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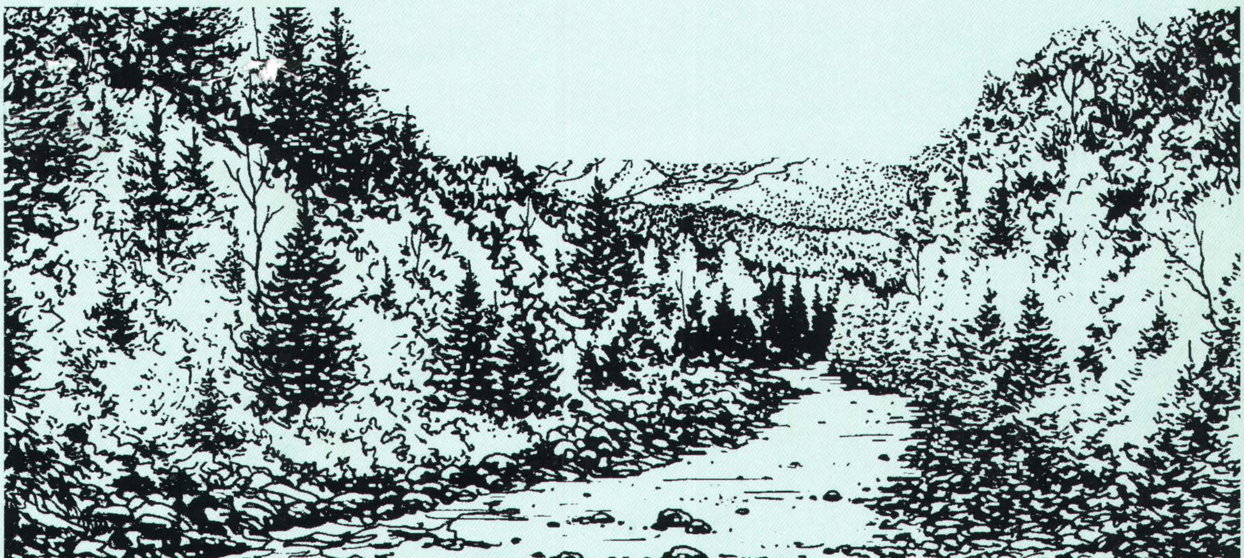
Environmental Characteristics and Water Quality of Hydrologic Benchmark Network Stations in the West–Central United States, 1963–95

Circular 1173–C



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

By Melanie L. Clark, Cheryl A. Eddy-Miller, *and* M. Alisa Mast

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

Robert M. Hirsch

Robert M. Hirsch
Chief Hydrologist

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
cubic meter per second (m^3/s)	35.31	cubic foot per second
kilometer (km)	0.6214	mile
liter (L)	0.2642	gallon (US)
meter (m)	3.28	foot
microequivalent per liter calcium (µeq/L)	0.0200	milligram per liter calcium
microequivalent per liter magnesium (µeq/L)	0.0122	milligram per liter magnesium
microequivalent per liter sodium (µeq/L)	0.0230	milligram per liter sodium
microequivalent per liter potassium (µeq/L)	0.0391	milligram per liter potassium
microequivalent per liter ammonium (µeq/L)	0.0140	milligram per liter ammonium (as N)
microequivalent per liter alkalinity (µeq/L)	0.0500	milligram per liter alkalinity (as $CaCO_3$)
microequivalent per liter sulfate (µeq/L)	0.0480	milligram per liter sulfate
microequivalent per liter chloride (µeq/L)	0.0354	milligram per liter chloride
microequivalent per liter nitrite plus nitrate (µeq/L)	0.0140	milligram per liter nitrite plus nitrate (as N)
micromole per liter silica (µmol/L)	0.0601	milligram per liter silica

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

$$°F = 9/5\ (°C) + 32.$$

Additional abbreviations and acronyms used in this report:

microsiemens per centimeter at 25 degrees Celsius (µS/cm)
micrometer (µm)
Atomic Absorption (AA)
EStimate TREND (ESTREND)
Hydrologic Benchmark Network (HBN)
Inductively Coupled Plasma (ICP)
LOcally WEighted Scatter-plot Smoothing (LOWESS)
National Atmospheric Deposition Program (NADP)
National Water Information System (NWIS)
National Water Quality Lab (NWQL)
U.S. Geological Survey (USGS)
Volume-Weighted Mean (VWM)

