200 μeq/L compared to 57 μeq/L in precipitation. The main source of stream-water sulfate probably is weathering of calcium sulfate minerals, such as gypsum and anhydrite in the marine sedimentary rocks. The median nitrate concentration of stream water was similar to precipitation, and stream-water ammonium concentrations were considerably lower. Although these stream-water nitrogen concentrations are low compared to concentrations considered indicative of human-related pollution (Kross, 1990), the nitrate concentrations were substantially higher than at most other stations in the HBN, indicating human activities have some effect on nutrient concentrations in stream water at this station.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 11). Most solutes were weakly correlated with discharge, except for sodium (rho = –0.733), chloride (rho = –0.669), and nitrogen (rho = 0.703). For the solutes, the strongest correlations were found among the weathering-derived solutes, particularly calcium, magnesium, and alkalinity. The strong inverse correlations of sodium and chloride with discharge simply may be due to dilution

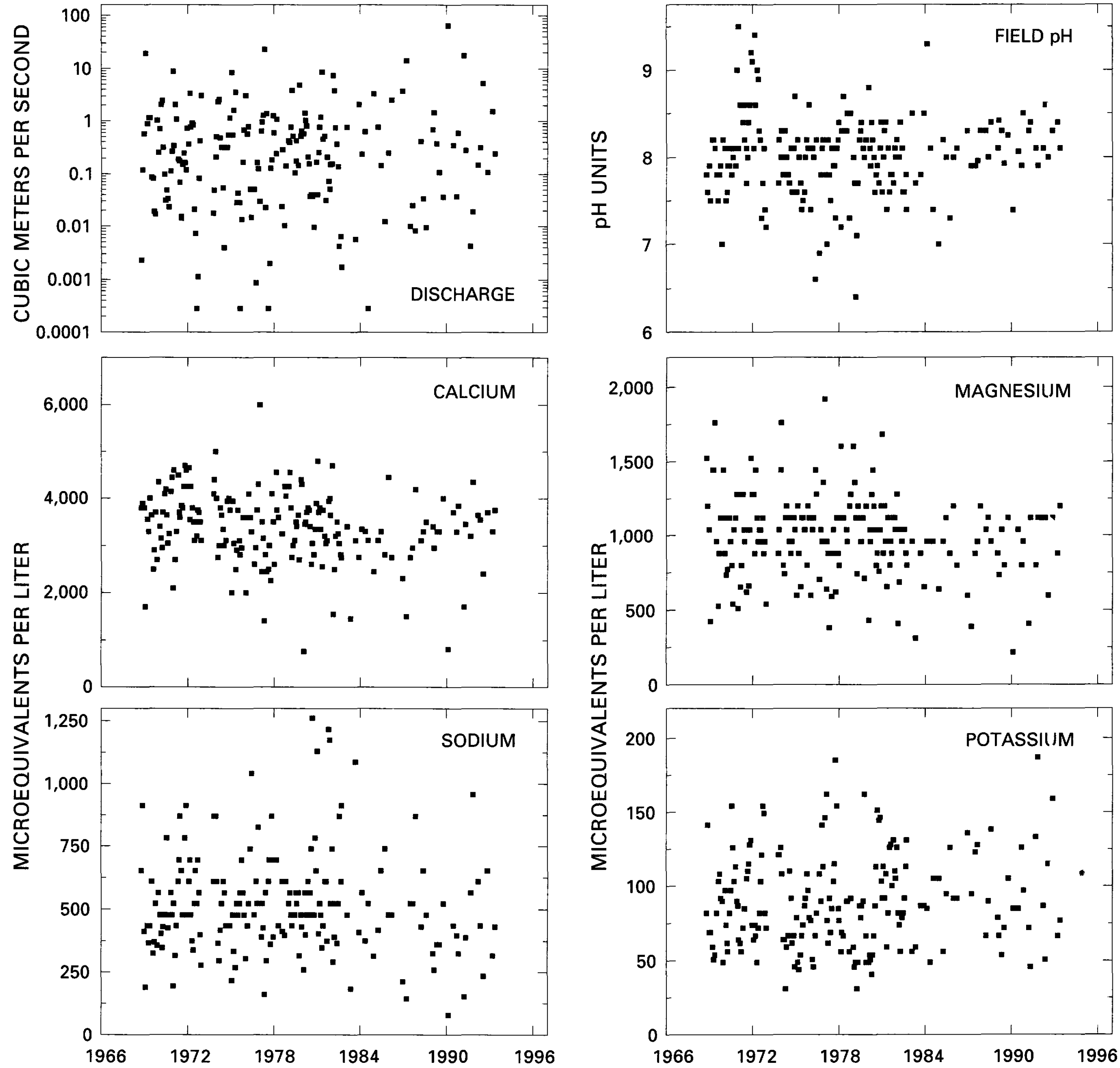


Figure 7. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at South Hogan Creek, Indiana.

of wastewater discharge during periods of increased discharge. Alternatively, these correlations may indicate that human activities have resulted in the contamination of the local ground-water system. Although nitrate also is derived primarily from human-related sources, it had a positive correlation with discharge. This indicates that nitrate primarily is transported during periods of high flow, probably due to surface runoff from agricultural lands and livestock yards. The strong correlations among calcium, magnesium, and alkalinity reflect the weathering of carbonate minerals, but the lack of correlation with discharge was somewhat unexpected. A more detailed examination of the data revealed that the concentrations of these

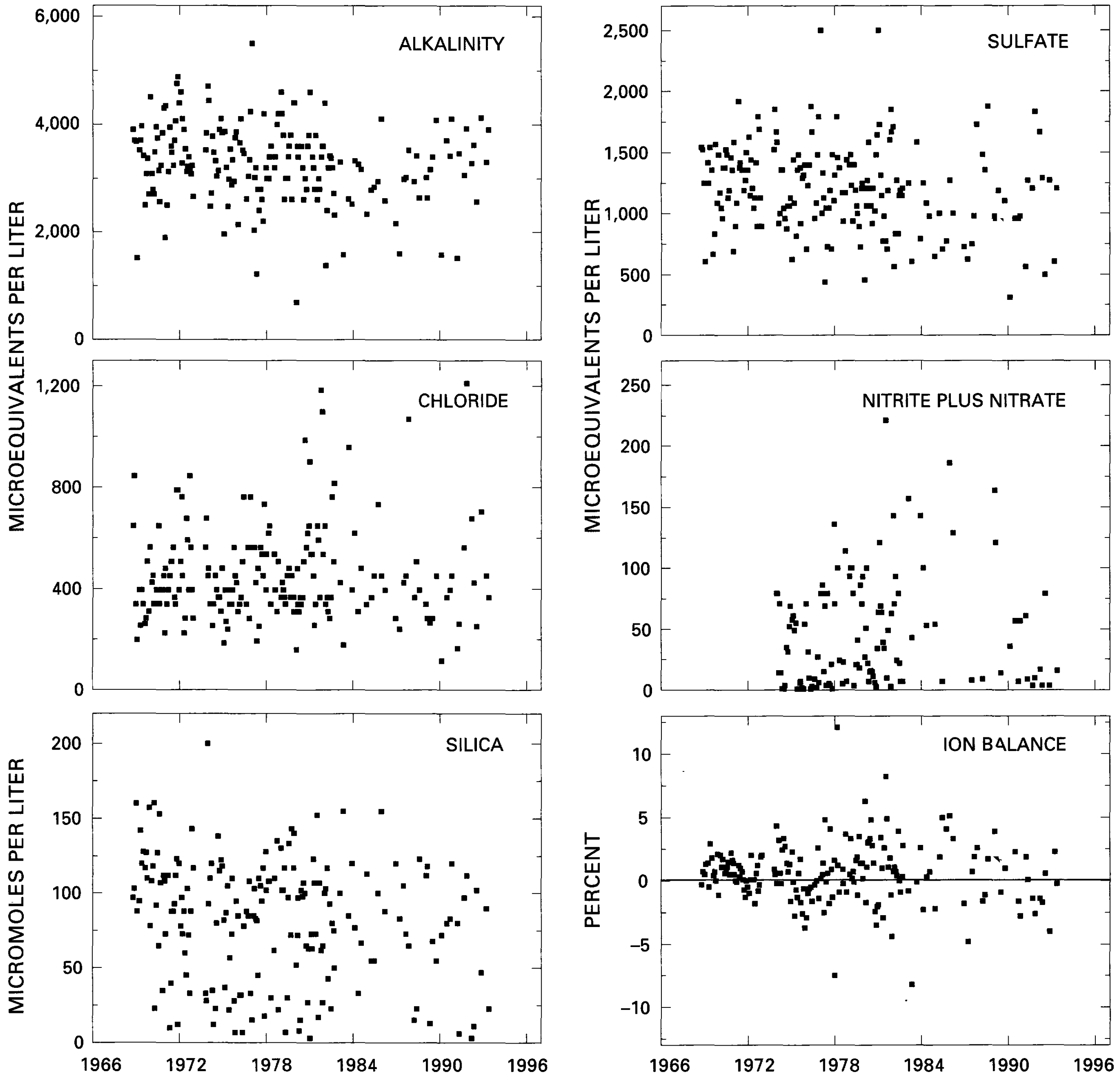


Figure 7. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at South Hogan Creek, Indiana—Continued.

constituents were, in fact, related to discharge, but the relation was not monotonic. Concentrations had the expected inverse correlation with discharge, but only for discharges greater than 0.03 m^3/s. At flows less than 0.03 m^3/s, stream-water concentrations were fairly constant as a function of discharge, perhaps reflecting a uniform source of streamflow from the bedrock aquifer.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are listed in table 12. No statistically significant trends were observed at the South Hogan Creek Station at the 0.01 probability level. Upward trends in flow-adjusted pH and sulfate concentrations were detected at a slightly less significant level of $p \leq 0.02$. The lack of trends in most dissolved constituents, particularly sodium,

Table 10. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major dissolved constituents measured in water-quality samples from South Hogan Creek, Indiana, October 1968 through May 1993, and volume-weighted mean concentrations in wet precipitation collected at the Oxford Station, Ohio

[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	
Inst. discharge	0.0003	0.045	0.25	0.76	64	187	--
Spec. cond., field	120	420	470	520	720	188	28
pH, field	6.4	7.8	8.1	8.3	9.5	187	4.3[b]
Calcium	750	3,000	3,30	3,800	6,000	189	6.9
Magnesium	220	850	1,070	1,150	1,920	189	2.0
Sodium	78	400	480	610	1,260	188	3.2
Potassium	31	67	85	110	190	188	.5
Ammonium	<.7	1.4	2.1	2.9	11	57	16
Alkalinity, laboratory	700	2,800	3,320	3,760	5,500	188	--
Sulfate	310	960	1,200	1,410	2,500	189	57
Chloride	120	340	390	540	1,210	188	4.2
Nitrite plus nitrate	<.7	7.1	24	71	220	130	24[c]
Silica	.7	55	88	110	200	189	--

[a] Data are volume-weighted mean concentrations for 1984–95.

[b] Laboratory pH.

[c] Nitrate only.

Table 11. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major dissolved constituents, South Hogan Creek, Indiana, 1969–93

[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	0.345									
Ca	–.250	0.303								
Mg	–.333	.252	0.866							
Na	–.733	–.206	.416	0.555						
K	–.550	–.320	.033	–.052	0.487					
Alk	–.264	.250	.914	.846	.388	–0.010				
SO_4	–.429	.224	.728	.734	.617	.145	0.628			
Cl	–.669	–.164	.406	.393	.871	.639	.354	0.569		
N	.703	.122	–.020	–.230	–.426	–.316	–.126	–.216	–0.292	
Si	.227	–.139	–.286	–.521	–.287	.221	–.358	–.399	–.126	0.478

chloride, and nitrate, indicates that land-use activities in the basin, such as road salting, agricultural runoff, and wastewater discharge, have remained fairly constant during the period of record. The source of trends in flow-adjusted pH and sulfate concentrations are less clear. Atmospheric deposition of sulfate has decreased substantially in the industrialized Midwest since the 1970's (Husar and others, 1991); however, changes in precipitation chemistry probably would not have much of an effect on stream chemistry in this basin because of the large internal source of sulfate from weathering. The trends in sulfate and pH also might be caused by changes in land use; however, there are few human-related activities that would impact pH and sulfate concentrations without also affecting the concentrations of the other dissolved constituents, particularly chloride, sodium, and nitrate.

Table 12. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major dissolved constituents, South Hogan Creek, Indiana, October 1968 through May 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; inst., instantaneous; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	–0.001	0.294	--	--
pH	.02	.025	0.02	0.015
Calcium	–4.4	.446	–3.1	.649
Magnesium	<.1	.225	–1.8	.221
Sodium	.1	.698	–1.4	.494
Potassium	.6	.064	.6	.113
Alkalinity	–3.3	.688	1.0	.887
Sulfate	–7.7	.111	–7.6	.020
Chloride	1.8	.331	2.6	.139
Nitrite plus nitrate	.3[a]	.763	--	--
Silica	–.6	.108	–.8	.053

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

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling in the South Hogan Creek Basin on November 5 and 6, 1991, are listed in table 13, and the locations of the sampling sites are shown in figure 6. During the sampling period, discharge at the gaging station was about 0.01 m^3/s compared to the median discharge of 0.15 m^3/s for November (Lawrence, 1987), indicating that the basin was sampled during low-flow conditions for that time of year. Because of the low-flow conditions, solute concentrations measured at site 1 were greater than the third-quartile concentrations reported for the HBN station during the entire period of record (table 10). The tributary streams were similar in composition to stream water collected at the gaging station (site 1); calcium and magnesium were the predominant cations, and bicarbonate and sulfate were the predominant anions. Ion balances for the synoptic samples were around zero (range –2.4 to 2.4 percent), indicating that unmeasured constituents, such as organic anions, did not seem to be an important component of stream water during the sampling period.

Considerable spatial variability in stream chemistry was measured in the South Hogan Creek Basin, particularly for sodium, chloride, and nitrate, which seems to be related to wastewater discharge from treatment facilities in the towns of Milan and Moores Hill. For example, chloride concentrations in tributaries sampled downstream from the towns of Moores Hill (site 8) and Milan (site 9) were 1,940 and 2,510 μeq/L (table 13), respectively, compared to the average concentration of 580 μeq/L at background sites in the

Table 13. Physical properties and major dissolved constituents from surface-water sampling sites in the South Hogan Creek Basin, Indiana, collected November 5–6, 1991

[Site locations shown in fig. 6; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeters at 25 degrees Celsius; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Cl, chloride; NO_3, nitrate; SO_4, sulfate; Alk, alkalinity; Si, silica; concentrations in microequivalents per liter, except silica in micromoles per liter; WTP, wastewater-treatment plant; --, not reported; criteria used in selection of sampling sites: BG = bedrock geology, MT = major tributary, LU = land use]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria	Remarks
1	3276700	0.0096	720	8.2	4,650	1,200	1,090	160	4,000	2,040	1,320	0.7	110	--	Gaging station
2	390241085031600	--	670	8.5	4,600	1,280	830	62	3,540	2,710	850	.4	120	MT	Downstream from Moores Hill
3	390246085034400	.0079	650	8.1	3,800	1,040	1,130	200	3,700	1,440	730	.6	87	MT, BG	Limestone bedrock
4	390456085074700	--	590	7.6	3,900	1,200	370	250	4,700	400	560	3.4	170	MT, BG	Glacial till
5	390500085095100	--	660	8.2	3,500	2,000	780	160	5,300	500	730	3.5	160	BG	Glacial till
6	390502085092800	--	320	7.8	1,850	620	130	200	2,480	180	160	.6	63	BG	Glacial till
7	390550085100300	--	640	7.9	3,350	2,000	870	460	5,620	520	510	3.4	230	BG	Glacial till
8	390620085053700	.0017	100	8.0	4,100	1,680	3,740	240	5,680	1,650	1,940	590	270	LU	Downstream from WTP
9	390706085073700	.0059	830	7.4	2,650	960	3,000	440	1,520	1,480	2,510	1,710	120	LU	Downstream from WTP
10	390715085073500	.0006	560	7.7	3,300	1,120	610	150	2,780	1,400	760	29	110	LU	Upstream from WTP

basin (sites 3–7, 10). Sodium concentrations were 3,740 and 3,000 μeq/L at sites 8 and 9, respectively, compared to the average background concentration of 650 μeq/L. The most substantial difference in concentration was measured for nitrate, which had a concentration of 590 μeq/L at site 8 and 1,710 μeq/L at site 9 compared to the average background concentration of less than 10 μeq/L. The synoptic samples also demonstrate that the water quality downstream at the HBN station was impacted by the wastewater-treatment facilities based on the elevated chloride concentration measured at site 1. By contrast, the nitrate concentration measured at site 1 was similar to background concentrations, implying that, at least during low-flow conditions, the biota were capable of consuming excess nitrate upstream from the HBN station. In contrast to sodium, chloride, and nitrate, the concentration patterns of the weathering-derived constituents were more uniform across the basin. For example, calcium concentrations ranged from 1,850 to 4,600 μeq/L, and magnesium ranged from 620 to 2,000 μeq/L. This pattern not only reflects the widespread presence of carbonate minerals in the glacial till and bedrock, but indicates that the towns of Milan and Moores Hill did not greatly affect the concentrations of these constituents in surface water. Sulfate concentrations were much lower in tributaries in the western one-half of the basin compared to the eastern one-half. For example, the average sulfate concentration at sites 4, 5, 6, and 7 was 400 μeq/L compared to the average concentration of 1,740 μeq/L at sites 2, 3, 8, 9, and 10. One explanation for this spatial pattern is a difference in bedrock mineralogy between these two areas of the basin. The streams in the northwestern part of the basin drain areas covered by glacial till, whereas drainages in the southeastern part of the basin are incised into the Ordovician bedrock, which, in places, contains evaporite beds of gypsum and anhydrite.

Elk Creek near Decatur City, Iowa (Station 06897950)

Site Characteristics and Land Use

The Elk Creek HBN Basin is located in the Central Lowland physiographic province in southern Iowa in the landform region known as the Southern Iowa Drift Plain (fig. 8). The landscape is formed by a broad loess-covered drift plain strongly incised by streams to form rolling hills and ridges. The HBN basin drains 136 km^2 of this dissected terrain and ranges in elevation from 282 m at the gaging station to 360 m on the surface of the almost level upland divide. The USGS gaging station is located 9.2 km southwest of Decatur City, Iowa, at latitude 40°43'18" and longitude 93°56'12". Elk Creek flows southeast into the Grand River, a tributary of the Missouri River, and has a channel length of about 15.8 km upstream from the gaging station and an average stream gradient of 3.3 m/km. Mean monthly discharge at the gaging station ranges from 0.36 m^3/s in August to 1.9 m^3/s in April; there are occasional periods of no flow in fall and early winter (September through December). Average annual runoff from the basin was 23 cm from 1968 through 1994 (Southard and others, 1994). The climate is characterized by cold winters and hot summers (DeWitt, 1990). Average daily air temperatures range from –6.6°C in January to 24.6°C in July. Average annual precipitation is 92 cm, of which about two-thirds falls from April through September (DeWitt, 1990). The average seasonal snowfall is 67 cm, and on average, 43 days each year have at least 2 cm of snow on the ground.

The Elk Creek Basin is in the Prairie Parkland ecoregion, which is characterized by intermingled prairie, groves, and strips of deciduous trees (Bailey and others, 1994). Forest vegetation covers about 10 percent of the basin and is concentrated along the flood plains and on steep upland hillslopes. The upland forests consist of white oak, northern red oak, black oak, bur oak, shagbark hickory, bitternut hickory, honeylocust, and eastern red cedar (DeWitt, 1990). The principal species along the flood plain are eastern cottonwood, silver maple, willow, green ash, basswood, and black walnut. Forests in the area are generally of poor quality because of the cumulative effects of selective cutting practices and cattle grazing (DeWitt, 1990). The native prairie grasses are big bluestem, little bluestem, switchgrass, and Indian grass; however, little of this vegetation type exists because most of the basin is cultivated. Soils on the hillslopes and uplands are classified as Alfisols (Hapludalfs) and are mapped in the Gara-Armstrong-Lineville soil association (DeWitt, 1990; Boeckman, 1992). These are moderately well-drained, silty, and loamy soils formed in glacial till and loess. The soil profiles are characterized by a surface layer of dark grayish-brown friable loam that is 15 to 30 cm thick overlying a subsoil of mottled, yellowish-brown firm clay loam or loam that extends to a depth of 150 cm. Soils developed in the flood plain are primarily mapped in the Nottaway-Lawson-Zook association (DeWitt, 1990). These are flat-lying, moderately to poorly drained, silty soils formed in alluvium.

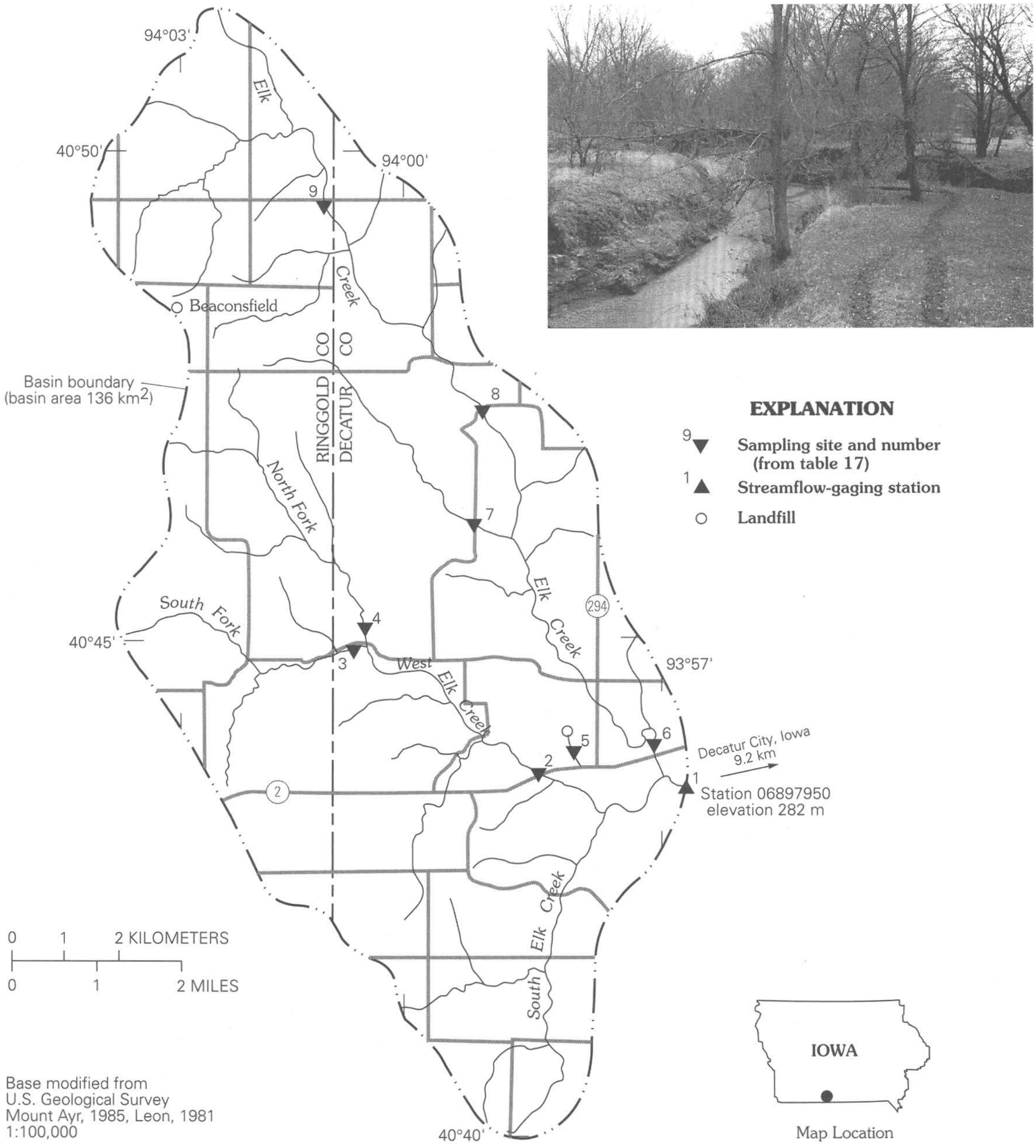


Figure 8. Map showing study area in the Elk Creek Basin and photograph of the North Fork of West Elk Creek.

Bedrock in the basin consists of flat-lying marine sediments of the Lansing and Kansas City Groups of Pennsylvanian age (Arey, 1916; Cagle and Heinitz, 1978). The Lansing Group consists of thin-bedded limestones and interbedded red and green shales and overlies the Kansas City Group, which consists of alternating beds of limestone and shale. Limestone beds in the Kansas City Group are quite permeable and form an important aquifer in the area (Cagle and Heinitz, 1978). The topography of the bedrock surface is a result of a complex system of ancient drainages, but is covered almost everywhere by unconsolidated deposits of glacial drift, loess, and alluvium as much as 60 m thick (Cagle, 1973). The drift consists predominantly of sand, pebbly clay, and gravel deposits of varying thickness and extent. Aquifers in the drift are an important source of small water supplies for domestic and livestock use (Cagle, 1967).

The Elk Creek Basin drains parts of Ringgold and Decatur Counties in southern Iowa. Land ownership in the basin is 98 percent private and 2 percent county and State (Kevin Reynolds, U.S. Department of Agriculture Natural Resources Conservation Service, written commun., 1996). Roughly 120 km of paved and gravel roads provide access to most areas of the basin. A 9-km segment of State Highway 2 runs from east to west in the southern one-half of the basin. County and State roads are plowed and salted in winter. Access to waterways is limited to rights-of-way at public road crossings.

Land use in the Elk Creek Basin is 10 percent forest, 55 percent row crops, and 35 percent pasture land (Kevin Reynolds, written commun., 1996). The percentage of agricultural land in the basin has changed very little since the HBN station was established, except for a slight increase in cropland and a decrease in cattle production. The primary row crops are corn and soybeans, and the major hay crops are legume-grass mixtures. Forested areas, which are used for timber harvesting and grazing, are primarily located along the main channel of Elk Creek and along upland tributaries. In addition to agricultural lands, the basin contains several cattle feedlots, hundreds of stockponds, a number of rural residences, and the small community of Beaconsfield (population 27). Most residents use shallow ground water as a domestic water supply. The county landfill located in the basin was built in the late 1970's. Between 1985 and 1995, about 25 percent of agricultural land in the basin was converted to permanent vegetation types through the Conservation Reserve Program (CRP) (Wayde Ross, written commun., 1996). The U.S. Department of Agriculture instituted the CRP in 1985 as a means of reducing soil erosion from highly erodible croplands. Under the CRP, farmers are paid in exchange for planting permanent vegetation types, such as sod-forming grasses and legumes, and implementing erosion controls, such as creating riparian buffer strips (Wayde Ross, U.S. Department of Agriculture Natural Resources Conservation Service, written commun., 1996).

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for the Elk Creek HBN Station for this report includes 154 water-quality samples that were collected from February 1968 through August 1994. Sampling frequency ranged from bimonthly to monthly from 1968 through 1982 and quarterly from 1983 through 1994. Water-quality samples in the early part of the period of record were probably analyzed at a USGS laboratory in Lincoln, Nebr., that operated until 1973 (Durum, 1978). After the establishment of the central laboratory system, samples were analyzed at a laboratory in Salt Lake City, Utah, from 1973 through 1975 and at the NWQL in Arvada, Colo., from 1976 through 1994. Daily discharge records are available for Elk Creek (station 06897950) from October 1967 through September 1994. The gaging station was moved about 90 m downstream on June 21, 1974, because of serious bank erosion at the upstream location (Joe Gorman, U.S. Geological Survey, oral commun., 1997).

Calculated ion balances for 146 samples with complete major-ion analyses are shown in figure 9. Ion balances ranged from –18 to 23 percent, and more than 95 percent of samples had values within the ±5 percent range, indicating that the analytical measurements were of high quality. The average charge balance for all samples was 1.0 percent, indicating that unmeasured constituents, such as organic anions, do not seem to contribute substantially to the ion balance of stream water at this station. Time-series plots of the major constituents were inspected for evidence of method-related effects (fig. 9). No unusual patterns were apparent, except for a slight decrease in data scatter for most constituents in the later one-half of the period of record. This pattern in data scatter may be related to a change in the distribution of sample discharge values due to a reduction in sampling frequency in 1983. Alternatively, the decrease in data scatter may reflect improvements in analytical methods during the period of record.

Median concentrations and ranges of major constituents in stream water at the Elk Creek Station and VWM concentrations in wet-only deposition measured at the McNay Research Center NADP Station are listed in table 14. Precipitation chemistry at the NADP station, which is located about 57 km east of the HBN station, was dilute and slightly acidic with a VWM pH of 4.9 for 12 years of record. The predominant cations were ammonium, which contributed 39 percent of the total cation charge, and calcium and hydrogen, which accounted for 28 and 22 percent, respectively. Sulfate composed 58 percent of the total anions and nitrate contributed 36 percent. The predominance of strong acid anions at this site indicates that precipitation may be affected by anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain. In addition, the relatively high ammonium concentrations in precipitation may be linked to the high density of livestock in this region of the country.

Stream water in Elk Creek is fairly concentrated and strongly buffered; specific conductance ranged from 90 to 900 µS/cm, and the alkalinity was between 1,040 and 7,300 µeq/L. Calcium and magnesium were the predominant cations, and bicarbonate was the predominant anion. The high concentrations of these solutes in stream water is attributed to the presence of limestone bedrock and of carbonate minerals in the near-surface till and loess deposits. The median concentration of chloride in stream water was 230 µeq/L, which is more than 70 times greater than VWM concentration of 3.1 µeq/L in precipitation. This large difference in concentration indicates that most stream-water chloride is derived from sources other than precipitation. Stream-water chloride at this site probably is derived from a combination of natural and human-related sources; however, fertilizer and road salt are probably the largest contributors. Sulfate concentrations also were much higher in stream water than in precipitation. The main source of sulfate, other than atmospheric deposition, probably is dissolution of gypsum and anhydrite minerals present in variable amounts in the limestones and shales (Kross, 1990). Stream water at this site had low, but detectable, concentrations of inorganic nitrogen species. The median stream-water concentrations of nitrate and ammonium were 25 and 7.2 µeq/L, respectively, compared to 20 and 22 µeq/L, respectively, in precipitation. Although stream-water nitrate concentrations were low compared to the concentration of 3 mg/L (214 µeq) considered indicative of human-related pollution in Iowa (Kross, 1990), they were substantially higher than nitrate concentrations at most stations in the HBN, indicating that agricultural activities had a small, but detectable, effect on the stream-water nutrient concentrations at this station.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 15). The major weathering constituents had strong correlations with discharge, except for potassium, sulfate, and silica. These inverse correlations are consistent with a hydrologic system where more concentrated ground water, which provides most of the discharge during low-flow conditions, is diluted with water from shallower ground-water sources during periods of increased discharge. In contrast, nitrate was positively correlated with discharge (rho = 0.670), which may be due to surface runoff from agricultural lands and livestock yards. Fertilizer and manure are sources of nitrate that are most likely to be transported to the stream during periods of increased discharge. The lack of correlation between sulfate and discharge (rho = –0.179) was somewhat unexpected because most of the sulfate probably is derived from bedrock sources. A more detailed examination of the data indicated that sulfate concentrations did vary with discharge, but the relation was not monotonic. Sulfate had the expected inverse relation with discharge, but only for discharges greater than 0.03 m^3/s. At flows less than 0.03 m^3/s, sulfate concentrations generally decreased with decreasing

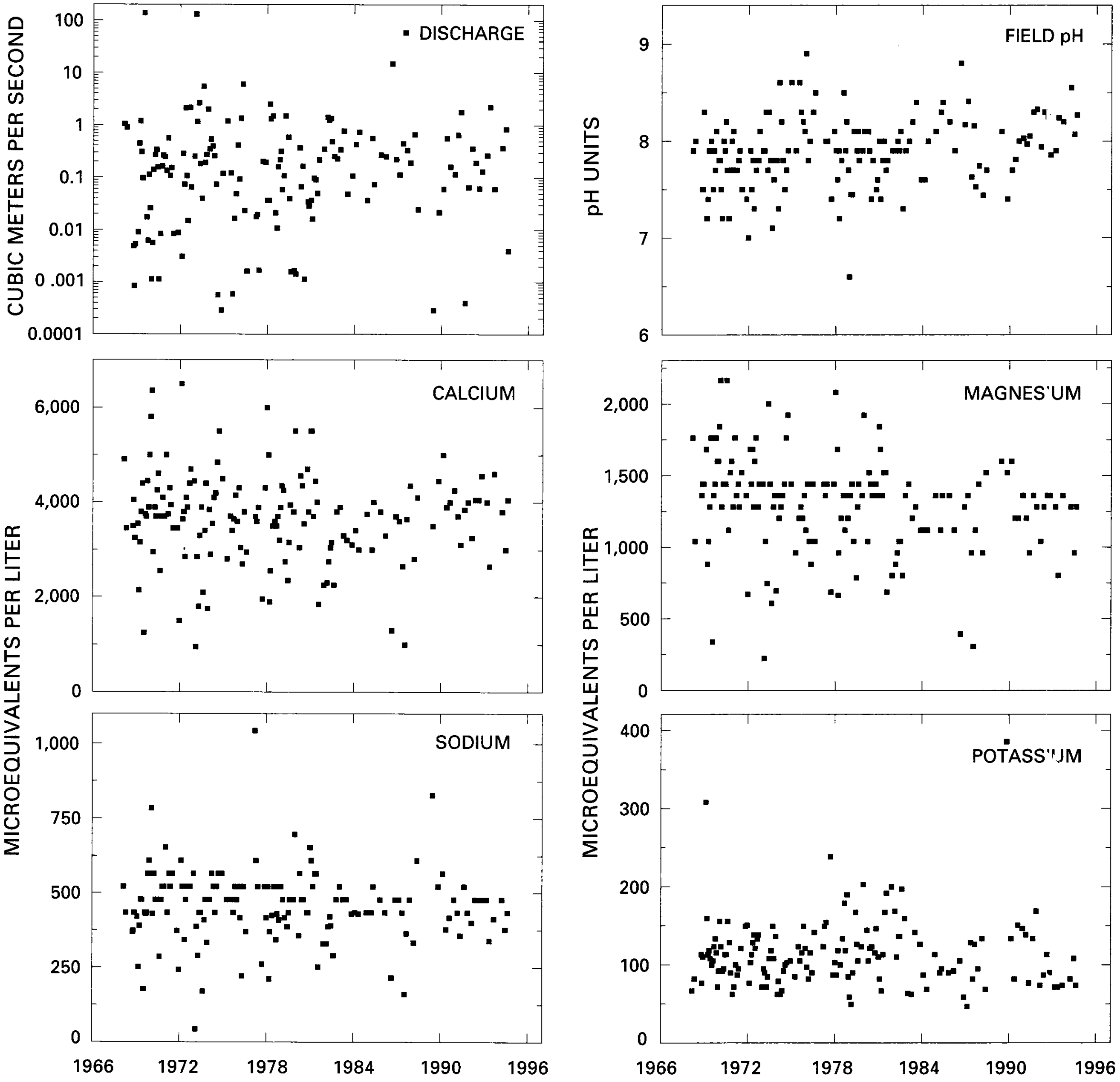


Figure 9. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Elk Creek, Iowa.

discharge. One explanation for this pattern is variation in ground-water chemistry. Simpkins and Burkart (1996) studied shallow ground water in a small agricultural basin in central Iowa and found that an unoxidized zone existed below about 4 m and that in this zone, much of the sulfate was being removed by sulfate reduction. Because ground water would be an increasingly important component of streamflow during low-flow conditions, the presence of a reducing zone in the ground-water aquifer might explain the decrease in stream-water sulfate concentrations at very low flows.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are listed in table 16. No statistically significant trends were observed at the Elk Creek Station at the 0.01

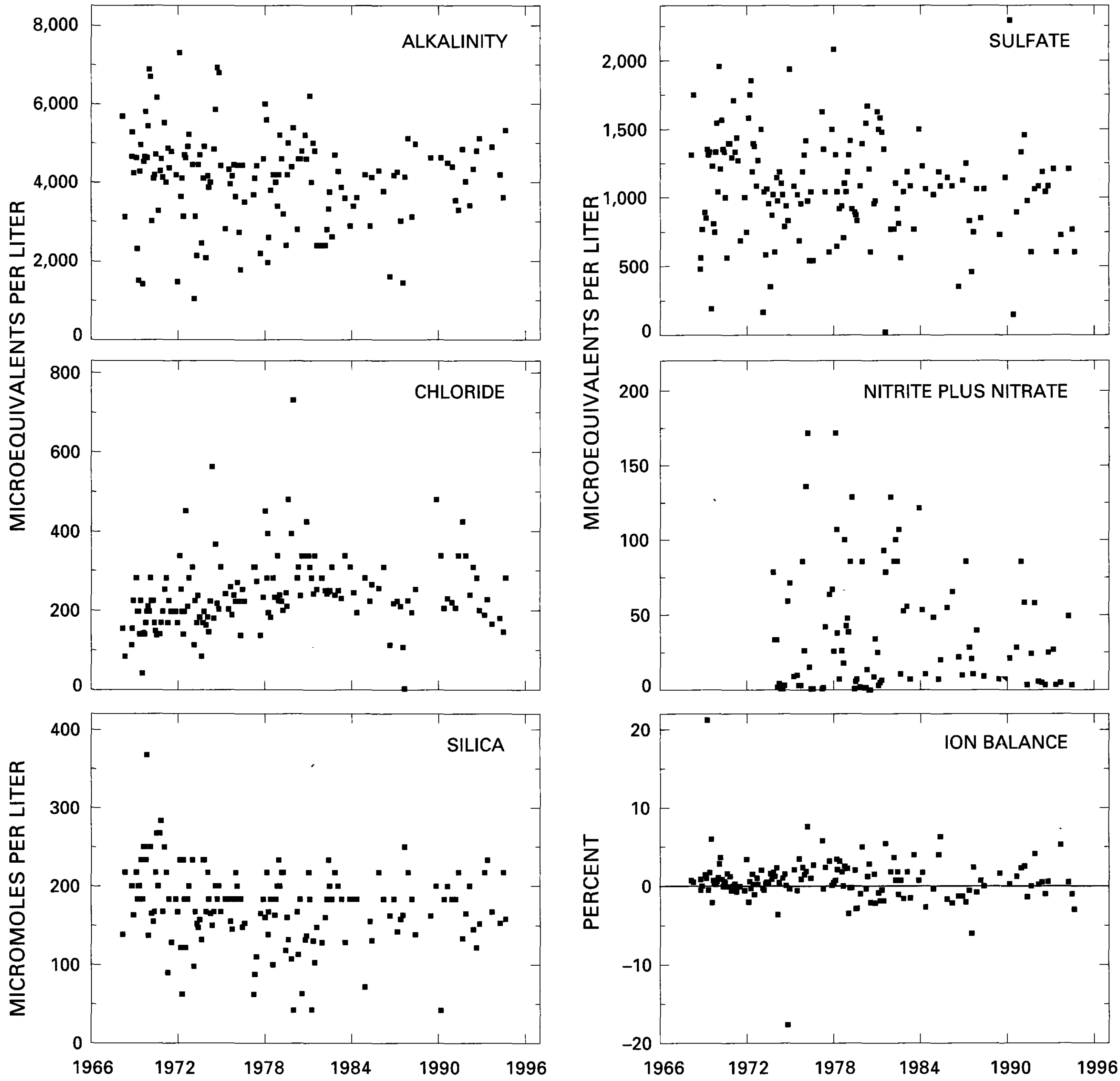


Figure 9. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Elk Creek, Iowa—Continued.

probability level. Downward trends in magnesium and silica and an upward trend in chloride were detected at a slightly less significant level of $p \leq 0.05$. The significance of all three trends increased to $p \leq 0.02$ after the concentrations were adjusted for streamflow variability. The observed trends in stream chemistry at this station are more likely related to changes in land-use activities rather than to trends in atmospheric deposition, considering that stream water is substantially more concentrated than precipitation. A number of land-use practices could have caused an increase in stream-water chloride, including road salting, fertilizer application, or leaching of the county landfill that was constructed in the early 1970's. The cause of the downward trends in magnesium and silica concentrations is not clear. Because

Table 14. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major dissolved constituents measured in water-quality samples from Elk Creek, Iowa, February 1968 through August 1994, and volume-weighted mean concentrations in wet precipitation collected at the McNay Research Center Station, Iowa

[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.	0.0001	0.034	0.16	0.42	140	152	--
Spec. cond., field	90	440	500	560	900	151	13
pH, field	6.6	7.7	7.9	8.1	8.9	151	4.9[b]
Calcium	950	3,150	3,700	4,230	6,500	154	16
Magnesium	230	1,150	1,400	1,480	2,220	153	2.4
Sodium	44	410	480	520	1,040	154	2.8
Potassium	46	87	110	130	380	151	.9
Ammonium	.6	3.3	7.2	17	170	37	22
Alkalinity, laboratory	1,040	3,415	4,200	4,710	7,300	148	--
Sulfate	21	830	1,060	1,330	2,290	154	32
Chloride	<2.8	190	230	280	730	153	3.1
Nitrite plus nitrate	<.7	5.8	25	59	170	100	20[c]
Silica	42	150	180	200	370	153	--

[a] Data are volume-weighted mean concentrations for 1984–95.

[b] Laboratory pH.

[c] Nitrate only.

Table 15. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major dissolved constituents, Elk Creek, Iowa, 1968–94

[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	0.150									
Ca	–.671	–0.159								
Mg	–.789	–.165	0.877							
Na	–.685	–.047	.746	0.901						
K	–.175	–.172	–.138	–.060	–0.125					
Alk	–.770	–.125	.904	.883	.749	–0.176				
SO_4	–.179	–.144	.506	.512	.592	–.203	0.244			
Cl	–.641	–.129	.277	.438	.416	.401	.296	0.141		
N	.670	–.102	–.648	–.695	–.612	.185	–.755	–.101	–0.264	
Si	.488	–.108	–.134	–.268	–.287	–.225	–.208	–.042	–.429	0.543

both of these constituents primarily are derived from weathering, one possible explanation is a decrease in sedimentation to streams as a result of reductions in soil erosion from agricultural lands. Although estimates of erosion rates are not available for the Elk Creek Basin, a reduction in soil erosion may have occurred as a result of the CRP, which resulted in the conversion of about 25 percent of cropland in the basin to permanent vegetation types between 1985 and 1995.

Table 16. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major dissolved constituents, Elk Creek, Iowa, February 1968 through August 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; inst., instantaneous; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	0.001	0.111	--	--
pH	<.01	.469	([a])	--
Calcium	<.1	.937	1.5	0.853
Magnesium	–5.3	.028	–5.2	.015
Sodium	<.1	.287	–1.0	.194
Potassium	–.2	.507	–.2	.579
Alkalinity	–5.0	.701	–2.5	.820
Sulfate	–7.0	.163	–6.3	.131
Chloride	2.6	.032	2.6	.014
Nitrite plus nitrate	.9[b]	.421	--	--
Silica	–1.2	.043	–1.5	.020

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

[b] Trend calculated for 1974–94 using a trend test for censored data.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling in the Elk Creek Basin on April 6 and 7, 1993, are listed in table 17, and the locations of sampling sites are shown in figure 8. During the sampling period, discharge at the gaging station was about 0.4 m^3/s compared to the median daily discharge of 0.5 m^3/s for April (Lawrence, 1987), indicating that the basin was sampled during normal flow conditions for that time of year. Solute concentrations measured at site 1 during the synoptic sampling were below the median concentrations reported for the HBN station during the entire period of record, except for silica (table 14). The tributary streams were similar in composition to stream water collected at the gaging station (site 1); calcium and magnesium were the predominant cations, and bicarbonate was the predominant anion. Ion balances for all samples were close to zero (range –0.5 to 1.8 percent), indicating that unmeasured ions, such as organic anions, did not seem to be an important component of stream water during the sampling period.

In general, concentrations of the major solutes did not vary markedly among the sampled tributary sites. For example, alkalinity ranged from a minimum of 3,260 µeq/L at site 9 to a maximum of 5,180 µeq/L at site 5 (table 17). Calcium concentrations ranged from 2,650 to 4,000 µeq/L, and magnesium ranged from 1,040 to 1,600 µeq/L. Sulfate concentrations had a slightly broader range of concentrations—from 580 µeq/L at site 5 to 1,250 µeq/L at site 7. The widespread presence and rapid weathering rates of carbonate minerals in the bedrock and in surfical deposits are the most likely reasons for the lack of

Table 17. Physical properties and major dissolved constituents from surface-water sampling sites in the Elk Creek Basin, Iowa, collected April 6 and 7, 1993

[Site locations shown in fig. 8; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeters 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; Si, silica; concentrations in microequivalents per liter, except silica in micromoles per liter; --, not reported; criteria used in selection of sampling sites: MT = major tributary, LU = land use]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria	Remarks
1	6897950	0.43	480	8.2	3,400	1,200	410	74	3,820	1,020	170	18	220	--	Gaging station
2	404337093580900	.32	490	8.1	3,500	1,200	420	77	3,840	1,000	160	12	220	MT, LU	Pasture and cropland
3	404501094002800	--	450	8.2	3,250	1,120	360	51	3,580	980	99	2.4	200	MT, LU	Pasture and cropland
4	404504094002600	--	440	8.1	3,000	1,040	360	64	3,520	880	100	5.6	220	MT, LU	Pasture and cropland
5	404343093573900	.0028	560	8.0	4,000	1,600	650	46	5,180	580	450	29	200	LU	Downstream from landfill
6	404348093564000	.34	460	8.1	3,200	1,120	430	72	3,680	880	180	22	220	MT, LU	Pasture and cropland
7	404611093590600	.050	470	8.1	3,100	1,120	430	72	3,360	1,250	150	13	200	LU	Pasture land and feedlots
8	404723093585800	--	420	8.1	2,800	1,040	390	38	3,400	730	150	19	220	LU	Pasture land and feedlots
9	404932094005800	.11	400	8.0	2,650	1,040	380	59	3,260	630	170	21	200	LU	Pasture land

much spatial variation in the concentrations of the major solutes. The slightly broader range of sulfate concentrations may reflect local variations in the distribution of evaporite beds in the underlying Pennsylvanian shales and limestones. Chloride and sodium concentrations were fairly uniform across the basin, with the exception of site 5. The chloride concentration at this site was 450 μeq/L compared to the average concentration of 150 μeq/L for the other eight sampling sites. This stream was sampled just downstream from the county landfill, indicating that the landfill may be a point source of contaminants to surface water. Nitrate concentrations ranged from 2.4 to 29 μeq/L and were low, considering the amount of agricultural activity in the basin.