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

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Abstract

The U.S. Geological Survey Hydrologic Benchmark Network program 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 a reference for separating natural from manmade changes in other streams. Most stations were established by the late 1960's and, after a few changes in the 1970's, the network eventually consisted of 58 stations in 39 States. This report describes the environmental characteristics and water-quality characteristics of 14 benchmark basins in the West-Central United States. The basins and physiographic provinces are as follows: Kings Creek, Kansas, Beaver Creek, North Dakota, and the Little Vermillion River, South Dakota, in the Central Lowland Province; Rock Creek, Montana, Dismal River, Nebraska, Bear Den Creek, North Dakota, and Castle Creek, South Dakota, in the Great Plains Province; Halfmoon Creek, Colorado, Vallecito Creek, Colorado, Rio Mora, New Mexico, and Encampment River, Wyoming, in the Southern Rocky Mountains Province; Cache Creek, Wyoming, in the Middle Rocky Mountains Province; Swiftcurrent Creek, Montana, in the Northern Rocky Mountains Province; and Mogollon Creek, New Mexico, in the Basin and Range Province. The information in this report was compiled to aid in the interpretation and application of historical water-quality data collected through the Hydrologic Benchmark Network program.

The site characteristics are variable for Hydrologic Benchmark Network stations in the West-Central United States. Land-use activities in the basins range from recreational use and timber harvesting on publicly owned forested land to agriculture and minor residential development on privately owned land. The streams drain a variety of geologic settings, including Precambrian metamorphic and igneous rocks, Paleozoic sedimentary rocks, and Tertiary volcanic rocks. Vegetation ranges from alpine tundra and subalpine coniferous forest to tallgrass prairie. The streamflow characteristics of the stations are variable. Some of the sites are dominated by steady ground-water flows, and others have snow-dominated hydrographs where a large part of the flow results from the melting of the annual snowpack.

Stream-water chemistry at the Hydrologic Benchmark Network stations in the West-Central United States appears to be controlled by the interaction of mildly acidic precipitation with underlying soils and bedrock and evaporative processes. Most of the stream waters are alkaline, calcium bicarbonate types. With few exceptions, temporal trends generally could not be identified at most stations for most of the flow-adjusted concentrations of calcium, magnesium, sodium, potassium, alkalinity, chloride, and silica. A few common trends were observed across stations, including downward trends in sulfate and upward trends in pH at several stations. These trends are consistent with trends in regional precipitation chemistry and regional declines in atmospheric sulfur-dioxide

emissions. Interpretation of the historical sulfate and pH data, however, is complicated by changes in analytical methods or field instrumentation, respectively, over the study period.

INTRODUCTION

In 1962, L.B. Leopold, then Chief Hydrologist of the U.S. Geological Survey (USGS), proposed to establish a network of hydrologic benchmarks to make long-term measurements of various hydrologic characteristics in areas that were free from the effects of human activities (Leopold, 1962). The main purpose of the network was to provide a long-term hydrologic data base to be used to study temporal trends of hydrologic characteristics and to serve as a reference for separating natural from manmade changes on other streams. The Hydrologic Benchmark Network (HBN) was started in 1963, and sites were selected on the basis of four criteria: (1) Little or no manmade storage, regulation, or diversion was to exist in the basin; (2) ground water in the basin was not to be affected by pumping from wells; (3) conditions were to be favorable for accurate measurement of streamflow and water quality; and (4) the potential was 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 58 stations—57 streamflow-gaging stations and 1 lake-stage station—in 39 States (fig. 1). Several modifications to the HBN program occurred in the 1990's. Eight stations were discontinued and two stations were replaced for the following four reasons: (1) The sites were operated as discharge-only stations during the period of record (Tallulah River, Ga.; Swiftcurrent Creek, Mont.; and Little Vermillion River, S. Dak.); (2) site conditions resulted in poor discharge records 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 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). In addition, water-quality sampling frequency was decreased at all HBN stations in October 1995, and sampling was discontinued in October 1996 owing to funding limitations. Currently (2000), discharge continues to be measured at the 49 remaining HBN streamflow-gaging stations.