Big Creek at Pollock, Louisiana (Station 07373000)

Site Characteristics and Land Use

The Big Creek HBN Basin is located in the Alluvial Plains region of the Coastal Plain physiographic province in central Louisiana (fig. 10). The 132-km^2 basin ranges in elevation from 23 to 80 m and drains a landscape dissected by numerous small streams with narrow, gently sloping ridgetops and steep-sided hillslopes. The USGS gaging station is located 1.3 km north of the town of Pollock, La., at latitude 31°32'10" and longitude 92°24'30". Big Creek flows southeast into the Little River, a tributary of the Atchafalaya River, and has a channel length of about 16 km upstream from the gaging station and an average stream gradient of 2.1 m/km. The main channel is perennial, and mean monthly discharge varies from a minimum of 0.71 m^3/s in August to a maximum of 3.1 m^3/s in February. Average annual runoff from the basin was 44 cm from 1943 through 1995 (Garrison and others, 1996). High infiltration rates and substantial ground-water storage result in well-sustained, constant base flows during dry months of the year. The climate is subtropical and is characterized by frequent and sometimes abrupt changes in weather. Average daily air temperatures range from 8.2°C in January to 27.8°C in July (Kilpatrick and others, 1986). Precipitation averages 148 cm annually and is slightly greater in the winter and the spring than in the summer and the fall (Kilpatrick and others, 1986). Average annual snowfall is less than 3 cm and only rarely are there days in winter when the air temperature does not rise above freezing.

The Big Creek Basin is in the Outer Coastal Plain Mixed Forest ecoregion and is covered by a subclimax pine forest, which has an understory of grasses and sedges (Bailey and others, 1994). Before European settlement, the vegetation was dominated by longleaf pine forests; however, past management practices and the exclusion of wildfire have eliminated most of this native ecosystem. Forest cover presently consists of 75 percent yellow pine (loblolly, shortleaf, and slash pines) and about 25 percent longleaf pine. Pine forests are interspersed with hardwoods and flowering species, such as dogwoods, redbud, and magnolia. Vegetation along the flood plain is dominated by hardwoods, including hickory, cypress, oak, and gum. Forests in the Big Creek Basin were heavily affected by the southern pine beetle epidemic in the mid-1980's. Most soils in the basin are classified as Ultisols (Paleudults) and are mapped in the Smithdale-Ruston soil association, which includes well-drained soils developed in terrace deposits of Quaternary age (Kilpatrick and others, 1986). The Ruston soils develop on narrow ridgetops, and the Smithdale soils are on steeper side slopes. A typical soil in this association has a brown surface layer of fine sandy loam as much as 15 cm thick overlying a yellowish-red subsoil of sand clay loam that extends to 190 cm. These soils are typically acidic (pH 4.5 to 5.5), have low cation-exchange capacities (7 to 13 meq/100 g), and high concentrations of exchangeable aluminum (Kilpatrick and others, 1986). The predominant clay minerals in these soils are kaolinite and vermiculite.

The basin is underlain by gently dipping terraces of Pleistocene age that were deposited by large braided river complexes during interglacial periods (Maher, 1941). The terrace deposits consist of silty clays, sands, and gravels that range in color from mottled pink to reddish brown in fresh exposures to deep red or orange in weathered exposures (Fisk, 1938). The sediments range from 15 to 30 m in thickness and overlie the Catahoula Formation of Miocene age. The Catahoula Formation consists of alternating beds of sand, silt, and clay deposited under predominantly non-marine conditions (Martin and Whiteman, 1986). The Catahoula Formation forms an important aquifer in Louisiana; however, most domestic wells in Grant Parish are completed in the overlying terrace deposits (Gaydos and others, 1973).

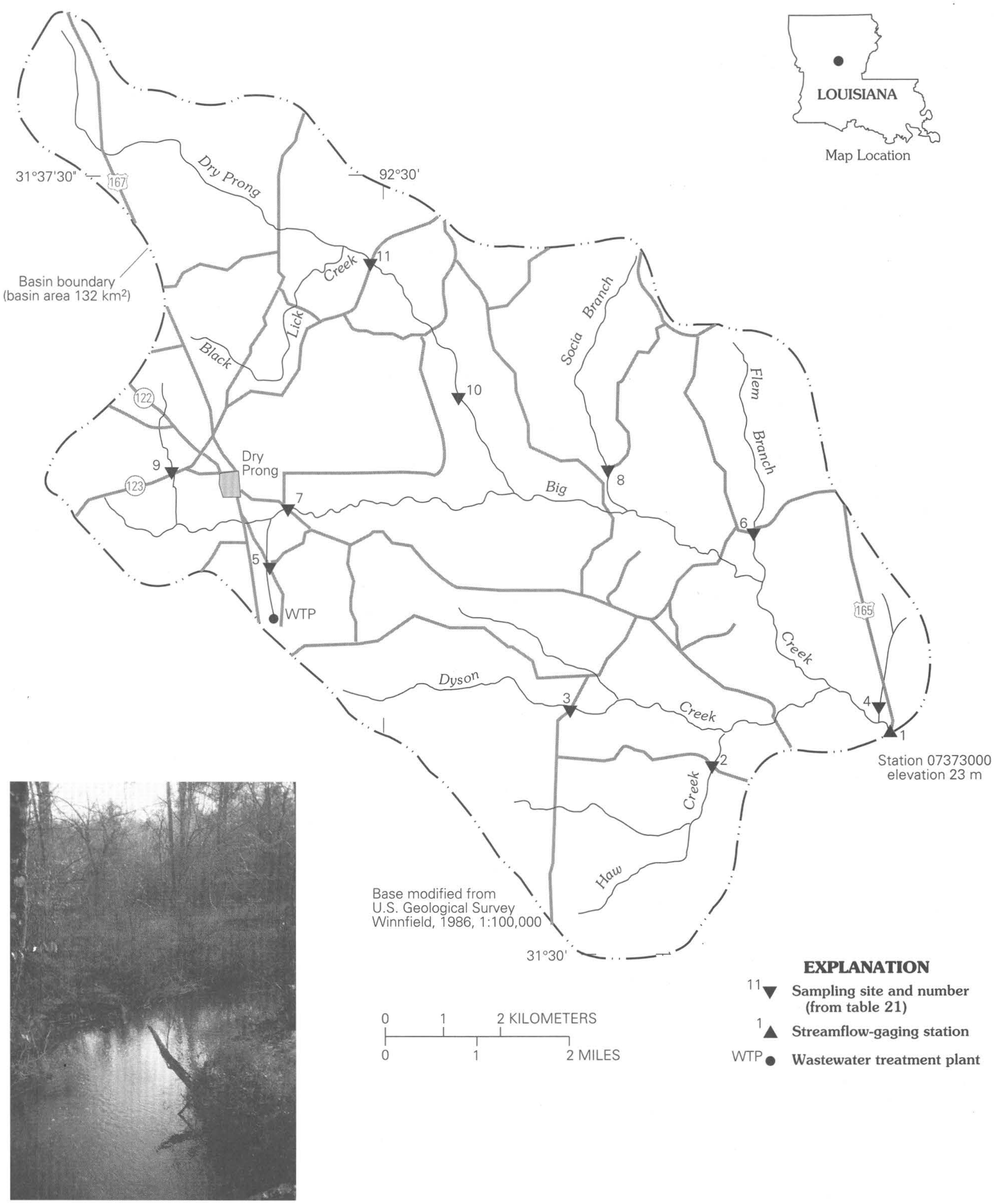


Figure 10. Map showing study area in the Big Creek Basin and photograph of the Haw Creek tributary.

The Big Creek Basin drains the central part of Grant Parish in central Louisiana and is within the boundaries of the Catahoula Ranger District of the Kisatchie National Forest. About 44 percent of land in the basin is privately owned (John Novosad, U.S. Department of Agriculture Forest Service, written commun., 1997). Privately owned land is concentrated along the main channel of Big Creek and the Dyson Creek and Dry Prong tributaries, and about 80 percent is owned by large timber companies (U.S. Department of Agriculture, 1985a). A dense network of forest roads provides access to most areas of the basin. Roads tend to follow the ridgelines rather than parallel the drainages.

Land cover in the basin is about 90 percent forest, 7 percent agricultural, and 3 percent residential (John Novosad, U.S. Department of Agriculture Forest Service, written commun., 1997). The primary land-use activities on National Forest and on private land are timber harvesting and livestock grazing. National Forests in the basin are managed on an even-aged basis with 120-year rotations for longleaf pine and 100-year rotations for shortleaf pine and hardwoods. During the past 10 years, about 10 percent of National Forest land in the basin has been clearcut, and 20 percent has been treated by intermediate cuts (Finnis Harris, U.S. Department of Agriculture Forest Service, written commun., 1997). The Forest Service also has a controlled grazing program and issues grazing permits in areas dominated by longleaf and yellow pine forest types. Grazing on forest land in the basin presently is limited to about 40 head of cattle on about 280 ha (Finnis Harris, written commun., 1997). Other human-related features in the basin include a dense network of roads, the community of Dry Prong (population 380), a few gravel pits, several rural residences and small farms, stock ponds, and a gas pipeline and pumping station at the head of Flem Branch. The town of Dry Prong has a wastewater-treatment facility that discharges into the headwaters of Big Creek. Most residents obtain domestic water from ground-water wells in the terrace deposits. There have been no major changes in land use in the basin since the establishment of the HBN site, other than a small increase in residential population and slight decrease in timber harvesting on National Forest lands (John Novosad, U.S. Department of Agriculture Forest Service, written commun., 1997).

Historical Water-Quality Data and Time-Series Trends

The data set for the Big Creek HBN Station analyzed for this report includes 233 water-quality samples that were collected from March 1967 through August 1995. Sampling frequency was monthly from 1968 through 1982 and quarterly from 1983 through 1995. Water-quality samples in the early part of the period of record were analyzed at a USGS laboratory in Baton Rouge, La., which analyzed surface-water samples until 1973 (Durum, 1978). After establishment of the central laboratory system, samples were analyzed at a laboratory in Atlanta, Ga., from 1973 through 1985 and at the NWQL in Arvada, Colo., from 1986 through 1995. Daily discharge records for Big Creek (station 07373000) are available beginning in January 1942. Records of daily water temperature at the gaging station are available from October 1964 through September 1973 and from October 1974 through September 1976.

Calculated ion balances for 224 samples with complete major-ion analyses are shown in figure 11. Ion balances ranged from −18 to 17 percent, and 95 percent of samples had values in the ±10 percent range, indicating that the analytical measurements were of good quality. The average ion balance for all samples was –0.1 percent, indicating that unmeasured constituents, such as organic anions, did not contribute substantially to the ion balance of stream water at this station. Time-series plots of the major constituents were inspected for evidence of method-related effects (fig. 11). Several patterns are evident at this station; for example, calcium, magnesium, and sodium concentrations had noticeable decreases in data scatter after 1983. Procedural changes that may have affected the concentration patterns of these constituents include a change in the analytical method for cations and trace metals 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/admin/memo/, accessed 1997) and a change in the NWQL in 1985. Some of this variation also may be related to the decrease in sampling frequency after 1983. Several patterns also are apparent in the sulfate data. For example, lower than average concentrations were more common in the late 1960's and in the early 1970's, and higher than average concentrations were apparent in the late 1970's and the 1980's. The low concentrations in the early part of the period of record are coincident with the period when samples were analyzed at the USGS laboratory in Baton Rouge, La. The pattern in the latter part of the period of record may be an artifact of different methods used to analyze sulfate including a colorimetric method, which was used between 1976 and 1984; a turbidimetric method, which was used from 1983 through 1989; and ion chromatography, which was used after 1990. Another notable pattern in figure 11 is the apparent decrease in ion balance beginning in the mid-1980's. The cause of this decrease could not be identified, although it is coincident with a switch to the NWQL in Arvada, Colo., that occurred in 1985.

Median concentrations and ranges of major constituents in stream water at the Big Creek Station and VWM concentrations in wet-only deposition measured at the NADP Southeast Research Station are listed in table 18. Precipitation chemistry at the NADP station, which is located about 220 km east of the HBN station, was dilute and slightly acidic with a VWM pH of 4.8 for 13 years of record. The predominant cations were hydrogen, sodium, and ammonium, which accounted for 33, 25, and 23 percent of the total cation charge, respectively. The predominant anions were sulfate, which contributed 47 percent of the anion charge, and chloride and nitrate, which contributed 29 and 24 percent, respectively. These results indicate that precipitation at the nearby NADP station may be affected by anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain, as well as salt from marine aerosols.

Stream water in Big Creek is dilute and weakly buffered; specific conductance ranged from 24 to 59 µS/cm, and alkalinity was between 60 and 420 µeq/L (table 18). The major cations in stream water were sodium and calcium, and the major anions were bicarbonate and chloride. The low concentrations of the weathering-derived solutes, particularly bicarbonate, are attributed to the lack of weatherable minerals in the underlying Pleistocene terrace deposits. The median concentration of chloride in stream water was 120 µeq/L, which is about nine times greater 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 about a threefold increase in the chloride concentration of precipitation, indicating that most stream-water chloride is derived from sources other than precipitation. Because of the proximity of this site to the Gulf of Mexico, stream-water chloride probably is contributed by dry deposition of marine aerosols. Small amounts of chloride also may be derived from brackish waters stored in the Catahoula Formation (Maher, 1941). The median sulfate concentration of stream water was 42 µeq/L compared to the VWM concentration of 23 µeq/L in precipitation. The difference in concentration is somewhat smaller than expected based on evapotranspiration and indicates that some atmospherically deposited sulfate is retained in the basin. Possible mechanisms of sulfate retention include adsorption on clays and organic matter in the soil or sulfate reduction in swampy areas along the flood plain. The basin also seems to be a substantial sink of atmospheric nitrogen based on the lower concentrations of nitrate and ammonium in stream water compared to precipitation. Because weathering supplies only minor amounts of base cations and alkalinity to stream water, the retention of sulfate and nitrate may play an important role in buffering surface waters in the basin from the effects of acidic deposition.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 19). The weathering-derived solutes, sodium, alkalinity, and silica, were strongly correlated with discharge, which is consistent with a hydrologic system where weathering-enriched base flow is diluted by waters from shallow sources during periods of increased discharge. Among the solutes, the strongest correlations were among sodium, alkalinity, and silica. These correlations are consistent with the weathering stoichiometry of feldspar minerals, which are present in the terrace deposits and in underlying sandstones of the Catahoula Formation. The moderately strong positive correlation between sodium and chloride (rho = 0.638) indicates that some sodium probably also is derived from dissolution of salt. Calcium and magnesium were poorly correlated with the feldspar-weathering products and had only weak correlations with discharge. These patterns indicate that the concentrations of these cations may be regulated by processes other than weathering, such as cation exchange and nutrient cycling in the soil and shallow ground-water environments.

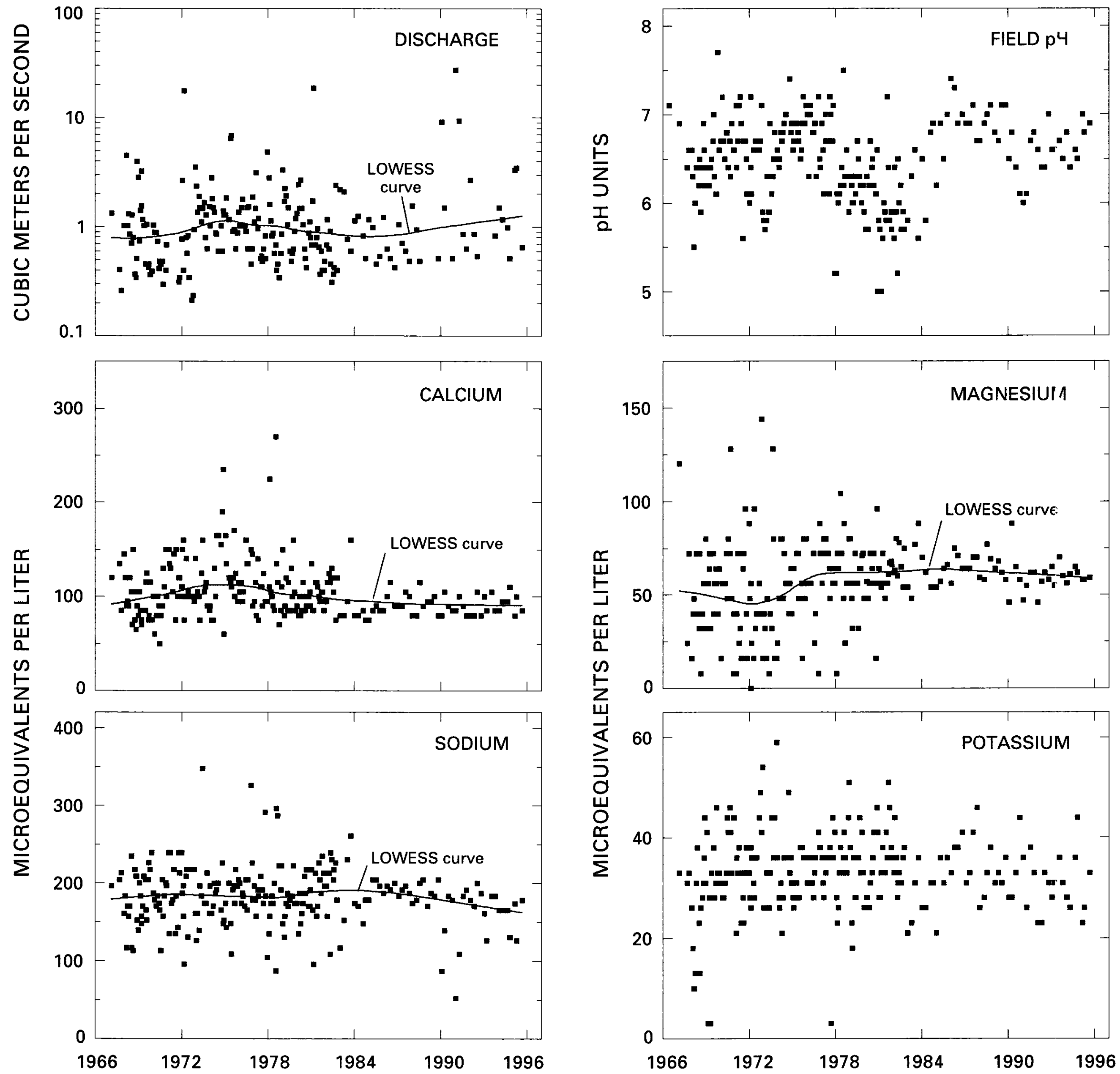


Figure 11. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Big Creek, Louisiana.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are listed in table 20. Statistically significant trends were observed in discharge and unadjusted calcium, magnesium, sodium, and sulfate concentrations at the 0.01 probability level. Statistically significant trends were not detected in the flow-adjusted sodium and sulfate concentrations, indicating that these trends were probably caused by the upward trend in stream discharge. The trends in calcium and magnesium were similar for the unadjusted and flow-adjusted concentrations, indicating that they were not caused by the observed trend in stream discharge. The LOWESS curves in figure 11 reveal slightly different trend patterns for calcium and magnesium. For example, the upward trend in magnesium is primarily caused by a period of low concentrations in the early part of the period of record. Since the mid-1970's, magnesium concentrations have remained

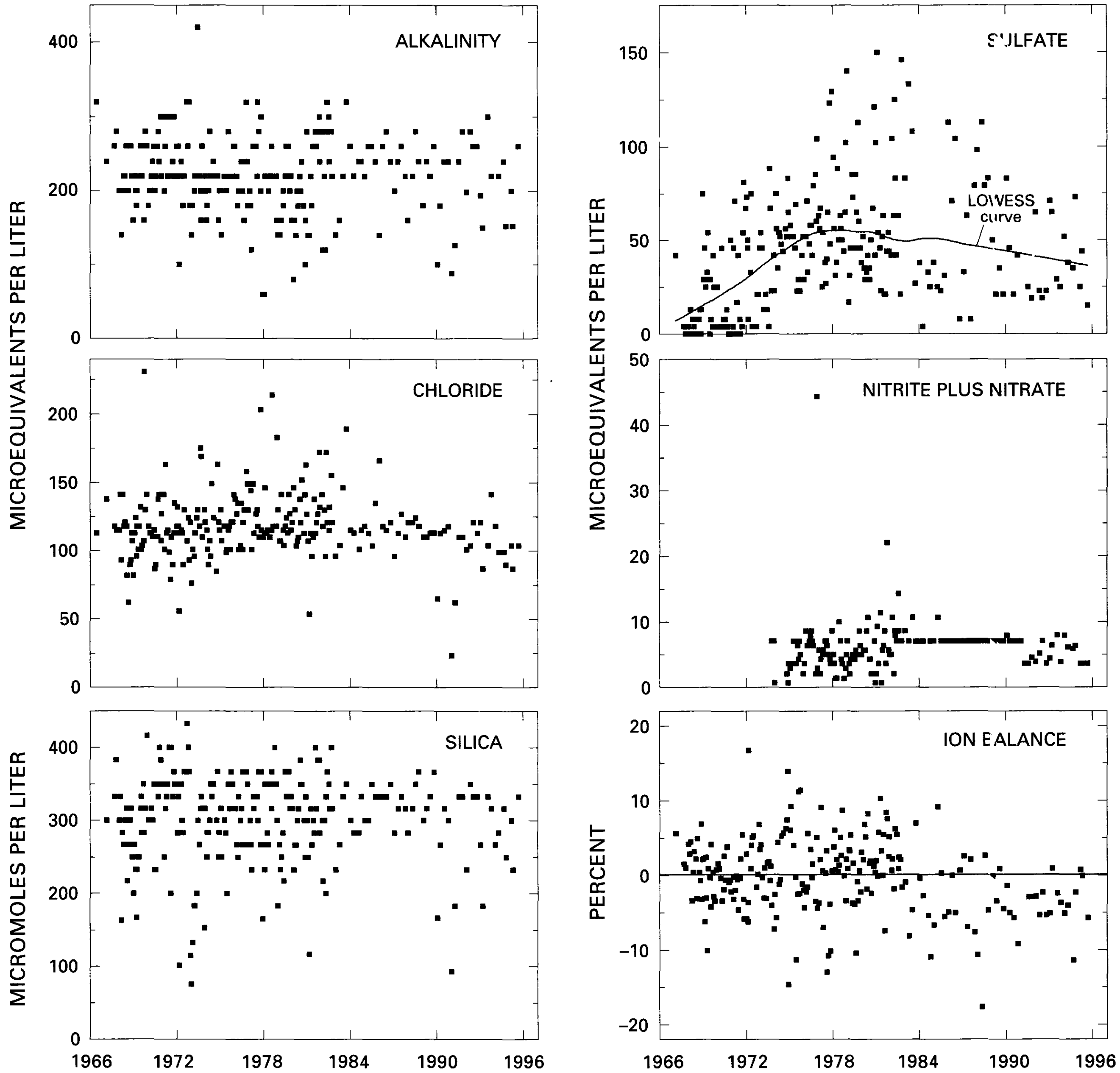


Figure 11. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Big Creek, Louisiana—Continued.

relatively constant. The greatest change in calcium concentrations occurred in the late 1970's and early 1980's, and since about 1983, calcium concentrations have remained relatively constant. Trends in stream-water calcium and magnesium at this station may reflect changes in environmental factors, such as land-use activities or precipitation chemistry. The effect of land use on stream chemistry at this site probably is minimal because the basin is primarily forested, and there have been no major changes in land use during the period of record other than a slight increase in residential population and decrease in logging activity. Trends in precipitation chemistry at this site are difficult to confirm because no long-term records are available for the entire period of record. Lynch and others (1995) reported declines in calcium, magnesium, and sulfate concentrations at a number of NADP stations in the south-central

Table 18. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major dissolved constituents measured in water-quality samples from Big Creek, Louisiana, March 1967 through August 1995, and volume-weighted mean concentrations in wet precipitation collected at the Southeast Research Station, Louisiana

[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.	0.21	0.54	0.89	1.42	27	232	--
Spec. cond., field	24	37	39	42	59	231	12
pH, field	5.0	6.2	6.5	6.8	7.7	233	4.8[b]
Calcium	50	85	100	120	270	229	4.8
Magnesium	8.0	50	58	74	150	228	3.3
Sodium	52	170	180	200	350	231	12
Potassium	<2.6	28	33	38	59	232	.7
Ammonium	<.7	1.1	2.1	4.8	50	75	11
Alkalinity, laboratory	60	200	220	260	420	231	--
Sulfate	<2.1	23	42	63	150	231	23
Chloride	23	110	120	130	230	231	14
Nitrite plus nitrate	<.7	<7.1	7.1	7.1	43	147	12[c]
Silica	75	270	300	330	430	233	--

[a] Data are volume-weighted mean concentrations for 1983–95.

[b] Laboratory pH.

[c] Nitrate only.

Table 19. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major dissolved constituents, Big Creek, Louisiana, 1967–95

[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	−0.129								
Ca	−.375	0.178							
Mg	−.469	.150	0.496						
Na	−.711	.097	.265	0.476					
K	−.554	.036	.389	.374	0.396				
Alk	−.714	.186	.169	.374	.745	0.284			
SO_4	.089	−.170	.312	.133	−.127	.024	−0.321		
Cl	−.388	−.122	.265	.368	.638	.336	.330	0.153	
Si	−.732	.288	.077	.370	.770	.370	.751	−.293	0.453

region of the United States from 1982 through 1990. Stream-water concentrations of calcium and magnesium have remained relatively constant since 1983, indicating that the observed trends in stream chemistry probably are not related to changes in atmospheric deposition. Another possibility is that the trends are artifacts of method-related factors. For example, the low magnesium concentrations in the early part of the record are coincident with a period when samples were analyzed at a USGS laboratory in Baton Rouge, La. (Durum, 1978). Another method-related factor that may have affected calcium and magnesium concentrations was a change in the analytical method used for cations and trace metals 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/admin/memo/, accessed 1997).

Table 20. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major dissolved constituents, Big Creek, Louisiana, March 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; inst., instantaneous; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	0.01	0.006	--	--
pH, field	.01	.140	0.01	0.089
Calcium	–.8	.001	–.7	.003
Magnesium	.6	.000	.7	.000
Sodium	–.9	.002	–.4	.076
Potassium	<.1	.882	<.1	.920
Alkalinity, laboratory	<.1	.481	.2	.602
Sulfate	.9	.003	.7	.071
Chloride	–.5	.013	–.2	.331
Nitrite plus nitrate	.1[a]	.022	--	--
Silica	–.6	.053	.2	.832

[a]Trend calculated for 1974–95 using a trend test for censored data.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling in the Big Creek Basin on January 20 and 21, 1991, are listed in table 21, and the locations of the sampling sites are shown in figure 10. During the sampling period, discharge at the gaging station was about 2.1 m^3/s compared to the median discharge of about 1.3 m^3/s for January (Lawrence, 1987), indicating that the basin was sampled during somewhat higher than normal flow conditions for that time of year. Solute concentrations measured at site 1 during the synoptic sampling were less than the first-quartile concentrations reported for the HBN station during the entire period of record, except for magnesium and sulfate (table 18). The tributary streams were similar in composition to stream water collected at the gaging station (site 1); sodium was the predominant cation, and chloride and alkalinity were the dominate anions. Ion balances were positive for all samples but one (range –2.0 to 11 percent), indicating the unmeasured anions, such as organic anions, were probably an important component of stream water during the sampling period.

In general, chemistry of the tributary streams was dilute and did not vary markedly among the sampling sites. For example, specific conductance ranged from 25 to 44 μS/cm (table 21), and most dissolved constituents did not vary by more than a factor of three. These surface-water characteristics primarily reflect the uniform composition of and lack of weatherable minerals in the underlying Pleistocene terrace deposits and Miocene sands. Some subtle

Table 21. Physical properties and major dissolved constituents from surface-water sampling sites in the Big Creek Basin, Louisiana, collected January 20–21, 1991

[Site locations shown in fig. 10; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeters 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; Si, silica; concentrations in microequivalents per liter, except silica in micromoles per liter; WTP, wastewater-treatment plant; --, not reported; criteria used in selection of sampling sites: MT = major tributary, LU = land use]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria	Remarks
1	07373000	2.1	34	6.5	85	60	130	24	110	92	45	4.3	220	--	Gaging station
2	313153092262300	.15	32	6.5	90	54	130	26	130	58	85	2.1	200	LU	Primarily forested
3	313224092275500	.15	39	6.3	130	61	140	23	140	110	82	1.4	270	MT, LU	Primarily forested
4	313232092243100	--	35	6.7	65	58	150	33	120	33	150	7.1	230	LU	Downstream from agricultural operation
5	313348092311200	--	27	5.6	90	62	78	24	74	63	62	4.3	120	LU	Downstream from WTP
6	313406092255300	.10	31	6.4	65	45	130	21	90	60	110	1.4	230	LU	Pipeline pumping station, logging
7	313419092305800	.17	42	6.4	130	58	150	38	120	94	110	14	180	LU	Downstream from WTP and Dry Prong
8	313440092273100	.20	27	6.1	60	37	100	17	43	79	90	1.4	220	LU	Primarily forest
9	313441092321900	.016	44	5.9	120	78	200	44	200	42	120	27	280	LU	Residential area
10	313522092290800	.37	25	6.1	55	44	100	20	69	50	82	2.1	200	MT, LU	Primarily forested
11	313641092300800	.34	26	6.0	65	51	96	19	54	58	73	2.9	200	LU	Primarily forested

variations in stream chemistry are evident, however, which may reflect factors other than geology. Chloride concentrations seemed to be slightly elevated in tributaries draining developed subbasins (sites 4, 6, 7, and 9) compared to tributaries draining forested subbasins (sites 2, 3, 8, 10, and 11). For example, the average chloride concentration for the forested tributaries was 82 µeq/L compared to the average concentration of 120 µeq/L for the developed tributaries. Because chloride often is an indicator of human activities, these results may indicate that residential development and agriculture in the basin may have a detectable effect on surface-water chemistry. Site 5 was the one tributary that did not seem to fit the land-use pattern. The chloride concentration of 62 µeq/L at site 5 was lower than all of the forested tributaries, despite the fact that the sampling site was not far downstream from a wastewater-treatment facility. Interestingly, the sample collected at the gaging station (site 1) had a lower chloride concentration than any of the upstream tributaries, perhaps due to inputs of low chloride ground water along the lower reaches of the Big Creek stream channel. Nitrate concentrations were low at all the sampling sites (range 1.4 to 27 µeq/L); however, the two highest concentrations were measured downstream from Dry Prong (sites 7 and 9), indicating that the town had a small, but detectable, effect on stream-water nutrient concentrations at these two sites.

Washington Creek at Windigo, Michigan (Station 04001000)

Site Characteristics and Land Use

The Washington Creek HBN Basin is located in the Superior Upland physiographic province on the southwest end of Isle Royale, which is the largest island in Lake Superior (fig. 12). The 34-km^2 basin ranges in elevation from 184 to 425 m and drains a landscape of narrow northeast-trending ridges separated by flat stream valleys with numerous wetlands. The USGS gaging station is located 1.3 km northeast of the Windigo Ranger Station at latitude 47°55'23" and longitude 89°08'42". Washington Creek, which flows into Windigo Harbor in Lake Superior, has a channel length of about 10.9 km upstream from the gaging station and an average stream gradient of 9.7 m/km. The main channel is perennial, and mean monthly discharge varies from 0.10 m^3/s in February to 2.0 m^3/s in April during snowmelt. Streamflow normally peaks a second time in October and November owing to increased precipitation and low rates of evapotranspiration. Average annual runoff from the basin was 42 cm from 1965 through 1995 (Blumer and others, 1996). The climate is continental with short, cool summers and cold winters. The mean annual air temperature is 3.4°C, and average annual precipitation is 77 cm (Hansen and others, 1973). Winter snowfall generally begins in October and accumulates in a seasonal snowpack that typically reaches 45 to 60 cm in depth.

The Washington Creek Basin is in the Laurentian Mixed Forest ecoregion, which is between the boreal forest and the deciduous forest zones (Bailey and others, 1994). The boreal forest type primarily grows in the northern part of the basin closest to the shoreline (Slavich and Janke, 1993). The predominant species in this area are white spruce, balsam fir, aspen, and paper birch. Farther south in the basin, the soils are thicker, and the climate is somewhat warmer; the forest primarily consists of mature stands of sugar maple and yellow birch. Wetland areas situated between the upland ridges are dominated by black spruce, white cedar, and fir, and some south-facing slopes have stands of jack pine. Most soils in the basin are classified as Spodosols and are mapped in the Graveraet-Michigamme-Rock outcrop soil association (U.S. Department of Agriculture, 1990a). This association is characterized by rock outcrops interspersed with moderately deep (60 to 90 cm), sandy to coarse loamy soils formed in glacial till and loamy mantle material over glacial till (Stottlemyer and Hanson, 1989). The soils tend to be acidic (pH 3.8 to 5.0) and have low exchangeable bases and organic-matter contents in the mineral horizon (Stottlemyer and Hanson, 1989).

Bedrock underlying Isle Royale consists of a thick sequence of basaltic and andesitic lava flows with interbedded conglomerates and sandstones collectively referred to as the Portage Lake Volcanics of Precambrian age (Huber, 1973a, b). The lava flows and sedimentary layers dip to the southeast and

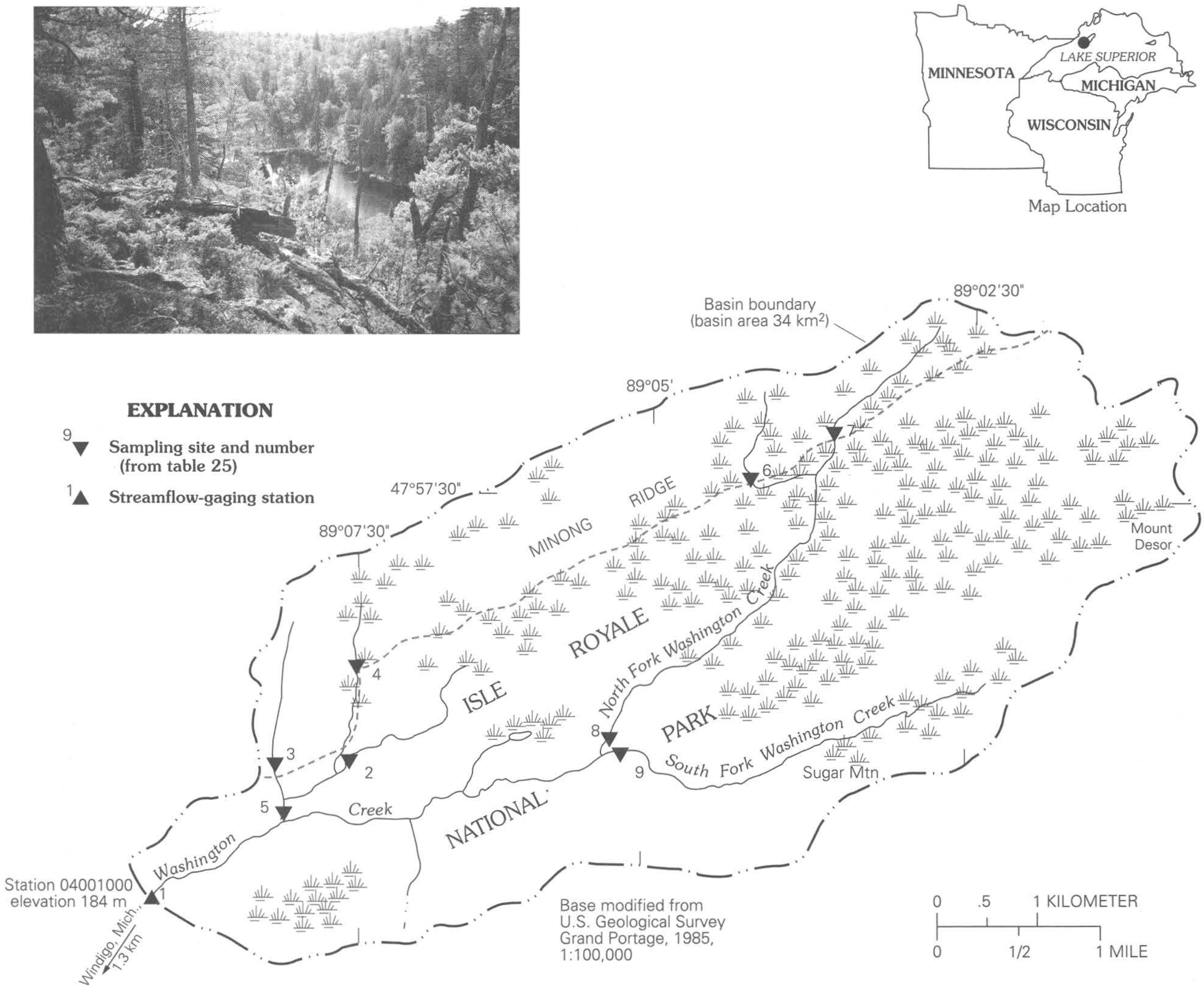


Figure 12. Map showing study area in the Washington Creek Basin and photograph of the landscape of the basin.

are eroded to form a series of long, parallel ridges and valleys. The Washington Creek Basin is primarily underlain by flood basalts, which locally include some sedimentary units. The flood basalts are composed of plagioclase (An_{60}) and pyroxene, which is predominantly augite. Ilmenite and magnetite are major accessory minerals, and chloride, sericite, and calcite are common secondary minerals (Huber, 1973b). Most bedrock in the basin is covered by talus, slopewash, and glacial drift deposits of Pleistocene age. Till deposits are deepest and most extensive in the southwestern part of the basin. The tills have a high carbonate content that probably is derived from calcareous deposits brought south from Hudson Bay by Pleistocene glaciers (Huber, 1973b).

The Washington Creek Basin is located in Keweenaw County in Michigan on the western end of Isle Royale in Lake Superior and is entirely in the boundaries of Isle Royale National Park. The basin is accessible by way of Windigo, on the western end of the island, by using seaplane service from Houghton, Mich. (118 km to the south), or by ferry service from Grand Portage, Minn. (35 km to the west). The park is open to the general public from April 15 to November 1, and regular transportation services operate from mid-June through October. During the winter, the site is accessible by ski plane or helicopter. The gaging station can be reached by a 1.7-km hiking trail from Windigo. The basin is undeveloped, except for two maintained hiking trails. A campground, ranger station, and weather station are located at Windigo, which is downstream from the gaging station.

Although the basin has remained undisturbed since the establishment of the National Park, the ecosystem has been modified by land uses in the past (Shelton, 1975). Mineral exploration for native copper deposits occurred in the Windigo area from 1889 to 1893, including an extensive drilling project to locate ore deposits. Although few deposits were ever mined, fire was commonly used by prospectors to remove vegetation from the bedrock. The only logging in the HBN basin occurred in the 1890's when white cedar and pine were cut along Washington Creek. Part of the basin was burned in 1936 when a logging-related fire destroyed almost one-third of the forest cover on the island. Natural factors also have affected the forests of Isle Royale, including spruce budworm epidemics and trends in the moose population (Hansen and others, 1973). The Civilian Conservation Corps constructed trails, fire towers, and buildings on the island in the 1930's, and the Isle Royale National Park was formally established in 1940. The management policies of Isle Royale National Park are described in the most recent version of the general management plan for the park (U.S. Department of the Interior, 1998). In addition to Washington Creek, water quality on Isle Royale also is monitored at the Wallace Lake study site (Stottlemyer and Hanson, 1989) located on the east end of Isle Royale approximately 40 km east of the HBN station. The Wallace Lake study site was established in 1982 as part of a network of field research sites in National Parks designed to study the structure and function of environmentally sensitive ecosystems and their response to disturbance, such as atmospheric contaminant inputs and global climate change (URL http://www.mesc.usgs.gov/norocky, accessed 1998).

Historical Water-Quality Data and Time-Series Trends

The data set for the Washington Creek HBN Station analyzed for this report includes 146 water-quality samples that were collected from September 1967 through August 1995. Sampling frequency was monthly in 1968 and 1969, bimonthly from 1970 through 1982, and quarterly from 1983 through 1995. Water-quality samples in the early part of the period of record were analyzed at a USGS laboratory in Columbus, Ohio, that operated until 1973 (Durum, 1978). After establishment of the central laboratory system, samples were analyzed at a laboratory in Atlanta, Ga., from 1973 through 1985 and at the NWQL in Arvada, Colo., from 1986 through 1995. Daily discharge records for Washington Creek (station 04001000) are available beginning in October 1964. Records of daily water temperature at the gaging station are available from October 1964 through September 1991.

Calculated ion balances for 139 samples with complete major-ion analyses are shown in figure 13. Ion balances ranged from –8.9 to 13 percent, and about 80 percent of samples had values within the ±5 percent range, indicating that the analytical results are of high quality. The average ion balance was 1.5 percent, and 68 percent of the samples had positive ion balances, indicating a slight excess of measured cations over anions in solution. Time-series plots of the major dissolved constituents were inspected for evidence of method-related effects (fig. 13). The most notable pattern was observed 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 in Arvada, Colo., between March 1986 and December 1989 (Fishman and others, 1994). In 1989, the laboratory determined that sulfate concentrations can be overestimated by this method 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/admin/memo/, accessed 1997). The bias was most pronounced in dilute waters, although it was not consistent among samples and seemed to be affected by factors such as color and turbidity (Schertz and others, 1994). The positive bias in sulfate concentrations also is reflected in the ion balance, which was consistently lower than average during this period of record.

Median concentrations and ranges of major constituents in stream water at the Washington Creek Station and VWM concentrations in wet-only deposition measured at the Wallace Lake NADP Station are listed in table 22. Precipitation chemistry at the NADP station, which is about 40 km east of the HBN station on the east end of Isle Royale, is dilute and slightly acidic with a VWM pH of 4.8 for 11 years of record. The predominant cations in precipitation were hydrogen and ammonium, which contributed 35 and 38 percent of the total cation charge. The predominant anions were sulfate, which accounted for 61 percent of the total anions, and nitrate, which accounted for 36 percent. The predominance of strong acid anions indicates that precipitation on Isle Royale may be affected by anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain (Stottlemyer and Hanson, 1989).