The original network design to study temporal trends was first evaluated by testing 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-chemistry 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 sampling and analytical methods, could have caused the observed trends. Some of the method changes are documented in Alexander and others (1996). However, documentation of environmental characteristics was minimal for most HBN stations because characteristics other than stream discharge and chemistry were seldom recorded for the stations. In addition, if the HBN is to be useful as a reference for separating natural from manmade changes in other streams, an understanding of the natural and human factors that affect water quality in these basins is needed. About 1990, the USGS began an evaluation of the HBN program to provide detailed information for sites within the network and to determine the suitability of each site with regard to the original design criteria. Synoptic sampling was conducted to investigate within-basin variability in surface-water chemistry at selected tributary streams, lakes, or springs in each basin.

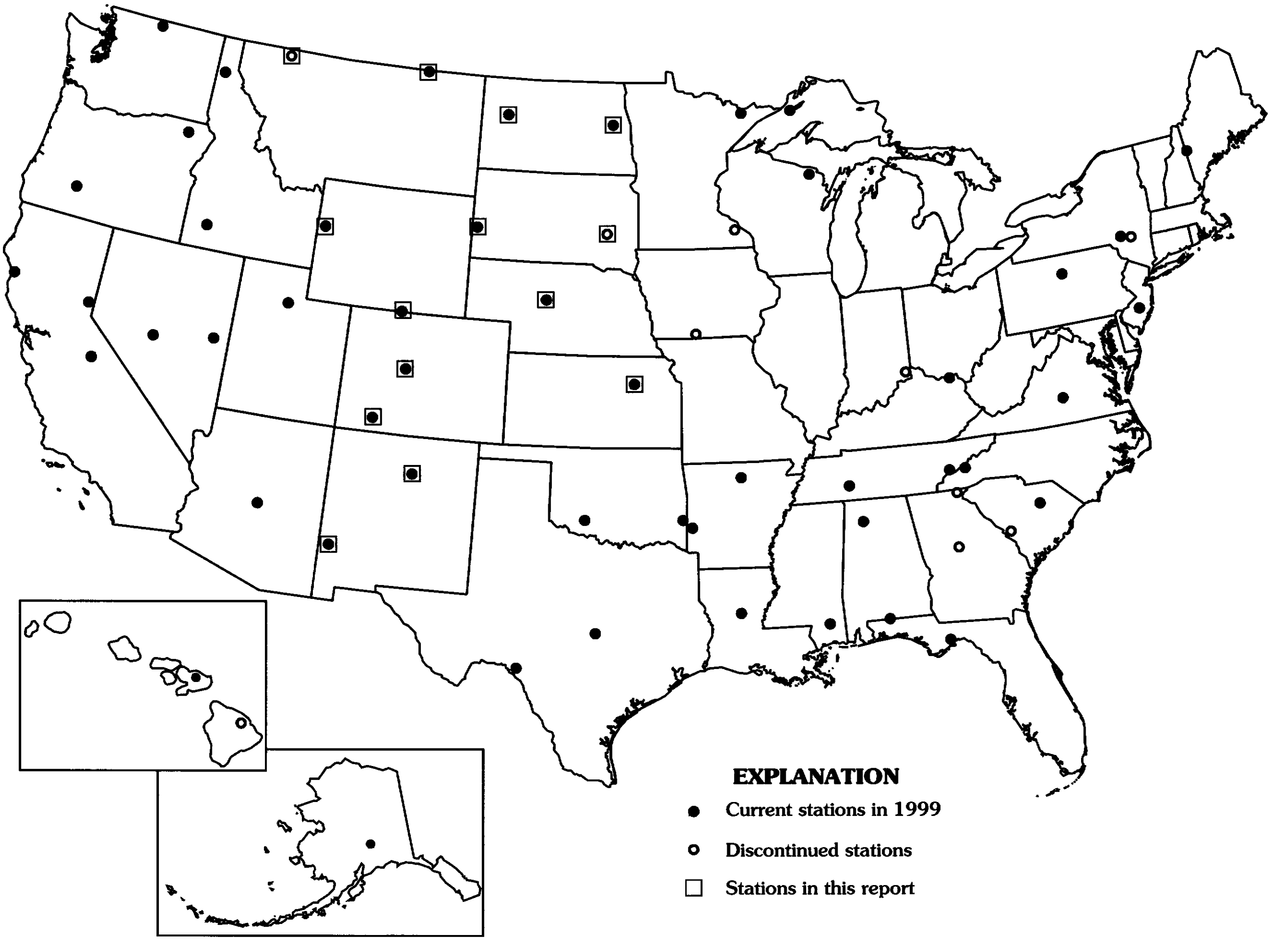

Figure 1. Map showing locations of current and discontinued stations in the Hydrologic Benchmark Network.

Purpose and Scope

The purpose of this report is to describe the environmental characteristics and water quality of HBN stream basins within the West-Central United States. These stream basins, in order of presentation, are: Halfmoon Creek near Malta, Colo.; Vallecito Creek near Bayfield, Colo.; Kings Creek near Manhattan, Kans.; Rock Creek below Horse Creek near International Boundary, Mont.; Swiftcurrent Creek at Many Glacier, Mont.; Dismal River near Thedford, Nebr.; Mogollon Creek near Cliff, N. Mex.; Rio Mora near Tererro, N. Mex.; Bear Den Creek near Mandaree, N. Dak.; Beaver Creek near Finley, N. Dak.; Castle Creek above Deerfield Reservoir, S. Dak.; Little Vermillion River near Salem, S. Dak.; Cache Creek near Jackson, Wyo.; and Encampment River above Hog Park Creek near Encampment, Wyo. This report has 14 sections, one for each HBN station, in which the following information is presented: (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 that were collected at the streamflow-gaging station in each basin for the period of record, including data quality, water-quality characteristics, time-series trends, and precipitation chemistry at nearby precipitation stations; and (3) an interpretation of within-basin variability in surface-water chemistry at selected tributary streams, lakes, or springs in each basin. Site names and numbers of the synoptic sampling locations are contained in Appendix A. The sections for Swiftcurrent Creek and Little Vermillion River do not include a complete analysis of historical water-quality records because water-quality samples were not routinely collected at these stations. 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. In addition to the water-quality data, a list of reference maps was compiled for each study area, including 7.5-minute quadrangle maps, soil surveys, geologic maps, and other miscellaneous maps. This information is presented by study area in Appendix B.

Previous Work

Although the HBN has been in existence for more than 30 years, only a few studies have undertaken an assessment or analysis of the entire network data base. 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 characteristics in undisturbed HBN stations with those in major streams that drain similar hydrologic regions of the United States. Smith and Alexander (1983) examined time trends in pH, alkalinity, and sulfate at 47 HBN stations to investigate the long-term effects of acidic deposition on water quality in undeveloped basins. Lins (1986) used a principal component analysis to determine whether patterns in stream sulfate at 30 stations in the network could be used as analogues for regional patterns in sulfate deposition from the atmosphere. Lawrence (1987) presented a compilation of streamflow characteristics for 58 HBN stations, including an analysis of time trends in streamflows for the period of record through 1980. Process-level investigations and site-specific investigations have been conducted on only a few individual network basins, and those have been primarily in the Eastern United States (Hainly and Ritter, 1986; Johnsson and Barringer, 1993; Lord and others, 1990). Campbell and Turk (1988) investigated the effects of sulfur-dioxide emissions on stream chemistry at sites in the Western United States. The HBN basins included in their study were Halfmoon Creek, Colo., Vallecito Creek, Colo., Dismal River, Nebr., Rio Mora, N. Mex., Castle Creek, S. Dak., and Encampment River, Wyo. The results of that study indicated that short-term (year-to-year) fluctuations in stream sulfate loads in stream water were evident on a regional scale, but they were primarily controlled by regional precipitation patterns rather than regional sulfur-dioxide emissions fluctuations.