Stream water in Washington Creek is moderately concentrated and well buffered; specific conductance ranged from 57 to 250 µS/cm, and alkalinity was generally between 820 and 2,120 µeq/L (table 22). The major cations in stream water are calcium and magnesium, and bicarbonate is the predominant anion. The predominance of these solutes in stream water is attributed to the weathering of mafic minerals in the metavolcanic rocks and of carbonate minerals in glacial till. The median concentration of chloride in stream water was 85 µeq/L, which is about 50 times greater than the VWM concentration of 1.6 µeq/L in precipitation. On the basis of the difference between annual precipitation and runoff, evapotranspiration can account for not more than a twofold increase in the chloride concentration in precipitation, indicating that most stream-water chloride is derived from sources other than precipitation. The source of additional stream-water chloride is not obvious. Because the basin is undeveloped, the only plausible source of stream-water chloride is weathering of sedimentary rock fragments in the underlying glacial till. The median concentration of sulfate in stream water was 120 µeq/L compared to 29 µeq/L in precipitation, indicating as much as one-half of stream-water sulfate is derived from sources other than wet deposition. In a study on the east end of Isle Royale, Stottlemyer and Hanson (1989) determined that the flux of sulfate from dry deposition was almost twice that in wet-only precipitation, indicating that most stream-water sulfate at this station can be accounted for by atmospheric deposition. Concentrations of inorganic nitrogen species in stream water were less than the VWM concentrations 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, including chloride, had strong inverse correlations with discharge. These results are consistent with a hydrologic system where weathering-enriched base flow is diluted by water from shallow or surficial sources during periods of increased discharge, particularly spring snowmelt. Among the solutes, strong positive correlations were found among calcium, magnesium, sodium, alkalinity, chloride, and silica. Strong associations between base cations and silica probably reflect the weathering of plagioclase and pyroxene minerals in the volcanic rocks. The strong correlations between chloride and the weathering-derived solutes provide additional evidence that chloride is derived primarily from geologic sources in the basin. Likewise, the poor correlations between sulfate and the weathering-derived constituents are consistent with the assumption that sulfate is derived primarily from atmospheric sources.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are listed in table 24. A statistically significant (0.01 probability level) upward trend in pH and a downward trend in potassium were detected in the unadjusted and flow-adjusted concentrations. After flow adjustment, statistically significant trends also were detected in calcium, magnesium, and chloride concentrations. The LOWESS curves in figure 13 show that the trend in pH was primarily caused by a period of low pH values before 1980, and that most of the decrease in potassium concentrations occurred during the late 1970's and early 1980's. Because changes in pH and potassium occurred during relatively short

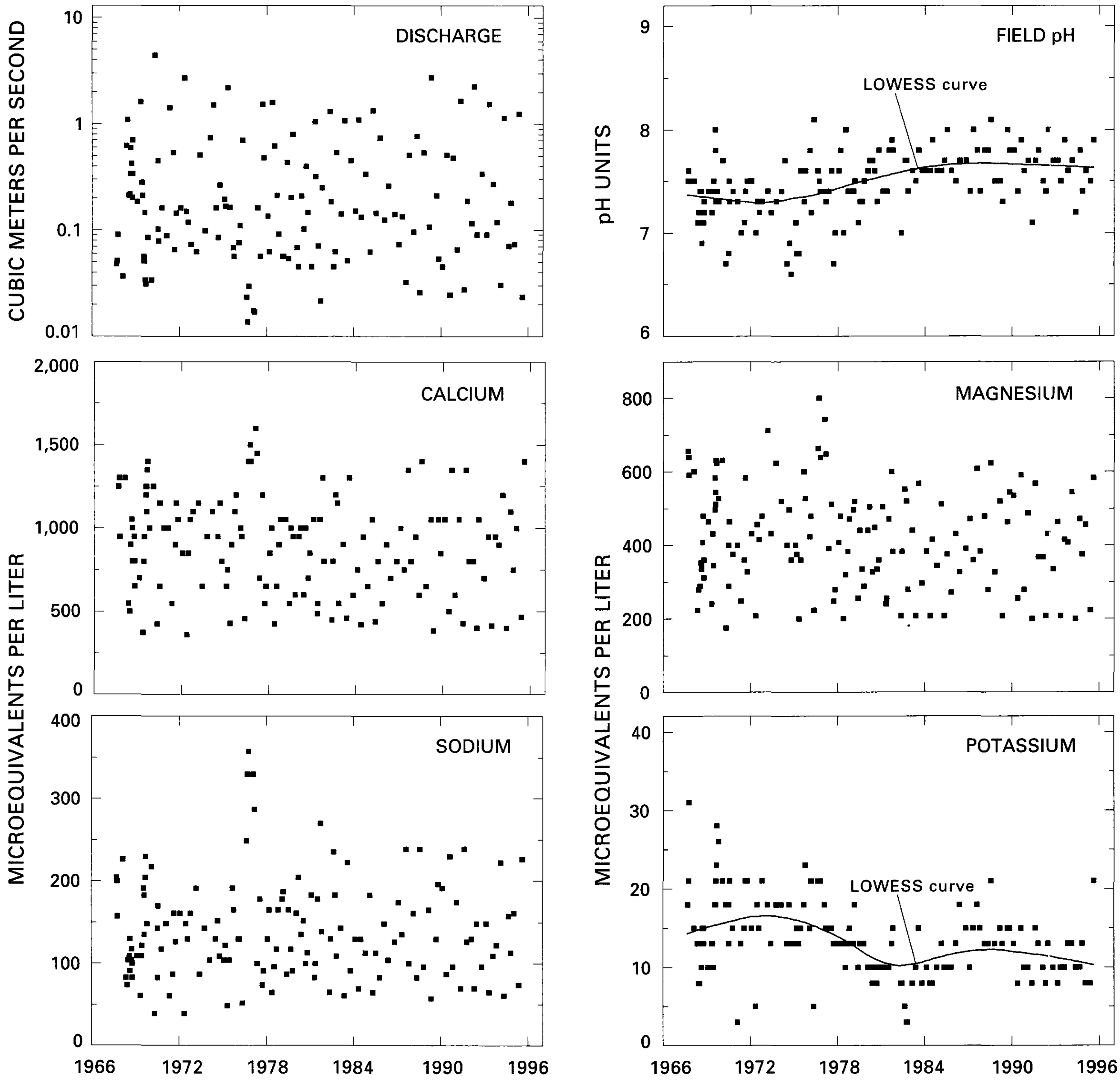


Figure 13. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Washington Creek, Michigan.

periods of time, they may have been caused by method-related factors rather than by environmental change. The trend in field pH may have been caused by changes in field instruments and pH probes, whereas potassium concentrations probably were affected by changes in laboratory facilities or analytical methods. The trends in calcium, magnesium, and chloride concentrations probably were caused by environmental change rather than by method-related factors because the trends were only detected in flow-adjusted concentrations. Because the Washington Creek Basin has remained undisturbed since the establishment of the National Park, trends in stream chemistry probably do not reflect changes in land use. Other environmental factors that may have affected stream chemistry include long-term variations

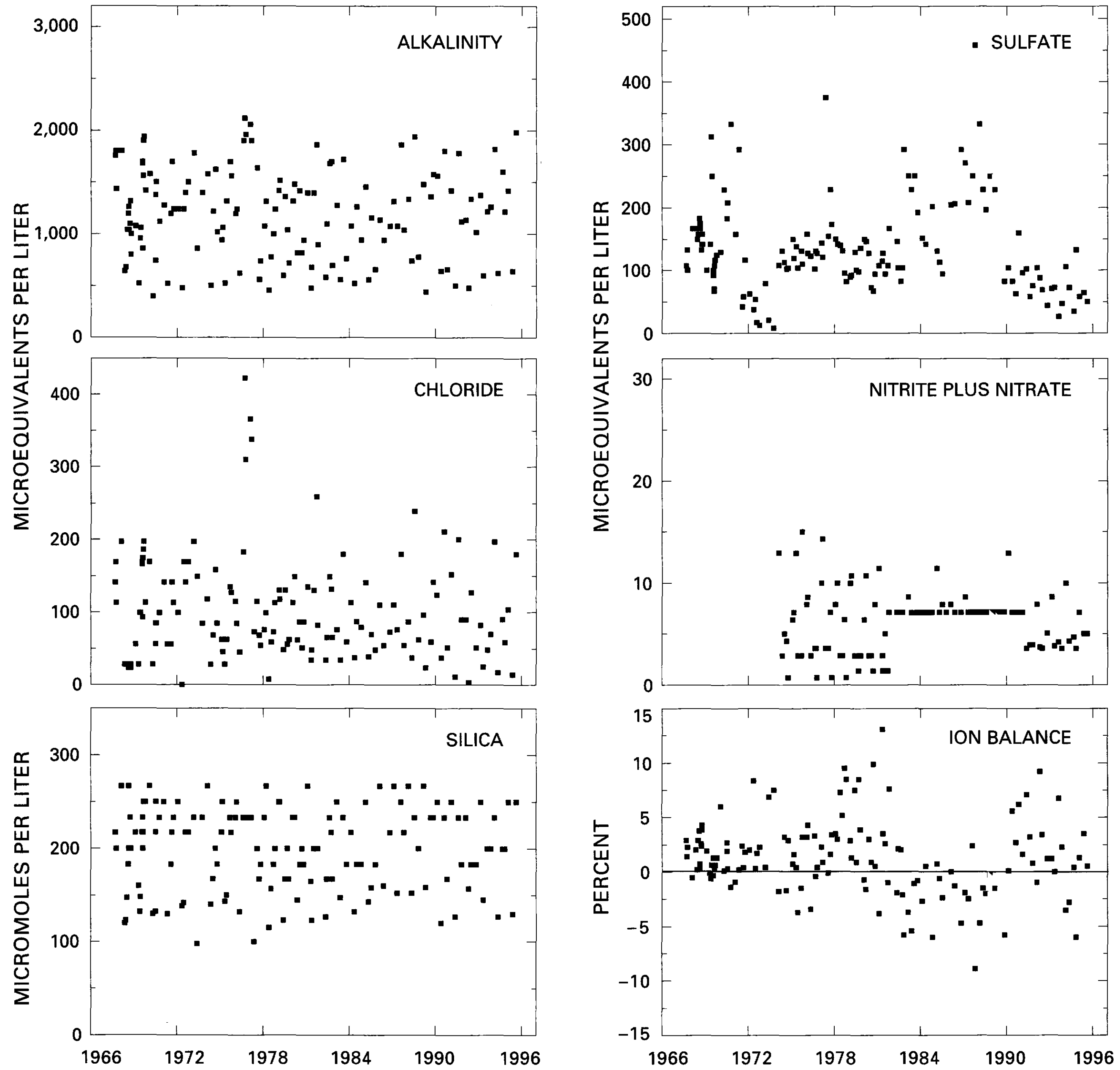


Figure 13. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Washington Creek, Michigan—Continued.

in climate and changes in atmospheric deposition. Analysis of long-term climatic records is beyond the scope of the report; however, Lawrence (1987) reported a statistically significant decline in annual mean discharge at the Washington Creek gaging station from 1965 through 1980, which was probably caused by trends in precipitation amount. Long-term records of precipitation chemistry are not available to help establish a link between trends in stream chemistry and changes in atmospheric deposition. However, Lynch and others (1995) did report statistically significant declines in calcium, magnesium, and chloride at several NADP stations in the north-central United States between 1980 and 1992.

Table 22. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major dissolved constituents measured in water-quality samples from Washington Creek, Michigan, September 1967 through August 1995, and volume-weighted mean concentrations in wet precipitation collected at the Wallace Lake Station, Michigan

[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.	0.014	0.065	0.15	0.48	4.4	145	--
Spec. cond., field	57	98	130	170	250	141	13
pH, field	6.6	7.3	7.5	7.7	8.1	145	4.8[b]
Calcium	360	650	900	1,050	1,600	145	7.9
Magnesium	180	330	420	530	800	145	2.2
Sodium	39	96	130	170	360	145	1.4
Potassium	<2.6	10	13	15	31	145	.7
Ammonium	<.7	1.4	2.1	2.9	26	61	17
Alkalinity, laboratory	400	820	1,220	1,510	2,120	145	--
Sulfate	8.3	92	120	160	460	142	29
Chloride	<2.8	51	85	140	420	146	1.6
Nitrite plus nitrate	<.7	3.6	7.1	7.1	15	102	17[c]
Silica	98	160	200	230	270	146	--

[a] Data are volume-weighted mean concentrations for 1985–95.

[b] Laboratory pH.

[c] Nitrate only.

Table 23. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major dissolved constituents, Washington Creek, Michigan, 1968–95

[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	−0.478								
Ca	−.925	0.541							
Mg	−.942	.539	0.967						
Na	−.970	.496	.936	0.967					
K	−.327	.311	.400	.413	0.350				
Alk	−.957	.539	.963	.976	.955	0.361			
SO_4	.151	−.091	−.147	−.078	−.068	.211	−0.177		
Cl	−.955	.483	.896	.920	.957	.340	.919	−0.053	
Si	−.744	.287	.793	.843	.783	.345	.782	.076	0.747

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling in the Washington Creek Basin on September 20 and 21, 1992, are listed in table 25, and the locations of the sampling sites are shown in figure 12. During the sampling period, discharge at the gaging station was about 0.2 m^3/s compared to the median daily discharge of 0.1 m^3/s for September and 0.2 m^3/s for October (Lawrence, 1987), indicating that the basin was sampled during normal flow conditions for that time of year. The solute concentrations measured at site 1 were between the first-quartile and median concentrations reported for the HBN station during the entire period of record (table 22), except for sulfate, which was less than the first-quartile concentration. The tributary streams were similar in composition to stream water collected at the gaging station (site 1); calcium and magnesium were the predominant cations, and bicarbonate was the predominant anion. Although not measured, organic anions probably were an important component of stream chemistry based on the tealike color of the stream water and the positive ion balances of most of the synoptic samples (range 0.1 to 8.5 percent). Concentrations of the weathering-derived solutes did not vary by more than a factor of two among the sampled tributaries, probably reflecting the small basin size and the relatively homogeneous composition of the underlying bedrock and glacial till deposits. Calcium, for example, ranged from 650 to 1,050 µeq/L, and alkalinity ranged from 860 to 1,620 µeq/L. The lowest concentrations of weathering constituents were measured at sites 6 and 7, perhaps because of the large wetland areas in these two subbasins. Among the minor solutes, chloride and sulfate concentrations had the most variability; chloride concentrations ranged from 8.5 to 59 µeq/L, and sulfate concentrations ranged from 15 to 81 µeq/L. Chloride was higher at the HBN station than at any of the upstream sampling sites, indicating that ground-water discharge along the lower reach of the stream channel is probably the source of most stream-water chloride at the HBN station. The range of stream-water sulfate concentrations probably cannot be accounted for by differences in atmospheric deposition because of the small basin size. Alternatively, this variation may reflect the influence of wetland areas along the streams where sulfate may be removed because of reducing conditions in the wetland soils.

Table 24. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major dissolved constituents, Washington Creek, Michigan, September 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; inst., instantaneous; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge, inst.	–0.001	0.602	--	--
pH, field	.01	.000	0.02	0.000
Calcium	–1.6	.264	–2.2	.006
Magnesium	–.4	.482	–1.2	.009
Sodium	<.1	.672	<.1	.975
Potassium	–.2	.000	–.2	.000
Alkalinity, laboratory	1.3	.592	–.5	.711
Sulfate	–1.7	.069	–1.7	.104
Chloride	–.7	.095	–.8	.001
Nitrite plus nitrate	.1[a]	.064	--	--
Silica	<.1	.724	<.1	.992

[a] Trend calculated for 1974–95 using a trend test for censored data.

Table 25. Physical properties and major dissolved constituents from surface-water sampling sites in the Washington Creek Basin, Michigan, collected September 20–21, 1992

[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; Si, silica; concentrations in microequivalents per liter, except silica in micromoles per liter; --, not reported]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Remarks
1	4001000	0.19	120	7.8	800	370	100	9.5	1,160	33	59	1.1	180	Gaging station
2	475547089074700	.024	110	7.9	750	390	96	12	1,100	23	20	2.1	170	
3	475601089075000	--	160	7.8	1,050	540	110	13	1,620	81	14	1.4	280	
4	475608089075300	.0056	110	7.7	700	380	100	12	1,060	58	17	1.6	120	
5	475553089074800	.0046	120	7.7	750	410	100	12	1,140	65	8.5	1.6	140	
6	475735089041600	.0069	100	7.5	700	380	100	6.2	980	29	25	.4	170	Primarily wetlands
7	475751089033900	--	90	6.8	650	340	96	7.2	860	23	42	.8	200	Primarily wetlands
8	475613089051900	.10	100	7.4	700	340	87	6.2	1,000	15	39	.9	150	Major tributary
9	475611089051700	.038	130	7.8	900	380	91	11	1,320	40	8.5	2.3	200	Major tributary

Kawishiwi River near Ely, Minnesota (Station 05124480)

Site Characteristics and Land Use

The Kawishiwi River HBN Basin is in the Superior Upland physiographic province in the northeastern corner of Minnesota (fig. 14). The 655-km^2 basin ranges in elevation from 442 to 643 m and drains an area of rolling bedrock ridges interspersed with irregular shallow basins occupied by hundreds of lakes and peatlands (Heinselman, 1996). The USGS gaging station is located 22.5 km east of the town of Ely, Minn., at latitude 47°55'22" and longitude 91°32'06". The Kawishiwi River flows west into the Basswood River, a tributary of the Rainy River, and has an average stream gradient of 1.4 m/km and a channel length upstream from the gaging station of about 77 km, of which about 40 percent consists of on-channel lakes (Siegel and Ericson, 1980). The main channel is perennial, and discharge is strongly seasonal with mean monthly flows that range from 1.6 m^3/s in March under ice cover to 18.6 m^3/s in May during spring breakup and snowmelt. Average annual runoff from the basin was 28 cm from 1966 through 1995 (Mitton and others, 1996). The climate is classified as continental with short summers and long, cold winters. Average monthly air temperatures range from −14.4°C in January to 19.2°C in July (National Climatic Data Center, 1996). Average annual precipitation is about 70 cm, of which about 40 percent falls as snow (Pettyman, 1978). In most

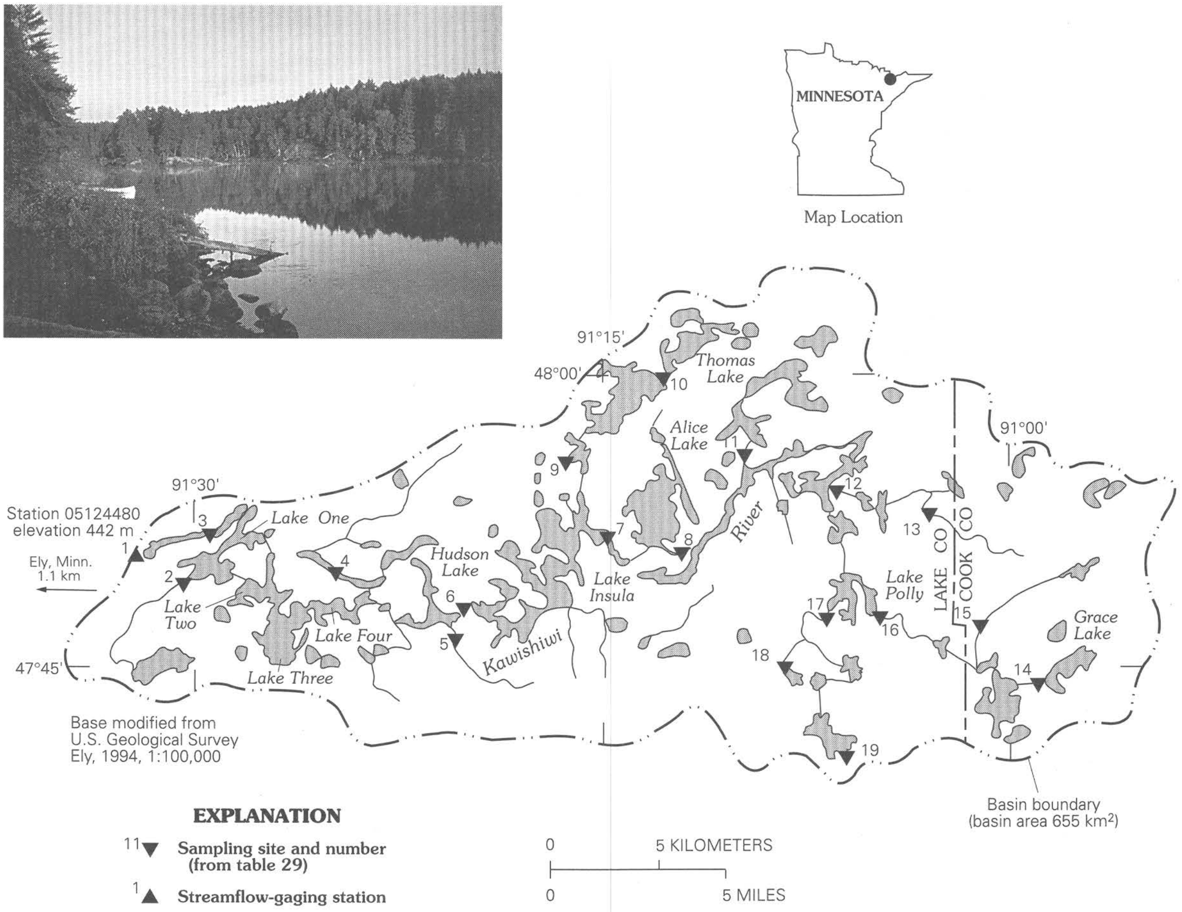


Figure 14. Map showing study area in the Kawishiwi River Basin and photograph of a typical lake in the basin.

winters, permanent ice cover is established on almost all lakes and streams, and a seasonal snowpack covers the basin from about mid-November to mid-April.

The Kawishiwi River Basin is in the Laurentian Mixed Forest ecoregion (Bailey and others, 1994), and vegetation is representative of the extreme southern part of the boreal forest zone (Pettyman, 1978). The upland areas are dominated by jack pine, quaking aspen, and birch and commonly have an understory of northern red oak, black spruce, or fir. Shrubs common in the upland forests include juneberry, beaked hazel, mountain maple, willow, and American green alder. The once common red and white pine species are only in isolated, scattered stands because of the past effects of logging and fire. In the wetter lowland areas and bogs, the predominant tree species are black spruce, northern white cedar, and tamarack; speckled alder is the common shrub. Most soils in the basin are mapped in the Mesaba-Barto-Mucky peats association (Pettyman, 1978). The Barto and Mesaba series include well-drained soils that formed in loamy glacial material and range in thickness from 20 to 100 cm. A typical soil profile has a thin surface layer of organic matter over a subsoil of gravelly, sandy loam that has an accumulation of organic matter and iron and aluminum oxides. These soils generally are acidic and have low cation-exchange capacities (<10 meq/100 g soil) and low base saturation (Cook and Jager, 1991). Mucky peats are poorly drained soils that form in bogs and lowland areas surrounding lakes and streams. These soils consist of dark-brown, partly decomposed organic materials extending to depths of 130 cm (Pettyman, 1978).

Bedrock in the basin belongs to the Duluth Complex of Proterozoic age, which consists of gabbroic and troctolitic anorthosites, which have been intruded by several types of mafic and felsic rocks. The anorthosites are composed mostly of calcic plagioclase (greater than 80 percent) and variable amounts of olivine, pyroxene, and iron oxide minerals (Davidson, 1969). Some anorthosites in the area have been weakly mineralized and contain small amounts of pyrite, chalcopyrite, and pyrrhotite (Davidson, 1969). Most bedrock in the basin is mantled by a thin layer of brown Wisconsin till, usually less than 5 m in thickness. The till is stony with a sandy matrix and contains cobbles and boulders consisting of mafic and felsic rock types (Grout and others, 1959). Topographic features in the basin trend northeast-southwest and reflect both structures in the Proterozoic bedrock and the general direction of glaciation (Siegel, 1981).

The Kawishiwi River Basin drains parts of Lake and Cook Counties in Minnesota and is entirely within the boundaries of the Boundary Waters Canoe Area Wilderness (BWCAW). The BWCAW is part of the National Wilderness Preservation System and is administered by the Superior National Forest (U.S. Department of Agriculture, 1993). The interior of the basin is accessible by canoe from hundreds of portage-linked lakes and streams, although there are only three road-accessible launch points along the perimeter of the basin. The gaging station can be reached in summer by canoe from an access point about 2.4 km upstream. Most lakes and streams are ice covered during the winter, and the gaging station is accessible only by snowshoes or skis. A wilderness travel permit issued by the Forest Service is required for all overnight visits in the BWCAW from May 1 through September 30. Camping is permitted only at developed campsites, which have wilderness box latrines.

The history of land use and vegetation disturbance in the BWCAW is described in detail by Heinselman (1996). The forest ecosystem of the BWCAW was changed substantially by two periods of timber harvesting, the big-pine era from 1895 to 1930 and the pulpwood era from 1935 to 1978. During the big-pine era, as much as 70 percent of big white and red pines were harvested in BWCAW, and several major fires burned large areas of forest. The logging, in combination with slash fires, converted the former pine forests to paper birch and aspen stands that still persist today. The Superior National Forest was created in 1909 near the end of the big-pine era, and management efforts were initially focused on controlling fire, acquiring land, and improving timber stands. This improvement of forest resources, in combination with the development of a wood-pulp industry, resulted in the pulpwood era of logging that lasted from 1935 to 1978. During this second period of logging, large amounts of jack pine and black spruce were cut in the BWCAW, and an intense network of unpaved roads penetrated the area, including the southern and eastern parts of the Kawishiwi River Basin. In 1964, the BWCAW became part of the National Wilderness Preservation System, although logging, mining, and motorized travel still were permitted in the wilderness boundary. In 1978, the BWCAW Act finally ended logging and greatly decreased motorboat usage in the wilderness area. Since 1978, land use has been limited primarily to backcountry recreational use, and the BWCAW has become the most heavily used wilderness area in the United States. Visitor use has increased threefold since the early 1960's, and more than 100,000 people camp in the backcountry each year. The major visitor effects on the ecosystem are disturbance of vegetation and soils and degradation of water quality around established campsites. The most heavily used areas in the Kawishiwi River Basin are around Lake One, Lake Two, Lake Three, and Lake Insula (U.S. Department of Agriculture, 1993).

Historical Water-Quality Data and Time-Series Trends

The data set for the Kawishiwi River HBN Station analyzed for this report includes 132 water-quality samples that were collected from July 1966 through July 1995. Sampling frequency ranged from bimonthly to monthly from 1967 through 1970 and quarterly from 1971 through 1995. Additional water-quality samples were collected at the HBN station in 1976 as part of an environmental impact study to evaluate the possible effects of mining on hydrologic systems in northeastern Minnesota (Siegel and Ericson, 1980). Samples that were collected in the early part of the period of record were analyzed at a USGS laboratory in Columbus, Ohio, that operated until 1973 (Durum, 1978). After establishment of the central laboratory system, samples were analyzed at a laboratory in Salt Lake City, Utah, from 1973 through 1975 and at the NWQL in Arvada, Colo., from 1976 through 1995. Daily discharge records for the Kawishiwi River (station 05124480) are available beginning in June 1966. Records of daily water temperatures at the gaging station are available from July 1966 through September 1981.

Calculated ion balances for 127 samples with complete major-ion analyses are shown in figure 15. Ion balances ranged from –27 to 19 percent, and over 30 percent of the samples had values outside the ±10 percent range. This large range of ion balances was not unexpected considering the difficulties in making precise analytical measurements at the low solute concentrations typical of this station. The average ion balance was 1.0 percent, and 60 percent of the samples had positive ion balances, indicating a slight excess of measured cations over anions in solution, perhaps reflecting the presence of unmeasured organic anions. Time-series plots of the major dissolved constituents were inspected for evidence of method-related effects (fig. 15). The most notable pattern observed was in sulfate, which showed 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 in Arvada, Colo., between March 1986 and December 1989 (Fishman and others, 1994). In 1989, the NWQL determined that sulfate concentrations can be overestimated by this method 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/admin/memo/, accessed 1997). The bias was most pronounced in dilute water, although it was not consistent among the samples and seemed to be affected by factors such as color and turbidity (Schertz and others, 1994). The positive bias in sulfate concentrations also is reflected in the ion balances, which were consistently negative between 1986 and 1989. In addition to sulfate, elevated concentrations of calcium and chloride were evident in a number of samples that were collected in the mid-1970's. The cause of these high concentrations could not be determined; however, the samples were collected during the period when chemical analyses were conducted at the central laboratory in Salt Lake City, Utah.

Median concentrations and ranges of major constituents in stream water collected at the Kawishiwi River Station and VWM concentrations in wet-only deposition measured at the Fernberg NADP Station are listed in table 26. Precipitation chemistry at the NADP station, which is about 4 km northeast of the HBN station, was dilute and slightly acidic with a VWM pH of 5.0 for 16 years of record. The predominant cations in precipitation were ammonium, hydrogen, and calcium, which contributed 38, 27, and 22 percent of the total cation charge, respectively. Sulfate and nitrate were the predominant anions, accounting for 55 and 39 percent of the total anion charge, respectively. The predominance of strong acid anions indicates that precipitation at the NADP station may be affected by anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain (Glass and Loucks, 1986).

Stream water in the Kawishiwi River is dilute and weakly buffered; specific conductance ranged from 19 to 50 µS/cm, and alkalinity was between 120 and 320 µeq/L (table 26). The river also has brownish tea-colored water, which is characteristic of surface runoff from hundreds of wetlands in the basin (Heinselman, 1996). The major cations in stream water were calcium and magnesium, and bicarbonate was the predominant anion. The predominance of these solutes in stream water is attributed to the weathering of calcium-rich plagioclase and pyroxene minerals in the bedrock and till. The median concentration of chloride in stream water was 17 µeq/L, which is about eight times greater than the VWM concentration of 2.1 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 chloride concentration of precipitation, indicating that some stream-water chloride is derived from sources other than wet precipitation. Because there is no development in the basin, the only plausible source for additional stream-water chloride is weathering of mafic minerals in the bedrock (Peters, 1991). The median concentration of sulfate in stream water was 90 µeq/L compared to 21 µeq/L in precipitation, which is slightly larger than would be expected solely from the effects of evapotranspiration. Assuming that geologic sources are minor, most of the additional stream-water sulfate probably is derived from dry deposition from the atmosphere. Baker (1991) estimated that dry deposition was about 27 percent of total sulfate deposition in the region, which seems to be consistent with sulfate concentrations in the river. Concentrations of inorganic nitrogen species in stream water were less than the concentrations in precipitation, indicating 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 27). The major dissolved constituents were poorly correlated with discharge, except for weak inverse correlations with calcium (rho = –0.444) and magnesium (rho = –0.447). Although discharge in the Kawishiwi River is strongly seasonal, the lack of correlation with solutes probably reflects streamflow that is mostly derived from a well-mixed reservoir of water stored in on-channel lakes. Among the solutes, the strongest correlations were between calcium and magnesium (rho = 0.629) and calcium and sodium (rho = 0.526), which may reflect common mineralogic sources for these solutes. The most abundant mineralogic source of calcium and magnesium is pyroxene in the mafic rocks, whereas plagioclase is the only common weathering source of both calcium and sodium.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are listed in table 28. Statistically significant downward trends were detected in the unadjusted calcium, sulfate, chloride, and silica concentrations at the 0.01 probability level. Trends in flow-adjusted concentrations were not calculated for calcium, sulfate, and chloride because the flow models were not statistically significant at the 0.10 probability level. Results were similar for unadjusted and flow-adjusted silica concentrations, indicating that the trend was not caused by variations in stream discharge. A statistically significant trend also was detected in potassium concentrations; however, the magnitude of the trend was less than 2 µeq/L over the entire 30-year period of record. The LOWESS curves in figure 15 showed slightly different trend patterns for calcium, sulfate, chloride, and silica. The downward trend in calcium was largely driven by high concentrations and greater scatter in the early part of the period of record. By contrast, most of the decline in sulfate concentrations occurred in the later part of the period of record, except for a period of elevated concentrations in the 1980's, which was caused by analytical bias. Chloride and silica had somewhat similar patterns with small increases in concentration at the beginning of the period of record followed by declines. Trends in stream-water sulfate and calcium at the Kawishiwi River Station may be linked to changes in atmospheric deposition. Although early records of precipitation chemistry are not available, Lynch and others (1995) reported declines in sulfate and calcium concentrations at several NADP stations in the north-central part of the United States from 1980 through 1992. Although a decline in atmospheric deposition of sulfate could explain most of the trend in stream-water sulfate, the trend in calcium deposition is not consistent with the timing of the trend in stream-water calcium, which remained nearly constant after 1980. Analytical bias may provide a more reasonable explanation for the downward trend in calcium. The decrease in concentration and the data scatter that is shown in figure 15 occurred about the time that a new

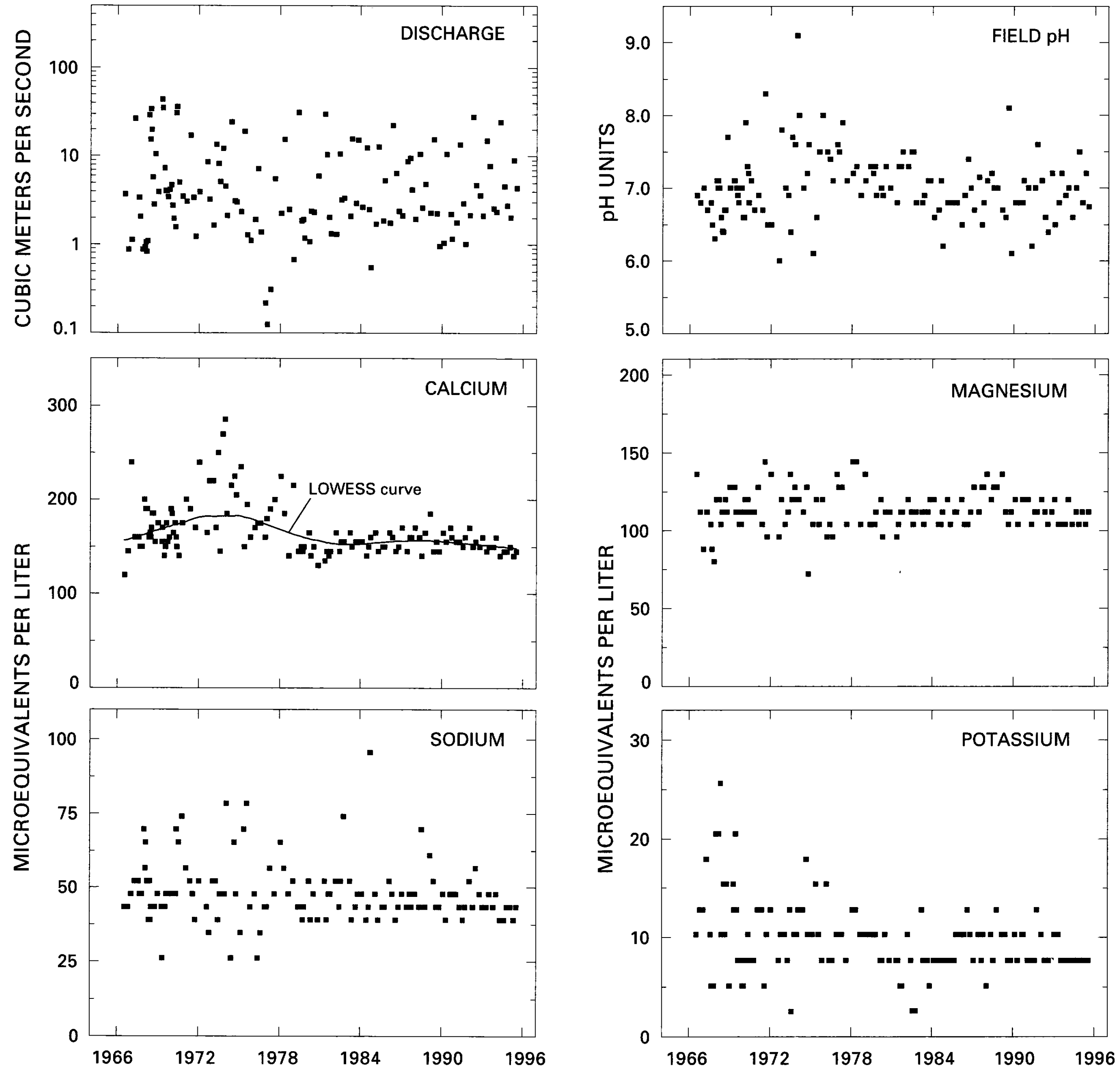


Figure 15. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Kawishiwi River, Minnesota.

procedure was adopted for the analysis of major cations and trace metals (Office of Water Quality Technical Memorandum No. 82.18, *National Water-Quality Networks*, issued September 28, 1982, at URL http://water.usgs.gov/admin/memo/, accessed 1997). The cause of the downward trends in silica and chloride could not be identified. Environmental factors that may have affected these constituents include the termination of logging in 1978, declines in atmospheric deposition (Lynch and others, 1995), or an increase in backcountry visitor use, the latter of which would probably have caused upward rather than downward trends. Laboratory bias also may have affected the concentration patterns of chloride and silica, including the use of two different laboratories during the period of record as well as improvements and modifications of the analytical methods (Fishman and others, 1994).

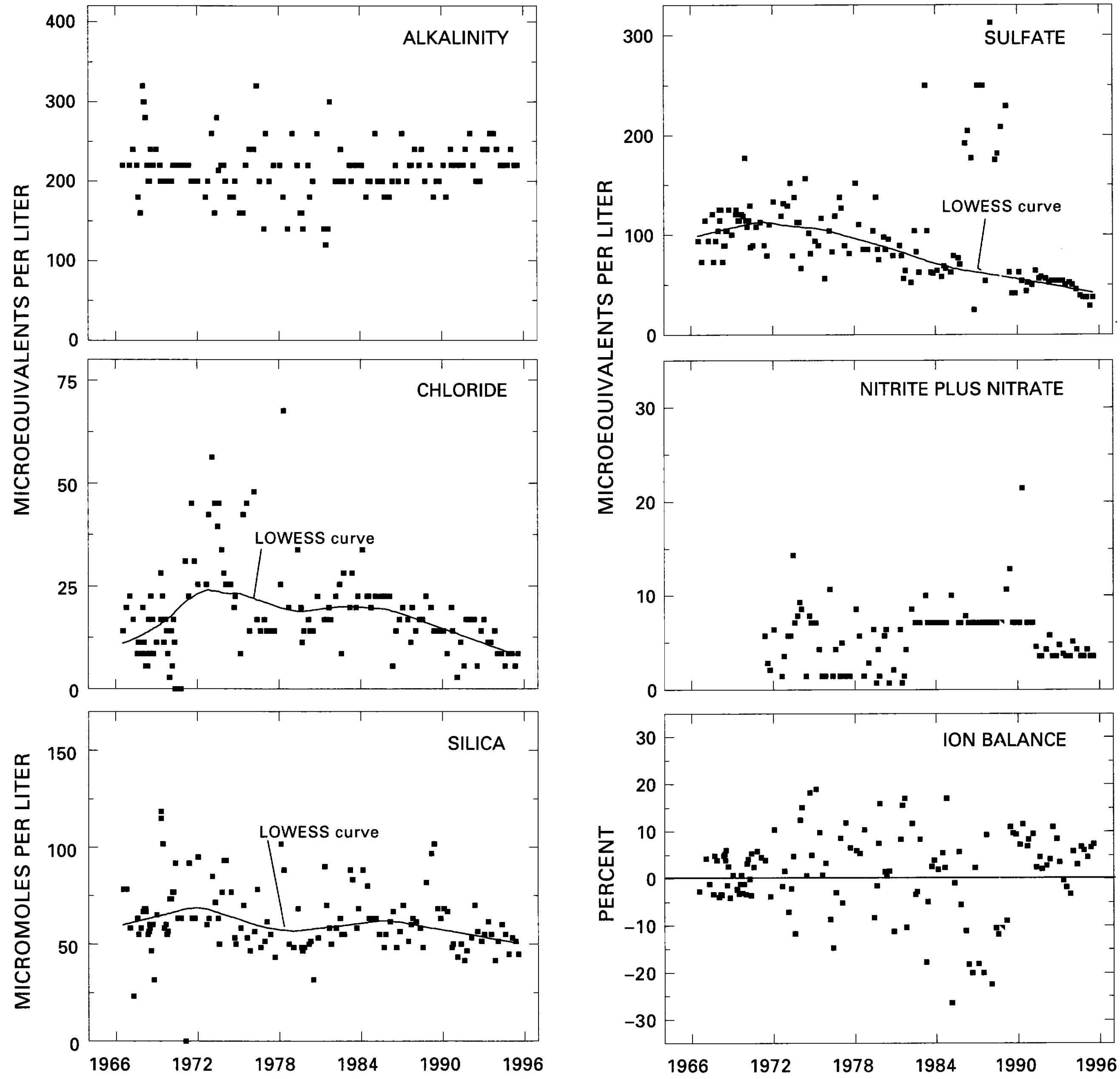


Figure 15. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Kawishiwi River, Minnesota—Continued.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling in the Kawishiwi River Basin on September 11–14, 1992, are listed in table 29, and the locations of the sampling sites are shown in figure 14. During the sampling period, discharge at the gaging station was about 3.1 m^3/s compared to the median daily discharge of 2.0 m^3/s for September (Lawrence, 1987), indicating that the basin was sampled during higher than normal flow conditions for that time of year. Solute concentrations measured at site 1 were less than the first-quartile concentrations reported for the HBN station during the entire period of record (table 26), except for calcium and silica concentrations, which were higher. Stream water at all the upstream sampling sites was very dilute and similar in composition to stream water collected at

Table 26. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major dissolved constituents measured in water-quality samples from Kawishiwi River, Minnesota, July 1966 through July 1995, and volume-weighted mean concentrations in wet precipitation collected at the Fernberg Station, Minnesota

[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 VWM[a]
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge, inst.	0.12	1.95	3.23	9.11	44	133	--
Spec. cond., field	19	29	31	35	50	133	9.2
pH, field	6.0	6.7	7.0	7.2	9.1	135	5.0[b]
Calcium	120	150	160	175	290	134	8.2
Magnesium	72	100	110	140	150	135	2.5
Sodium	26	43	48	52	96	132	2.0
Potassium	<2.6	7.7	10	10	26	132	.6
Ammonium	<.7	1.4	1.4	2.1	26	60	14
Alkalinity, laboratory	120	200	220	220	320	134	--
Sulfate	25	63	90	120	310	134	21
Chloride	<2.8	11	17	23	68	134	2.1
Nitrite plus nitrate	<.7	3.6	6.4	7.1	21	99	15[c]
Silica	23	52	60	69	120	133	--

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

[b] Laboratory pH.

[c] Nitrate only.

Table 27. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major dissolved constituents, Kawishiwi River, Minnesota, 1966–95

[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	–0.087								
Ca	–.444	–0.157							
Mg	–.447	–.153	0.629						
Na	–.357	–.133	.526	0.489					
K	–.128	.025	.282	.159	–0.020				
Alk	–.157	.049	.298	.389	.185	–0.100			
SO_4	.041	.072	.188	.126	.138	.271	–0.177		
Cl	–.073	–.019	.181	.246	.135	.133	–.129	0.484	
Si	.351	–.333	.139	.043	.128	–.028	–.224	.224	0.344

the gaging station (site 1); calcium was the predominant cation, and bicarbonate was the predominant anion. Although not measured, dissolved organic carbon seemed to be an important component of stream water based on the tealike color of the water and the large positive ion balances of the synoptic samples (range 6.6 to 55 percent). The most notable spatial pattern in stream chemistry was that concentrations of the weathering-derived cations varied by less than a factor of two, whereas alkalinity varied by almost a factor of eight. For example, calcium concentrations ranged from 110 to 210 µeq/L compared to alkalinity, which ranged from 49 to 400 µeq/L (table 29). Dissolved organic carbon seemed to be related to the variation in alkalinity, as evidenced by the strong inverse correlation between alkalinity and ion balance (rho = –0.820), indicating that organic ligands may be important in controlling the acid-base status of surface water in the basin. Chloride and nitrate were uniformly low throughout the basin; chloride concentrations ranged from 2.5 to 8.7 µeq/L, and nitrate concentrations varied from 0.4 to 2.5 µeq/L. These results are consistent with the low concentrations of these constituents in precipitation and with the minimal amount of human activity in the basin. Sulfate concentrations ranged from 16 to 77 µeq/L, which is slightly more than might be expected from variations in atmospheric deposition. These results may indicate that biological processes are important in controlling stream chemistry, particularly in wetland areas where reducing conditions in the soils may remove sulfate from the surface-water system. Silica concentrations varied from 32 to 150 µmol/L and were not correlated with patterns in the other weathering-derived constituents. As with sulfate, this pattern may be related to biological processes, such as the removal of silica by diatoms in the large number of lakes in the basin.

Table 28. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major dissolved constituents, Kawishiwi River, Minnesota, July 1966 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; inst., instantaneous; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge, inst.	–0.02	0.292	--	--
pH, field	<.01	.341	<0.01	0.315
Calcium	–.7	.000	(a)	--
Magnesium	<.1	.669	<.1	.789
Sodium	<.1	.063	–.2	.047
Potassium	<.1	.001	<.1	.001
Alkalinity, laboratory	<.1	.087	.2	.198
Sulfate	–2.4	.000	(a)	--
Chloride	–.4	.001	(a)	--
Nitrite plus nitrate	.1[b]	.064	(a)	--
Silica	–.4	.002	–.4	.003

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

[b] Trend calculated for 1971–95 using a trend test for censored data.

Table 29. Physical properties and major dissolved constituents from surface-water sampling sites in the Kawishiwi River Basin, Minnesota, collected September 11–14, 1992

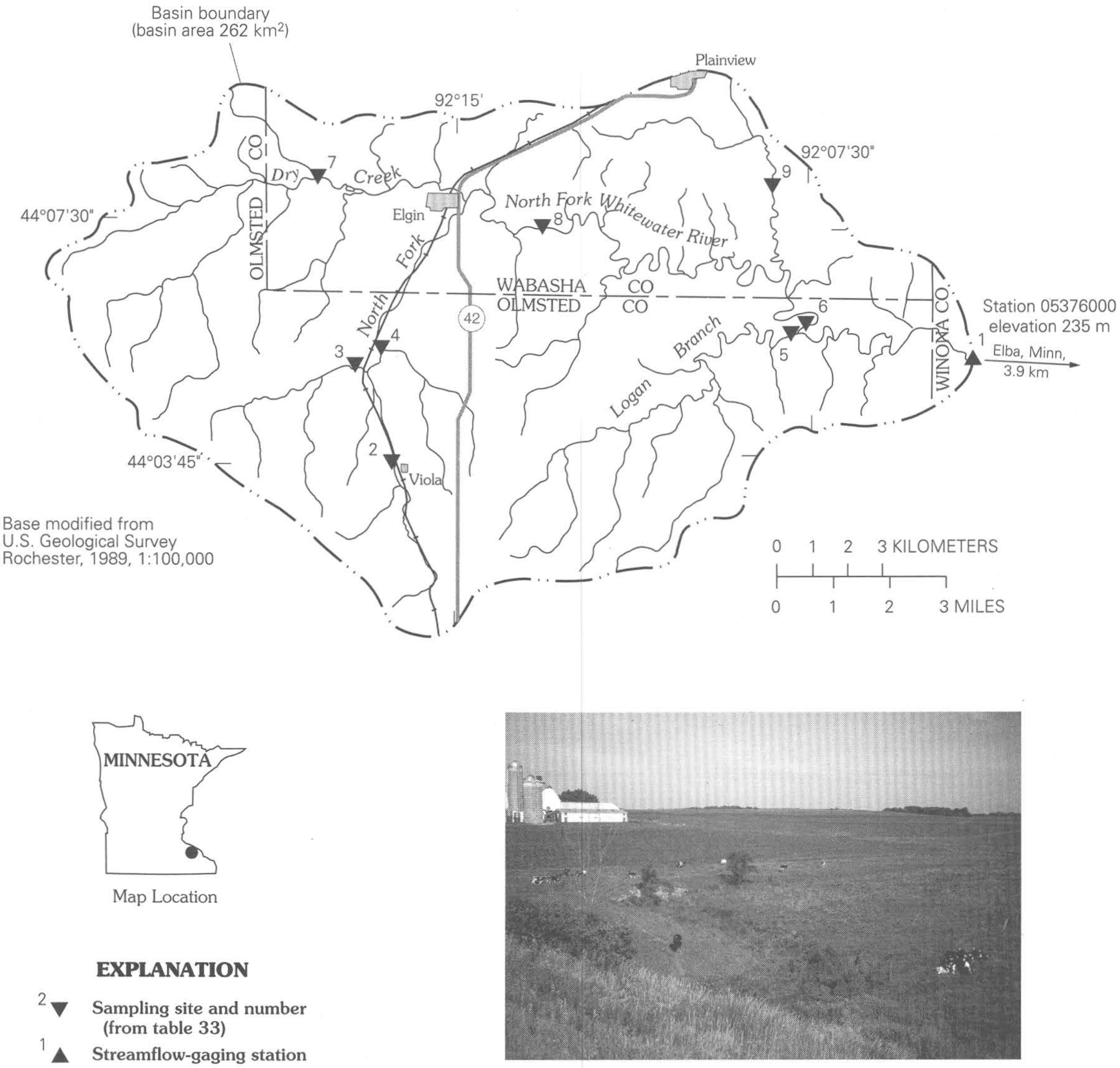
[Site locations shown in fig. 14; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; Si, silica;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

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Remarks
1	05124480	3.1	30	7.0	160	100	39	7.9	150	54	6.2	1.1	70	Gaging station
2	475436091303600	--	33	6.3	180	170	48	8.5	150	31	8.7	1.6	110	Downstream from boat access
3	475558091292100	.23	30	6.9	170	96	39	7.9	180	50	7.3	0.4	63	Lake outflow
4	475504091250500	.12	35	6.8	160	180	43	3.6	200	50	5.4	2.5	65	Lake outflow
5	475303091203300	.11	49	6.7	210	280	48	3.8	400	27	4.8	0.4	110	No lakes in subbasin
6	475357091200100	2.0	29	7.0	160	88	43	6.2	190	50	6.2	0.7	67	Lake outflow
7	475550091144500	1.9	28	7.0	160	80	43	5.9	170	50	5.6	1.5	65	Lake outflow, gabbroic bedrock
8	475527091122000	3.3	27	6.8	160	76	39	6.2	160	44	4.5	1.1	50	Lake outflow, gabbroic bedrock
9	475730091161800	.0082	35	6.8	160	150	39	5.9	240	58	5.9	0.5	43	Lake outflow
10	475946091124600	.19	34	7.1	190	100	43	7.2	210	77	7.3	0.6	60	Lake outflow, greenstone
11	475800091094600	.14	32	6.9	180	96	43	4.9	220	48	5.4	0.6	38	Lake outflow
12	475702091064900	--	25	6.7	170	75	35	4.4	96	27	4.5	1.0	70	Main tributary
13	475620091025900	.30	21	6.6	140	59	35	2.6	82	29	3.7	1.1	120	Intermediate volcanic rocks
14	475210090585500	.61	20	6.6	110	55	30	4.9	89	48	3.7	0.8	88	Lake outflow, granitic bedrock
15	475256091013200	--	21	5.9	140	65	35	2.1	49	16	3.7	1.0	150	Intermediate volcanic rocks
16	475355091050900	1.6	23	6.5	150	72	39	5.1	110	33	4.5	2.1	82	Main tributary
17	475344091065700	.65	24	6.6	150	69	43	3.6	110	35	3.7	0.8	72	Main tributary
18	475228091080500	.047	23	6.6	140	58	35	5.6	100	29	3.7	1.5	32	Lake outflow, gabbroic bedrock
19	474206091061500	--	30	7.0	160	100	39	2.6	150	54	6.2	1.1	70	Gabbroic bedrock

North Fork Whitewater River near Elba, Minnesota (Station 05376000)

Site Characteristics and Land Use

The North Fork Whitewater River HBN Basin is located in the Wisconsin Driftless Section of the Central Lowland physiographic province in the southeastern corner of Minnesota (fig. 16). The basin drains an area of 262 km^2 and ranges in elevation from 235 to 400 m. The gently rolling landscape in the upper part of the basin is formed by a plateau of erosion-resistant rock. In the lower part of the basin, the plateau surface is strongly dissected by several steep-sided stream channels. The USGS gaging station is located 3.9 km west of Elba, Minn., at latitude 44°05'30" and longitude 92°03'57". The North Fork Whitewater River drains east into the Whitewater River, a tributary of the Mississippi River, and has a channel length of 47 km upstream from the gaging station and an



Base modified from U.S. Geological Survey Rochester, 1989, 1:100,000

Figure 16. Map showing study area in the North Fork Whitewater River Basin and photograph of agricultural land in the basin.

average stream gradient of 1.9 m/km. Mean monthly discharge varies over a narrow range from 0.86 m^3/s in January to 2.5 m^3/s in March, and average annual runoff from the basin was 17 cm from 1933 through 1995 (Mitton and others, 1996). The climate is characterized by moderately warm summers and cold winters. Average daily air temperatures range from −10.7°C in January to 22.7°C in July (Lueth, 1994). Precipitation averages 84 cm annually and more than 70 percent falls from April through September. The average seasonal snowfall is 120 cm and, on average, 95 days of the year have at least 2 cm of snow cover (Lueth, 1994).

The North Fork Whitewater River Basin is in the Eastern Broadleaf Forest (Continental) ecoregion (Bailey and others, 1994), but only 16 percent of the basin is forested. Most forested areas are localized along the steep-sided slopes of the drainages in the lower part of the basin. Oak, shagbark hickory, bitternut hickory, aspen, and paper birch are the most common species. Large areas of the uplands at one time were covered by white oak, red oak, elm, basswood, maple, wild cherry, and pine that since have been cleared for farming. Soils in the basin are classified as Alfisols and mapped in the Seaton-NewGlarus-Palsgrove and Lacrescent-Lamoille soil associations (Lueth, 1994). The Seaton-NewGlarus-Palsgrove soils are well-drained silt loams developed in loess on the upland areas of the basin. A typical soil profile has a surface layer of grayish-brown silt loam that is 20 cm thick overlying a subsoil of dark yellowish-brown silt loam that extends to a depth of 150 cm. The soils generally have pH values between 5.1 and 7.3 and an organic-matter content of less than 3 percent in the upper 20 cm (McCleary and others, 1989). Soils in the Lacrescent-Lamoille series develop in loess and colluvium on steep-sided slopes along the drainages and consist of well-drained silt loams that contain between 20 and 60 percent cobbles and gravel.

Bedrock in the basin consists of gently dipping marine sedimentary rocks of Paleozoic age. The uplands plateau surface is capped by the resistant limestones of the Galena Formation and dolomite beds belonging to the Prairie du Chien Group of Paleozoic age (Mossler and Book, 1984). The softer shales and sandstones of the Decorah Shale, Platteville Formation, Glenwood Formation, St. Peter Sandstone, and Jordan Sandstone of Paleozoic age primarily crop out along the walls of the stream valleys (Mossler and Book, 1984). The Prairie du Chien Group and the Jordan Sandstone form the Prairie du Chien aquifer, which is the major water supply in the southeastern corner of Minnesota (Smith and Nemetz, 1996). The bedrock, particularly in the upland areas of the basin, is covered by till deposits of Pleistocene age. The till consists of a mixture of sand, silt, and clay that is calcareous where unweathered. A thin layer of loess mantles the till and the bedrock and ranges in thickness to as much as 3 m (Hobbs, 1988). The loess consists of a brownish silt loam that is leached of carbonate to a depth of 2 to 3 m. The steep walls along the stream channels are mantled by unsorted colluvium consisting of clasts of bedrock in a silt matrix derived from loess (Hobbs, 1984).

The North Fork Whitewater River Basin drains parts of Wabasha, Olmsted, and Winona Counties of Minnesota. Land ownership is 94 percent private and 6 percent State (W. Lorenzen, U.S. Department of Agriculture Natural Resources Conservation Service, written commun., 1996). Most State-owned land is part of the Whitewater State Forest and is located along a deeply incised section of the main channel of the North Fork Whitewater River in the lower part of the basin. More than 100 km of State and county roads traverse most areas of the basin. The incised section of the main river channel is accessible by hiking trails on State forest land; access to most tributaries is limited to rights-of-way at public road crossings. Many roads in the basin are plowed and heavily salted in winter.

Land cover in the basin is 64 percent cropland, 8 percent pasture land, 16 percent forest, 6 percent wetland, and 6 percent residential and urban land (W. Lorenzen, written commun., 1996). Feed grain and forage for dairy cattle and other livestock are the major farming enterprises in the watershed. Recent trends in the farm economy have shown a shift from dairy operations to cash crop production, including cannery crops (U.S. Department of Agriculture, 1996). The average farm is 254 acres in size, and approximately one-third of farms are dairies. Other human-related features in the basin include the townships of Viola (population 604), Elgin (population 761), and part of Plainview (population 2,768);

a wastewater-treatment plant at Plainview; a State park campground; and a railroad line that parallels the upper reach of the main river channel. Controlling erosion from croplands is the principal land-management concern in the region (Argabright and others, 1996). Implementation of conservation practices, such as terracing, strip cropping, and reducing tillage, caused a reduction in soil erosion rates in the region of nearly 50 percent between 1930 and 1992 (Argabright and others, 1996). The U.S. Department of Agriculture instituted the CRP in 1985 as an additional means of reducing soil erosion from highly erodible croplands. Under the program, farmers were paid in exchange for planting permanent vegetation types, such as sod-forming grasses and legumes. About 25 percent of cropland in the basin was planted in grasses under the CRP program; however, as much as 50 percent of that grass cover has come back into production since 1996 (W. Lorenzen, written commun., 1996). In 1996, a long-term watershed implementation plan was adopted for the drainage basin of the Whitewater River, of which the North Fork Whitewater River is one of four major tributaries (U.S. Department of Agriculture, 1996). The goal of the plan is to improve water quality, reduce sedimentation and flooding, and improve wildlife habitat in the Whitewater River Basin by developing a partnership among watershed citizens, governmental agencies, environmental groups, and businesses.

Historical Water-Quality Data and Time-Series Trends

The data set for the North Fork Whitewater River HBN Station analyzed for this report includes 218 water-quality samples that were collected from August 1967 through September 1993. Sampling frequency ranged from 8 to 12 samples per year during the period 1968 through 1982 and bimonthly from 1983 through 1993. Water-quality samples in the early part of the period of record were probably analyzed at a USGS laboratory in Columbus, Ohio, that operated until 1973 (Durum, 1978). After establishment of the central laboratory system, samples were analyzed at a laboratory in Salt Lake City, Utah, from 1973 through 1975 and at the NWQL in Arvada, Colo., from 1976 through 1995. Daily discharge records are available for the North Fork Whitewater River (station 05376000) from May 1939 through September 1941 and from July 1967 through September 1993.

Calculated ion balances for 210 samples with complete major-ion analyses are shown in figure 17. Ion balances ranged from −16 to 20 percent, and more than 98 percent of samples had values in the ±10 percent range, indicating that the analytical measurements were of high quality. The average ion balance for all samples was slightly positive (1.2 percent), which probably is due to the fact that nitrite plus nitrate was not included in the calculation of the ion balance. The average nitrite-plus-nitrate concentration at this station was 220 μeq/L, which is slightly less than 2 percent of the total ionic charge in solution. Time-series plots of the major dissolved constituents were inspected for evidence of method-related effects (fig. 17). No unusual patterns were apparent, except perhaps for nitrite plus nitrate, which had a pattern of elevated concentrations between 1980 and 1986 and again in 1992. The period of elevated nitrite-plus-nitrate concentrations in the 1980's seems to coincide with a change in the protocol for field preservation of nutrient samples. Before 1980, samples were preserved by chilling to 4°C; from 1980 through 1985, samples were preserved with mercuric chloride tablets; and beginning in 1986, the tablets were replaced by ampoules of mercuric chloride solution (Schertz and others, 1994). Schertz and others observed elevated organic plus ammonium nitrogen and ammonia nitrogen concentrations in several streams in Texas between 1980 and 1986, which were attributed to a positive bias in the data caused by the addition of mercuric chloride tablets. In 1986, when the tablets were replaced by the ampoules, the concentrations returned to normal levels of variation. Although Schertz and others (1994) only observed a bias in ammonium species, the pattern in the North Fork Whitewater River indicates that, perhaps, the mercuric chloride tablets may have biased the nitrite-plus-nitrate concentrations as well.

Median concentrations and ranges of major constituents in stream water at the North Fork Whitewater River Station and VWM concentrations in wet-only deposition measured at the Wildcat Mountain NADP station are listed in table 30.

Precipitation chemistry at the NADP station, which is about 120 km east of the HBN station, was dilute and slightly acidic with a VWM pH of 4.8 for 6 years of record. The predominant cations were ammonium, which contributed 45 percent of the total cation charge, and calcium and hydrogen, which accounted for 26 and 20 percent, respectively. Sulfate accounted for 56 percent of the total anions and nitrate contributed 39 percent. The predominance of strong acid anions at this site indicates that precipitation may be affected by anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain. In addition, the relatively high ammonium concentrations at this NADP station may be linked to the high density of livestock in this region of the country.

Stream water in the North Fork Whitewater River is concentrated and strongly buffered; specific conductance ranged from 200 to 690 µS/cm, and alkalinity was between 1,240 and 5,700 µeq/L (table 22). Calcium and magnesium were the predominant cations, and bicarbonate was the predominant anion. The predominance of these solutes in stream water is attributed to the presence of limestone bedrock and carbonate minerals in the overlying till and loess deposits. The median concentration of chloride in stream water was 240 µeq/L, which is almost 100 times greater than the VWM concentration of 2.5 µeq/L in precipitation. This large difference in concentration indicates that most stream-water chloride is derived from sources other than precipitation. Most stream-water chloride probably is derived from a combination of natural and human-related sources; however, road salt, sewage effluent, and fertilizer are probably the largest contributors. Sulfate concentrations also were much higher in stream water than in precipitation. The main source of sulfate, other than atmospheric deposition, probably is calcium sulfate minerals present in variable amounts in the limestone and shale bedrock. The median concentrations of nitrate and ammonium in stream water were 210 and 2.1 µeq/L compared to 23 and 27 µeq/L in precipitation, indicating that a substantial amount of inorganic nitrogen is exported from the basin. The most likely sources of stream-water nitrate in the basin include fertilizers, animal wastes, and wastewater effluent.The median stream-water nitrate concentration was similar to the concentration of 210 µeq/L (3 mg/L), which is considered indicative of human-related pollution of ground water in southeastern Minnesota (Smith and Nemetz, 1995).

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 31). Discharge was poorly correlated with the major dissolved constituents, except for a weak positive correlation with nitrite plus nitrate (rho = 0.573). There also were few strong correlations among the solutes, except for a positive correlation between calcium and nitrate (rho = 0.764). The lack of strong correlations among these solutes probably is related to hydrologic factors. Streamflow is supplied primarily by groundwater discharge from a carbonate aquifer, which maintains a relatively constant flow rate and stream composition throughout most of the year. The correlations between nitrate and discharge and nitrate and calcium probably result from leaching of inorganic nitrogen from agricultural land and livestock yards during high-flow periods when discharge from shallow flow paths may be an important component of streamflow.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are listed in table 32. Statistically significant trends were observed in discharge and most of the major dissolved constituents at the 0.01 probability level. Trends in calcium, magnesium, sodium, alkalinity, chloride, nitrite plus nitrate, and silica were similar for unadjusted and flow-adjusted concentrations, indicating that trends were not caused by the trend in stream discharge. The LOWESS curves in figure 17 show several different trend patterns at this station. The largest relative increases occurred in sodium, chloride, and nitrite-plus-nitrate concentrations, which at least doubled during the period of record. Most of the increase in sodium and chloride concentrations occurred before 1985; however, the magnitude of the trend in flow-adjusted chloride [10 (µeq/L)/yr] was twice that of flow-adjusted sodium [5 (µeq/L)/yr]. The upward trend in nitrite plus nitrate was more erratic than the trends in sodium and chloride, perhaps owing, in part, to analytical bias. By contrast, the increases in calcium, magnesium, potassium, alkalinity, sulfate, and silica concentrations were small (4 to 18 percent). Upward trends in sodium and chloride

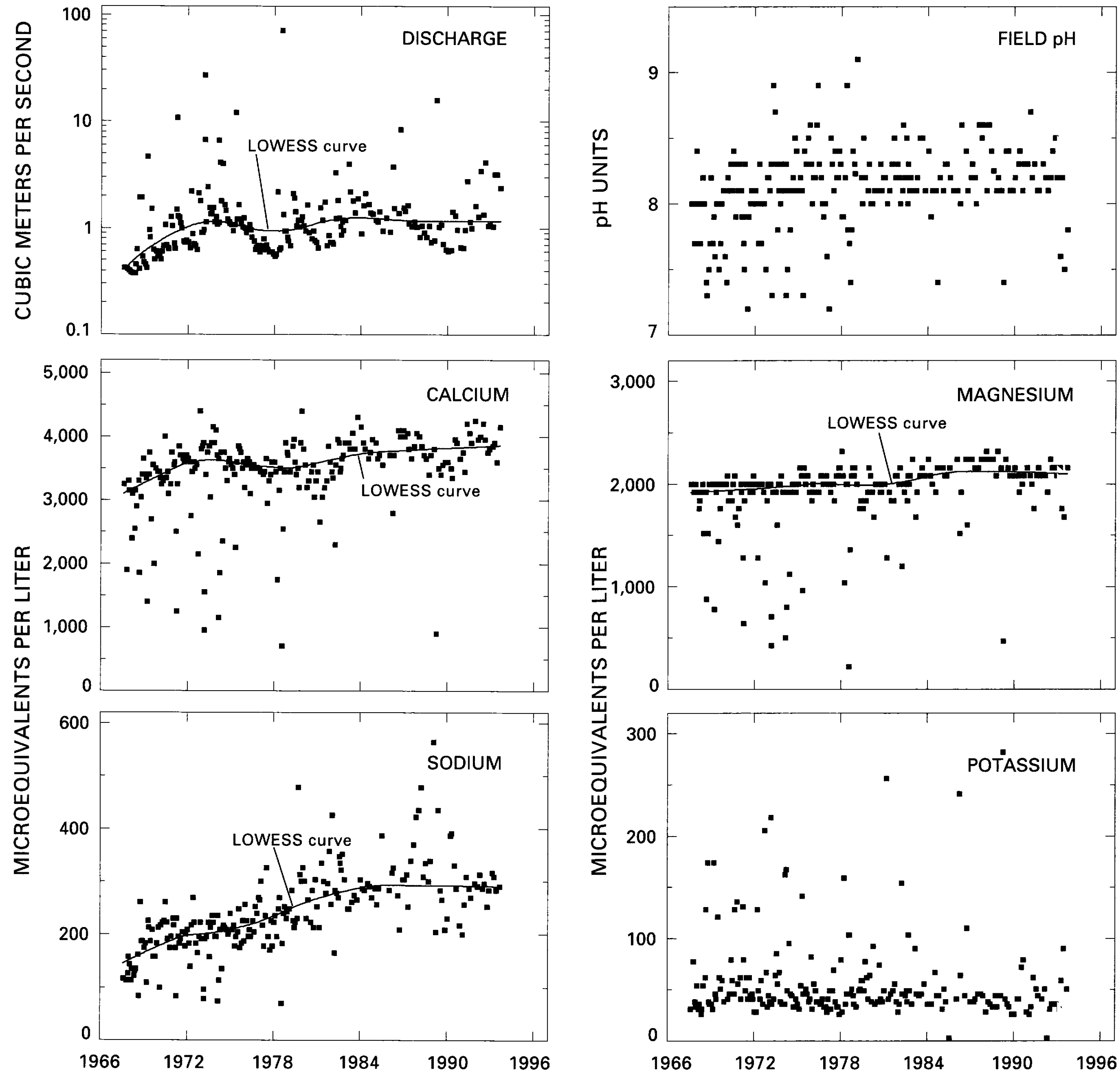


Figure 17. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at North Fork Whitewater River, Minnesota.

most likely are caused by changes in land-use activities in the basin, such as increased use of deicing salts, discharge from septic systems and the wastewater-treatment facility, and application of fertilizers to croplands. The difference in magnitude between the sodium and chloride trends was somewhat unexpected and may indicate part of the sodium from human-related sources is replacing calcium and magnesium on cation-exchange sites in the soil (Rittmaster and Shanley, 1995). The upward trend in nitrite-plus-nitrate concentrations probably also reflects changes in land-use activities because stream-water nitrogen is primarily derived from fertilizer and animal wastes. The source of trends in the remaining constituents is less

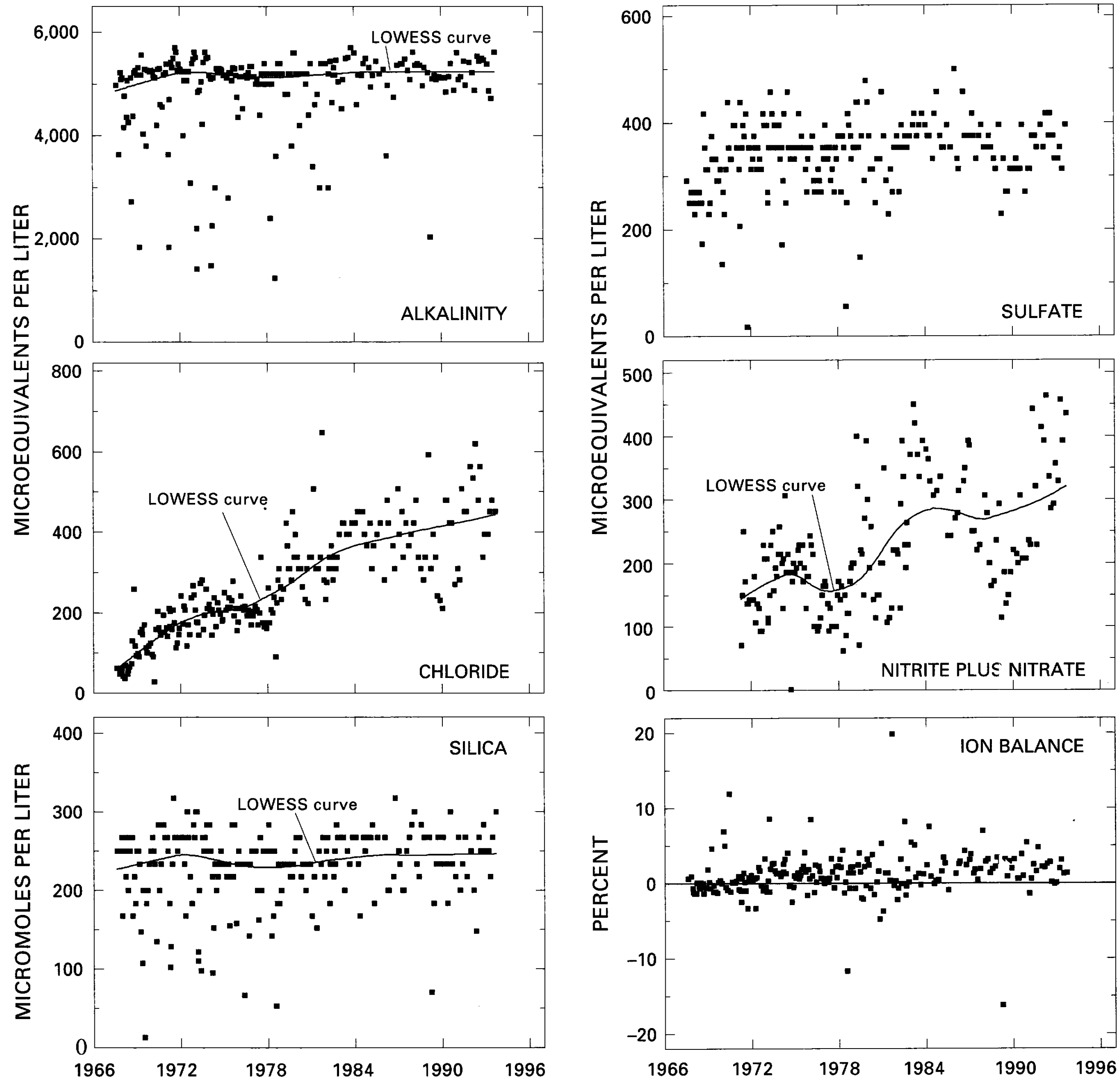


Figure 17. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at North Fork Whitewater River, Minnesota—Continued.

clear. Landscape disturbance associated with croplands and residential areas has the potential to increase rates of base cation leaching and may result in higher stream-water alkalinity (Stoddard and Murdoch, 1991). Because sulfate and silica also are derived from geologic sources, landscape disturbance may affect stream-water concentrations of these solutes as well.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling in the North Fork Whitewater River Basin on August 20, 1992, are listed in table 33, and the locations of the sampling sites are shown in figure 16. During the sampling period, discharge at the gaging station was about 1.1 m^3/s compared to the median

Table 30. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major dissolved constituents measured in water-quality samples from North Fork Whitewater River, Minnesota, August 1967 through September 1993, and volume-weighted mean concentrations in wet precipitation collected at the Wildcat Mountain Station, Wisconsin

[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.	0.37	0.70	1.0	1.4	71	219	--
Spec. cond., field	220	490	530	560	690	219	15
pH, field	7.2	8.0	8.2	8.3	9.1	216	4.8[b]
Calcium	700	3,350	3,600	4,00	4,400	218	12
Magnesium	220	1,980	2,060	2,140	2,320	218	3.1
Sodium	70	200	230	290	570	218	2.2
Potassium	<2.6	36	44	59	280	215	.6
Ammonium	<.7	1.1	2.1	3.9	130	78	27
Alkalinity, laboratory	1,240	4,880	5,180	5,40	5,700	217	--
Sulfate	17	310	350	370	500	218	33
Chloride	28	170	240	340	650	219	2.5
Nitrite plus nitrate	<7.1	150	210	280	460	177	23[c]
Silica	13	220	230	270	320	218	--

[a] Data are volume-weighted mean concentrations for 1989–95.

[b] Laboratory pH.

[c] Nitrate only.

Table 31. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major dissolved constituents, North Fork Whitewater River, Minnesota, 1967–93

[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	–0.192									
Ca	.345	0.106								
Mg	–.374	.254	0.428							
Na	–.126	.097	.127	0.363						
K	.480	–.167	–.065	–.596	–0.097					
Alk	–.228	.196	.471	.606	.183	–0.342				
SO_4	.257	–.010	.556	.261	.118	.021	0.329			
Cl	.471	–.007	.523	.106	.402	.191	.108	0.359		
N	.573	–.053	.764	.092	.041	.096	.230	.532	0.602	
Si	–.163	–.102	.337	.356	.197	–.067	.389	.167	.005	0.207

discharge of 0.9 m^3/s for November (Lawrence, 1987), indicating that the basin was sampled during normal flow conditions for that time of year. The concentrations of most solutes measured at site 1 during the synoptic sampling were between the first- and third-quartile concentrations reported for the HBN station during the entire period of record (table 30). The tributary streams were similar in composition to stream water collected at the gaging station (site 1); calcium and magnesium were the predominant cations, and bicarbonate was the predominant anion. Ion balances were slightly negative for all samples and ranged from –0.4 to –2.1 percent.

Table 32. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major dissolved constituents, North Fork Whitewater River, Minnesota, August 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; inst., instantaneous; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge, inst.	0.02	0.000	--	--
pH	<.01	.120	0.01	0.021
Calcium	22.8	.000	26.3	.000
Magnesium	8.1	.000	15.4	.000
Sodium	6.1	.000	5.0	.000
Potassium	–.3	.080	–1.0	.000
Alkalinity, laboratory	8.4	.005	22.7	.000
Sulfate	1.4	.034	.2	.000
Chloride	14.8	.000	10.0	.000
Nitrite plus nitrate	7.8[a]	.000	7.2[a]	.000
Silica	1.0	.005	1.4	.002

[a] Trend calculated for 1971–93.

The concentrations of the weathering-derived constituents did not vary markedly among the sampled tributary sites (table 33). For example, alkalinity ranged from a minimum of 4,980 µeq/L at site 3 to a maximum of 5,800 µeq/L in Dry Creek upstream from Elgin (site 7). Calcium concentrations ranged from 3,550 to 4,650 µeq/L, and magnesium ranged from 2,000 to 2,880 µeq/L. The widespread presence and rapid weathering rates of carbonate minerals in the bedrock and surfical deposits are the most likely reasons for the lack of substantial spatial variation in the concentrations of these solutes. Differences in the concentration of the remaining solutes seem to be related largely to human activities in the basin. Several solutes were elevated downstream from the wastewater-treatment plant at Plainview (site 9) compared to other sampling sites in the basin. For example, sodium and chloride concentrations were 6,090 and 5,630 µeq/L, respectively, at site 9 compared to the average sodium and chloride concentrations of 310 and 700 µeq/L, respectively, at the other sampling sites in the basin. The wastewater-treatment plant also apparently had a slight effect on streamwater potassium and sulfate concentrations based on the elevated concentrations of these solutes at site 9. Despite the high concentrations at site 9, the wastewater-treatment plant did not seem to substantially affect the surface-water chemistry at the gaging station (site 1), probably because of the low discharge at site 9 compared to the discharge at the gage. Nitrate concentrations at the sampling sites ranged from 240 µeq/L at site 1 to 860 µeq/L at site 2. All sites had nitrate concentrations greater than the background concentration of 210 µeq/L (3 mg/L) for ground water in southeastern Minnesota (Smith and Nemetz, 1996), and two of the tributaries (sites 2 and 4) had concentrations at or greater than the drinking-water standard of 710 µeq/L (10 mg/L), indicating widespread nitrate contamination of stream water in the basin.

Table 33. Physical properties and major dissolved constituents from surface-water sampling sites in the North Fork Whitewater River Basin, Minnesota, collected August 20, 1992

[Site locations shown in fig. 16; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeters 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; Si, silica; concentrations in microequivalents per liter, except silica in micromoles per liter; WTP, wastewater-treatment plant; criteria used in selection of sampling sites: MT = major tributary, LU = land use]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria	Remarks
1	5376000	1.1	560	8.1	3,750	2,080	270	62	5,240	330	390	240	250	--	Gaging station
2	440350092161400	.020	700	8.3	4,450	2,480	340	44	5,440	440	850	860	300	LU	Cropland
3	440520092165900	.0085	600	8.6	4,200	2,000	280	79	4,980	500	730	430	220	LU	Cropland
4	440535092163400	.031	670	8.6	4,350	2,320	300	72	5,340	460	850	700	270	LU	Cropland
5	440554092074700	.14	640	8.3	4,150	2,480	250	49	5,580	400	510	480	270	MT	Forested along stream
6	440603092072900	.48	600	8.2	3,550	2,160	440	79	5,000	400	700	320	200	MT	Forested along stream
7	440721092193800	.017	680	8.6	4,650	2,400	280	51	5,800	440	820	520	300	MT, LU	Cropland
8	440743092141700	.10	640	8.1	4,100	2,080	310	92	5,240	480	730	430	230	LU	Downstream from Elgin
9	440806092081400	.048	1,380	8.2	3,850	2,880	6,090	236	5,720	1,080	5,630	680	320	LU	Downstream from WTP

Upper Twin Creek at McGaw, Ohio (Station 03237280)

Site Characteristics and Land Use

The Upper Twin Creek HBN Basin is in the Allegheny Mountain section of the Appalachian Plateaus physiographic province along the southern border of Ohio (fig. 18). The landscape is unglaciated and characterized by narrow ridgetops, steep hillslopes, and narrow stream valleys. The basin drains 31.6 km^2 of strongly dissected terrain and ranges in elevation from 164 m at the gaging station to more than 395 m along the northern basin divide. The USGS gaging station is located 1.1 km upstream from McGaw, Ohio, at latitude 38°38'37" and longitude 83°12'57". Upper Twin Creek is a southeast-flowing tributary of the Ohio River and has a channel length of 11.1 km upstream from the gaging station and an average stream gradient of 12.7 m/km. Mean monthly discharge varies from 0.07 m^3/s in October to 0.83 m^3/s in March, and periods of no flow occur most years between October and December. Streamflow generally is highly variable in summer because of severe thundershowers. Average annual runoff from the basin was 38 cm from 1963 through 1995 (Shindel

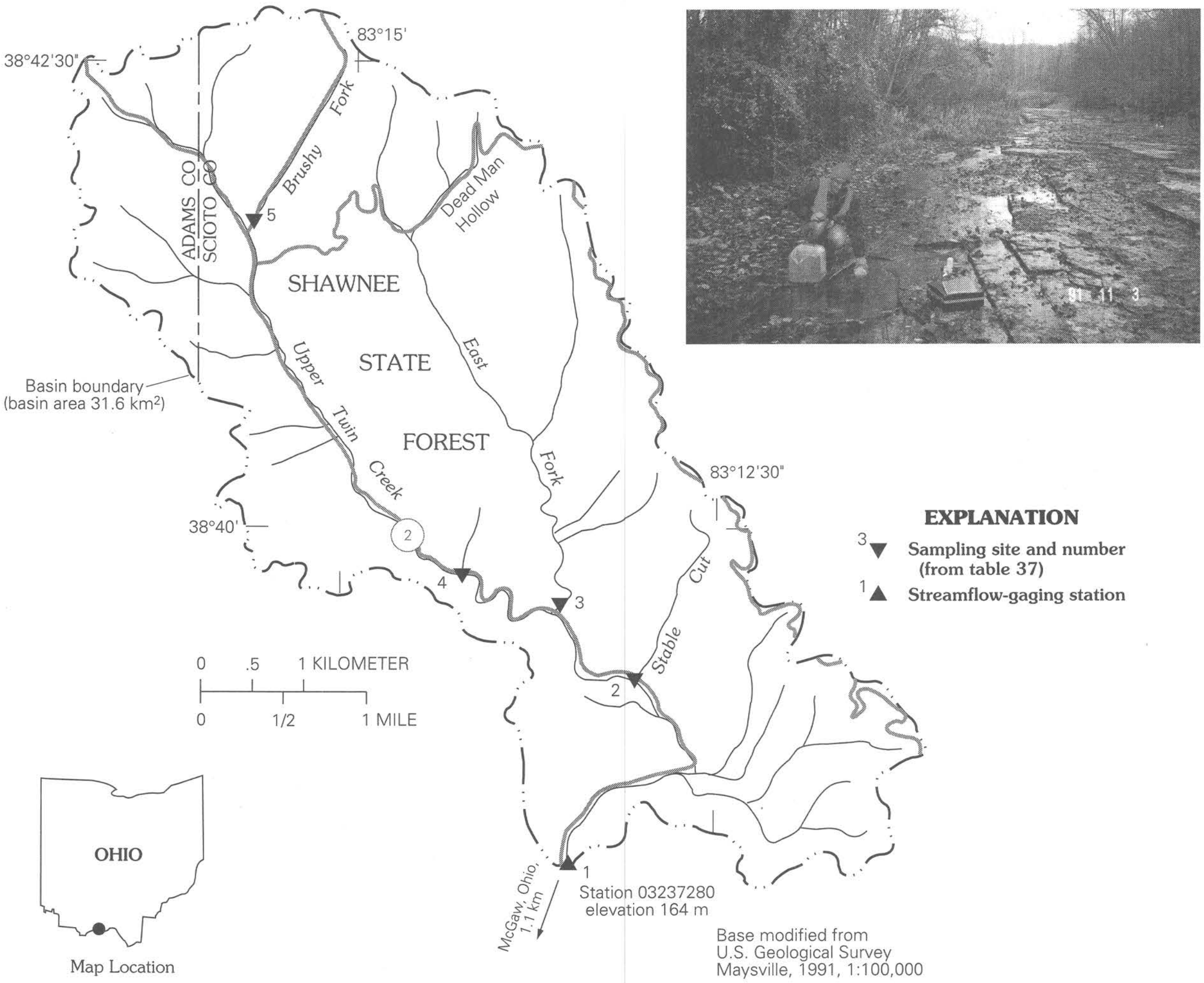


Figure 18. Map showing study area in the Upper Twin Creek Basin and photograph of the main stream channel.

and others, 1996). The climate is characterized by fairly warm summers and cold, snowy winters. Average daily air temperatures range from 0.0°C in January to 24.4°C in July (McCleary and others, 1989). Precipitation averages 105 cm annually and is fairly evenly distributed during the year. Average annual snowfall is 45 cm, but mid-winter thaws preclude the accumulation of a seasonal snow cover.

The basin is in the Eastern Broadleaf Forest (Oceanic) ecoregion, which is characterized by temperate deciduous forests that form a dense, continuous canopy (Bailey and others, 1994). Several species of oaks and hickories, as well as sassafras, pitch pine, and shortleaf pine, populate the drier ridges (Shawnee State Forest, written commun., 1997). Midslope areas are dominated by oaks and hickories, as well as maples, basswoods, yellow poplar, buckeyes, blackgum, white ash, red elm, northern hackberry, and quaking aspen. Sweetgum, American beech, black cherry, black walnut, eastern sycamore, river birch, and bitternut are common in moist areas in bottomlands and coves. Soils in the basin are classified as Ultisols (Hapludults) and mapped in the Shelocta and Brownsville soil associations (McCleary and others, 1989). These are deep, well-drained soils on side slopes and ridgetops that were formed in colluvium and residuum derived from siltstone, sandstone, and shale. A typical soil profile has a surface layer of pale brown silt loam that is about 15 cm thick overlying a subsoil of yellowish-brown silt loam that extends down to 130 cm. Below the subsoil is a 25- to 50-cm layer of yellowish-brown silt loam that contains as much as 15 percent of thin, flat rock fragments of sandstone and shale. Most soils are acidic (pH 3.6 to 5.5) and have an organic-matter content of less than 3 percent in the upper 20 cm (McCleary and others, 1989).

Bedrock in the basin consists of gently dipping marine sedimentary rocks of Lower Mississippian age, including the Berea Sandstone, the Sunbury Shale, and the Cuyahoga and Logan Formations (Hyde, 1953). The Berea Sandstone consists of 70 percent sandstone and 30 percent siltstone and shale and is locally calcareous. The Sunbury Shale is a pyritiferous dark-gray to black carbonaceous fissile shale that generally is less than 10 m thick. The Cuyahoga and Logan Formations crop out on the upper hillslopes and ridges. The Cuyahoga Formation consists of a gray shale interbedded with silty shale and siltstone, and the Logan Formation consists of light-gray siltstone with occasional beds of shale (Sheppard, 1964).

The Upper Twin Creek Basin drains the southwestern corner of Scioto and Adams Counties in Ohio, and most land is in the Shawnee State Forest, which is administered by the Ohio Department of Natural Resources. Land on the west side of Upper Twin Creek, which accounts for about 23 percent of the basin, is designated as a State wilderness area. Privately owned parcels account for about 4 percent of the basin, and most parcels are located along the flood plain just upstream from the gaging station. State Forest Road 2 enters the basin at the gaging station and parallels the entire length of Upper Twin Creek. Forest roads also access Brushy Fork and Dead Man Hollow in the upper one-half of the basin. Roads are surfaced with limestone gravel, except a 2-km stretch of Forest Road 2, which is chipped and sealed upstream from the gaging station. Roads are occasionally plowed in winter but are not salted (Benjamin Hamilton, Shawnee State Forest, written commun., 1997). The wilderness area is accessible by hiking and equestrian trails.

Land cover in the basin is 98 percent forest, 1 percent open, and 1 percent agricultural (Benjamin Hamilton, Shawnee State Forest, written commun., 1997). The principal land-use activity on State-owned lands on the east side of the creek is timber harvesting. State-owned lands on the west side of the creek were designated as wilderness in 1972, and since then, timber harvesting and motorized vehicles have been prohibited. Timber harvesting on State lands is done to the highest standards to minimize the effects on surface water and to improve wildlife habitat (Benjamin Hamilton, written commun., 1997). Timber is harvested on a sustained-yield basis by selective harvesting and clearcutting. Since the 1950's, about 885 ha of timber in the basin have been selectively harvested and 75 ha have been clearcut (Benjamin Hamilton, written commun., 1997). Wildfires are common in the region, and the policy of the Shawnee State Forest is to suppress fires that occur on public and private lands in and surrounding the State forest. Land use on private land is primarily residential, but there is a small amount of agriculture, including corn, tobacco, and livestock. Two groups of trailer homes (five to six each) and accompanying onsite sewage disposal systems and domestic trash dumps are situated along the creek, one just upstream from the gaging station and the other in the headwaters. Very few changes in land use have occurred in the basin since the establishment of the HBN station, the most important change being the designation of the State wilderness area in 1972.

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for the Upper Twin Creek HBN Station for this report includes 299 water-quality samples that were collected from August 1967 through September 1995. Except for a few years, samples were collected monthly during the entire period of record. Water-quality samples in the early part of the period of record were probably analyzed at a USGS laboratory in Columbus, Ohio, that operated until 1973 (Durum, 1978). After establishment of a central laboratory system, samples were analyzed at a laboratory in Atlanta, Ga., from 1973 through 1985 and at the NWQL in Arvada, Colo., from 1986 through 1995. Daily discharge records are available for Upper Twin Creek (station 03237280) beginning in June 1963. Daily records of pH and specific conductance at the gaging station are available from March 1985 through September 1995, and daily water temperature is available from 1963 through 1966, from 1967 through 1970, from 1972 through 1982, and from 1984 through 1995.

Calculated ion balances for 299 samples with complete major-ion analyses are shown in figure 19. Ion balances ranged from −16 to 14 percent, and more than 98 percent of samples had values in the ±10 percent range, indicating that the analytical measurements were of good quality. The average charge balance for all samples was −1.1 percent, indicating that unmeasured constituents, such as organic anions, did not contribute substantially 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. 19). A few questionable patterns are evident in the Upper Twin Creek data, particularly for chloride and field pH. For example, chloride concentrations showed a noticeable decrease in scatter in the early 1970's. This pattern is coincident with a switch from the USGS laboratory in Columbus, Ohio, to the central laboratory in Atlanta, Ga., in 1973 and may reflect a difference in the precision of the chloride analyses reported by these two facilities. The temporal pattern in field pH showed a rather abrupt decrease in pH values in 1973, followed by a gradual increase between 1973 and 1992, and a decrease again around 1992. Although this pattern in pH may have been caused by environmental factors, a change in methods would be more likely to produce abrupt changes in the pH values (Schertz and others, 1994), such as those observed in 1973 and again in 1992.

Median concentrations and ranges of major constituents in stream water at the Upper Twin Creek Station and VWM concentrations in wet-only deposition measured at the Clark State Fish Hatchery NADP Station are listed in table 34. Precipitation chemistry at the NADP station, which is located about 65 km southwest of the HBN station, is dilute and acidic with a VWM pH of 4.4 for 13 years of record. The predominant cations were hydrogen and ammonium, which accounted for 62 and 19 percent of the total cation charge, respectively. The predominant anions were sulfate, which contributed 66 percent of the anion charge, and nitrate, which contributed 29 percent. The predominance of strong acid anions and the low pH 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 Upper Twin Creek is fairly concentrated but only moderately buffered; specific conductance ranged from 60 to 220 µS/cm, and alkalinity was between 100 and 600 µeq/L (table 34). The major cations in stream water were magnesium and calcium, and the predominant anion was sulfate. Although the Ohio Valley has some of the highest rates of sulfate deposition in the United States, the high stream-water sulfate concentrations probably are derived primarily from weathering of the sedimentary rocks rather than atmospheric deposition. The two most likely sources of sulfate are oxidation of disseminated pyrite in the Sunbury Shale and Berea Sandstone and dissolution of minor gypsum beds in the marine shales. High concentrations of magnesium and calcium also are attributed to bedrock weathering, although the mineralogic sources, particularly for magnesium, are difficult to confirm. Weathering of carbonate minerals releases calcium and magnesium to surface water, whereas dissolution of gypsum releases only calcium. Ion exchange from clays in the marine shales is another potential source of cations, the primary mechanism being neutralization of sulfuric acid generated from the oxidation of pyrite. The median chloride concentration in stream water was 56 μeq/L, which is about 16 times higher than the VWM chloride concentration of 3.5 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 chloride concentration of precipitation, indicating that stream-water chloride also is derived from sources other than precipitation. Anthropogenic sources of chloride probably are minimal because roads are not salted in winter and there are only a few residences in the basin. The excess stream-water chloride, therefore, probably is derived from dissolution of salts from the marine sedimentary rocks. Concentrations of nitrite plus nitrate and ammonium were lower in stream water than in precipitation, indicating that most atmospherically deposited 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 35). All solutes showed strong inverse correlations with discharge (−0.652 > rho > −0.854), with the exception of silica (rho = −0.121). Inverse correlations between solutes and discharge are consistent with a hydrologic system where weathering-enriched base flow is diluted by water from shallow sources during periods of increased discharge. Strong positive correlations were observed among all the weathering-derived constituents, except for silica. The strong correlations between chloride and the weathering solutes provide additional evidence that most stream-water chloride is derived from the dissolution of salts in the sedimentary bedrock. The processes that control silica concentrations in stream water are not clear, particularly because the concentrations varied little for a wide range of streamflows. Weathering of quartz and clay minerals in the sandstones and shales is the most likely source of silica to the stream during low-flow conditions. During high-flow conditions, however, dissolution of amorphous silica phases, biological activity, and sorption reactions in shallow ground-water or soil environments may be the predominant 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 are listed in table 36. Statistically significant upward trends were observed for pH, calcium, magnesium, alkalinity, and sulfate at the 0.01 probability level. The results were similar for unadjusted and flow-adjusted concentrations, indicating that the trends were not caused by variations in stream discharge. The LOWESS curves in figure 19 indicate slightly different trend patterns for these five constituents. For example, field pH declined in the early part of the period of record and then increased steadily between 1973 and 1993. The greatest change in calcium and alkalinity concentrations occurred in the later one-half of the period of record. Most of the increase in alkalinity occurred during a short period in the early 1990's, whereas the increase in calcium was more gradual. By contrast, most of the increase in magnesium and sulfate concentrations occurred in the first one-half of the period of record.

Trends in stream chemistry at Upper Twin Creek Station may reflect changes in environmental factors such as precipitation chemistry or land-use activities. Estimates of sulfur emissions indicate that atmospheric sulfate deposition has decreased substantially in the industrialized Midwest since the 1970's (Husar and others, 1991). Lynch and others (1995) reported declines in calcium, magnesium, and sulfate concentrations at NADP stations in the Midwestern United States from 1982 through 1990. The upward trends in stream-water calcium, magnesium, and sulfate at the HBN station are inconsistent with the trends in precipitation chemistry reported by Lynch and others (1995), indicating that the stream-water trends probably were not caused by

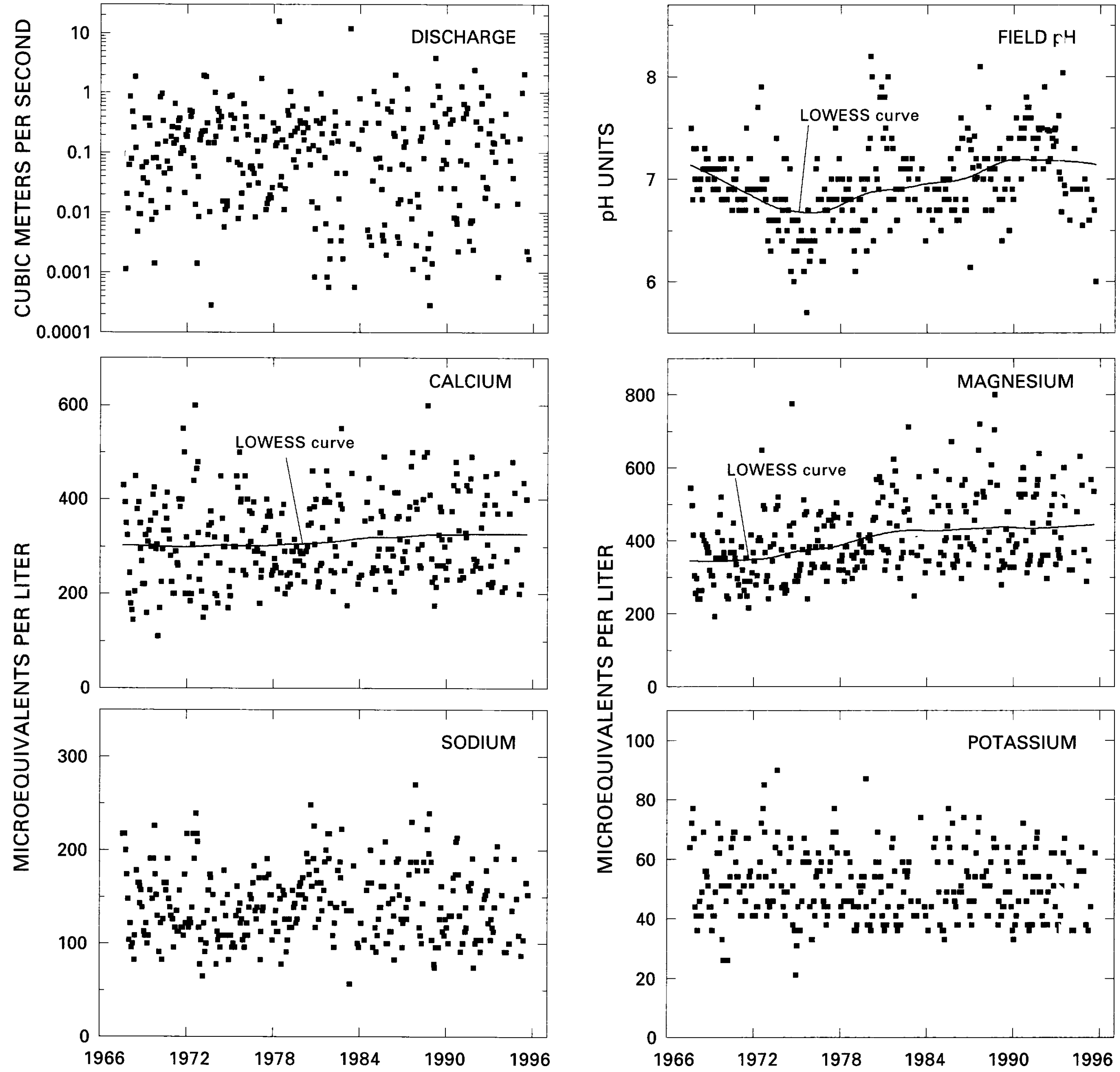


Figure 19. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Upper Twin Creek, Ohio.

changes in atmospheric deposition. Trends in stream chemistry at this station may more likely reflect human activities in the basin. Although most of the State-owned land is fairly undisturbed, there are several rural residential areas and small farms along Upper Twin Creek, as well as a network of gravel roads. Landscape disturbance associated with the residential areas and farms has the potential to increase rates of base cation leaching and may result in higher stream-water alkalinity and pH (Stoddard and Murdoch, 1991). Because sulfate also is derived from geologic sources, landscape disturbance may impact stream-water sulfate concentrations as well. Changes in stream-water chemistry also may be

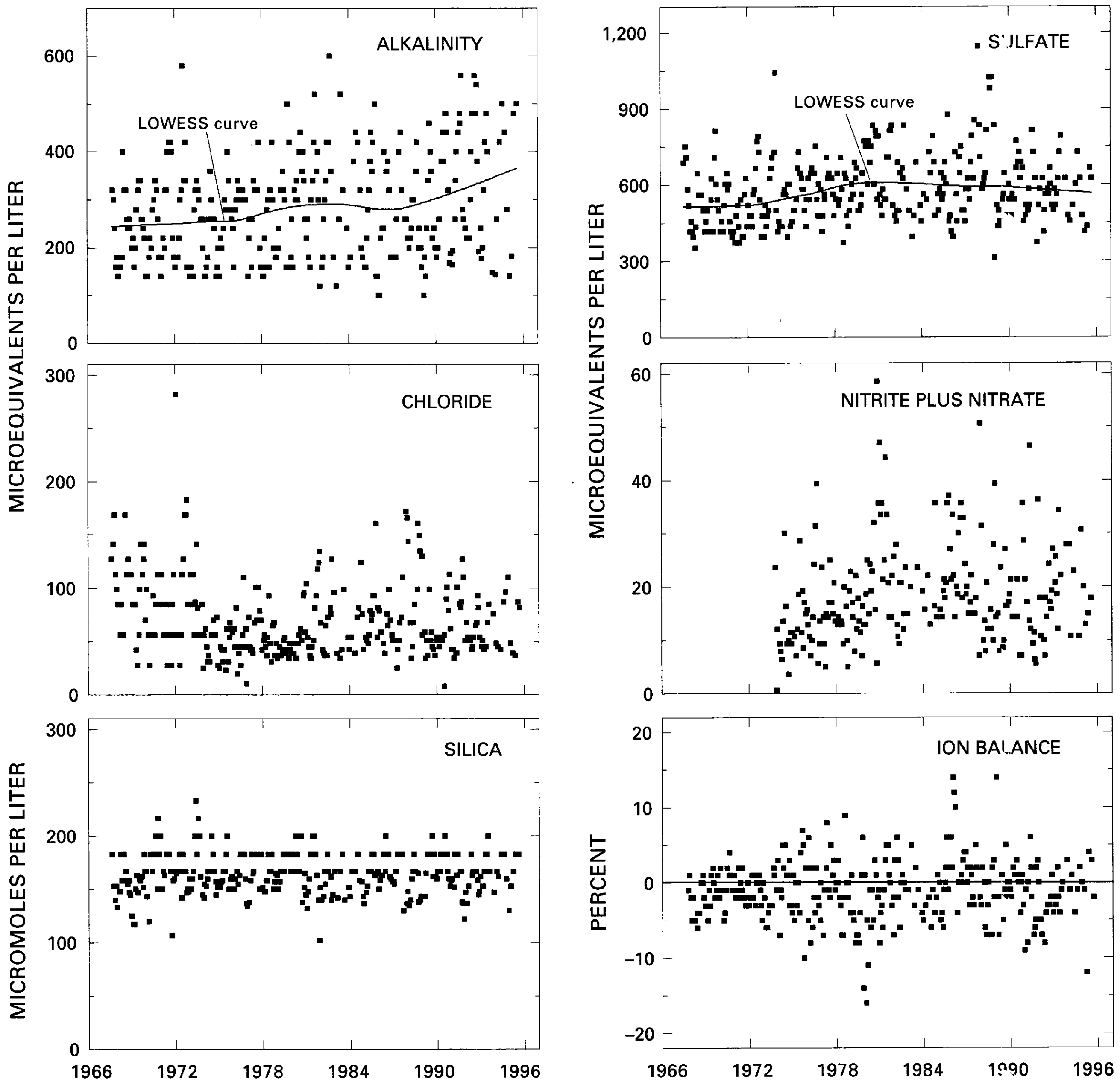


Figure 19. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Upper Twin Creek, Ohio—Continued.

related to the network of roads. Most roads in the basin are covered with limestone gravel and should provide a readily soluble source of calcium, magnesium, and alkalinity to the stream, particularly during storms and snowmelt when direct runoff from the roads to the stream channel is more likely.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling in the Upper Twin Creek Basin on November 3, 1991, are listed in table 37, and the locations of the sampling sites are shown in figure 18. During the sampling period, discharge at the gaging station was 0.003 m^3/s

Table 34. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major dissolved constituents measured in water-quality samples from Upper Twin Creek, Ohio, August 1967 through September 1995, and volume-weighted mean concentrations in wet precipitation collected at the Clark State Fish Hatchery Station

[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.	0.0003	0.017	0.12	0.34	16	302	--
Spec. cond., field	60	70	100	120	220	306	20
pH, field	5.7	6.7	6.9	7.2	8.2	306	4.4[b]
Calcium	110	250	300	390	750	306	7.0
Magnesium	200	350	400	490	800	305	1.8
Sodium	57	110	140	170	270	306	2.7
Potassium	20	41	49	59	90	305	.8
Ammonium	<.7	<.7	<.7	1.4	10	148	12
Alkalinity, laboratory	100	190	260	340	600	302	--
Sulfate	310	480	560	640	1,140	306	45
Chloride	8.5	45	56	85	280	306	3.5
Nitrite plus nitrate	<3.6	14	14	21	86	231	20[c]
Silica	100	150	160	180	230	306	--

[a] Data are volume-weighted mean concentrations for 1983–95.

[b] Laboratory pH.

[c] Nitrate only.

Table 35. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major dissolved constituents, Upper Twin Creek, Ohio, 1967–95

[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	0.011								
Ca	–.864	0.113							
Mg	–.864	.086	0.968						
Na	–.785	.038	.848	0.900					
K	–.653	.008	.752	.715	0.632				
Alk	–.670	.152	.821	.781	.661	0.695			
SO_4	–.748	.080	.777	.830	.851	.536	0.570		
Cl	–.764	.011	.805	.776	.632	.541	.617	0.592	
Si	–.121	–.082	.161	.178	.251	.471	.236	.155	–0.099

compared to the median discharge of 0.02 m^3/s for October and 0.06 m^3/s for November (Lawrence, 1987), indicating that the basin was sampled during low-flow conditions for that time of year. Because of the low-flow conditions, solute concentrations measured at site 1 were greater than the third-quartile concentrations reported for the HBN station during the entire period of record (table 34). The tributary streams were similar in composition to stream water collected at the gaging station (site 1); magnesium and calcium were the predominant cations, and sulfate and bicarbonate were the predominant anions. Ion balances were negative for all samples and ranged from −3.1 to −5.8 percent. This result was somewhat unexpected because of the high solute concentrations at this station and may indicate a bias in one of the analytical measurements.

Most of the spatial variability in stream chemistry in the Upper Twin Creek Basin was measured in the weathering-derived constituents. For example, alkalinity ranged from 320 µeq/L in the East Fork (site 3) to 2,280 µeq/L in Brushy Fork (site 5) (table 37). Similar spatial patterns were measured in the magnesium and calcium concentrations. Magnesium ranged from 420 to 1,280 µeq/L and calcium ranged from 250 to 1,200 µeq/L. These differences in stream chemistry may reflect differences in the mineralogy of the underlying sedimentary rocks. For example, the shales and siltstones, which are more common in the upper part of the basin, contain a greater percentage of carbonate minerals and marine clays than the sandstones that underlie the lower one-half of the basin. The concentrations of the remaining solutes did not vary markedly among the sampling sites. For example, sulfate concentrations ranged 540 to 790 µeq/L, and silica ranged from 130 to 180 µmol/L. Because both of these solutes also are derived from weathering, these results may reflect uniformity in the mineralogic sources for these solutes. Chloride concentrations also varied over a narrow range but seemed to be elevated in streams draining residential or agricultural development (sites 1, 2, and 4) compared to streams where there was little or no development (sites 3 and 5). Nitrate concentrations were low at all the sampling sites (range <3.6 to 7.9 µeq/L), indicating that human activities had a minor effect on the nutrient concentrations of surface water during the sampling period.

Table 36. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major dissolved constituents, Upper Twin Creek, August 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, inst.	<−0.01	0.206	--	--
pH, field	.01	.007	(a)	--
Calcium	1.7	.003	1.1	0.007
Magnesium	4.1	.000	3.5	.000
Sodium	<.1	.862	−.3	.134
Potassium	−.1	.302	−.3	.083
Alkalinity, laboratory	2.9	.000	2.4	.000
Sulfate	3.3	.000	2.9	.000
Chloride	−.5	.534	−.3	.204
Nitrite plus nitrate	.3[b]	.149	.3[b]	.130
Silica	<.1	.232	<.1	.506

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

[b] Trend calculated for 1974–95.

Table 37. Physical properties and major dissolved constituents from surface-water sampling sites in the Upper Twin Creek Basin, Ohio, collected November 3, 1991

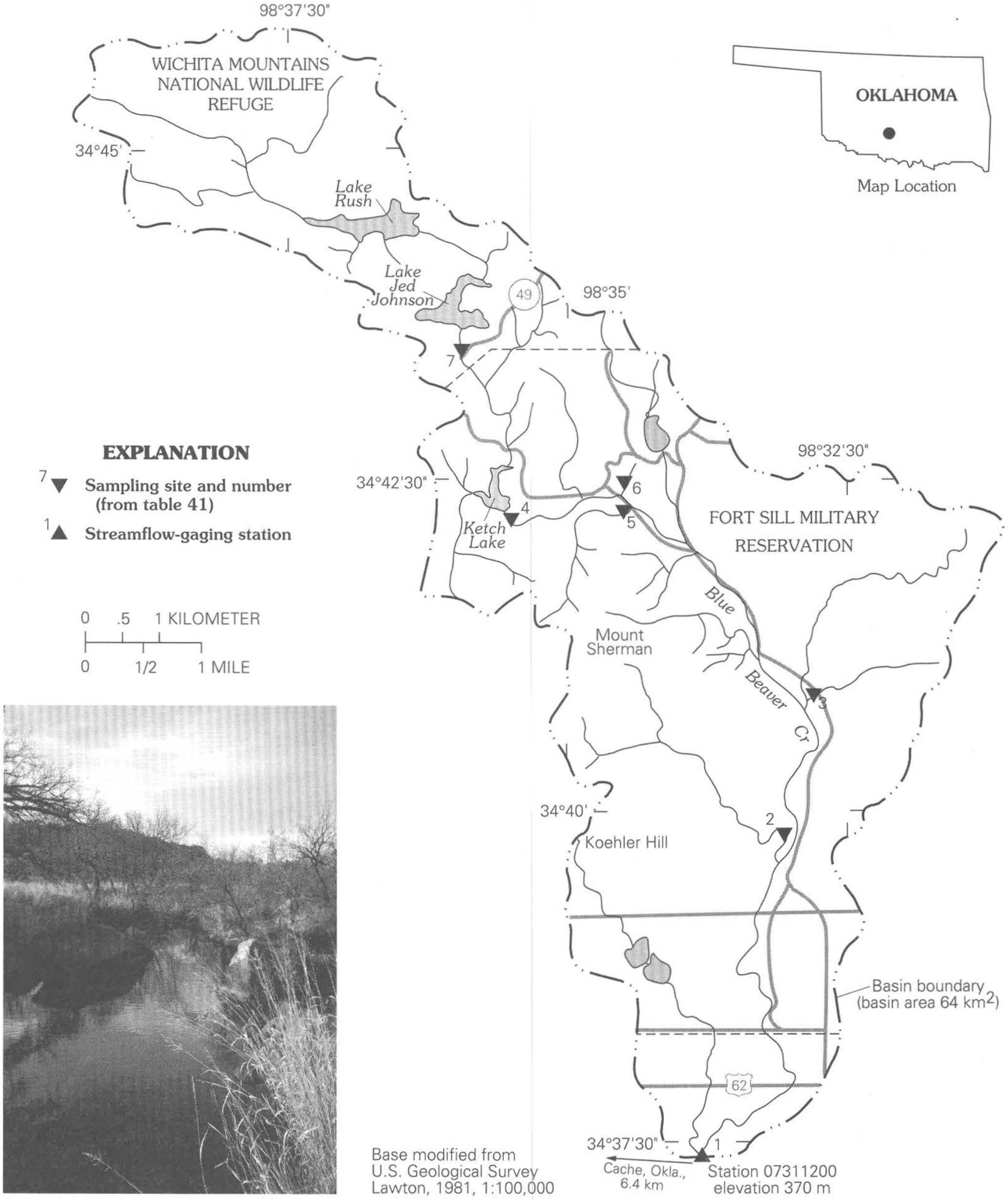
[Site locations shown in fig. 18; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeters at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; Si, silica; concentrations in microequivalents per liter, except silica in micromoles per liter; <, less than; --, not reported; criteria used in selection of sampling sites: MT = major tributary, LU = land use]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria[a]	Remarks
1	3237280	0.0034	160	7.3	430	640	200	54	520	790	150	7.9	150	--	Gaging station
2	383911083130000	--	140	7.1	420	580	160	54	660	560	110	<3.6	180	MT	
3	383935083133200	--	100	6.4	250	420	150	56	320	540	85	<3.6	170	MT, LU	Undeveloped
4	383941083135600	--	250	7.8	900	1,040	210	54	1,660	650	160	5.0	130	MT, LU	Residential development
5	384137083154100	--	280	7.1	1,200	1,280	170	82	2,280	540	79	<3.6	180	LU	Undeveloped, headwaters

Blue Beaver Creek near Cache, Oklahoma (Station 07311200)

Site Characteristics and Land Use

The Blue Beaver Creek HBN Basin is in the Wichita Mountains section of the Central Lowland physiographic province in southwestern Oklahoma (fig. 20). The 64-km^2 basin ranges in elevation from 370 to 732 m and drains a landscape of smooth rounded hills flanked by a broad, gently rolling plain. The USGS gaging station is located 6.4 km east of the town of Cache, Okla., at latitude 34°37'24" and longitude 98°33'48". Blue Beaver Creek flows south into Cache Creek, a tributary of the Red River, and has a channel length of about 26 km upstream from the gaging station and an average stream gradient of 6.9 m/km. Mean monthly discharge varied from



Base modified from U.S. Geological Survey Lawton, 1981, 1:100,000

Figure 20. Map showing study area in the Blue Beaver Creek Basin and photograph of the main stream channel below Lake Jed Johnson.

0.04m^3/s in July to 1.1 m^3/s in May, and annual runoff from the basin was 19 cm from 1964 through 1995 (Blazs and others, 1996). In most years, there are periods of no flow at the gaging station, particularly during July through October. The climate is temperate continental with long, hot summers and short, mild winters. Average monthly air temperatures range from 3.0°C in January to 27.8°C in July (National Climatic Data Center, 1997). Precipitation averages 77 cm annually and is greatest in May (13.1 cm) and least in January (2.9 cm). Snowfall averages 12 cm annually and normally melts within a few days of falling.

The Blue Beaver Creek Basin is in the Great Plains Steppe and Shrub ecoregion (Bailey and others, 1994) and is covered by short- and mixed-grass prairies with oak savanna communities usually along the drainages. Common grass species include bluestem, indian grass, switchgrass, blue grama, and side-oats grama, and the predominant woody species are live oak, post oak, blackjack oak, and bigtooth maple. Most soils in the basin are classified as Mollisols and are mapped in the Lawton soil series (Mobley, 1967). The Lawton series consists of deep, loamy soils that formed in old alluvium of mixed rock type derived from the Wichita Mountains. A typical profile has a surface layer of brown loam to a depth of 35 cm overlying a subsoil of reddish-brown clay loam and yellowish-red sandy clay loam that extends to a depth of 150 cm. In most places, the soils have granitic sand and pebbles throughout the profile. The Stony Rock Land-Cobble Rock Land association is mapped on the slopes of the Wichita Mountains and includes a combination of exposed bedrock, shallow soils over bedrock, and cobble land, which consists of deep reddish-brown loams with between 25 and 70 percent cobblestones (Mobley, 1967).

The headwaters of Blue Beaver Creek originate in the Wichita Mountains, which are a series of igneous knobs of Cambrian age that protrude through sedimentary rocks of Permian age (Gilbert, 1982). The Cambrian rocks in the basin belong to the Carlton Rhyolite Group, which includes highly silicified rhyolitic lavas, consisting of phenocrysts of perthite and quartz in a groundmass of quartz and orthoclase. The main channel of Blue Beaver Creek cuts across the Post Oak Conglomerate and Garber Sandstone of Permian age, which were derived from sediment and debris eroded from the core of the Wichita Mountains (Havens, 1983). The Post Oak Conglomerate contains rounded boulders and cobbles of igneous rock types and fragments of limestone, dolomite, and shale eroded from older sedimentary rocks. Farther from the mountain flanks, the Post Oak Conglomerate becomes increasingly finer and eventually grades into red-brown, fine-grained sandstones and mudstones typical of the Garber Sandstone (Havens, 1983). Recent alluvium consisting of unconsolidated sand, silt, and clay was deposited along the flood plain. This alluvium ranges from 1 to 15 m in thickness and is the main source of water for domestic wells and stock supplies in the Wichita Mountains (Havens, 1983).

The Blue Beaver Creek Basin drains the western part of Comanche County in Oklahoma, and all land in the basin is publicly owned. The lower 75 percent of the basin is in the Fort Sill Military Reservation and the upper 25 percent is in the Wichita Mountains Wildlife Refuge. Land in the refuge in managed by the U.S. Fish and Wildlife Service to provide prairie grassland habitat for herds of buffalo, longhorn cattle, elk, and deer. The part of the wildlife refuge north of Lake Rush is set aside for wildlife use and is closed to the general public. Visitor use is concentrated near Lake Rush and Lake Jed Johnson where fishing and small motorized boats are permitted. These two small reservoirs and Ketch Lake to the south have a combined surface area of 53 ha. Land in the military reservation is used by the U.S. Army for tactical maneuvers (moving heavy equipment across the landscape) and foot patrols. Fort Sill uses standard erosion control and revegetation techniques to minimize the effects of intensive military training on the environment (Toni Hodgkins, U.S. Department of the Army, written commun., 1996). Since 1990, several roads in the basin have been improved, and more than 15 stream crossings have been constructed using limestone riprap to reduce erosion (Toni Hodgkins, written commun., 1996).

Historical Water-Quality Data and Time-Series Trends

The data set for the Blue Beaver Creek HBN Station analyzed for this report includes 138 water-quality samples that were collected from April 1967 through July 1995. Samples were collected monthly from 1968 through 1973 and quarterly from 1971 through 1995. Samples in the early part of the period of record were probably analyzed at a USGS laboratory in Oklahoma City, Okla., that operated until 1973 (Durum, 1978). After establishment of the central laboratory system, samples were analyzed at a laboratory in Salt Lake City, Utah, from 1973 through 1975 and at the NWQL in Arvada, Colo., from 1976 through 1995. Daily discharge records for Blue Beaver Creek (station 07311200) are available beginning in July 1964.

Calculated ion balances for 120 samples with complete major-ion analyses are shown in figure 21. Ion balances ranged from –6.4 to 16 percent, and 95 percent of samples had values within the ±5 percent range, indicating that the analytical results are of high quality. The average ion balance was –0.1 percent, indicating that unmeasured constituents, such as organic anions, do not seem to contribute substantially 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. 21). The only notable pattern was the presence of several elevated potassium concentrations in the mid-1970's. Although there are no documented

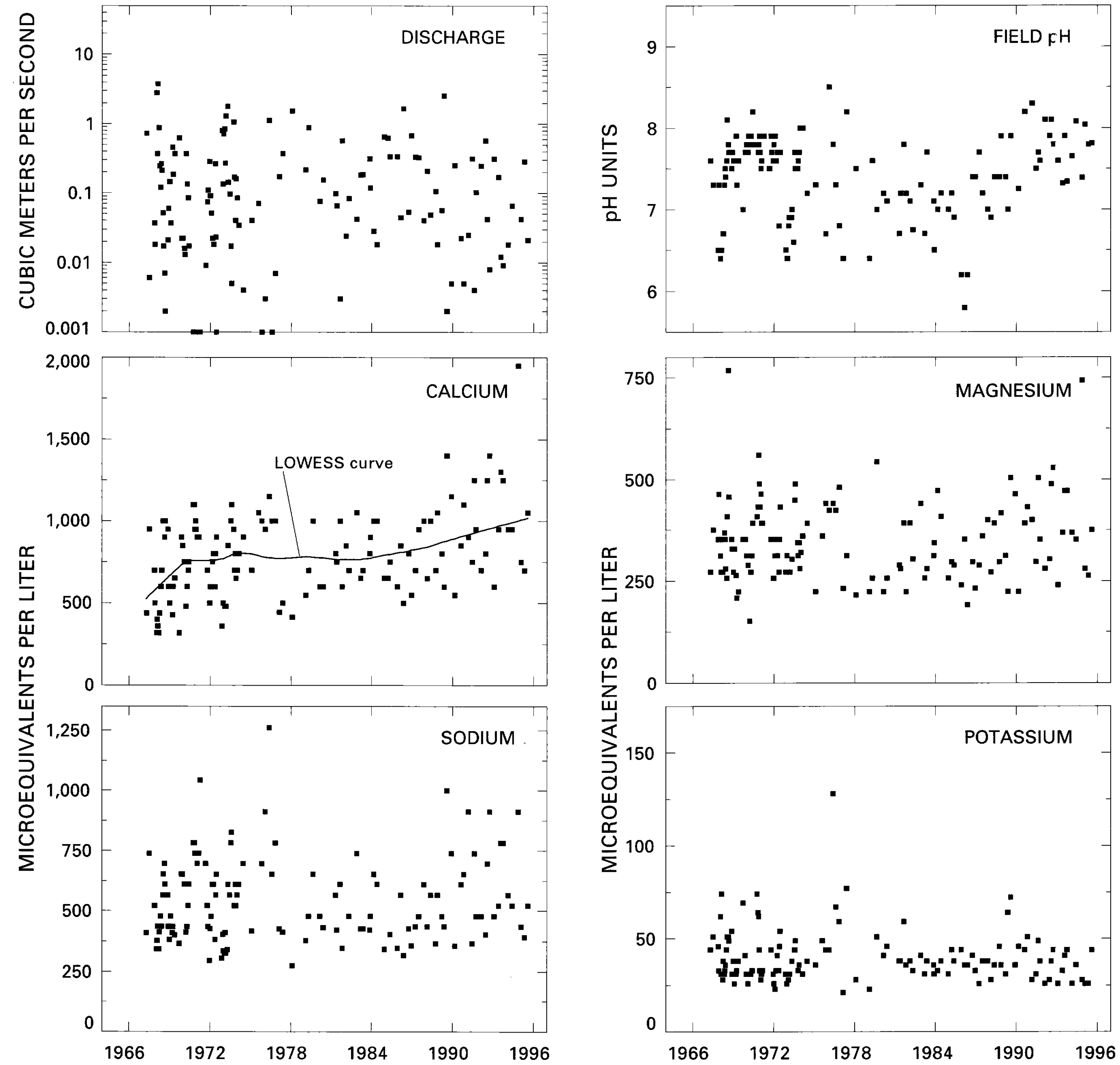


Figure 21. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Blue Beaver Creek, Oklahoma.

changes in field or laboratory methods during this period, the possibility of a method-related bias cannot be completely ruled out.

Median concentrations and ranges of major constituents in stream water at the Blue Beaver Creek Station and VWM concentrations in wet-only deposition measured at the Great Plains Apiaries NADP Station are listed in table 38. Precipitation chemistry at the NADP station, which is about 100 km northeast of the HBN station, is dilute and slightly acidic with a VWM pH of 5.0 for 13 years of record. The predominant cations were calcium and ammonium, which accounted for 31 and 29 percent of the total cation charge, respectively. Sulfate and nitrate were the predominant anions, contributing 53 and 35 percent of the total anion charge, respectively. The predominance of strong acid anions indicates that precipitation at the NADP station may be affected by anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain.

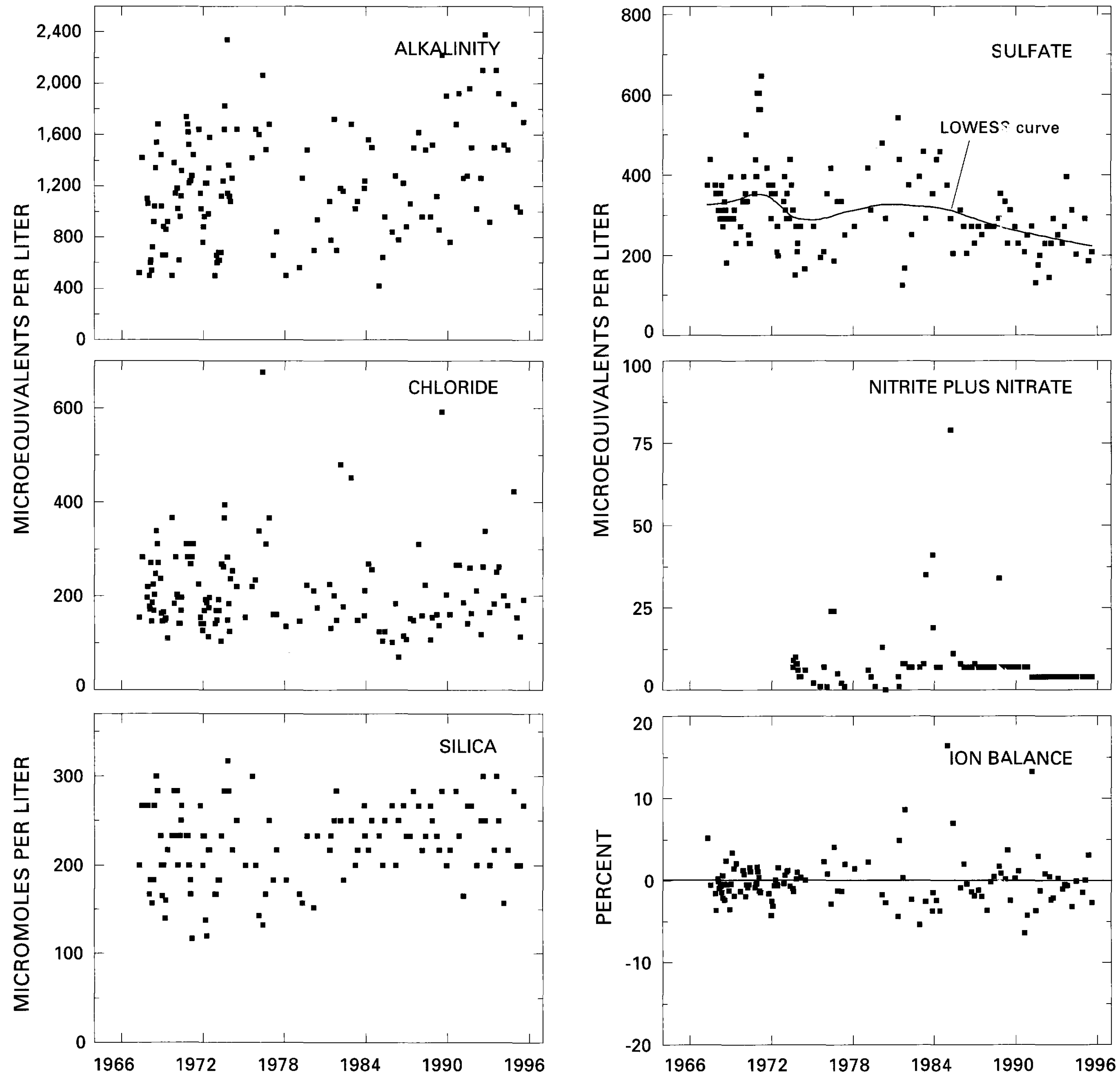


Figure 21. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Blue Beaver Creek, Oklahoma—Continued.

Stream water in Blue Beaver Creek is moderately concentrated and well buffered; specific conductance ranged from 89 to 400 µS/cm, and alkalinity was between 420 and 2,380 µeq/L (table 38). The major cation in stream water was calcium, and the predominant anion was bicarbonate. The predominance of these solutes in stream water is attributed to the weathering of calcareous rock fragments in the Permian conglomerates and sandstones. The median concentration of chloride in stream water was 190 µeq/L, which is more than 30 times greater than the VWM concentration of 5.3 µeq/L in precipitation. On the basis of the difference between annual precipitation and runoff, evapotranspiration can account for about a fourfold increase in the chloride concentration of precipitation, indicating that most chloride in stream water is derived from sources other than precipitation. Because the basin is undeveloped, the only reasonable source of additional stream-water chloride is dissolution of salts in the underlying conglomerates. The median concentration of sulfate in stream water was 290 µeq/L compared to 23 µeq/L in precipitation, indicating that a substantial amount of stream-water sulfate probably is derived from weathering of the sedimentary bedrock. Concentrations of inorganic nitrogen species in stream water were generally less than the VWM concentrations 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 39). The weathering-derived constituents had strong inverse correlations with discharge, except for silica (rho = –0.180). These results are consistent with a hydrologic system where weathering-enriched base flow is diluted by water from shallow or surficial sources during periods of increased discharge. Strong positive correlations were found among calcium, magnesium, and alkalinity (0.911 < rho < 0.946), which is consistent with weathering of carbonate minerals in the Permian conglomerates. The strong positive correlation between sodium and chloride (rho = 0.847) may indicate that the primary source of chloride is weathering of halite in the sedimentary bedrock. Sulfate and silica were not correlated with discharge or other dissolved constituents, despite the fact that both solutes are presumably derived from weathering.

Table 38. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major dissolved constituents measured in water-quality samples from Blue Beaver Creek, Oklahoma, April 1967 through July 1995, and volume-weighted mean concentrations in wet precipitation collected at the Great Plains Apiaries Station, Oklahoma

[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 VWM[a]
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge, inst.	0.0006	0.018	0.075	0.28	3.8	136	--
Spec. cond., field	89	130	160	220	400	135	10
pH, field	5.8	7.0	7.5	7.8	8.6	135	5.0[b]
Calcium	320	600	750	950	1,950	131	15
Magnesium	150	270	340	400	770	131	2.8
Sodium	270	420	520	650	1,260	134	5.0
Potassium	20	31	37	44	130	127	1.5
Ammonium	<.7	<1.1	2.1	4.3	15	53	14
Alkalinity, laboratory	420	880	1,170	1,510	2,380	137	--
Sulfate	130	250	290	350	650	135	23
Chloride	70	150	190	260	680	136	5.3
Nitrite plus nitrate	<.7	3.6	7.1	7.3	78	75	15[c]
Silica	120	200	230	270	320	128	--

[a] Data are volume-weighted mean concentrations for 1983–95.

[b] Laboratory pH.

[c] Nitrate only.

Table 39. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major dissolved constituents, Blue Beaver Creek, Oklahoma, October 1967–95

[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
pH	−0.347								
Ca	−.827	0.397							
Mg	−.837	.353	0.962						
Na	−.825	.339	.854	0.868					
K	−.204	−.051	.211	.212	0.250				
Alk	−.783	.469	.945	.912	.843	0.229			
SO_4	−.176	−.386	.052	.077	.205	.004	−0.086		
Cl	−.715	.124	.666	.682	.847	.204	.671	0.322	
Si	−.180	.130	.397	.379	.103	.386	.386	−.174	0.097

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are listed in table 40. Statistically significant trends were detected in the unadjusted calcium and sulfate concentrations at the 0.01 probability level. Results were similar for the flow-adjusted concentrations, indicating that trends in calcium and sulfate were not driven by variations in stream discharge. After flow adjustment, a statistically significant upward trend also was detected in stream-water alkalinity. The LOWESS curves in figure 21 show that the downward trend in sulfate and the upward trend in calcium are primarily due to changes in concentrations since the mid-1980's. Although not shown in figure 21, the pattern in flow-adjusted alkalinity was similar to the pattern for unadjusted calcium concentrations. Trends in stream chemistry at the Blue Beaver Creek Station may reflect changes in environmental factors, such as precipitation chemistry or land-use activities. Lynch and others (1995) reported a decline in the sulfate concentration of precipitation at a nearby NADP station in Arkansas from 1982 through 1990. Although the direction of the trend in sulfate deposition is consistent with the stream-water trend, the precipitation trend [−0.3 (μeq/L)/yr] is an order of magnitude smaller than the stream-water trend [−3.2 (μeq/L)/yr], indicating that atmospheric deposition alone cannot account for the trend in stream-water sulfate. The large increases in stream-water calcium [9.5 (μeq/L)/yr] and alkalinity [14.1 (μeq/L)/yr] also cannot be accounted for by trends in atmospheric deposition and may be linked to land-use activities in the basin. Military training exercises, particularly those involving the movement of heavy vehicles, have caused serious land damage and have caused increased sedimentation to some streams on the military reservation (Toni Hodgkins, U.S. Department of the Army, written commun., 1996). Since 1990, however, Fort Sill has implemented techniques to control erosion, such as revegetation, road improvements, and construction of hardened stream crossings. Although most of these measures might be expected to decrease land-use effects on streams, the hardened crossings are constructed of limestone riprap, which could provide a readily soluble source of dissolved calcium and alkalinity to the stream.

Table 40. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major dissolved constituents, Blue Beaver Creek, Oklahoma, April 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; inst., instantaneous --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge, inst.	<0.01	0.634	--	--
pH, field	.01	.230	0.01	0.066
Calcium	7.1	.009	9.5	.000
Magnesium	<.1	.957	1.1	.175
Sodium	<.1	.706	1.1	.325
Potassium	−.2	.037	−.2	.247
Alkalinity, laboratory	7.2	.088	14.1	.000
Sulfate	−3.5	.002	−3.2	.004
Chloride	−1.5	.097	−.7	.365
Nitrite plus nitrate	<.1[a]	.759	--	--
Silica	<.1	.880	<.1	.999

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

Table 41. Physical properties and major dissolved constituents from surface-water sampling sites in the Blue Beaver Creek Basin, Oklahoma, collected February 2–3, 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; Si, silica; concentrations in microequivalents per liter, except silica in micromoles per liter; <, less than; --, not reported; criteria used in selection of sampling sites: BG = bedrock geology, LU = land use]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria[a]	Remarks
1	7311200	0.065	130	7.8	650	260	390	22	950	230	120	<4.1	180	BG, LU	Downstream from Fort Sill
2	343946098330200	--	77	6.9	320	170	250	17	500	170	70	.7	230	BG	Mixed lithology
3	344050098325000	.0003	120	6.9	420	190	480	22	700	250	140	<5.5	250	BG	Mixed lithology
4	344214098353300	.017	71	7.8	350	150	200	31	430	140	70	1.4	80	BG, LU	Rhyolite, below reservoirs
5	344216098342700	--	38	6.6	140	74	150	9	140	180	42	.7	250	BG	Rhyolite
6	344224098342700	--	77	7.1	340	160	220	13	230	310	140	1.4	170	BG	Rhyolite
7	344327098355700	.0042	65	7.3	320	140	170	26	450	110	48	2.1	140	BG, LU	Rhyolite, upstream from Fort Sill

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling in the Blue Beaver Creek Basin on February 2 and 3, 1991, are listed in table 41, and the locations of the sampling sites are shown in figure 20. During the sampling period, discharge at the gaging station was about 0.07 m^3/s compared to the median daily discharge of about 0.06 m^3/s for February (Lawrence, 1987), indicating that the basin was sampled during normal flow conditions for that time of year. The concentrations of most solutes measured at site 1 during the synoptic sampling were similar to the first-quartile concentrations reported for the HBN station during the entire period of record (table 38). The composition of the tributary streams was similar to stream water collected at site 1, with calcium and sodium the dominant cations and bicarbonate and sulfate the dominant anions. Ion balances for all the synoptic samples were positive (range 0.4 to 6.1 percent), indicating that unmeasured constituents, such as organic anions, may have been an important component of stream water during the sampling period. Stream-water chemistry in the basin was quite variable, particularly for the weathering-derived constituents. For example, calcium ranged from a minimum of 140 μeq/L at site 5 to 650 μeq/L at site 1 and alkalinity, which ranged from 140 μeq/L at site 5 to 950 μeq/L at site 1. This pattern in stream chemistry seems to reflect the distribution of bedrock types in the basin. Sites with higher concentrations (sites 1 and 3) drain areas underlain by the Permian conglomerates, whereas the more dilute sites (sites 2, 4, 5, and 7) drain large areas of Carlton Rhyolite. Spatial patterns in sulfate and chloride concentrations also seemed to be related to bedrock type; higher concentrations were at sites 1 and 3, and lower concentrations were at sites 2, 4, 5, and 7. Site 6 was the one tributary that did not fit the general pattern by having a low alkalinity similar to streams draining igneous rocks, but having elevated sulfate and chloride similar to streams draining sedimentary rocks. The low silica concentration at site 4 compared to site 7 was somewhat unexpected and may indicate silica removal by diatoms in Ketch Lake. The effect of military activities on water quality in the basin was difficult to evaluate because the sedimentary rocks underlie the same part of the basin that is used for military training. Therefore, it was not possible to determine if differences in water quality between site 7 (upstream from military activities) and site 1 (basin outlet) predominantly reflected the influence of geology or the effect of military activities in the basin.

Kiamichi River near Big Cedar, Oklahoma (Station 07335700)

Site Characteristics and Land Use

The Kiamichi River HBN Basin is located in the Ouachita Mountains section of the Ouachita physiographic province in southeastern Oklahoma (fig. 22). The 104-km^2 basin ranges in elevation from 270 to 810 m and drains an area of steep east-west-trending ridges separated by a broad, flat-bottomed stream valley. The USGS gaging station is located 3.4 km east of the town of Big Cedar, Okla., at latitude 34°38'18" and longitude 94°36'45". The Kiamichi River is an east-flowing tributary of the Red River and has a channel length of about 19 km upstream from the gaging station and an average stream gradient of 11.1 m/km. Mean monthly discharge varies from 0.22 m^3/s in August to 4.2 m^3/s in March, although periods of no flow occur during most years in August and September. Average annual runoff from the basin was 74 cm from 1966 through 1995 (Blazs and others, 1996). The climate is characterized as subtropical with hot, humid summers and mild winters

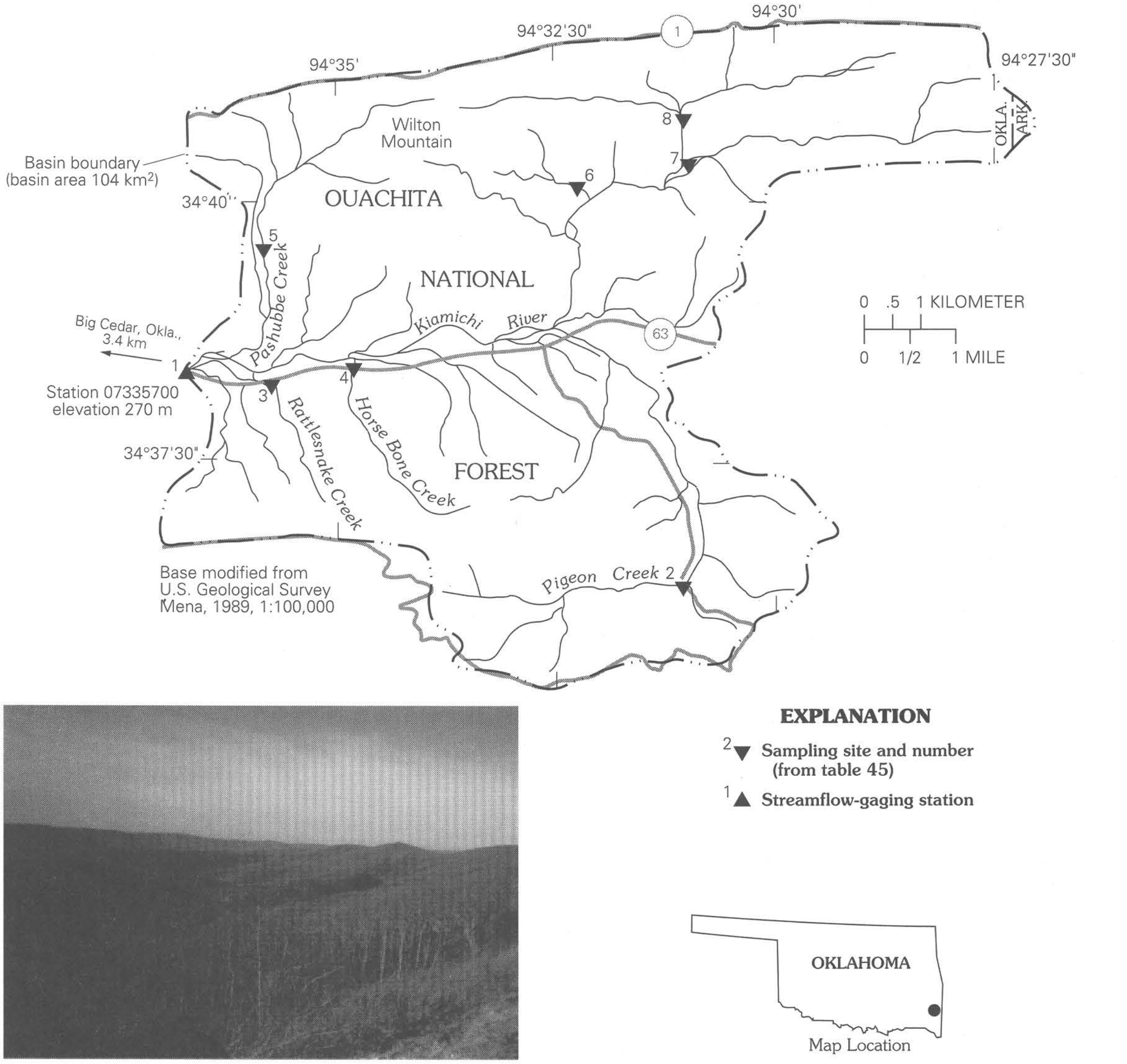


Figure 22. Map showing study area in the Kiamichi River Basin and photograph of the landscape of the basin.

(U.S. Department of Agriculture, 1990c). Average daily air temperatures range from 4.9°C in January to 27.2°C in July (Abernathy and Olszewski, 1983). Precipitation averages 130 cm annually with October, November, and December generally the driest months (National Climatic Data Center, 1997).

The Kiamichi River Basin is in the Ouachita Mixed Forest-Meadow ecoregion (Bailey and others, 1994), and forests are dominated by second growth (50 to 70 years old) oak, hickory, and pine vegetation types (U.S. Department of Agriculture, 1990b). Drier south- and west-facing slopes are dominated by shortleaf pine and minor amounts of loblolly pine. Pines and hardwoods grow together on wetter north- and east-facing slopes. The predominant hardwood species in these areas are white oak, black oak, post oak, blackjack oak, black hickory, pignut hickory, and mockernut hickory. Hardwoods predominant on the rich bottomlands of the stream valleys. Soils in the basin are classified as Ultisols and are mapped in the Carnaswa-Octavia-Pirum and Neff-Kenn-Ceda soil associations (Abernathy and Olszewski, 1983). The Carnaswa-Octavia-Pirum soils are mapped along the ridges and hillslopes and include well-drained, moderately deep soils developed in sandstone and shale. A typical soil profile has a surface layer of brown stony loam up to 20 cm thick overlying a subsoil of red clay loam and clay that extends to 150 cm. These soils are generally acidic (4.5 to 5.5), have a low organic-matter content (0.2 to 2 percent), and contain as much as 40 percent cobbles and gravel of sandstone and shale (Abernathy and Olszewski, 1983). The Neff-Kenn-Ceda soils are mapped along the flood plain of the Kiamichi River and are primarily level soils that have developed in loamy alluvium and are subject to flooding. A typical profile has a 20-cm surface layer of dark brown silt loam overlying a subsoil of dark yellowish-brown silty clay loam that extends to depths of 150 to 200 cm.

The Ouachita Mountains are composed of sedimentary rocks of Paleozoic age that have been intensely deformed into a series of east-west-trending, tightly folded anticlines and synclines that strongly control the local topography (Seeley, 1963; Briggs, 1973). The Paleozoic formations underlying the basin include the Tenmile Creek Formation of Mississippian age and Jackfork Group of Pennsylvanian age. The Tenmile Creek Formation consists of dark gray shales and interbedded siltstone and sandstone layers; it is easily weathered and forms the floor of the Kiamichi River Valley. The Jackfork Group consists of alternating layers of sandstone and shale, of which sandstones account for more than 60 percent (Briggs, 1973). Rocks in the Jackfork Group are more resistant to weathering than the shales of the Tenmile Creek Formation and form the long, narrow ridges of the Kiamichi River Valley. Bedrock along the flood plain of the river is covered by recent alluvial deposits consisting of unconsolidated sand, silt, and clay that reach as much as 10 m thick (Abernathy and Olszewski, 1983).

The Kiamichi River drains the southeastern part of Le Flore County in Oklahoma and is entirely in the boundaries of the Kiamichi Ranger District of the Ouachita National Forest. About 35 percent of land in the northwestern part of the basin is in the Upper Kiamichi River Wilderness, which is accessible by several foot trails (Frank Yerby, U.S. Department of Agriculture Forest Service, written commun., 1996). Privately owned lands, which are concentrated along the main channel of the Kiamichi River, account for 9 percent of land in the National Forest boundary. Several paved and gravel roads traverse the basin, including a section of State Highway 63 that parallels the lower reach of the main river channel. Because of the infrequent occurrence of snow or ice events, there is no salting or plowing of roads in the basin.

Land cover in the basin is 98 percent forest and 2 percent pasture (Frank Yerby, U.S. Department of Agriculture Forest Service, written commun., 1996). Land-use activities in the basin include timber harvesting, recreation, and a small amount of cattle grazing. National Forest land in the basin is divided into two management areas, wilderness and general forest (Frank Yerby, written commun., 1996). The management policy for Upper Kiamichi River Wilderness is to preserve or enhance the wilderness resource for the protection and perpetuation of natural conditions. In the wilderness, motorized travel is prohibited and the forests are unavailable for harvesting. The remainder of National Forest land in the basin is classified as suitable for timber production (U.S. Department of Agriculture, 1990b). These forests are managed as southern yellow pine and mixed pine-hardwood types, using a combination of even-aged and uneven-aged silvicultural systems. During the past 10 years, about 600 ha of forest land in the basin have been harvested using a combination of thinning cuts, uneven-aged cuts, clearcuts, and seed-tree cuts (Frank Yerby, written commun., 1996). Most privately owned land is located along the lower reaches of the river and includes permanent rural residences and recreation retreats owned by absentee landowners. About 200 ha, or 25 percent, of private land is open pasture, which is used for cattle grazing. The only major change in land use in the basin during the past 30 years was the designation of the Upper Kiamichi River Wilderness in 1988 (U.S. Department of Agriculture, 1990b).

Historical Water-Quality Data and Time-Series Trends

The data set for the Kiamichi River HBN Station analyzed for this report includes 226 water-quality samples that were collected from January 1966 through August 1995. Sampling frequency ranged from 8 to 12 samples per year from 1966 through 1982, and then was quarterly from 1983 through 1995. Samples in the early part of the period of record were probably analyzed at a USGS laboratory in Oklahoma City, Okla., that operated until 1973 (Durum, 1978). After the establishment of the central laboratory system, samples were analyzed at a laboratory in Salt Lake City, Utah, from 1973 through 1975 and at the NWQL in Arvada, Colo., from 1976 through 1995. Daily discharge records for the Kiamichi River (station 07335700) are available beginning in October 1965, and precipitation amount at the gaging station is available beginning in October 1993.

Calculated ion balances for 198 samples with complete major-ion analyses are shown in figure 23. Ion balances ranged from –35 to 28 percent, and only 70 percent of samples had values within the ±10 percent range. This wide range of values was not unexpected and reflects the difficulties of making precise analytical measurements at the low solute concentrations typical of this station. The average ion balance was –4.3 percent, and 70 percent of the samples had negative balances, indicating a slight excess of measured anions over cations in solution. Natural waters commonly have an excess of cations in solution owing to 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. One possibility is a positive bias in the laboratory alkalinity measurements, which were determined by fixed endpoint titration to pH 4.5. In low ionic-strength water, the endpoint is often closer to pH 5.0, which can result in an overestimation of alkalinity by as much as 25 μeq/L (Barnes, 1964). Time-series plots of the major dissolved constituents were inspected for evidence of other method-related effects (fig. 23). The most notable pattern was observed in the sulfate concentrations, which had a period of elevated concentrations during the 1980's, followed by a period of low concentrations at the end of the period of record. The elevated sulfate concentrations coincided with the use of a turbidimetric titration method at the NWQL between 1983 and 1989 (Fishman and others, 1994). Sulfate concentrations were later determined to be frequently overestimated by this method, and the bias was most pronounced in dilute waters, although the bias was not consistent among samples and appeared to be affected by factors such as color and turbidity (Schertz and others, 1994). The sulfate 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/admin/memo/, accessed 1997), which is coincident with the low concentrations observed during the last 6 years of record.

Median concentrations and ranges of major constituents in stream water at the Kiamichi River Station and VWM concentrations in wet-only deposition measured at the Caddo Valley NADP Station are listed in table 42. Precipitation chemistry at the NADP station, which is located 150 km east of the gaging station, is dilute and slightly acidic with a VWM pH of 4.7 for 12 years of record. The predominant cations in precipitation were hydrogen and ammonium, which contributed 44 and 22 percent of the total cation charge, respectively. The predominant anions were sulfate and nitrate, which accounted for 56 and 30 percent of the total anion charge, respectively. The predominance of strong acid anions indicates that precipitation at the NADP station may be affected by anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain.

Stream water in the Kiamichi River is dilute and weakly buffered; specific conductance ranged from 12 to 58 μS/cm, and alkalinity was between 20 and 320 μeq/L (table 42). The major cations in stream water were sodium, calcium, and magnesium, and alkalinity was the predominant anion. The low stream-water concentrations of weathering-derived constituents, particularly alkalinity, are attributed to the lack of weatherable minerals in the underlying sandstone and shale bedrock. The median concentration of chloride in stream water was 59 μeq/L, which is about nine times the VWM concentration of 6.6 μeq/L in precipitation. On the basis of the difference between annual precipitation and runoff, evapotranspiration can account for roughly a twofold increase in the chloride concentration of precipitation, indicating that most stream-water chloride is derived

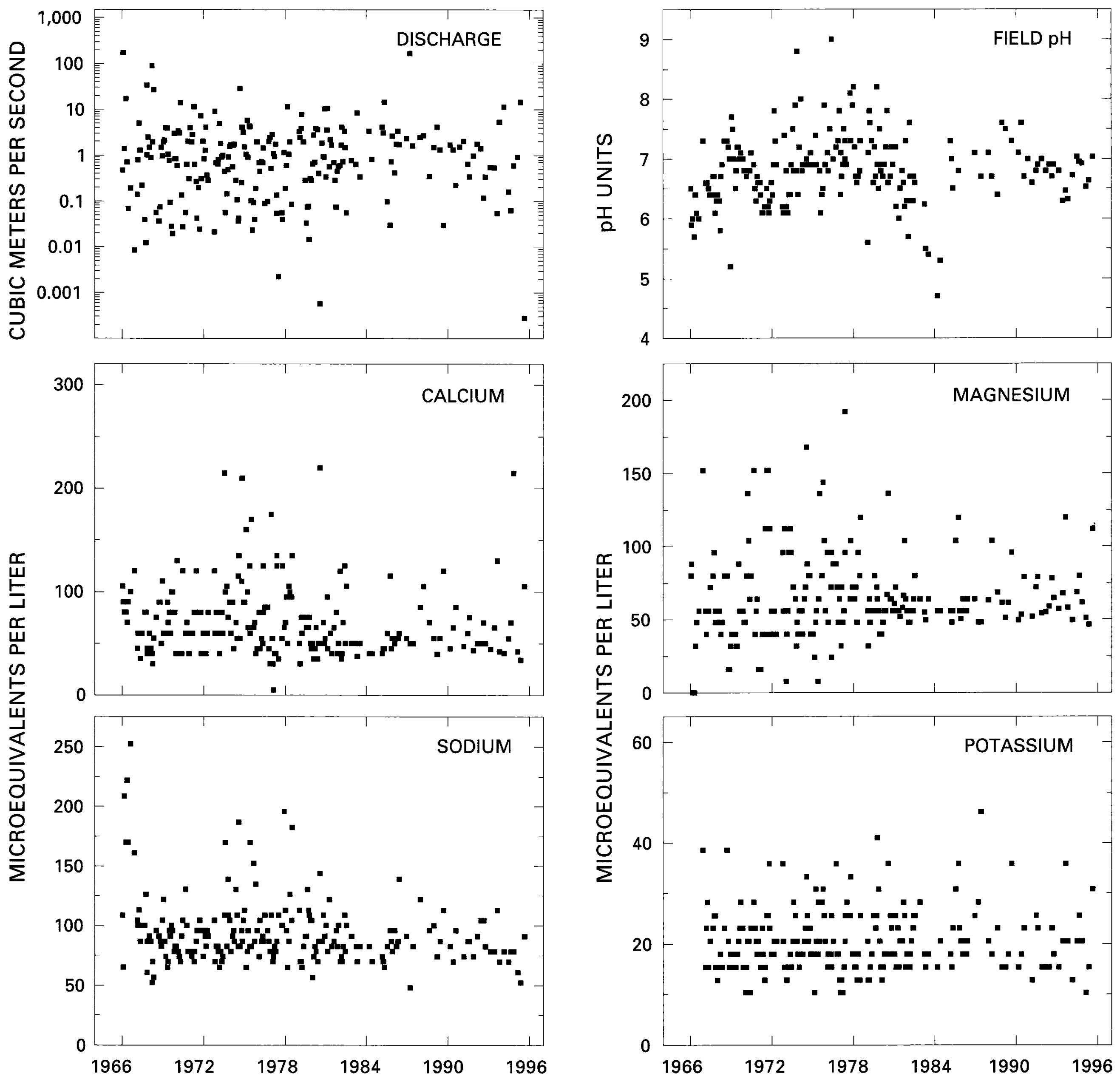


Figure 23. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Kiamichi River, Oklahoma.

from sources other than precipitation. The most likely source of additional stream-water chloride is weathering of salts in the underlying marine sedimentary rocks, although some chloride may be derived from rural residences and pasture land along the lower reach of the river channel. The median concentration of sulfate in stream water was 71 µeq/L compared to 26 µeq/L in precipitation, which is slightly larger than would be expected from the effects of evapotranspiration. Additional sources of stream-water sulfate include dry deposition from the atmosphere and weathering of small amounts of pyrite in the underlying shales. The low concentrations of nitrate and ammonium in stream water compared to precipitation indicate that nitrogen is strongly retained by soils and vegetation in the basin. The low stream-water nitrogen concentrations also indicate that strips of grazing land bordering the stream do not seem to greatly affect the nutrient composition of stream water at the HBN station.

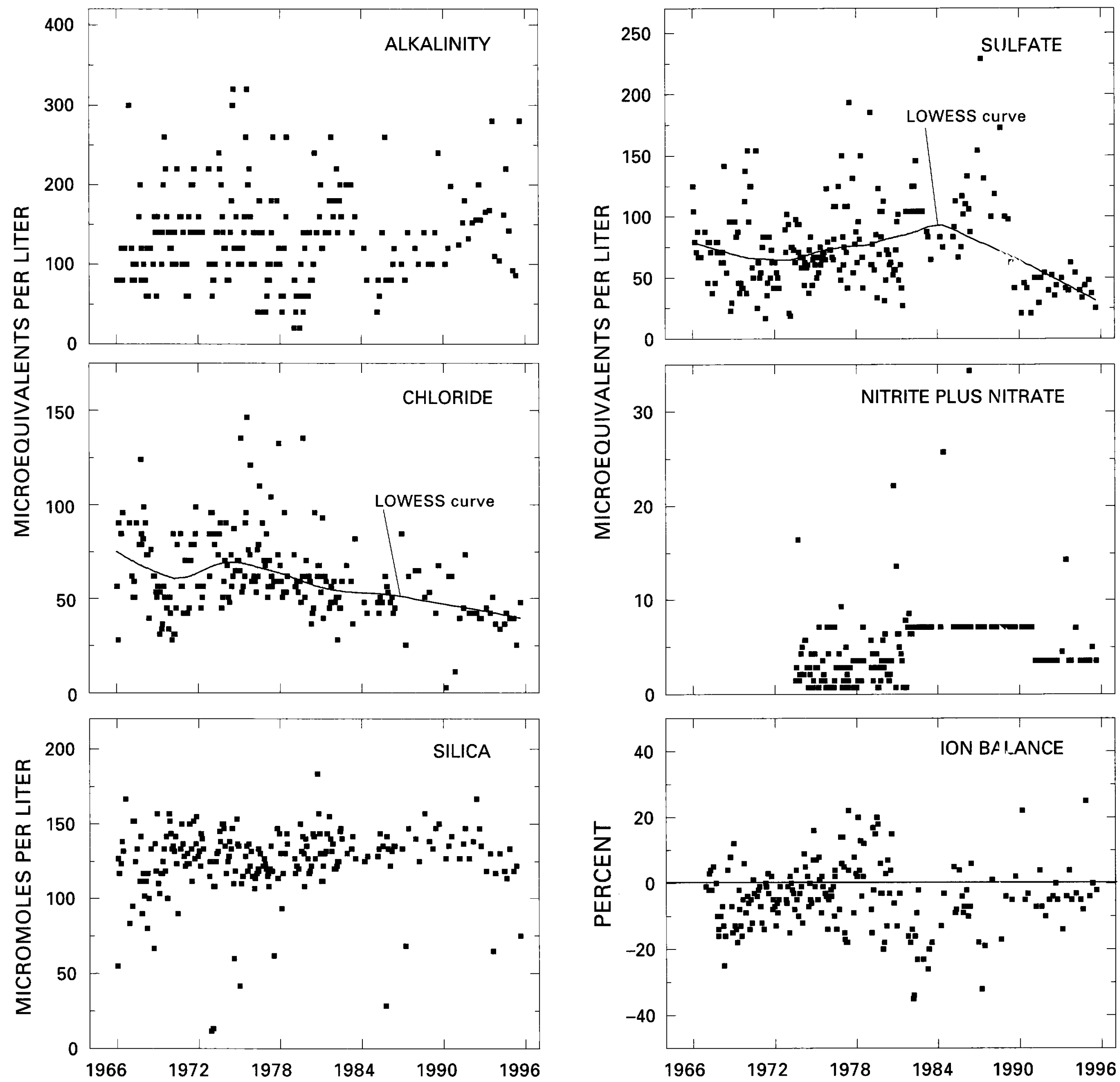


Figure 23. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Kiamichi River, Oklahoma—Continued.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 43). Most of the weathering-derived constituents had weak inverse correlations with discharge, except for silica (rho = −0.008). Most solutes had weak positive correlations; the strongest correlations were between calcium and magnesium (rho = 0.641) and magnesium and potassium (rho = 0.607). The positive correlations between calcium and magnesium and magnesium and potassium are consistent with the weathering of carbonate minerals and clays in the sandstone and shale bedrock. The moderate correlation between sodium and chloride (rho = 0.525) provides additional evidence that chloride is derived from weathering of salts in the underlying sedimentary rocks.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are listed in table 44. Statistically significant trends were

Table 42. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major dissolved constituents measured in water-quality samples from the Kiamichi River, Oklahoma, January 1966 through August 1995, and volume-weighted mean concentrations in wet precipitation collected at the Caddo Valley Station, Arkansas

[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 VWM[a]
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge, inst.	0.0003	0.26	0.88	2.28	170	223	--
Spec. cond., field	12	21	25	29	58	208	13
pH, field	4.7	6.5	6.8	7.1	9.0	208	4.7[b]
Calcium	5.0	50	60	85	220	217	5.9
Magnesium	<8.0	48	56	72	190	219	2.1
Sodium	48	78	87	100	370	221	6.4
Potassium	10	15	18	23	46	216	.8
Ammonium	<.7	1.4	2.1	4.3	11	68	10
Alkalinity, laboratory	20	100	120	160	320	219	--
Sulfate	17	50	71	96	230	225	26
Chloride	<2.8	48	59	73	190	223	6.6
Nitrite plus nitrate	<.7	2.3	3.6	7.1	34	146	14[c]
Silica	12	120	130	140	180	224	--

[a] Data are volume-weighted mean concentrations for 1984–95.
[b] Laboratory pH.
[c] Nitrate only.

Table 43. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major dissolved constituents, Kiamichi River, Oklahoma, 1966–95

[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
pH	0.005								
Ca	–.483	0.012							
Mg	–.609	.032	0.641						
Na	–.460	–.006	.556	0.563					
K	–.500	–.094	.560	.607	0.517				
Alk	–.484	–.284	.381	.453	.282	0.373			
SO_4	.191	–.146	–.030	–.153	.118	.139	–0.217		
Cl	–.261	.125	.352	.191	.525	.342	.005	0.272	
Si	–.008	–.008	.031	.083	.251	.177	–.016	.104	0.087

detected in the unadjusted sulfate and chloride concentrations at the 0.01 probability level. Results for the flow-adjusted chloride concentrations were similar to the unadjusted concentrations, indicating that the trend was not caused by variations in stream discharge. The trend in sulfate, however, was not statistically significant after the concentrations were adjusted for flow. The LOWESS curve for chloride shows a gradual decrease in concentrations beginning in the mid-1970's (fig. 23). It is unlikely that human activities caused the trend in stream-water chloride because there were few changes in land use during the period of record. Trends in atmospheric deposition at this site are difficult to confirm because no long-term records of precipitation chemistry are available for the area. Lynch and others (1995) reported significant declines in calcium, magnesium, and sulfate concentrations in precipitation at a nearby NADP station in Arkansas from 1982 through 1990, but detected no trend in chloride. Alternatively, the trend in stream-water chloride may have been caused by laboratory bias introduced by improvements and changes in analytical method for chloride during the 30-year period of record (Fishman and others, 1994).

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling in the Kiamichi River Basin on January 31 and February 1, 1991, are listed in table 45, and the locations of the sampling sites are shown in figure 22. During the sampling period, discharge at the gaging station was about 0.8 m^3/s compared to the median daily discharge of about 1.3 m^3/s for January and February (Lawrence, 1987), indicating that the basin was sampled during low-flow conditions for that time of year. The concentrations of most solutes measured at site 1 were less than the first-quartile concentrations reported for the HBN station during the entire period of record (table 42). The tributary streams were similar in composition to stream water collected at the gaging station (site 1); sodium was the predominant cation, and bicarbonate and sulfate were the predominant anions. Ion balances for the synoptic samples ranged –5.5 to 2.8 percent, indicating that unmeasured constituents, such as organic anions, did not seem to be an important component of stream water during the sampling period.

Table 44. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major dissolved constituents, Kiamichi River, Oklahoma, January 1966 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; inst., instantaneous; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge, inst.	<0.01	0.068	--	--
pH, field	<.01	.558	<0.01	0.728
Calcium	–.7	.011	–.7	.011
Magnesium	<.1	.406	.2	.234
Sodium	–.5	.011	–.4	.021
Potassium	<.1	.963	<.1	.505
Alkalinity, laboratory	<.1	.343	.6	.162
Sulfate	–.8	.004	–.6	.037
Chloride	–1.0	.000	–.9	.000
Nitrite plus nitrate	(a)	--	--	--
Silica	.3	.047	.4	.071

[a] Insufficient data to calculate trend.

In general, stream chemistry did not vary markedly among the sampling sites, although the weathering-derived solutes had the widest range of concentrations. For example, sodium ranged from 43 to 96 µeq/L, silica ranged from 90 to 170 µmol/L, and alkalinity ranged from 23 to 120 µeq/L. Although small, this variability in surface-water chemistry seems to be related to the distribution of the sedimentary units in the basin. For example, the highest concentrations of cations, alkalinity, and silica were measured at sites 3 and 4, which are downstream from areas underlain by

Table 45. Physical properties and major dissolved constituents from surface-water sampling sites in the Kiamichi River Basin, Oklahoma, collected January 31–February 1, 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; Si, silica; concentrations in microequivalents per liter, except silica in micromoles per liter; develop., development; <, less than; --, not reported; criteria used in selection of sampling sites: BG = bedrock geology, LU = land use]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO$_4$	Cl	NO$_3$	Si	Criteria	Remarks
1	7335700	0.82	19	6.8	36	46	70	13	73	58	39	2.1	120	LU	Downstream from develop.
2	343623094310200	.062	16	6.7	24	46	52	11	46	46	34	1.4	110	BG	Mixed lithology
3	343813094354800	.0084	24	6.4	50	64	96	14	120	60	48	1.4	170	BG	Predominantly shale
4	343822094344700	.011	18	6.3	33	45	74	12	70	52	39	4.3	140	BG	Predominantly shale
5	343929094355100	--	16	5.8	21	36	52	12	23	60	34	<.7	110	BG	Sandstone
6	344004094320900	--	15	6.5	22	31	52	12	45	40	39	<.7	110	BG	Sandstone
7	344020094305800	.042	13	6.4	19	31	43	10	33	48	34	<.7	92	BG, LU	Sandstone, above develop.
8	344045094310500	.11	13	6.1	19	37	48	11	23	50	34	<.7	90	BG	Sandstone

the Tenmile Creek Formation, and the lowest concentrations were measured at sites 7 and 8, which are in areas underlain by rocks of the Jackfork Group. Both of these formations consist of sandstones, shales, and mudstones; however, the Jackfork Group is predominantly shale and the Tenmile Creek Formation is predominantly sandstone. Concentrations of the remaining solutes showed less variability among the sampling sites. For example, sulfate concentrations ranged from 40 to 60 μeq/L, chloride ranged from 34 to 48 μeq/L, and nitrate concentrations at all sites were less than 5 μeq/L. Neither chloride nor nitrate concentrations were elevated at site 1 compared to the upstream sites, indicating that pasture land and rural residential areas that are concentrated along the lower reaches of the Kiamichi River did not affect stream chemistry at the gaging station during the sampling period.

Devils River at Pafford Crossing near Comstock, Texas (Station 08449400)

Site Characteristics and Land Use

The Devils River HBN Basin is in the Great Plains physiographic province in southwestern Texas (fig. 24). The 10,260-km^2 basin ranges in elevation from 345 to more than 820 m and drains the southern part of the Edwards Plateau, an arid upland of rough and broken limestone topography cut by narrow, steep-walled canyons (Barker and others, 1994). The gaging station on the Devils River is located 18.5 km east of Comstock, Tex., at latitude 29°40'35" and longitude 101°00'00". The Devils River is a south-flowing tributary of the Rio Grande and discharges into the Amistad Reservoir just downstream from the gaging station. Perennial streamflow occurs in the main channel of the

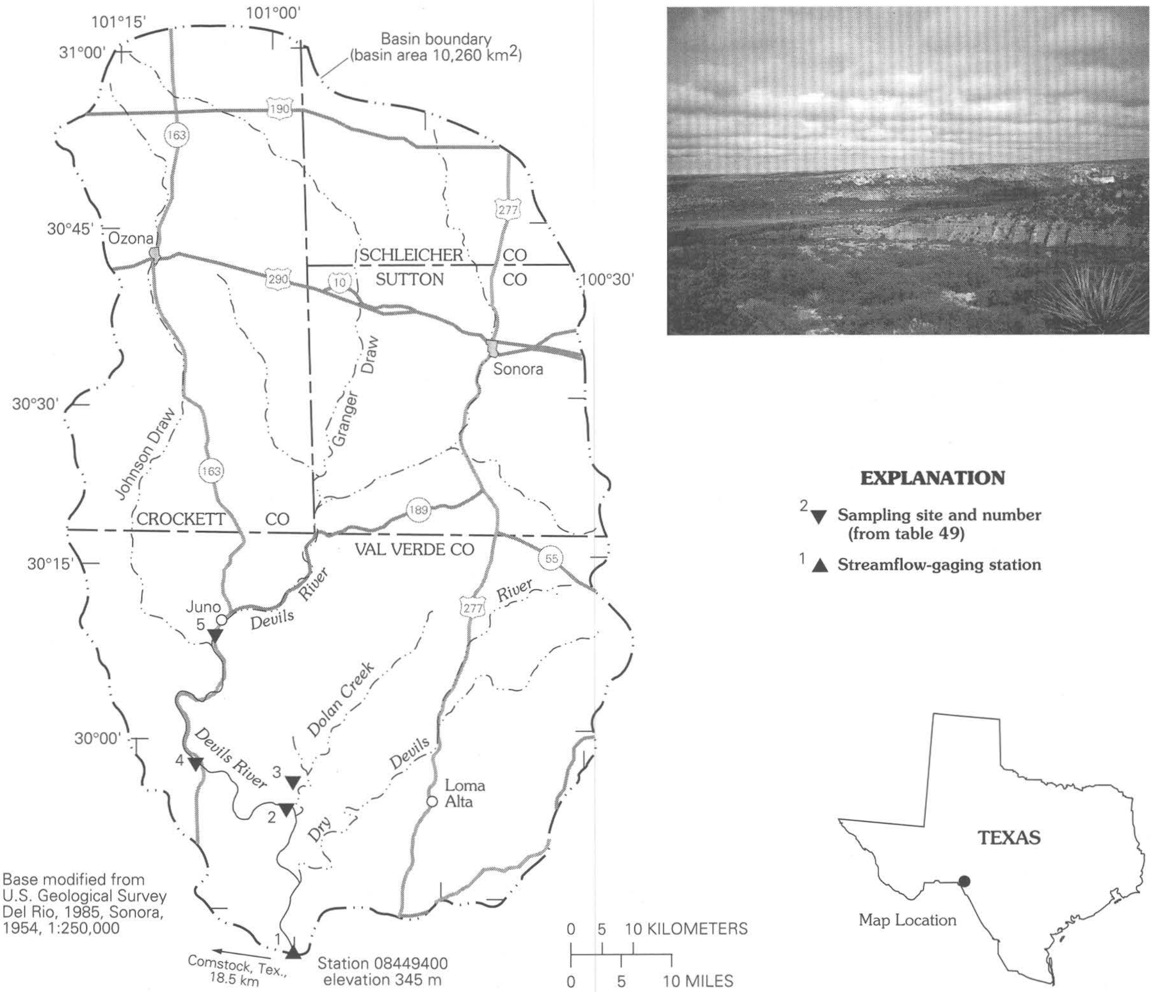


Figure 24. Map showing study area in the Devils River Basin and photograph of the landscape of the basin.

Devils River south of Juno because of ground-water discharge from several springs in the lower part of the basin (fig. 24). The perennial reach of the river has a channel length of about 65 km and an average stream gradient of 2.1 m/km. Discharge at the gaging station is uniform throughout the year, with average monthly discharges that range from of 7.3 m^3/s in February to 20.4 m^3/s in September (International Boundary and Water Commission, 1995). Major floods occur periodically that transport enormous quantities of gravel and rock in the channel and strip most vegetation from the banks (Texas Water Commission, 1992). Average annual runoff from the basin was 32 cm from 1960 through 1995. The climate is classified as semiarid, continental with dry winters and hot summers. Average daily air temperatures range from 10.4°C in January to 30.4°C in July (Golden and others, 1982). The average annual rainfall is 53 cm, and May and September generally are the months of greatest precipitation (International Boundary and Water Commission, 1995).

The Devils River Basin is in the Chihuahuan Desert ecoregion, which is characterized by extensive arid grasslands and thorny shrubs that frequently grow in open stands (Bailey and others, 1994). The predominant grasses are sideoats grama and hairy grama, which, when heavily grazed, are replaced by woody shrubs and red grama, fall witchgrass, and perennial three-awn (Golden and others, 1982). Some of the predominant woody plants are juniper, Texas persimmon, live oak, mesquite, catclaw, ocotillo, yucca, and cactus. Most soils in the basin are classified as Aridisols and are mapped in the Ector-Rock Outcrop association (Golden and others, 1982). This association consists of limestone outcrops interspersed with shallow, well-drained Ector soils on upland side slopes and ridges. A typical soil profile has a surface layer of alkaline, grayish-brown stony loam that is 20 to 30 cm thick overlying as much as 15 cm of highly fractured and indurated limestone with coatings of calcium carbonate on cracks and crevices. More than one-half of the soil surface is generally covered with limestone gravel and cobbles. Deep, loamy and clayey soils belonging to the Dev-Rio Diablo association are mapped on flood plains and terraces along the river (Golden and others, 1982).

The basin is underlain by marine sedimentary rocks of Cretaceous age, including the Segovia Member of the Edwards Limestone, the Devils River Limestone, and the Buda Limestone (Barnes, 1981). The aerially most extensive unit is the Segovia Member, consisting of beds of cherty limestone, dolomite, and marl. The Buda Limestone is primarily mapped in the northern part of the basin and forms a resistant cap over much of the plateau surface. The Devils River Limestone crops out south of Dolan Springs and includes limestone and dolomite units. The Devils River Formation is very permeable and porous (Barker and others, 1994) and probably is an important source of water to springs recharging the Devils River.

The Devils River Basin drains parts of Crockett, Sutton, Schleicher, and Val Verde Counties in Texas, and land ownership is predominantly private. The Devils River State Natural Area, located near the mouth of Dolan Creek, is managed by the Texas Parks and Wildlife Division and provides habitat for several rare endemic or peripheral species of fish that live in the Devils River (Texas Water Commission, 1992). The 2-km reach of the main channel upstream from the gaging station is in the boundaries of the Amistad National Recreation Area. A few State and Federal highways traverse the basin, although most of the basin is inaccessible because of private land ownership. The basin is sparsely populated, and the major land-use activity is ranching. The average ranch size is about 3,000 ha, and most of the income is generated from sheep, Angora goats, and cattle (Golden and others, 1982). The towns of Ozono (population 3,181) and Sonora (population 2,751), as well as several oil and gas fields, are located in the upper part of the basin more than 100 km north of the HBN station.

Historical Water-Quality Data and Time-Series Trends

The data set for the Devils River HBN Station analyzed for this report includes 104 water-quality samples that were collected from January 1978 through August 1995. Sampling frequency was monthly from 1978 through 1980, bimonthly from 1981 through 1986, and quarterly from 1987 through 1995. Water-quality samples were analyzed at the NWQL in Arvada, Colo., for the entire period of record. Daily discharge records are available for the Devils River (station 08449400) beginning in 1960. The gaging station is operated by the International Boundary and Water Commission (IBWC) as part of the 1944 Water Treaty requiring that the IBWC keep a record of the Rio Grande waters belonging to the United States and Mexico (http://www.ibwc.state.gov). Data from gaging stations and records of rainfall and evaporation stations operated by the IBWC are published annually.

Calculated ion balances for 100 samples with complete major-ion analyses are shown in figure 25. Ion balances ranged from –5.6 to 9.6 percent, and more than 95 percent of the samples had values in the ±5 percent range, indicating that the analyses are of high quality. The average ion balance for all samples was slightly positive (1.4 percent), which probably is due to the fact that the nitrite-plus-nitrate concentrations were not included in the ion balance calculation. The average nitrite-plus-nitrate concentration was 110 µeq/L, or 1.3 percent of the total ionic charge, which accounts for the average charge imbalance of 1.4 percent. Time-series plots of the major dissolved constituents were inspected for evidence of other method-related effects (fig. 25). The temporal pattern in field pH shows a period of low pH values in the first part of the period of record and high pH values in the later part. Although this trend in pH may have been caused by environmental factors, a change in analytical methods may provide a more reasonable explanation, particularly considering the sudden decrease in pH in 1980 and the subsequent increase in 1987. Similar trends in field pH measurements were reported at a number of streams throughout Texas during the same period of record (Schertz and others, 1994). Schertz and others

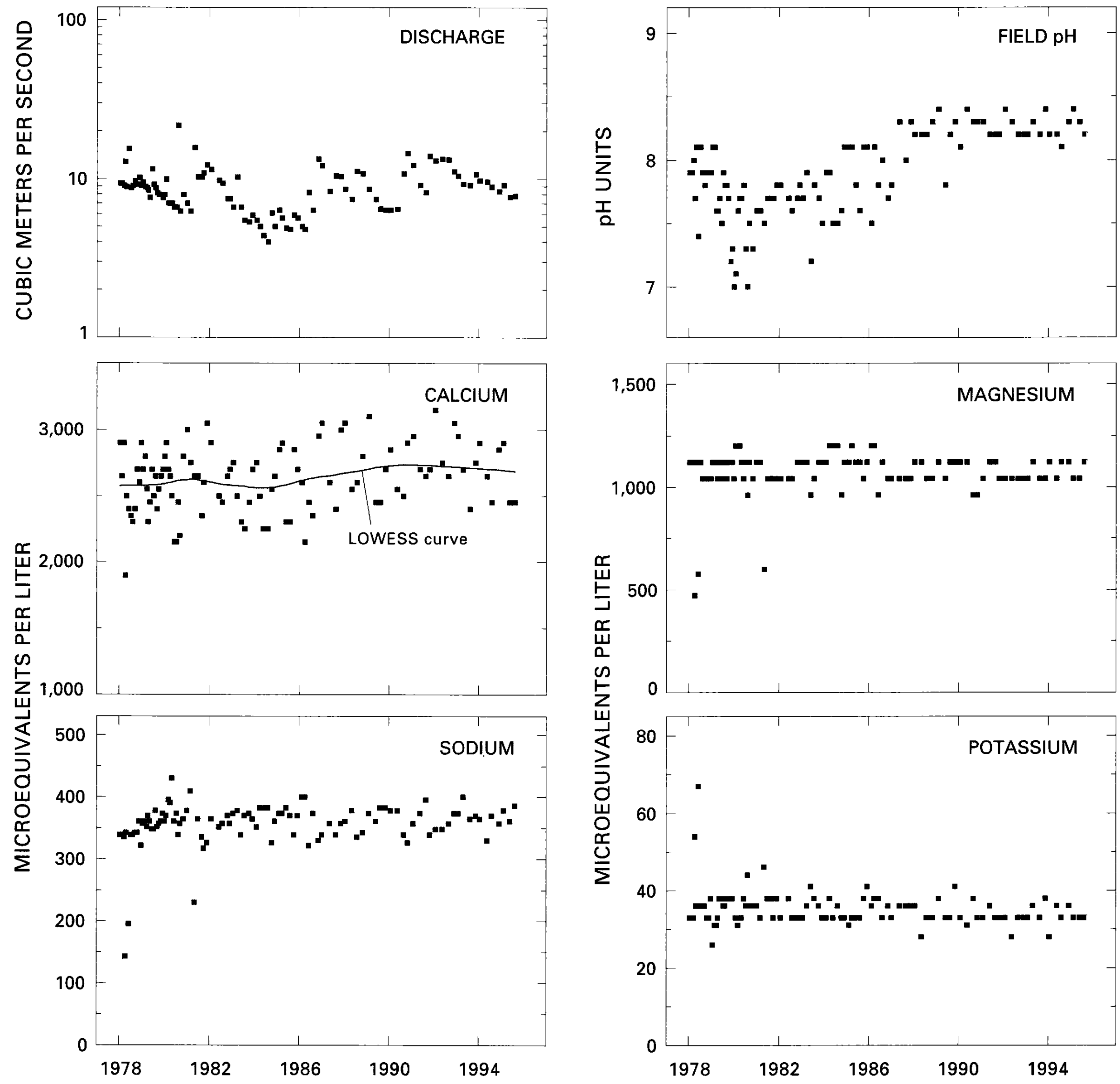


Figure 25. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Devils River, Texas.

determined the pH trends were probably caused by method-related factors because a single environmental change was unlikely to have caused a State-wide change in stream chemistry. Sulfate concentrations also had a few unusual patterns, including a period of high scatter and several elevated concentrations before 1982, followed by a period of less data scatter and low concentrations. Although natural variations in stream chemistry cannot be completely ruled out, these patterns probably were caused by changes in analytical methods used by the NWQL in Arvada, Colo. Two documented changes occurred during this period of record—the replacement of a colorimetric method by a turbidimetric method in 1982, followed by the replacement of the turbidimetric method by ion chromatography in 1990 (Fishman and others, 1994). Another notable pattern in figure 25 is the apparent increase in ion balance beginning in the mid-1980's. The cause of this increase could not be identified, although it is coincident with the change in analytical method for sulfate that occurred in 1982.

Median concentrations and ranges of major constituents in stream water at the Devils River Station and VWM concentrations in wet-only deposition measured at the Sonora NADP Station are listed in table 46. Precipitation chemistry at the NADP station,

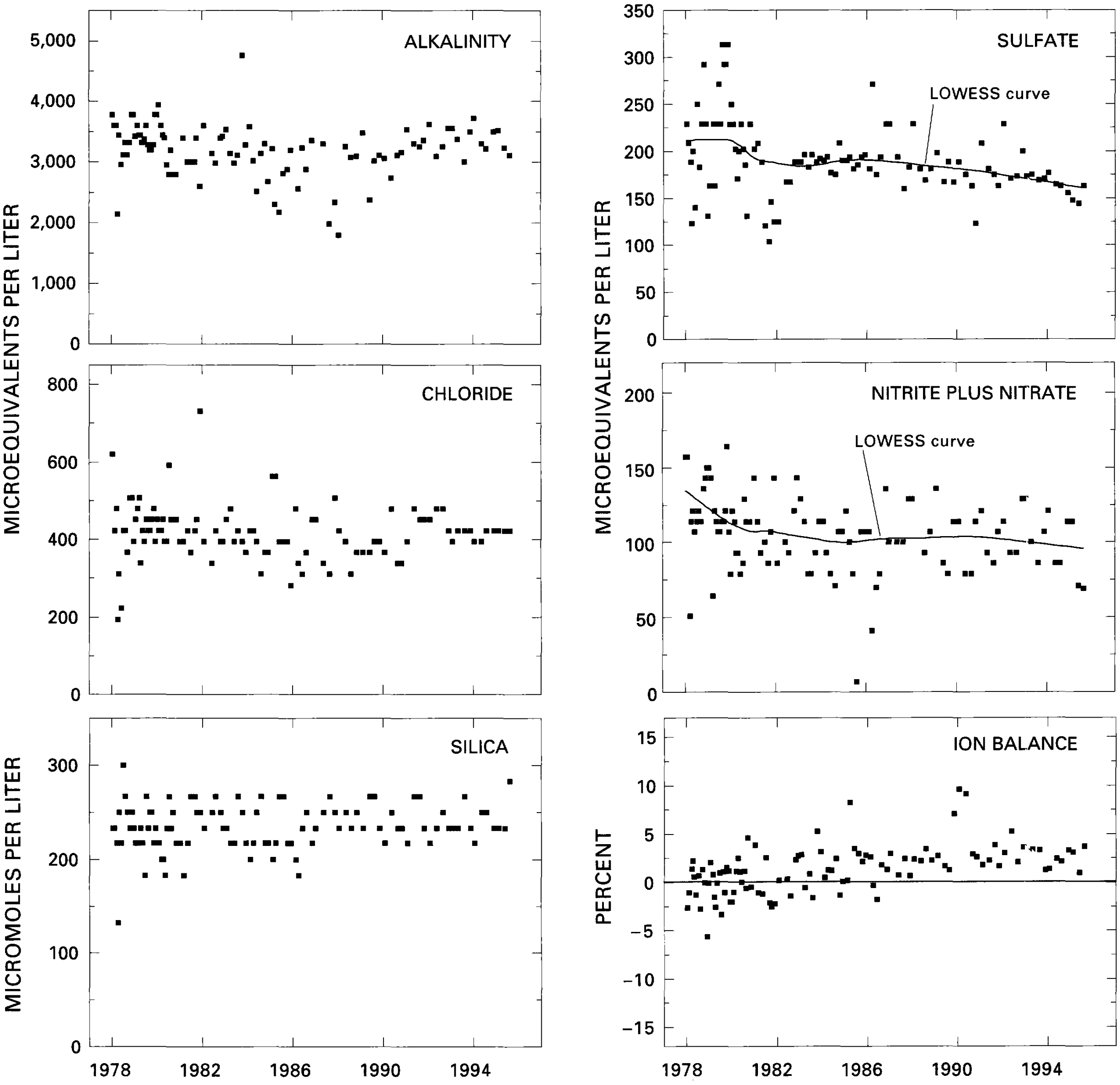


Figure 25. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Devils River, Texas—Continued.

which is located about 75 km northeast of the gaging station, is dilute and only slightly acidic with a VWM pH of 5.2 for 12 years of record. The predominant cations were calcium and ammonium, which contributed 34 and 29 percent of the total cation charge, respectively. Sulfate and nitrate were the predominant anions and accounted for 55 and 29 percent of the total anion charge, respectively.

Stream water in the Devils River is fairly concentrated and well buffered; specific conductance ranged from 250 to 460 µS/cm, and alkalinity was between 1,800 and 4,760 µeq/L. The major cations in stream water were calcium and magnesium, and bicarbonate was the predominant anion. The predominance of these solutes in stream water is attributed to the weathering of carbonate minerals in the underlying limestone and dolomite bedrock. The median concentration of chloride in stream water was 420 µeq/L, which is considerably higher than the VWM concentration of 6.2 µeq/L in precipitation. This large difference in concentration indicates that most stream-water chloride is derived from sources in the basin rather than atmospheric deposition, including dissolution of salts in the carbonate bedrock or perhaps oil field activities in the northern part of the basin. The median concentration of sulfate also was much higher in stream water than in precipitation, indicating that most sulfate also is derived from weathering of the bedrock. The median concentrations of nitrite plus nitrate in stream water was 10 times greater than the VWM concentration of 11 µeq/L in precipitation, indicating that a large amount of stream-water nitrogen is derived from sources other than precipitation. These fairly high nutrient concentrations were somewhat unexpected because of the sparse population and the type of land use in the Devils River Basin. Possible sources of nitrate might include dry deposition from the atmosphere, oil field activities, or possibly nitrogen fixation by legume species, such as mesquite.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 47). Most solutes were poorly correlated with discharge, except for weak inverse correlations with magnesium (rho = –0.611) and sodium (rho = –0.554). The solutes also were poorly correlated with each other, except for weak positive correlations between magnesium and sodium (rho = 0.698) and calcium and nitrite plus nitrate (rho = 0.691). The weak correlations between discharge and the major solutes reflect the importance of ground-water discharge, which maintains relatively constant flow rates and stream-water compositions in the Devils River throughout the year.

Table 46. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major dissolved constituents measured in water-quality samples from the Devils River, Texas, January 1978 through August 1995, and volume-weighted mean concentrations in wet precipitation collected at the Sonora Station, Texas

[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 VWM[a]
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge, inst.	4.0	6.6	8.7	10	22	104	--
Spec. cond., field	250	370	390	410	460	104	8.2
pH, field	7.0	7.7	7.9	8.2	8.4	104	5.2[b]
Calcium	1,900	2,450	2,650	2,800	3,150	104	14
Magnesium	470	1,040	1,120	1,150	1,200	104	2.2
Sodium	140	340	360	370	430	104	6.2
Potassium	26	33	33	38	67	103	.7
Ammonium	<.7	1.4	2.1	3.6	10	83	12
Alkalinity, laboratory	1,800	3,000	3,260	3,440	4,760	101	--
Sulfate	100	170	190	210	310	104	21
Chloride	190	390	420	450	730	104	6.2
Nitrite plus nitrate	7.1	89	110	120	160	103	11[c]
Silica	130	220	230	250	300	104	--

[a] Data are volume-weighted mean concentrations for 1984–95.

[b] Laboratory pH.

[c] Nitrate only.

Table 47. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major dissolved constituents, Devils River, Texas, 1978–95

[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	0.272									
Ca	.390	0.324								
Mg	–.611	–.124	–0.059							
Na	–.554	.011	–.090	0.698						
K	–.004	–.243	–.174	–.234	–0.183					
Alk	.242	.005	.414	.070	.052	–0.195				
Cl	.194	–.052	.205	.145	.002	–.124	0.138			
SO_4	–.241	–.312	.115	.212	.134	.213	.092	0.098		
N	.263	.036	.691	.051	–.091	–.083	.349	.230	0.189	
Si	.089	.163	–.421	–.159	–.058	.028	–.345	–.416	–.060	–0.379

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are listed in table 48. Statistically significant trends were detected in the unadjusted calcium, sulfate, and nitrite-plus-nitrate concentrations at the 0.01 probability level. Trend results for the flow-adjusted sulfate and nitrite-plus-nitrate concentrations were similar to those for the unadjusted concentrations. The trend in flow-adjusted calcium concentrations was not statistically significant; however, the trend in sodium became significant after correcting for flow. The LOWESS curves in figure 25 show slightly different trend patterns for sulfate and nitrite plus nitrate. The downward trend in sulfate was largely driven by high concentrations at the beginning of the period of record and low concentrations at the end. Nitrite-plus-nitrate concentrations declined in the early part of the period of record, then remained fairly constant after 1984. The cause of trends in stream chemistry at the Devils River Station is not known. Lynch and others (1995) found no statistically significant trends in precipitation chemistry at the Sonora NADP station from 1980–92, indicating that changes in atmospheric deposition probably were not an important factor. Land-use changes in the basin also have been minor, although the effect of human activities in the northern part of the basin is unknown. Method-related factors are another possible cause of stream-water trends, particularly for sulfate. As discussed previously, sulfate concentrations at the beginning and end of the period of record probably were biased by several changes in the analytical method for sulfate that occurred over the period of record.

Table 48. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major dissolved constituents, Devils River, Texas, January 1978 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; inst., instantaneous; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge, inst.	0.11	0.129	--	--
pH, field	<.01	.838	(a)	--
Calcium	12.6	.002	7.4	0.014
Magnesium	<.1	.324	1.6	.174
Sodium	.3	.475	1.0	.004
Potassium	<.1	.082	–.2	.014
Alkalinity, laboratory	3.8	.594	1.3	.999
Sulfate	–2.1	.000	–1.8	.001
Chloride	<.1	.808	(a)	--
Nitrite plus nitrate	–1.2	.004	–1.7	.000
Silica	<.1	.396	(a)	--

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

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling in the Devils River Basin on June 10 and 11, 1992, are listed in table 49, and the locations of sampling sites are shown in figure 24. During the sampling period, discharge at the gaging station was around 16 m^3/s compared to the median daily discharge of 8.7 m^3/s for June, indicating that the basin was sampled during above-normal flow conditions for that time of year. The solute concentrations measured at site 1 during

Table 49. Physical properties and major dissolved constituents from surface-water sampling sites in the Devils River Basin, Texas, collected June 10–11, 1992

[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; Si, silica; concentrations in microequivalents per liter, except silica in micromoles per liter; --, not reported]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si
1	8449400	16	390	8.2	2,750	1,040	350	36	3,420	180	510	86	250
2	295341100594100	--	430	8.1	3,000	1,040	400	38	3,700	160	560	110	270
3	295543100591600	--	520	7.5	3,800	1,200	410	38	4,680	190	650	160	250
4	295755101085000	--	490	8.0	3,550	1,120	400	41	4,140	210	560	110	270
5	300824101071100	--	430	8.1	2,500	1,360	480	51	3,640	400	680	53	370

the synoptic sampling were generally between the first- and third-quartile concentrations reported for the HBN station during the entire period of record (table 46). Stream chemistry did not vary markedly among the sampling sites, which was not unexpected considering the uniform geology of the basin and the large percentage of streamflow derived from ground water. For example, calcium ranged from 2,500 µeq/L at an upstream site on the main channel (site 5) to 3,800 µeq/L at the Jose Maria spring near Dolan Creek (site 3). A similar range of concentrations was measured for alkalinity, which ranged from 3,420 µeq/L at site 1 to 4,680 µeq/L at site 3. Comparison of samples along the main channel (sites 1, 2, 4, and 5) showed no substantial changes in chemistry along the transect, except for a slight decrease in magnesium, sodium, and chloride concentrations in the downstream direction. As was observed in the historical data records, fairly high concentrations of nitrate were measured at all the sampling sites (range 53 to 160 µeq/L). Although no anthropogenic sources of nitrogen could be identified in the basin, the sample collected at site 3 at the mouth of a large spring indicates that ground water is the primary source of nitrogen in stream water at the gaging station.

South Fork Rocky Creek near Briggs, Texas (Station 08103900)

Site Characteristics and Land Use

The South Fork Rocky Creek HBN Basin is in the Great Plains physiographic province in south-central Texas (fig. 26). The 86-km^2 basin ranges in elevation from 291 to 435 m and drains a hilly topography that has a stairstepped or benched appearance. The USGS gaging station is located 11.3 km west of the town of Briggs, Tex., at latitude 30°54'41" and longitude 98°02'12". South Fork Rocky Creek flows east into the San Gabriel River, a tributary of the Colorado River, and has a channel length of about 18.8 km upstream from the gaging station and an average stream gradient of 5.9 m/km. Mean monthly discharge at the gaging station ranged from 0.06 m^3/s in August to 0.66 m^3/s in May, and average annual runoff was 11 cm from 1963 through 1995 (Gandara and others, 1996). The main channel is ephemeral, and periods of no flow occur most years during August, September, and October. The climate is humid, subtropical with long, hot summers and short, mild winters. Precipitation averages 75 cm annually and is greatest in May and September (National Climatic Data Center, 1997). Potential evaporation is about twice the precipitation from May to October (Bailey and others, 1994). Average monthly air temperatures range from 8.4°C in January to 28.2°C in July.

The South Fork Rocky Creek Basin is in the Southwest Plateau ecoregion, which is characterized by arid grasslands in which shrubs and low trees grow singly or in bunches (Bailey and others, 1994). Native vegetation includes little bluestem, sideoats grama, and tall grama with scattered groves of live oak and Texas oak growing along the stream channels. Most soils in the basin are classified as Alfisols and are mapped in the Bracket series (Dittemore and Allison, 1979). These soils are shallow loamy soils on low rounded hills with exposed ledges of limestone and marl. A typical profile has a surface layer of brown clay loam that is 10 cm thick overlying a subsoil of yellowish-brown clay loam that extends to a depth of 30 cm.

Bedrock in the basin consists of sedimentary rocks of Cretaceous age that include the Glen Rose Limestone at lower elevations in the basin and the

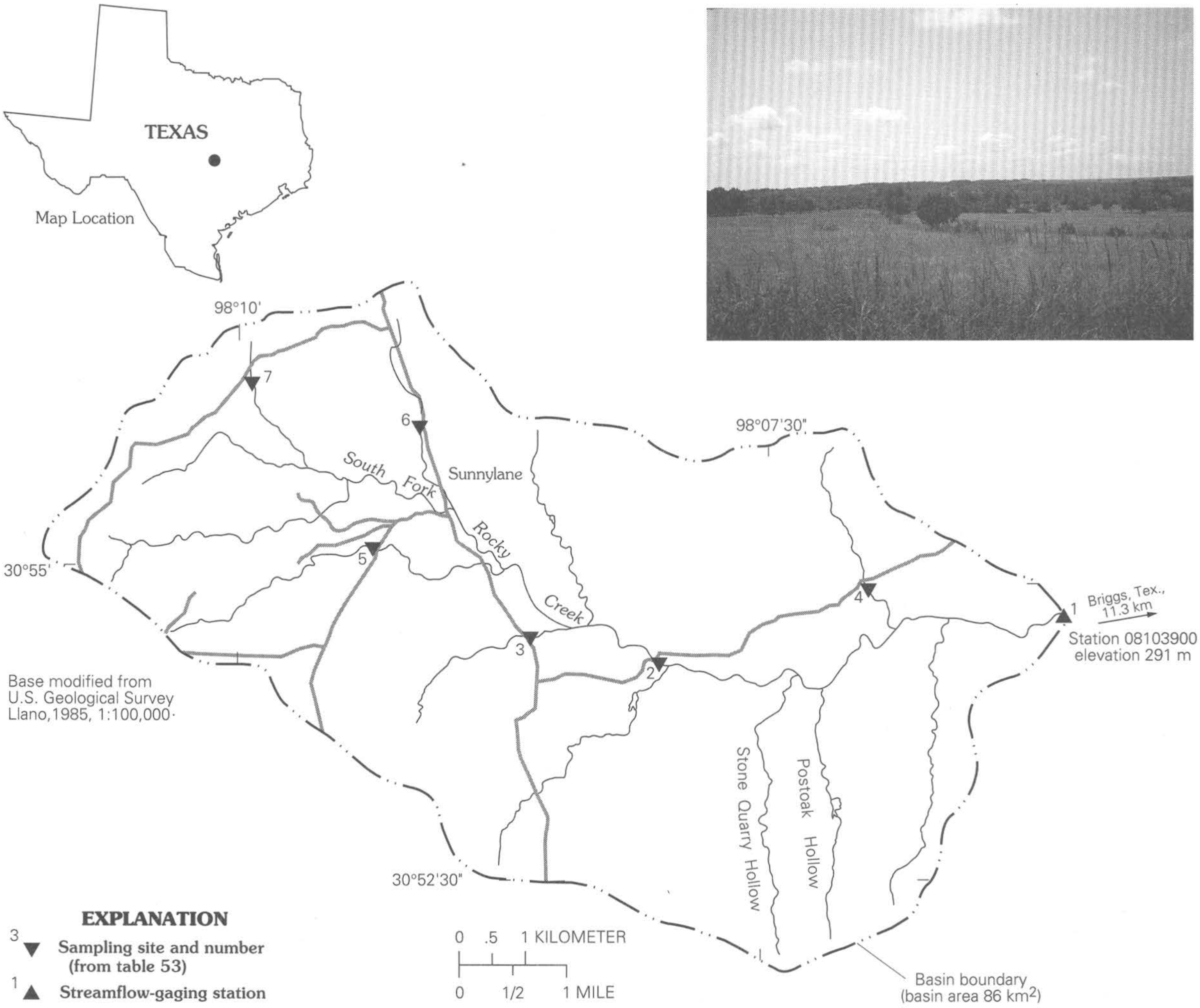


Figure 26. Map showing study area in the South Fork Rocky Creek Basin and photograph of the landscape of the basin.

Paluxy Sand and Walnut Formation along the basin divide (Texas Geological Survey, 1981). The Glen Rose Limestone is characterized by alternating beds of limestone, dolomite, and marl that weather unevenly to form the characteristic stairstepped topography of the area.

South Fork Rocky Creek drains the northeastern part of Burnet County in Texas, and land ownership is more than 98 percent private. Several kilometers of paved and gravel roads cross the basin, but access to streams is limited to public rights-of-way at road crossings. The basin is sparsely populated, and the major land-use activity is cattle ranching. Land cover is primarily native rangeland with less than 5 percent cropland, much of which has been revegetated with pasture grasses, such as coastal bermuda grass and Kleingrass, over the past 10 years (R.K. Ellis, U.S. Department of Agriculture Natural Resources Conservation Service, written commun., 1996). No major changes in land-use activities have occurred during the past 30 years, except for a slight decrease in cropland and construction of a few rural residential structures (R.K. Ellis, written commun., 1996). Several gravel pits, ranch houses, and stock ponds are scattered throughout the basin.

Historical Water-Quality Data and Time-Series Trends

The data set for the South Fork Rocky Creek HBN Station analyzed for this report includes 113 water-quality samples that were collected from January 1968 through June 1995. Sampling was scheduled for bimonthly from 1968 through 1982 and quarterly from 1983 through 1995, although fewer samples were collected in most years because of periods of no flow. Water-quality samples in the early part of the period of record were analyzed at a USGS laboratory in Austin, Tex., that operated until 1973 (Durum, 1978). After establishment of the central laboratory system, samples were analyzed at a laboratory in Salt Lake City, Utah, from 1973 through 1975 and at the NWQL in Arvada, Colo., from 1976 through 1995. Daily discharge records at the South Fork Rocky Creek (station 08103900) are available beginning in April 1963.

Calculated ion balances for 106 samples with complete major-ion analyses are shown in figure 27. Ion balances ranged from –6.4 to 8.0 percent, and more than 90 percent of samples had values within the ±5 percent range, indicating that the analytical measurements are of high quality. The average ion balance was –0.1 percent, indicating that unmeasured

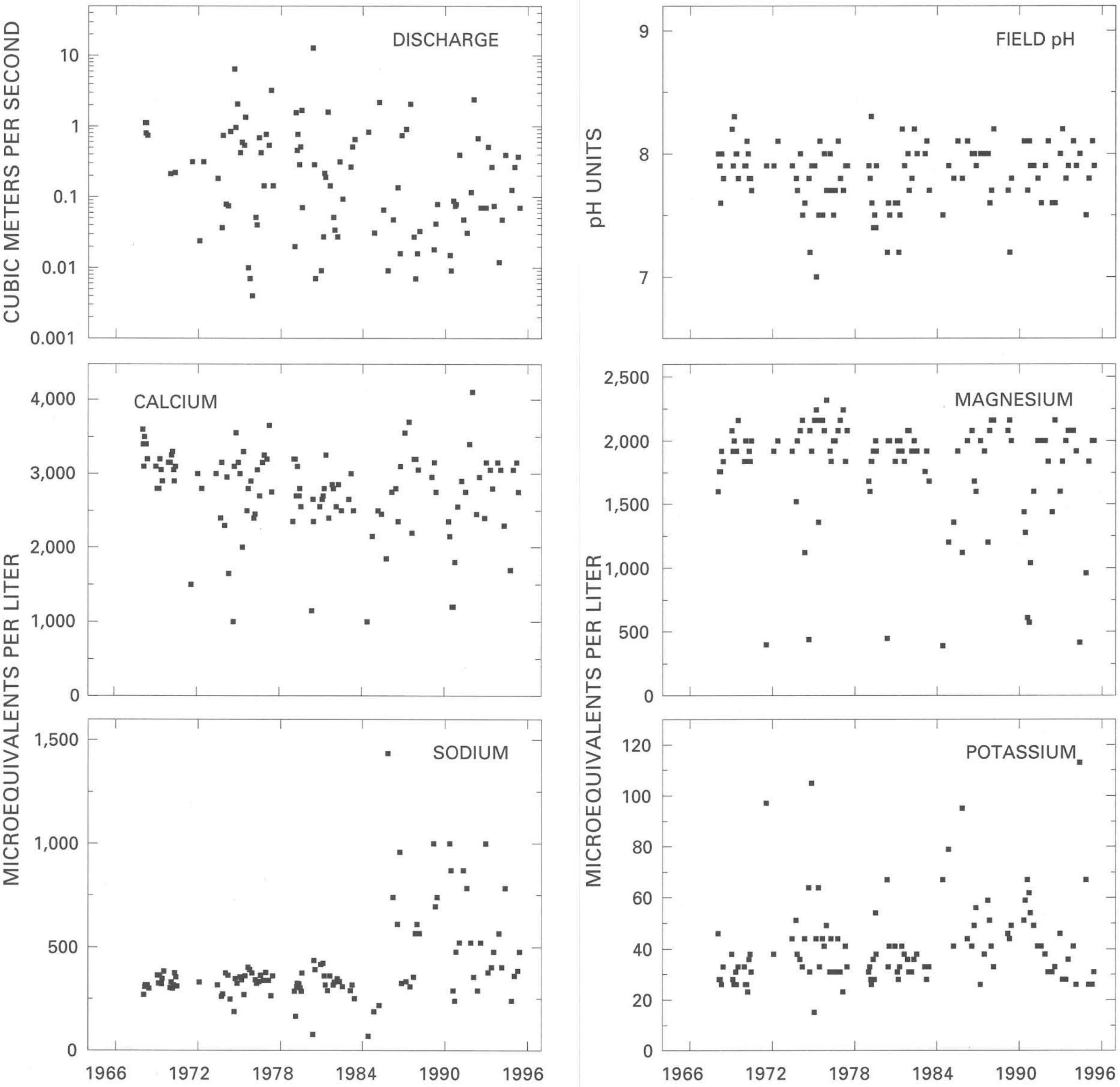


Figure 27. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at South Fork Rocky Creek, Texas.

constituents, such as organic anions, do not contribute substantially to the ionic composition of stream water at this station. Time-series plots of the major dissolved constituents were inspected for evidence of method-related effects (fig. 27). The most notable patterns are for sodium and chloride, which had elevated concentrations in samples that were collected after 1985. A more detailed analysis of the data revealed that samples with elevated sodium concentrations also had elevated chloride concentrations, indicating that analytical bias probably was not the cause. It also is unlikely that samples were contaminated during collection and processing procedures in the field (Frank Wells, U.S. Geological Survey, written commun., 1998), indicating that the elevated concentrations probably were caused by environmental change in the basin rather than a method-related factor.

Median concentrations and ranges of major constituents in stream water at the South Fork Rocky Creek Station and VWM concentrations in wet-only deposition measured at the L.B.J. National Grasslands

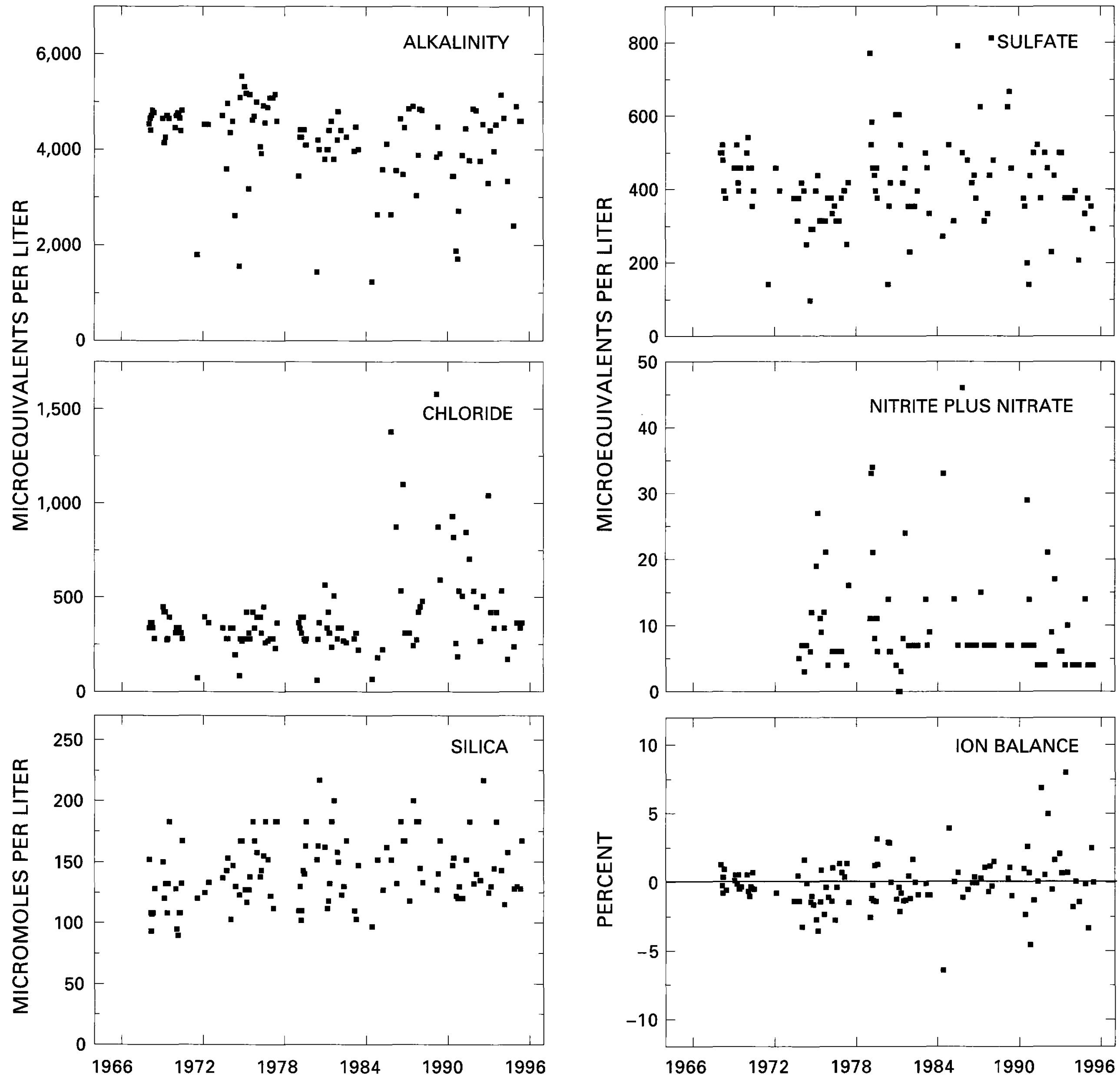


Figure 27. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at South Fork Rocky Creek, Texas—Continued.

NADP Station are listed in table 50. Precipitation chemistry at the NADP station, which is located about 275 km north of the HBN station, is dilute and slightly acidic with a VWM pH of 5.1 for 2 years of record. The predominant cations in precipitation were calcium and ammonium, which contributed 33 and 31 percent of the total cation charge, respectively. Sulfate and nitrate were the predominant anions in precipitation and accounted for 53 and 34 percent of the total anion charge, respectively. Stream water in South Fork Rocky Creek is fairly concentrated and well buffered; specific conductance ranged from 140 to 570 µS/cm, and alkalinity was between 1,240 and 5,540 µeq/L. The major cations in stream water were calcium and magnesium, and bicarbonate was the predominant anion. The predominance of these solutes in stream water is attributed to the weathering of carbonate minerals in the limestone and dolomite bedrock. The median concentration of chloride in stream water was 340 µeq/L, which is considerably higher than the VWM concentration of 5.5 µeq/L in precipitation. This large difference in concentration indicates that most stream-water chloride is derived from sources in the basin, such as weathering of the sedimentary rocks, discharge from rural septic systems, runoff from agricultural land, or oil-field activities. The high concentrations of sulfate in stream water (median of 400 µeq/L) compared to precipitation (23 µeq/L) also indicate that most sulfate is derived from internal sources, the most likely being dissolution of sulfate-bearing minerals in the bedrock. The median concentrations of inorganic nitrogen species in stream water were less than the VWM concentrations in precipitation, indicating that, overall, there was a net loss of nitrogen in the basin. However, about 25 percent of stream samples had nitrite-plus-nitrate concentrations greater than the VWM concentration in precipitation, which may indicate that upstream agricultural activities affect nutrient concentrations at the HBN station during some times of the year.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 51). Most solutes were poorly correlated with discharge, except for weak inverse correlations with sodium (rho = −0.591) and chloride (rho = −0.557). Among the solutes, the strongest correlations were found between calcium and alkalinity (rho = 0.842) and sodium and chloride

Table 50. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major dissolved constituents measured in water-quality samples from the South Fork Rocky Creek, Texas, January 1968 through June 1995, and volume-weighted mean concentrations in wet precipitation collected at the L.B.J. National Grasslands Station, Texas

[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.	0.0003	0.043	0.18	0.65	13	101	--
Spec. cond., field	140	450	490	510	570	112	9.2
pH, field	7.0	7.7	7.9	8.0	8.3	113	5.1[b]
Calcium	1,000	2,500	2,850	3,150	4,100	113	16
Magnesium	400	1,810	1,980	2,060	2,320	113	2.3
Sodium	70	310	340	400	1440	110	5.6
Potassium	15	31	36	44	110	111	.9
Ammonium	<.7	<.7	<1.1	3.9	11	55	15
Alkalinity, laboratory	1,240	3,880	4,420	4,720	5,540	112	--
Sulfate	96	330	400	460	810	113	23
Chloride	62	280	340	420	1,580	112	5.5
Nitrite plus nitrate	<.7	5.7	7.1	12	46	85	15[c]
Silica	90	120	140	160	220	113	--

[a] Data are volume-weighted mean concentrations for 1988–89.

[b] Laboratory pH.

[c] Nitrate only.

Table 51. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major dissolved constituents, South Fork Rocky Creek, Texas, 1968–95

[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
pH	–0.003								
Ca	.219	0.175							
Mg	–.262	–.064	0.649						
Na	–.591	.178	.091	0.374					
K	–.266	–.028	–.529	–.375	0.195				
Alk	.170	.174	.842	.673	.085	–0.617			
SO_4	–.211	–.004	.317	.286	.304	–.129	0.178		
Cl	–.557	.125	.179	.344	.832	.068	.117	0.554	
Si	–.218	–.039	.012	.259	.282	.325	.082	–.209	0.118

(rho = 0.832). The lack of correlation between solutes and stream discharge may reflect the high carbonate content of soils and bedrock in the basin, which produces soil and ground water of similar composition. The correlations among solutes are consistent with the assumption that carbonate minerals and salts are the major sources of solutes in stream water.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are listed in table 52. The only statistically significant trend was detected in the flow-adjusted sodium concentrations at the 0.01 probability level. Other than sodium, the trend analysis indicates that stream chemistry at this station has been fairly stable during the period of record, which is consistent with the sparse population of the basin and minimal change in land use during the period of record. In addition, there have been no detectable changes in atmospheric deposition since at least 1982 (Lynch and others, 1995). The upward trend in flow-adjusted sodium concentrations is largely driven by the elevated sodium concentrations observed beginning in 1985. As discussed previously, the elevated sodium and chloride concentrations at this station probably were caused by an environmental change in the basin rather than method-related factors. One possible explanation for the increase in stream-water sodium concentrations is leakage of brine water associated with oil-well activity. Although drilling activity in the basin in the mid-1980's could not be confirmed, contamination of surface waters by oil field brines is a common water-quality problem in many areas of Texas (Frank Wells, U.S. Geological Survey, written commun., 1998).

Table 52. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major dissolved constituents, South Fork Rocky Creek, Texas, January 1965 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; inst., instantaneous; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge, inst.	<0.01	0.916	--	--
pH, field	<.01	.247	([a])	--
Calcium	<.1	.842	([a])	--
Magnesium	–3.9	.279	–2.2	0.490
Sodium	3.7	.040	7.7	.008
Potassium	<.1	.585	–.1	.455
Alkalinity, laboratory	–19.9	.103	–14.9	.173
Sulfate	<.1	.785	1.2	.513
Chloride	3.0	.283	8.0	.046
Nitrite plus nitrate	–.3[b]	.266	--	--
Silica	.1	.340	.5	.239

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

[b] Trend test calculated for 1974–95 using a trend test for censored data.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling in the South Fork Rocky Creek Basin on June 8, 1992, are listed in table 53, and the locations of the sampling sites are shown in figure 26. During the sampling period, discharge at the gaging station was about 2.0 m^3/s compared to the median daily discharge of 0.3 m^3/s for May and 0.1 m^3/s for June (Lawrence,

Table 53. Physical properties and major dissolved constituents from surface-water sampling sites in the South Fork Rocky Creek Basin, Texas, collected June 8, 1992

[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; Si, silica; concentrations in microequivalents per liter, except silica in micromoles per liter; --, not reported; criteria used in selection of sampling sites: MT = major tributary, LU = land use]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	Si	Criteria[a]	Remarks
1	8103900	2.0	560	8.2	3,700	1,920	310	31	5,200	270	450	15	170	--	Gaging station
2	305420098060200	.89	540	8.1	3,500	1,840	310	25	5,160	310	340	12	180	MT	
3	305431098071100	.12	540	8.1	3,550	2,080	280	33	5,260	230	260	1.4	180	LU	Pasture land
4	305459098040500	.094	510	8.3	3,500	1,840	230	25	5,400	330	260	3.7	140	LU	Pasture land
5	305509098084300	.094	530	8.0	4,300	1,120	340	20	4,880	290	310	19	180	LU	Pasture land
6	305611098081600	.042	560	8.3	3,650	1,680	410	16	5,480	230	480	2.1	160	LU	Pasture land
7	305631098095800	--	630	7.9	5,000	1,120	330	12	5,740	210	540	230	250	LU	Stock ponds

1987), indicating that the basin was sampled during higher than normal flow conditions for that time of year. The solute concentrations measured at site 1 during the synoptic sampling were generally between the first- and third-quartile concentrations reported for the HBN station during the entire period of record (table 50). The tributary streams were similar in composition to stream water collected at the gaging station (site 1); calcium and magnesium were the predominant cations, and bicarbonate was the predominant anion. Ion balances for the synoptic samples ranged from −3.4 to 2.5 percent, indicating that unmeasured constituents, such as organic anions, did not seem to be an important component of stream water during the sampling period. The results presented in table 53 show relatively little variation in the stream chemistry among the sampling sites, particularly for the weathering-derived solutes. For example, calcium ranged from 3,500 to 5,000 μeq/L, magnesium ranged from 1,120 to 2,080 μeq/L, and alkalinity ranged from 4,880 to 5,740 μeq/L. This similarity in stream chemistry is probably largely due to the high carbonate content of soils and bedrock in the basin. The remaining solutes—sodium, potassium, sulfate, chloride, nitrate, and silica—did not vary markedly among the tributaries, except for nitrate, which was elevated at site 7. This tributary was sampled just downstream from a stock pond, indicating that livestock waste was probably the source of stream-water nitrate at this site.

Popple River near Fence, Wisconsin (Station 04063700)

Site Characteristics and Land Use

The Popple River HBN Basin is located in the Superior Upland physiographic province in the northeast corner of Wisconsin (fig. 28). The 360-km^2 basin ranges in elevation from 429 to 658 m and drains a hummocky landscape covered by forests, lakes, and wetlands (Oakes and others, 1973). The USGS gaging station is located 4.2 km northwest of Fence, Wis., at latitude 45°45'49" and longitude 88°27'47". The Popple River flows east into the Pine River, a tributary of the Menominee River, and has a channel length of 52 km upstream from the gaging station and an average stream gradient of 1.35 m/km. The river is slow moving along much of its reach, although bedrock outcrops form numerous riffles and small waterfalls (Sullivan and others, 1995). The main river channel is perennial, and mean monthly discharge varies from 1.3 m^3/s under ice cover in January and February to 8.6 m^3/s during snowmelt in April. Average annual runoff from the basin was 29 cm from 1964 through 1995 (Holmstrom and others, 1996). The climate is classified as humid continental, with short summers and long, snowy winters. Average monthly air temperatures range from −17.1°C in January to 20.9°C in July (National Climatic Data Center, 1997). Precipitation averages 78 cm annually with September being the wettest month (10.7 cm) and

February the driest (2.3 cm). Average annual snowfall is 138 cm, and the ground generally remains snow covered from mid-November to mid-April (Oakes and others, 1973).

The Popple River Basin is in the Laurentian Mixed Forest ecoregion, which lies between the boreal forest and the broadleaf deciduous forest zones (Bailey and others, 1994). Northern hardwoods, conifers, and aspen stands cover about 57 percent of the basin in areas where the water table is generally more than 1 m below the ground surface. Common hardwood species include sugar maple, red oak, white ash, basswood, and yellow birch; the conifer species are hemlock, white spruce, balsam fir, and white pine. Aspen is a common post-fire species that tends to grow on sandier soils than the soils dominated by hardwoods. Swamps and open bogs cover about 30 percent of the basin. In these areas, the water table is at or near the surface most of the year, and vegetation is dominated by black spruce, white cedar, black ash, tamarack, grass, sedge, and moss. Soils in the uplands are classified as Spodosols and are mapped in the Stambaugh and Goodman series (Hole and others, 1962). These series include well-drained acidic soils that range from 60 to 100 cm in depth. The Stambaugh soils are developed in loamy and sandy fluvial deposits, whereas the Goodman soils are developed in loamy glacial till. A typical soil profile has a thin organic horizon overlying a dark brown to reddish-brown layer of silt loam overlying a subsoil of coarse sand and gravel (Stambaugh) or loamy till (Goodman). The clay mineralogy of the

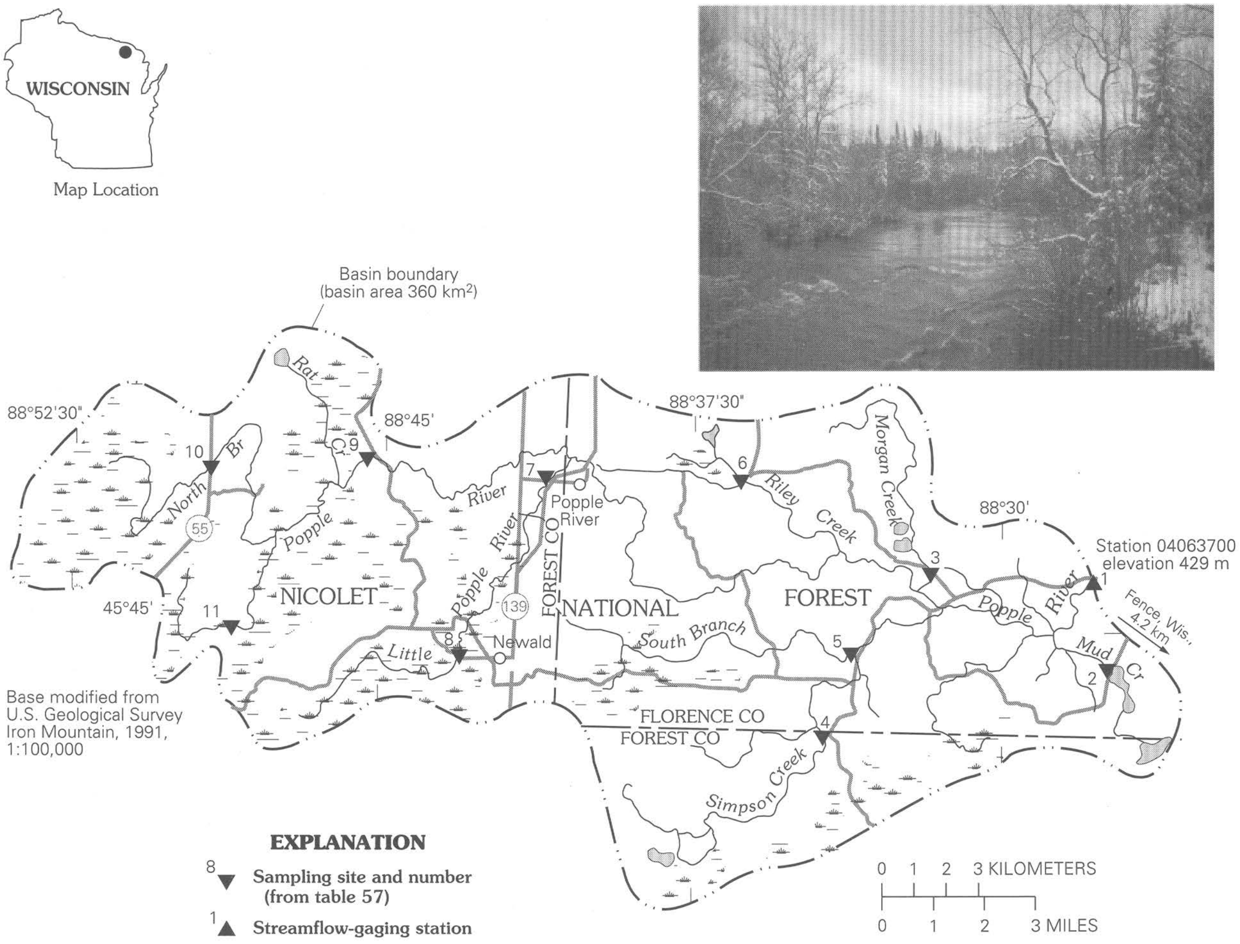


Figure 28. Map showing study area in the Popple River Basin and photograph of the main river channel.

loamy soils is dominated by illite and kaolinite with minor amounts of vermiculite and smectite (Simpkins and others, 1987). Wetland soils are scattered throughout the basin and consist largely of peat and muck that is typically a few meters thick.

The basin lies in the southern part of the Canadian Shield, which consists of crystalline rocks of Precambrian age covered by Pleistocene glacial deposits. Most of the bedrock consists of light-gray or pinkish-gray, medium-grained granite and granitoid gneiss that is composed of plagioclase, quartz, potassium feldspar, and biotite (Sims, 1990; Sims and others, 1992). Along the southern boundary, a small area of the basin is underlain by the Quinnesec Formation of Proterozoic age, which consists of thick metagabbro sills and thin interbeds of biotite schist and quartzite (Sims and others, 1992). The bedrock surface is irregular and, consequently, is covered by an uneven layer of glacial deposits that range in thickness from 0 to 50 m (Clayton, 1986). The glacial deposits consist of reddish-brown till and fluvial sands and gravels deposited by glacial meltwater streams. Pebbles and cobbles in the till consist of 95 percent igneous and metamorphic rock fragments and 5 percent sedimentary fragments, primarily dolomite (Clayton, 1986). The till is slightly calcareous but is generally leached of carbonates to a depth of 1 m. The fluvial sediments are similar in composition to the till, except that carbonates are leached to greater depths (Clayton, 1986).

The Popple River drains parts of Florence and Forest Counties in Wisconsin and is in the boundaries of the Florence District of the Nicolet National Forest. Approximately 40 percent of land in the National Forest is privately owned (D. Olson, U.S. Department of Agriculture Forest Service, written commun., 1996). Land cover in the basin is 61.1 percent forest, 35.1 percent wetland, 3.0 percent agricultural, 0.6 percent lakes, and 0.1 percent residential (Sullivan and others, 1995). The major land-use activities on publicly owned lands are timber harvesting and recreation. About 30 km^2 of forest land in the basin have been harvested during the last 10 years by using a combination of thinning, selection, shelterwood, and clearcuts (D. Olsen, U.S. Department of Agriculture Forest Service, written commun., 1996). The Forest Service maintains an 18-unit campground on Morgan Lake. Privately owned lands are mostly forested and have some abandoned agricultural fields. The primary land use on private land is residential, including two small towns, Popple River (population 42) and Newald, and a number of seasonal homes and hunting cabins. More than 100 km of paved and dirt roads traverse the basin, including State Highways 55 and 139, which are plowed and salted in winter, and a railroad line that parallels State Highway 139. The section of the Popple River downstream from Morgan Creek has State designation as a wild river. The river generally is accessible by canoe downstream from State Highway 139 from late April to early June.

Historical Water-Quality Data and Time-Series Trends

The data set for the Popple River HBN Station analyzed for this report includes 262 water-quality samples that were collected from October 1965 through September 1995. Sampling frequency was monthly from 1968 and 1982 and quarterly from 1983 through 1995. Additional samples were collected from March 1993 through May 1995 as part of the National Water-Quality Assessment Program in the Western Lake Michigan Drainages study unit (Sullivan and others, 1995). Water-quality samples in the early part of the record were analyzed at a USGS laboratory in Columbus, Ohio, that operated until 1973 (Durum, 1978). After establishment of the central laboratory system, samples were analyzed at a laboratory in Atlanta, Ga., from 1973 through 1985 and at the NWQL in Arvada, Colo., from 1986 through 1995. Daily discharge records are available for the Popple River (station 04063700) beginning in October 1963. Records of daily water temperature at the gaging station are available from March 1994 through December 1995.

Calculated ion balances for 256 samples with complete major-ion analyses are shown in figure 29. Ion balances ranged from –8.5 to 15 percent, and almost 90 percent of samples had values within the ±5 percent range, indicating that the analyses are of high quality. The average ion balance for all samples was 1.4 percent, and 65 percent of samples had positive ion balances, indicating that unmeasured constituents, such as organic anions, probably contributed 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). The most notable patterns are observed in the chloride and sulfate concentrations. For example, chloride concentrations had a high degree of scatter in the early part of the period of record, which was coincident with the period that samples were analyzed at the USGS laboratory in Columbus, Ohio (Durum, 1978). Sulfate had alternating periods of high and low concentrations that were not observed for the other major solutes. Sources of analytical bias in the early part of the period of record are difficult to confirm, although several different analytical methods were used for sulfate before 1985 (Fishman and others, 1994). The turbidimetric method, which was used at the NWQL between March 1986 and December 1989, often introduced a substantial positive bias in sulfate concentrations, 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/admin/memo/, accessed 1997). Ion chromatography replaced the turbidimetric method in 1990, which seems to correlate with the low sulfate concentrations measured at the end of the period of record.

Median concentrations and ranges of major constituents in stream water at the Popple River HBN Station and VWM concentrations in wet-only deposition measured at the Popple River NADP Station are listed in table 54. Precipitation chemistry at the NADP station, which is located about 6 km northeast of the HBN station, is dilute and slightly acidic with a VWM pH of 4.7 for 10 years of record. The predominant cations were hydrogen and ammonium, which each contributed 37 percent of the total cation charge. Sulfate and nitrate were the predominant anions and accounted for 56 and 39 percent of the total anion charge, respectively. The predominance of strong acid anions indicates that precipitation at the NADP station may be affected by anthropogenic emissions of sulfur and nitrogen compounds, which cause acid rain. The fairly high concentrations of ammonium at this NADP station may be linked to the high density of livestock in the Midwestern region of the country.

Stream water in the Popple River is moderately concentrated and well buffered; specific conductance ranged from 25 to 330 μS/cm, and alkalinity was between 400 and 2,700 μeq/L. Stream water at this station also has a tealike color owing to the leaching of tannins from the numerous wetlands in the basin (Sullivan and others, 1995). The major cations in stream water were calcium and magnesium, and bicarbonate was the predominant anion. The predominance of these solutes in stream water is attributed to the weathering of calcite and dolomite in the glacial deposits. The median concentration of chloride in stream water was 45 μeq/L, which is considerably higher than the VWM concentration of 2.4 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 chloride concentration of precipitation, indicating that most stream-water chloride is derived from sources other than precipitation. The most likely source of additional stream-water chloride is from deicing salts applied to roads in winter, although small amounts of chloride also might be contributed by septic systems in rural residential areas. The median concentration of sulfate in stream water was 140 μeq/L compared to 30 μeq/L in precipitation, which is slightly larger than would be expected from the effects of evapotranspiration. Assuming geologic sources are small, most of the additional stream-water sulfate probably is derived from dry deposition from the atmosphere. Baker (1991) estimated that dry deposition was about 27 percent of total sulfate deposition in the region, which seems to be consistent with sulfate concentrations in the stream. The low concentrations of nitrate and ammonium in stream water compared to precipitation indicate that atmospherically deposited nitrogen is strongly retained by soils and vegetation in the basin. The low stream-water nitrogen concentrations also indicate that rural residences in the basin do not seem to affect the nutrient composition of stream water at the HBN station.

The solute composition of stream water was further evaluated by analyzing correlations between solutes and stream discharge (table 55). The weathering-derived constituents, particularly calcium, magnesium, and alkalinity, had strong inverse correlations with discharge. These results are consistent with a hydrologic system where weathering-enriched base flow is diluted by water from shallow or surficial sources during periods of increased discharge, particularly spring snowmelt. Among the solutes, the strongest correlations were among calcium, magnesium, and alkalinity ($0.971 < \text{rho} < 0.983$), which is consistent with the weathering stoichiometry of carbonate minerals. In contrast, sulfate and chloride were weakly correlated with the other dissolved constituents, as well as discharge. The weak correlation between

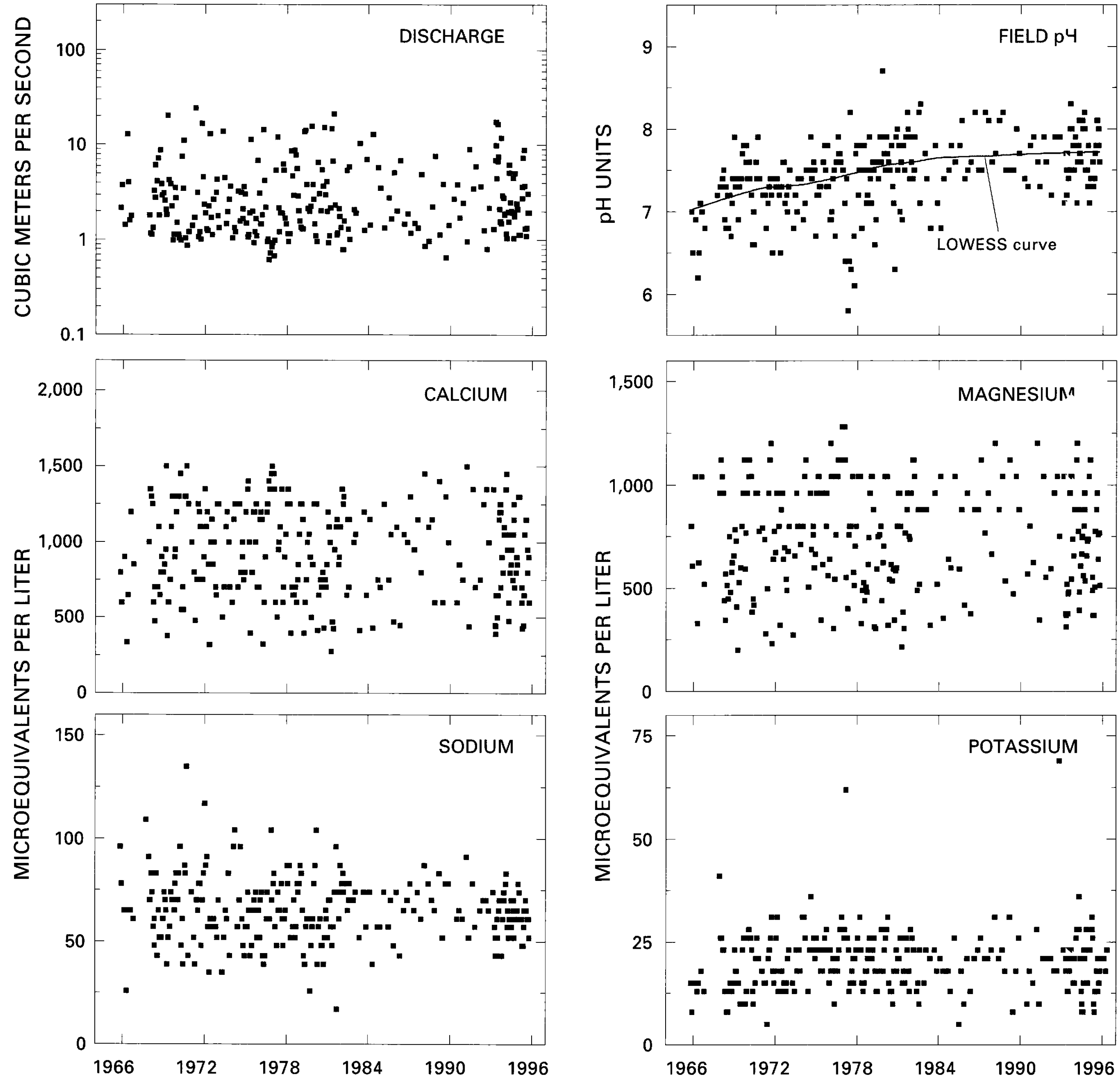


Figure 29. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Popple River, Wisconsin.

chloride and sodium (rho = 0.140) was somewhat unexpected because sodium also is a major component of deicing salts, indicating that some of the sodium from road salt may be exchanged for calcium and magnesium in the soils (Shanley, 1993). The poor correlations between sulfate and the carbonate solutes are consistent with the assumption that sulfate is derived primarily from atmospheric sources.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents are listed in table 56. A statistically significant upward trend of 0.02 units per year was detected in the unadjusted field pH at the 0.01 probability level. The trend result was similar for the flow-adjusted pH values, indicating that the trend was not caused by variations in stream discharge. The LOWESS curve in figure 29

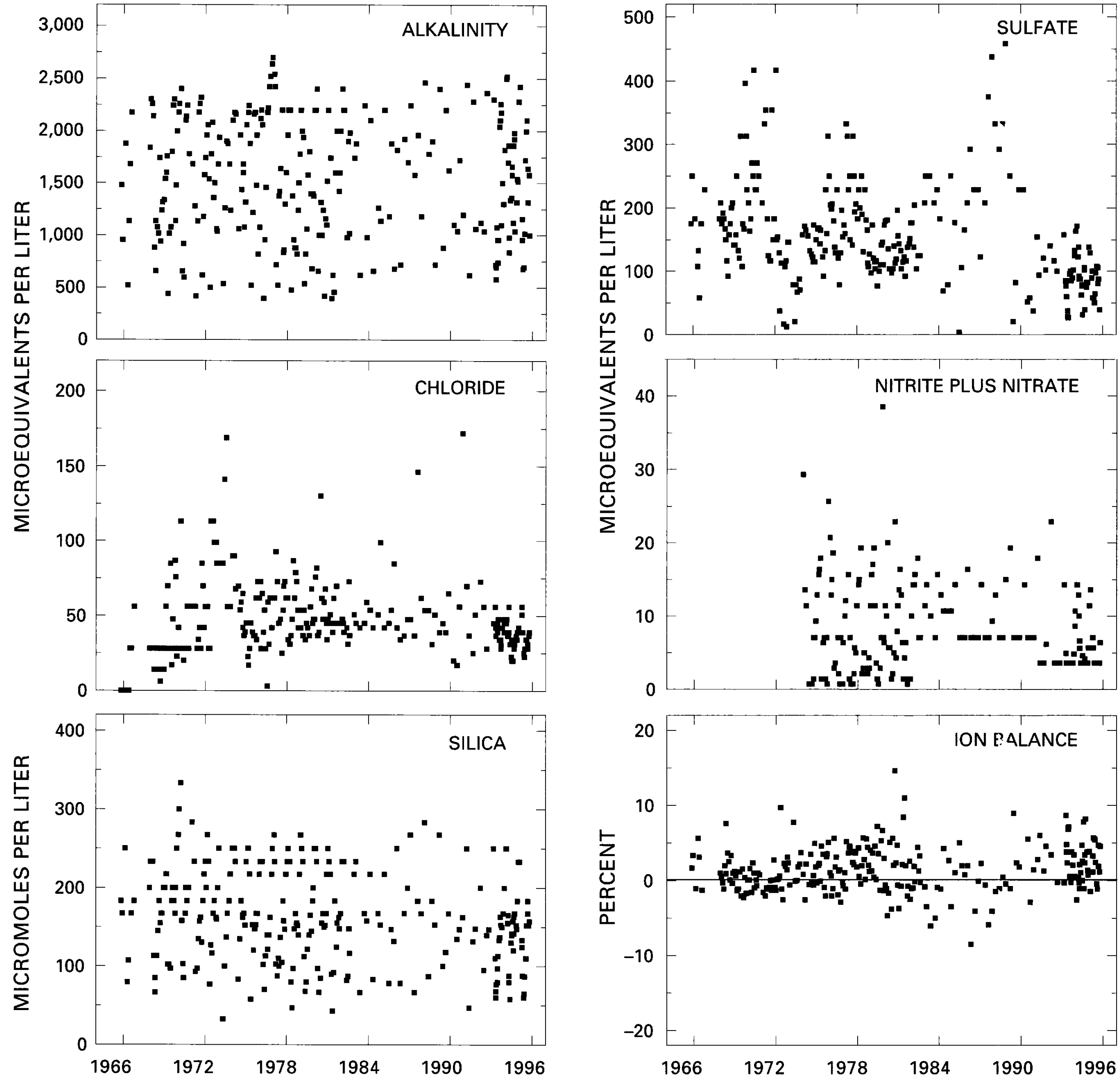


Figure 29. Temporal variation of discharge, field pH, major dissolved constituents, and ion balance at Popple River, Wisconsin—Continued.

indicates that the trend in pH has occurred over the entire period of record, although the rate of increase was slightly higher before 1984. Trends in stream-water pH at this site may reflect changes in environmental factors such as land use and precipitation chemistry. The effect of land use on stream chemistry at this site probably is minimal because the Popple River Basin is primarily forested, and there have been no changes in land use during the period of record, except for a slight decrease in timber harvesting (D. Olsen, U.S. Department of Agriculture Forest Service, written commun., 1996). Trends in precipitation chemistry at this site are difficult to confirm because no long-term records are available near this station. Husar and others (1991) estimated little change in sulfate deposition rates in the upper Midwest during

Table 54. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major dissolved constituents measured in water-quality samples from the Popple River, Wisconsin, October 1965 through September 1995, and volume-weighted mean concentrations in wet precipitation collected at the Popple River Station, Wisconsin

[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.	0.62	1.3	2.1	4.1	24	260	--
Spec. cond., field	25	120	170	210	330	261	14
pH, field	5.8	7.2	7.5	7.8	8.7	261	4.7^b
Calcium	280	700	950	1,200	1,500	261	9.1
Magnesium	200	540	760	960	1,280	261	2.4
Sodium	17	57	65	74	130	260	2.1
Potassium	5.1	15	20	23	69	260	.6
Ammonium	<.7	1.4	2.9	5.0	12	109	20
Alkalinity, laboratory	400	1,060	1,540	2,060	2,700	259	--
Sulfate	4.1	100	140	190	460	262	30
Chloride	<2.8	31	45	59	170	258	2.4
Nitrite plus nitrate	<.7	3.5	7.1	12	39	187	21^c
Silica	33	120	160	220	330	261	--

[a] Data are volume-weighted mean concentrations for 1986–95.

[b] Laboratory pH.

[c] Nitrate only.

Table 55. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major dissolved constituents, Popple River, Wisconsin, 1966–95

[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
pH	−0.363								
Ca	−.913	0.345							
Mg	−.910	.314	0.982						
Na	−.760	.198	.803	0.818					
K	−.308	−.035	.338	.366	0.351				
Alk	−.913	.353	.974	.972	.792	0.357			
SO_4	−.338	−.008	.390	.437	.436	.412	0.356		
Cl	.010	−.157	−.034	.011	.140	.186	−.045	0.359	
Si	−.531	−.077	.629	.686	.570	.389	.651	.491	0.253

the past 30 years, based on historical SO_2 emissions. Lynch and others (1995) reported declines in hydrogen ion [0.9 (μeq/L)/yr] and sulfate [1.0 (μeq/L)/yr] concentrations in precipitation at the Popple River NADP station from 1980 through 1992. Although the trend in precipitation acidity seems to be consistent with the upward trend in stream-water pH, a small change in the hydrogen ion concentration probably would not be detectable in the highly buffered water of the Popple River. The effect of decreasing sulfate deposition on stream-water sulfate probably also would be difficult to detect at this HBN station because of the large variations in stream-water sulfate concentrations that were caused by analytical bias. Method-related factors, particularly changes in field instruments and pH probes, also provide a possible explanation for the upward trend in stream-water pH. However, changes in field methods are not well documented for most stations in the HBN, particularly for the early part of the record.

Synoptic Water-Quality Data

Results of the surface-water synoptic sampling in the Popple River Basin on September 23 and 24, 1992, are listed in table 57, and the locations of the sampling sites are shown in figure 28. During the sampling period, discharge at the gaging station was about 4.2 m^3/s compared to the median daily discharge of 2.0 m^3/s for September and 2.3 m^3/s for October (Lawrence, 1987), indicating that the basin was sampled during higher than normal flow conditions for that time of year. The solute concentrations measured at site 1 during the synoptic sampling were close to the first-quartile concentrations reported for the HBN station during the entire period of record, except for sulfate, which was lower, and chloride, which was higher (table 54). The tributary streams spanned a wide range of concentrations that bracketed the concentrations in stream water collected at the gaging station (site 1). The average ion balance for all synoptic samples was 9.3 percent (range –3.7 to 37 percent), indicating that unmeasured constituents, probably organic anions, were an important component of stream water during the sampling period.

Table 56. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major dissolved constituents, Popple River, Wisconsin, October 1965 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; inst., instantaneous; <, less than; --, not calculated]

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge, inst.	–0.010	0.296	--	--
pH, field	.02	.001	0.02	0.001
Calcium	2.0	.205	.5	.647
Magnesium	2.1	.059	.2	.866
Sodium	<.1	.333	<.1	.827
Potassium	<.1	.223	<.1	.202
Chloride	<.1	.566	(a)	--
Sulfate	–.9	.170	(a)	--
Nitrite plus nitrate	(b)	--	--	--
Alkalinity, laboratory	8.0	.018	2.0	.259
Silica	–.5	.018	–.8	.045

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

[b] Insufficient data to calculate trend.

Table 57. Physical properties and major dissolved constituents from surface-water sampling sites in the Popple River Basin, Wisconsin, collected September 23–24, 1992

[Site locations shown in fig. 28; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeters at 25° Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO$_4$, sulfate; Cl, chloride; NO$_3$, nitrate; Si, silica; concentrations in microequivalents per liter, except silica in micromoles per liter; <, less than; --, not reported; criteria used in selection of sampling sites: BG = bedrock geology, LC = land cover, LU = land use]

Site	Station number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO$_4$	Cl	NO$_3$	Si	Criteria	Remarks
1	4063700	4.2	120	7.4	750	580	57	16	1,140	52	59	0.4	150	--	Gaging station
2	454440088281100	.13	260	8.1	1,250	1,200	74	20	2,580	75	85	1.0	87	LC	Upland forest
3	454558088314300	.092	160	7.4	850	720	48	16	1,600	46	28	.4	200	BG, LC	Felsic bedrock, upland forest
4	454312088341600	.19	130	7.6	800	630	52	16	1340	67	25	<.4	140	BG, LC	Mafic bedrock, upland forest
5	454439088353200	.17	210	7.7	1,150	960	65	19	2,300	100	34	.8	200	LC	Upland forest
6	454734088362200	.044	230	7.5	1,250	1,040	52	18	2,280	50	62	.6	180	BG, LC	Felsic bedrock, upland forest
7	454729088405500	.31	96	7.5	600	450	57	16	860	31	48	.4	130	LU	Downstream from Newald
8	454426088425900	--	72	6.9	480	360	52	13	620	35	42	.4	130	BG, LC	Mafic bedrock, wetland
9	454743088452300	--	62	6.5	450	330	52	7.4	540	31	34	.9	130	LC	Wetland
10	454727088491100	.43	46	6.2	350	270	39	2.1	260	27	14	.4	110	BG, LC	Felsic bedrock, wetland
11	454449088483100	.0037	39	5.7	270	200	43	2.1	200	25	51	.6	150	BG, LC	Mafic bedrock, wetland

The data presented in table 57 indicate that stream chemistry varied markedly in the Popple River Basin, particularly for the weathering-derived constituents. For example, calcium ranged from 270 µeq/L at site 11 to 1,250 µeq/L at sites 2 and 6. A similar pattern was observed for alkalinity, which ranged from 200 µeq/L at site 11 to 2,580 µeq/L at site 2. This variation in stream chemistry does not seem to be related to the distribution of different bedrock types in the basin. For example, there was no obvious difference in chemistry between sites 4, 8, and 11, which primarily are underlain by mafic bedrock, and sites 3, 6, and 10, which are underlain by felsic rock types. The one spatial pattern that does emerge seems to reflect the primary land-cover types in the basin. This pattern can be seen by comparing the chemistry of tributaries in the western one-half of the basin (sites 8–11) with tributaries in the eastern one-half of the basin (sites 2–7). In general, the western tributaries had lower specific conductances (36 to 96 µeq/L) and higher ion balances (8.8 to 37.2 percent) compared to the eastern tributaries, which had higher specific conductances (130 to 260 µS/cm) and lower ion balances (–3.7 to 2.3 percent). Because the western one-half of the basin contains more wetlands than the eastern one-half, these results probably reflect differences in the contributions of surface runoff and ground-water discharge to streamflow, with the western tributaries receiving greater inputs of dilute, organic-rich waters from large wetland areas in this part of the basin. The low silica concentration at site 2 was somewhat unusual and may be due to biological uptake in two large lakes located upstream from the sampling site. Human activities did not appear to have an effect on nutrient concentrations in stream water, as evidenced by the low nitrite-plus-nitrate concentrations at all sampling sites. The effect of road salting on water quality was somewhat difficult to assess not only because sampling occurred in September but also because roads cross through the headwater areas of the basin. The lowest chloride concentration, however, was measured at site 10, which is the only site sampled upstream from roads that are salted in winter.

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APPENDIXES

APPENDIX A. LIST OF MAP REFERENCES

A list of published topographic, geologic, soil, and miscellaneous maps covering all or parts of the HBN basins in the midwestern United States.

1. Cossatot River near Vandervoort, Arkansas (Station 07340300)

a. U.S. Geological Survey topographic maps:

Eagle Mountain, Arkansas (1:24,000), 1986, gaging station on this quadrangle
Nichols Mountain, Arkansas (1:24,000), 1986
Vandervoort, Arkansas (1:24,000), 1984
De Queen, Arkansas-Oklahoma (1:100,000), 1986

b. Geologic maps:

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Miser, H.D., and Purdue, A.H., 1929, Geology of the De Queen and Caddo Gap quadrangles: U.S. Geological Survey Bulletin 808, 195 p., scale 1:125,000.

c. Miscellaneous maps:

U.S. Department of Agriculture, 1984, Map of Ouachita National Forest (west half), Arkansas and Oklahoma: U.S. Department of Agriculture Forest Service, Southern Region, scale 1:126,720.

U.S. Geological Survey, 1986, Land-use series, De Queen, Arkansas; Oklahoma: U.S.Geological Survey Open-File Report 85–0323, scale 1:100,000.

2. North Sylamore Creek near Fifty Six, Arkansas (Station 07060710)

a. U.S. Geological Survey topographic maps:

Calico Rock, Arkansas (1:24,000), 1964
Fifty Six, Arkansas (1:24,000), 1972, gaging station on this quadrangle
Norfork SE, Arkansas (1:24,000), 1980
Onia, Arkansas (1:24,000), 1980
Bull Shoals Lake, Arkansas-Missouri (1:100,000), 1985
Mountain View, Arkansas (1:100,000), 1983

b. Geologic maps:

McFarland, J.D., Bush, W.V., Wise, O.A., and Holbrook, Drew, 1979, A guidebook to the Ordovician-Mississippian rocks of north-central Arkansas: Arkansas Geological Commission Report GB–79–1, 25 p.

c. Soil surveys:

U.S. Department of Agriculture, 1983, Soils survey of Baxter and Marion Counties, Arkansas: U.S. Department of Agriculture Soil Conservation Service, 136 p.

Ward, L.B., 1983, Soil survey of Stone County, Arkansas: U.S. Department of Agriculture Soil Conservation Service, 152 p.

d. Miscellaneous maps:

Imes, J.L., and Emmett, L.F., 1994, Geohydrology of the Ozark Plateaus aquifer system in parts of Missouri, Arkansas, Oklahoma, and Kansas: U.S. Geological Survey Professional Paper 1414–D, 127 p.

U.S. Department of Agriculture, 1986, Map of Ozark National Forest, Sylamore Ranger District, Arkansas: U.S. Department of Agriculture Forest Service, Southern Region, scale 1:126,720.

U.S. Geological Survey, 1987, Land use and land cover and associated maps for Mountain View, Arkansas: U.S. Geological Survey Open-File Report 87–311, scale 1:100,000.

3. South Hogan Creek near Dillsboro, Indiana (Station 03276700)

a. U.S. Geological Survey topographic maps:

Dillsboro, Indiana (1:24,000), 1980, gaging station on this quadrangle
Milan, Indiana (1:24,000), 1980
Pierceville, Indiana (1:24,000), 1980
Greensburg, Indiana (1:100,000), 1986

b. Geologic maps:

Gray, H.H., Forsyth, J.L., Schneider, A.F., and Gooding, A.M., 1972, Regional geologic map no. 7, Cincinnati sheet, part B: Bloomington, Indiana Geological Survey, 1 sheet, scale 1:250,000.

c. Soil surveys:

McWilliams, K.M., 1985, Soil survey of Ripley County and part of Jennings County, Indiana: U.S. Department of Agriculture Soil Conservation Service, 125 p.

Nickell, A.K., 1981, Soil survey of Dearborn and Ohio Counties, Indiana: U.S. Department of Agriculture Soil Conservation Service.

d. Miscellaneous maps:

U.S. Department of Agriculture, 1986, Important farmland, Ripley County, Indiana: U.S. Department of Agriculture Soil Conservation Service, scale 1:50,000.

4. Elk Creek near Decatur City, Iowa (Station 06897950)

a. U.S. Geological Survey topographic maps:

Ellston, Iowa (1:24,000), 1981
Grand River, Iowa (1:24,000), 1981
Kellerton, Iowa (1:24,000), 1981
Lamoni North, Iowa (1:24,000), 1981, gaging station on this quadrangle
Leon, Iowa-Missouri (1:100,000), 1981
Mount Ayr, Iowa-Missouri (1:100,000), 1985

b. Geologic maps:

Arey, M.F., 1920, Geology of Ringgold County: Iowa Geological Survey Report, v. 27, p. 33–64, scale 1:125,000.

Bain, H.F., 1898, Geology of Decatur County: Iowa Geological Survey Report, v. 8, p. 255–314, scale 1:125,000.

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Hansen, R.E., 1992, Bedrock topography of southwest Iowa: U.S. Geological Survey Miscellaneous Investigations Series I–2230, scale 1:250,000.

Hershey, H.G., 1969, Geologic map of Iowa: Iowa Geological Survey, scale 1:500,000.

c. Soil surveys:

Boeckman, L.E., 1992, Soil survey of Ringgold County, Iowa: U.S. Department of Agriculture Soil Conservation Service, 230 p.

DeWitt, T.A., 1990, Soil survey of Decatur County, Iowa: U.S. Department of Agriculture Soil Conservation Service, 224 p.

d. Miscellaneous maps:

Cagle, J.W, and Heinitz, A.J., 1978, Water resources of south-central Iowa: Iowa Geological Survey Water Atlas 5, 97 p.

Cagle, J.W., and Steinhilber, W.L., 1967, Availability of ground water in Decatur County, Iowa: Iowa Geological Survey Water Atlas 2, 28 p.

5. Big Creek at Pollock, Louisiana (Station 07373000)

a. U.S. Geological Survey topographic maps:

Dry Prong, Louisiana (1:24,000), 1985
Pollock, Louisiana (1:24,000), 1985, gaging station on this quadrangle
Williana, Louisiana (1:24,000), 1985
Winnfield, Louisiana (1:100,000), 1986

b. Geologic maps:

Fisk, H.N., 1938, Geology of Grant and La Salle Parishes: Louisiana Geological Survey Bulletin 10, scale 1:62,500.

c. Soil surveys:

Kilpatrick, W.W., Henry, C.H., Jr., Ragus, J., Ardoin, A., Mason, P., and Williams, E., 1986, Soil survey of Grant Parish, Louisiana: U.S. Department of Agriculture Soil Conservation Service, 141 p.

d. Miscellaneous maps:

U.S. Department of Agriculture, 1983, Map of Kisatchie National Forest, Catahoula and Winn Ranger Districts, Louisiana: U.S. Department of Agriculture Forest Service, Southern Region, scale 1:126,720.

6. Washington Creek at Windigo, Michigan (Station 04001000)

a. U.S. Geological Survey topographic maps:

Sugar Mountain, Michigan (1:24,000), 1985
Windigo, Michigan (1:24,000), 1985, gaging station on this quadrangle
Isle Royale National Park, Michigan (1:62,500), 1987
Grand Portage, Minnesota-Michigan (1:100,000), 1985

b. Geologic maps:

Huber, N.K., 1973, Geologic map of Isle Royale National Park, Michigan: U.S. Geological Survey Miscellaneous Geologic Investigations Map I–796, scale 1:62,500.

c. Soil surveys:

U.S. Department of Agriculture, 1990, General soil map, Isle Royale National Park, Michigan: U.S. Department of Agriculture Natural Resources Conservation Service [formerly Soil Conservation Series], scale 1:190,080.

d. Miscellaneous maps:

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National Park Service, 1979, Map of Isle Royale National Park, Michigan: Washington, D.C., U.S. Department of the Interior National Park Service, scale 1:176,000.

7. Kawishiwi River near Ely, Minnesota (Station 05124480)

a. U.S. Geological Survey topographic maps:

Alice Lake, Minnesota (1:24,000), 1986
Beth Lake, Minnesota (1:24,000), 1986
Gabbro Lake, Minnesota (1:24,000), 1986

Kawishiwi Lake, Minnesota (1:24,000), 1986
Isabella Lake, Minnesota (1:24,000), 1986
Kekekabic Lake, Minnesota (1:24,000), 1986
Kelso Mountain, Minnesota (1:24,000), 1986
Lake Insula, Minnesota (1:24,000), 1986
Lake Polly, Minnesota (1:24,000), 1986
Ogishkemuncie Lake, Minnesota (1:24,000), 1986
Ojibway Lake, Minnesota (1:24,000), 1986, gaging station on this quadrangle
Perent Lake, Minnesota (1:24,000), 1986
Quadga Lake, Minnesota (1:24000), 1986
Snowbank Lake, Minnesota (1:24,000), 1986
Basswood Lake, Minnesota (1:100,000), 1978
Ely, Minnesota (1:100,000), 1978

b. Geologic maps:

Davidson, D.M., Jr., 1969, Geologic map of Kawishiwi Lake quadrangle, Lake and Cook Counties, Minnesota: Minnesota Geological Survey Miscellaneous Map M–7, scale 1:24,000.

———1969, Geologic map of Perent Lake quadrangle, Lake County, Minnesota: Minnesota Geological Survey Miscellaneous Map M–8, scale 1:24,000.

———1977, Reconnaissance geologic map of Alice Lake quadrangle, Cook County, Minnesota: Minnesota Geological Survey Miscellaneous Map M–33, scale 1:24,000.

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———1977, Reconnaissance geologic map of Kelso Mountain quadrangle, Cook County, Minnesota: Minnesota Geological Survey Miscellaneous Map M–27, scale 1:24,000.

———1977, Reconnaissance geologic map of Lake Polly quadrangle, Cook County, Minnesota: Minnesota Geological Survey Miscellaneous Map M–34, scale 1:24,000.

Green, J.C., 1982, Bedrock geology, Two Harbors sheet, Minnesota: Minnesota Geological Survey, scale 1:250,000.

c. Soil surveys:

Pettyman, D.H., 1978, Soil survey of Kawishiwi area, Minnesota—Parts of Lake and Cook Counties in Superior National Forest: U.S. Department of Agriculture Soil Conservation Service, 35 p.

d. Miscellaneous maps:

U.S. Department of Agriculture, 1987, Map of BWCA wilderness entry points: Washington, D.C., U.S. Department of Agriculture Forest Service, 22 × 35 cm.

———1976, Map of the boundary waters canoe area—Superior National Forest, Minnesota: Washington, D.C., U.S. Department of Agriculture Forest Service, 28 × 39 cm.

———1994, Superior National Forest, Minnesota: Milwaukee, Wisconsin, U.S. Department of Agriculture Forest Service, Eastern Region, scale 1:253,000.

8. North Fork Whitewater River near Minnesota (Station 05376000)

a. U.S. Geological Survey topographic maps:

Beaver, Minnesota (1:24,000), 1977
Chester, Minnesota (1:24,000), 1972
Elba, Minnesota (1:24,000), 1977, gaging station on this quadrangle
Millville, Minnesota (1:24,000), 1972
Plainview, Minnesota (1:24,000), 1972
Plainview SW, Minnesota (1:24,000), 1972
Rochester, Minnesota (1:100,000), 1989

b. Geologic maps:

Balaban, N.H., ed., 1988, Geologic atlas of Olmstead County, Minnesota: St. Paul, Minnesota Geological Survey, 9 plates containing 1. base map, 2. bedrock geology, 3. surficial geology, 4. depth to bedrock and bedrock topography, 5. sensitivity of the ground-water system to pollution, 6. sinkholes and sinkhole probability, 7. geology and well construction, 8. geology and well construction, and 9. geologic resources, scale 1:100,000.

c. Soil surveys:

Lueth, R.A., 1994, Soil survey of Winona County, Minnesota: U.S. Department of Agriculture Soil Conservation Service, 278 p.

9. Upper Twin Creek at McGaw, Ohio (Station 03237280)

a. U.S. Geological Survey topographic maps:

Buena Vista, Ohio-Kentucky (1:24,000), 1967
Pond Run, Ohio-Kentucky (1:24,000), 1967, gaging station on this quadrangle

b. Geologic maps:

Sheppard, R.A., 1964, Geology of the Portsmouth quadrangle, Kentucky-Ohio and parts of the Wheelersburg and New Boston quadrangles: U.S. Geological Survey Geologic Quadrangle Map GQ–312, scale 1:24,000.

c. Soil surveys:

McCleary, F.E., Feusner, M.M., and Hamilton, S.J., 1989, Soil survey of Scioto County, Ohio: U.S. Department of Agriculture Soil Conservation Service, 207 p.

d. Miscellaneous maps:

Ohio Department of Natural Resources, 1995, Map of Shawnee State Forest and Backpack Trail: Columbus, Ohio, Department of Natural Resources Division of Forestry, scale 1.5 inches = 2 miles.

10. Blue Beaver Creek near Cache, Oklahoma (Station 07311200)

a. U.S. Geological Survey topographic maps:

Meers, Oklahoma (1:24,000), 1975
Mount Scott, Oklahoma (1:24,000), 1975
Quanah, Oklahoma (1:24,000), 1975
Saddle Mountain, Oklahoma (1:24,000), 1956
Taupa, Oklahoma (1:24,000), 1970, gaging station on this quadrangle
Lawton, Oklahoma (1:100,000), 1981

b. Geologic maps:

Hoffman, M.G., 1930, Geology and petrology of the Wichita Mountains: Oklahoma Geological Survey Bulletin 52, 83 p., scale 1:63,360.

c. Soil surveys:

Mobley, H.L., 1967, Soil survey, Comanche County, Oklahoma: U.S. Department of Agriculture Soil Conservation Service, 58 p.

d. Miscellaneous maps:

Havens, J.S., 1977, Reconnaissance of the water resources of the Lawton quadrangle, southwestern Oklahoma: Oklahoma Geological Survey Hydrologic Atlas HA–6, 4 sheets, scale 1:250,000.

Havens, J.S., 1983, Reconnaissance of groundwater in vicinity of Wichita Mountains, southwestern Oklahoma: Oklahoma Geological Survey Circular 85, 13 p., sheet 1 of 2, geologic map, scale 1:250,000.

11. Kiamichi River near Big Cedar, Oklahoma (Station 07335700)

a. U.S. Geological Survey topographic maps:

Lynn Mountain, Oklahoma (1:24,000), 1981
Mountain Fork, Arkansas-Oklahoma (1:24,000), 1979
Page, Oklahoma (1:24,000), 1981, gaging station on this quadrangle,
Zafra, Oklahoma-Arkansas (1:24,000), 1979
Mena, Oklahoma (1:100,000), 1975

b. Geologic maps:

Briggs, Garrett, 1973, Geology of the eastern part of the Lynn Mountain Syncline, Le Flore County, Oklahoma: Oklahoma Geological Survey Circular 75, scale 1:42,240.

Seely, D.R., 1963, Structure and stratigraphy Rich Mountain area: Oklahoma Geological Survey Bulletin 101, scale 1:50,000.

c. Soil surveys:

Abernathy, E.J., and Olszewski, K.M., 1983, Soil survey of Le Flore County, Oklahoma: U.S. Department of Agriculture Soil Conservation Service, 211 p.

d. Miscellaneous maps:

U.S. Department of Agriculture, 1978, Ouachita National Forest, Kiamichi Division, Oklahoma: Atlanta, Georgia, U.S. Department of Agriculture Forest Service, Southern Region, scale 1:126,720.

———1994, Map of Ouachita National Forest, Arkansas-Oklahoma: Atlanta, Georgia, U.S. Department of Agriculture Forest Service, Southern Region, scale 1:500,000.

12. Devils River at Pafford Crossing near Comstock, Texas (Station 08449400)

a. U.S. Geological Survey topographic maps:

Big Lake, Texas (1:100,000), 1985
Camp Wood, Texas (1:100,000), 1985
Comstock, Texas (1:100,000), 1985, gaging station on this quadrangle
Devils Draw, Texas (1:100,000), 1985
Ozona, Texas (1:100,000), 1985
Rocksprings, Texas (1:100,000), 1985
San Angelo, Texas (1:100,000), 1985
Sonora, Texas (1:100,000), 1985
Del Rio, Texas (1:250,000), 1969
Sonora, Texas (1:250,000), 1978

b. Geologic maps:

Barnes, V.E., 1977, Geologic atlas of Texas, Del Rio sheet: The University of Texas at Austin, Bureau of Economic Geology, scale 1:250,000.

———1981, Geologic atlas of Texas, Sonora sheet: The University of Texas at Austin, Bureau of Economic Geology, scale 1:250,000.

Freeman, V.L., 1965, Geologic map of the Barkers Crossing quadrangle, Val Verde County, Texas: U.S. Geological Survey Miscellaneous Geologic Investigations Map I–440, scale 1:62,500.

Sharps, J.A., and Freeman, V.L., 1965, Geologic map of the Mouth of Pecos and Feely quadrangles, Val Verde County, Texas: U.S. Geological Survey Miscellaneous Geologic Investigations Map I–434, scale 1:62,500.

c. Soil surveys:

Golden, M.L., Gabriel, W.J., and Stevens, J.W., 1982, Soil survey of Val Verde County, Texas: U.S. Department of Agriculture Soil Conservation Service, 138 p.

Wiedenfeld, C.C., and McAndrew, J.D., 1968, Soil survey of Sutton County, Texas: U.S. Department of Agriculture Soil Conservation Service, 33 p.

d. Miscellaneous maps:

U.S. Geological Survey, 1985, Land-use series, Sonora, Texas: U.S. Geological Survey Open-File Report 85–65, scale 1:250,000.

13. South Fork Rocky Creek near Briggs, Texas (Station 08103900)

a. U.S. Geological Survey topographic maps:

Bachelor Peak, Texas (1:24,000), 1967, gaging station on this quadrangle
Joppa, Texas (1:24,000), 1967
Lake Victor, Texas (1:24,000), 1967
Llano, Texas (1:100,000), 1985

b. Geologic maps:

Texas Geological Survey, 1981, Geologic atlas of Texas, Llano sheet: The University of Texas at Austin, Bureau of Economic Geology, scale 1:250,000.

c. Soil surveys:

Dittemore, W.H., Jr., and Allison, J.E., 1979, Soil survey of Blanco and Burnet Counties, Texas: U.S. Department of Agriculture Soil Conservation Service, 116 p.

14. Popple River near Fence, Wisconsin (Station 04063700)

a. U.S. Geological Survey topographic maps:

Alvin SE, Wisconsin (1:24,000), 1970
Armstrong Creek, Wisconsin (1:24,000), 1980
Crandon NE, Wisconsin (1:24,000), 1965
Florence SW, Wisconsin (1:24,000), 1962, gaging station on this quadrangle
Lake Gordon, Wisconsin (1:24,000), 1980
Long Lake, Wisconsin (1:24,000), 1970
Long Lake SE, Wisconsin (1:24,000), 1970
Newald, Wisconsin (1:24,000), 1981
Iron Mountain, Michigan-Wisconsin (1:100,000), 1991

b. Geologic maps:

Clayton, Lee, 1986, Pleistocene geology of Florence County, Wisconsin: Wisconsin Geological and Natural History Survey, Information Circular 51, scale 1:200,000.

Simpkins, W.W., McCartney, M.C., and Mickelson, D.M., 1987, Pleistocene geology of Forest County, Wisconsin: Wisconsin Geological and Natural History Survey, Information Circular 61, scale 1:100,000.

Sims, P.K., 1990, Geologic map of Precambrian rocks of Iron Mountain and Escanaba 1 × 2 quadrangles, northeastern Wisconsin and northwestern Michigan: U.S. Geological Survey Miscellaneous Investigations Series Map I–2056, scale 1:250,000.

c. Soil surveys:

Hole, F.D., Olson, G.W., Schmude, K.O., and Milfred, C.J., 1962, Soil survey of Florence County, Wisconsin: Wisconsin Geological and Natural History Survey, Bulletin 4, Soil Series 59, scale 1:63,360.

d. Miscellaneous maps:

U.S. Department of Agriculture, 1995, The Nicolet National Forest: Rhinelander, Wisconsin, U.S. Department of Agriculture Forest Service, Eastern Region, scale 1:126,720.

Oakes, Edward, Field, S.J., and Seeger, L.P., 1973, The Pine-Popple River Basin—Hydrology of a wild river area, northeastern Wisconsin: U.S. Geological Survey Water-Supply Paper 2006, scale 1:250,000, 8 maps including bedrock geology, surficial deposits, soils, hydrogeochemistry, and forest cover.

APPENDIX B. 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
COSSATOT RIVER BASIN, ARKANSAS		
1	07340300	COSSATOT RIVER NR VANDERVOORT AR
2	342249094133300	LONG BR NR VANDERVOORT AR
3	342408094083200	CANEY CR NR VANDERVOORT AR
4	342440094155700	ROCK CR NR VANDERVOORT AR
5	342549094075000	SUGAR CR NEAR SHADY AR
6	342551094080000	ROCKY MTN BR NR SHADY AR
7	342615094144200	NORTH FORK LITTLE BRUSHY CR NR SHADY AR
8	342615094144300	LITTLE BRUSHY CR NR SHADY AR
9	342643094060300	MINE CR NR SHADY AR
10	342659094071000	SULPHUR CR NR SHADY AR
11	342704094072200	COSSATOT R AT SHADY AR
12	342737094120500	BOAR TUSK MTN BR NR SHADY AR
13	342739094111700	SUGARTREE MTN BR NR SHADY AR
NORTH SYLAMORE CREEK, ARKANSAS		
1	07060710	NORTH SYLAMORE CREEK NR FIFTY SIX AR
2	360254092162200	BARKSHED CREEK AT MOUTH AR
3	360146092144200	BEAR PEN CREEK NR MOUTH AR
4	360107092150400	CAP FORK AT MOUTH AR
5	360256092162100	COLE FORK AT MOUTH AR
6	355943092124700	GUNNER CREEK AT MOUTH AR
7	360228092151000	SPRING BEECH CREEK AT MOUTH AR
8	360256092153100	STEWART FORK AT MOUTH AR
SOUTH HOGAN CREEK BASIN, INDIANA		
1	03276700	SOUTH HOGAN CR NR DILLSBORO IN
2	390241085031600	WHITAKER CR ABOVE DILLSBORO IN
3	390246085034400	S HOGAN CR AB CHANCE BRANCH NR DILLSBORO IN
4	390456085074700	S HOGAN CR AT HWY 101 NR MILAN IN
5	390500085095100	S HOGAN CR AT 525 EAST RD NR STRINGTOWN IN
6	390502085092800	NORTHEAST TRIB OF S HOGAN CR NR STRINGTOWN IN
7	390550085100300	S HOGAN CR AB HOG FARM NR STRINGTOWN IN
8	390620085053700	WHITAKER CR BLW MOORES HILL IN
9	390706085073700	MILAN CR BELOW WWTP AT MILAN IN
10	390715085073500	MILAN CR AB WWTP AT MILAN IN
ELK CREEK BASIN, IOWA		
1	06897950	ELK CR NR DECATUR CITY IA
2	404337093580900	WEST ELK CR NR DECATUR CITY IA
3	404501094002800	SOUTH FORK WEST ELK CR NR DECATUR CITY IA
4	404504094002600	NORTH FORK WEST ELK CR NR DECATUR CITY IA
5	404343093573900	LANDFILL CR NR DECATUR CITY IA
6	404348093564000	ELK CR AT HWY 2 NR DECATUR CITY IA
7	404611093590600	ELK CR IN SECT 17 NR DECATUR CITY IA
8	404723093585800	ELK CR IN SECT 8 NR DECATUR CITY IA
9	404932094005800	UPPER ELK CR NR DECATUR CITY IA

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
BIG CREEK BASIN, LOUISIANA		
1	07373000	BIG CR NR POLLOCK LA
2	313153092262300	HAW CR NR POLLOCK LA
3	313224092275500	DYSON CR NR POLLOCK LA
4	313232092243100	UNNAMED TRIB NR BIG CR NR POLLOCK LA
5	313348092311200	SEWAGE PLANT TRIB NR DRY PRONG LA
6	313406092255300	FLEM BR NR POLLOCK LA
7	313419092305800	BIG CR NR DRY PRONG LA
8	313440092273100	SOCIA BR NR POLLOCK LA
9	313441092321900	UNNAMED TRIB AT DRY PRONG LA
10	313522092290800	DRY PRONG BELOW BEAR BR NR POLLOCK LA
11	313641092300800	DRY PRONG NR DRY PRONG LA
WASHINGTON CREEK BASIN, MICHIGAN		
1	04001000	WASHINGTON CR AT WINDIGO ISLE ROYALE MI
2	475547089074700	TWICE TRIED TRIB ISLE ROYALE MI
3	475601089075000	TRIB AT TRAIL CROSSING ISLE ROYALE MI
4	475608089075300	BURN AREA TRIB ISLE ROYALE MI
5	475553089074800	FIRST DAY TRIB ISLE ROYALE MI
6	475735089041600	GRASSY TRIB ISLE ROYALE MI
7	475751089033900	SWAMPY TRIB ISLE ROYALE MI
8	475613089051900	N FORK WASHINGTON CR ISLE ROYALE MI
9	475611089051700	S FORK WASHINGTON CR ISLE ROYALE MI
KAWISHIWI RIVER BASIN, MINNESOTA		
1	05124480	KAWISHIWI R NR ELY MN
2	475436091303600	PAGAMI CREEK NR ELY MN
3	475558091292100	KAWISHIWI R BLW BOAT RAMP NR ELY MN
4	475504091250500	BRIDGE LAKE OUTFLOW NR ELY MN
5	475303091203300	AHMOO CREEK NR ELY MN
6	475357091200100	INSULA LAKE OUTFLOW NR ELY MN
7	475550091144500	KAWISHIWI R AB INSULA LAKE NR ELY MN
8	475527091122000	KAWISHIWI R AB ALICE LAKE NR ELY MN
9	475730091161800	KIANA LAKE OUTFLOW NR ELY MN
10	475946091124600	FRASER LAKE OUTFLOW NR ELY MN
11	475800091094600	TRAPLINE LAKE OUTFLOW NR ELY MN
12	475702091064900	LOUSE R AB MALBERG LAKE NR ELY MN
13	475620091025900	BARTO CR NR ELY MN
14	475210090585500	GRACE LAKE OUTFLOW NR ELY MN
15	475256091013200	WHELP CR NR ELY MN
16	475355091050900	PHOEBE R AB LAKE POLLY NR ELY MN
17	475344091065700	KAWISHIWI R AB LAKE POLLY NR ELY MN
18	475228091080500	BASKATONG LAKE OUTFLOW NR ELY MN
19	474206091061500	KAWISHIWI LAKE INFLOW NR ELY MN
NORTH FORK WHITEWATER RIVER BASIN, MINNESOTA		
1	05376000	N FORK WHITEWATER R NR ELBA MN
2	440350092161400	N FORK WHITEWATER R NR VIOLA MN
3	440520092165900	PIPELINE TRIB NR VIOLA MN

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
		NORTH FORK WHITEWATER RIVER BASIN, MINNESOTA—Continued
4	440535092163400	N FORK WHITEWATER R NR RR BEND NR VIOLA MN
5	440554092074700	LOGAN BRANCH NR ELBA MN
6	440603092072900	N FORK WHITEWATER R AB LOGAN BR NR ELBA MN
7	440721092193800	DRY CREEK ABOVE EGLIN MN
8	440743092141700	N FORK WHITEWATER R BLW ELGIN MN
9	440806092081400	PLAINVIEW TRIB NR ELBA MN
		UPPER TWIN CREEK BASIN, OHIO
1	03237280	UPPER TWIN CR AT MCGAW OH
2	383911083130000	UPPER TWIN CR BLW STABLE CUT NR MCGAW OH
3	383935083133200	EAST FORK NR MCGAW OH
4	383941083135600	UPPER TWIN CR AB EAST FORK NR MCGAW OH
5	384137083154100	BRUSHY FORK NR MCGAW OH
		BLUE BEAVER CREEK BASIN, OKLAHOMA
1	07311200	BLUE BEAVER CR NR CACHE OK
2	343946098330200	KOEHLER HILL TRIB NR CACHE OK
3	344050098325000	NEWT JONES HILL TRIB NR MEDICINE PK OK
4	344214098353300	BLUE BEAVER CR BELOW KETCH L NR THE HOLY CITY OK
5	344216098342700	MT SHERMAN TRIB NR THE HOLY CITY OK
6	344224098342700	KETCH RD TRIB NR THE HOLY CITY OK
7	344327098355700	BLUE BEAVER CR BELOW JED JOHNSON L OK
		KIAMICHI RIVER BASIN, OKLAHOMA
1	07335700	KIAMICHI R NR BIG CEDAR OK
2	343623094310200	PIGEON CR AT FR 6026 NR MTN FORK AR
3	343813094354800	RATTLESNAKE CR NR BIG CEDAR OK
4	343822094344700	HORSE BONE CR NR BIG CEDAR OK
5	343929094355100	PASHUBBE CR NR BIG CEDAR OK
6	344004094320900	PIDDLY CR NR MTN FORK AR
7	344020094305800	KIAMICHI R ABOVE SCENIC DR TRIB NR MTN FORK AR
8	344045094310500	SCENIC DR TRIB NR MTN FORK AR
		DEVILS RIVER BASIN, TEXAS
1	08449400	DEVILS R AT PAFFORD CROSSING NR COMSTOCK TX
2	295341100594100	DEVILS R AB DOLAN FALLS NR COMSTOCK TX
3	295543100591600	JOSE MARIA SPRING NR COMSTOCK TX
4	295755101085000	DEVILS R AT BAKER CROSSING NR COMSTOCK TX
5	300824101071100	DEVILS R AT JUNO TX
		SOUTH FORK ROCKY CREEK BASIN, TEXAS
1	08103900	S FORK ROCKY CR NR BRIGGS TX
2	305420098060200	S FORK ROCKY CR AT MAIN RD NR BRIGGS TX
3	305431098071100	FENCE CR NR BRIGGS TX
4	305459098040500	OVER ROAD TRIB NR BRIGGS TX
5	305509098084300	GRAVEL PIT TRIB NR BRIGGS TX
6	305611098081600	SUNNYLANE CR NR BRIGGS TX
7	305631098095800	COUBLE CR NR BRIGGS TX

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
		POPPLE RIVER BASIN, WISCONSIN
1	04063700	POPPLE R NR FENCE WI
2	454440088281100	MUD CR NR FENCE WI
3	454558088314300	MORGAN CR NR FENCE WI
4	454312088341600	SIMPSON CR NR FENCE WI
5	454439088353200	S POPPLE R NR FENCE WI
6	454734088362200	RILEY CR NR FENCE WI
7	454729088405500	L POPPLE R AT POPPLE R WI
8	454426088425900	L POPPLE R AT NEWALD WI
9	454743088452300	POPPLE R NR GENERAL MCARTHUR WHITE PINE WI
10	454727088491100	N POPPLE R AT HWY 55 WI
11	454449088483100	UPPER POPPLE R NR HWY 55 WI

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

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

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