Acknowledgments

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METHODS

Historical water-quality records for stations in the HBN are available from the USGS National Water Information System (NWIS). Water measurements made at most HBN stations have included a comprehensive suite of characteristics, including physical properties, major dissolved constituents, trace elements, radiochemical constituents, nutrients, and biological constituents (Alexander and others, 1996). A subset of the characteristics, including physical properties, major dissolved constituents, and nutrients, were compiled for this report. The parameter codes used in NWIS and the periods of record for the 19 physical properties and water-quality constituents retrieved are listed in table 1. In this report, nitrite plus nitrate is assumed to be equivalent to nitrate. The following modifications were made to the data before statistical and graphical analyses were performed: (1) Alkalinity values stored under parameter code 00410 before 1981 were combined with alkalinity values stored under parameter code 90410 to obtain a continuous record of laboratory alkalinity values; (2) dissolved and total nitrite plus nitrate and dissolved and total ammonium were combined to obtain more continuous records of these two nutrient species; (3) concentrations reported as "less than" were

Table 1. National Water Information System codes and periods of record of physical and water-quality parameters retrieved for this report

Parameter	Parameter code	Period of record
Discharge, instantaneous	00060, 00061	Entire period
Specific conductance, field	00095	Entire period
Specific conductance, laboratory	90095	After 1980
pH, field	00400	Entire period
pH, laboratory	00403	After 1980
Calcium, dissolved	00915	Entire period
Magnesium, dissolved	00925	Entire period
Sodium, dissolved	00930	Entire period
Potassium, dissolved	00935	Entire period
Ammonium, dissolved	00608, 71846	1969–79,[b] after 1980
Ammonium, total	00610, 71845	1971–79,[b] 1981–82, 1986–92
Alkalinity, laboratory	00410,[a] 90410, 00417	Entire period
Alkalinity, field	00410,[a] 39086, 00419	After 1984
Bicarbonate, field	00440, 00450, 00453	1965–78,[b] after 1985
Sulfate, dissolved	00945	Entire period
Chloride, dissolved	00940	Entire period
Nitrite plus nitrate, dissolved	00631	1974–77,[b] after 1979
Nitrite plus nitrate, total	00630	After 1971[b]
Silica	00955	Entire period

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

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

set equal to the detection limit value for the time-series plots and ion-balance calculations; (4) values reported as zero in the data base were retained in the data files but were set to the minimum reporting level for summary statistics; (5) concentrations were converted from units of milligrams per liter to microequivalents per liter except silica, which was 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. The period of record for all stations extends through water year 1995. 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 concentration minus the total anion concentration divided by the total concentration in solution. The cation concentration was calculated as the sum of the hydrogen ion (calculated from field pH measurements), calcium, magnesium, sodium, and potassium concentrations, and the anion concentration as the sum of the laboratory alkalinity, chloride, and sulfate concentrations. The inorganic nitrogen species—nitrite plus nitrate and ammonium—were excluded from the calculation because neither of these species was measured over the entire period of record. Omission of these constituents from the ion balance is not expected to produce bias because concentrations typically were at or near the detection limits of the analytical methods. Ion balance was calculated only for samples with complete chemical analyses. The water-quality records also were inspected for bias that may have been introduced by sampling or analytical methods and were compared to the chronology of activities and analytical methods that were used by USGS laboratories (Durum, 1978; Fishman and others, 1994) and to operational guidelines for the HBN that were documented in a series of USGS technical memoranda, which are available at URL http://water.usgs.gov/admin/memo/. Interpretation of the data was aided by the use of time-series plots. Summary statistics of physical properties and water-quality constituents were calculated from the historical water-quality records at each station. Spearman rank correlation coefficients (rho values) were calculated to measure the strength of monotonic associations among discharge and the major solutes. Values of rho fall between −1.0 to 1.0, with a value less than zero indicating an inverse correlation between constituents, a value of zero indicating no correlation between constituents, and a value greater than zero indicating a positive correlation between constituents. Correlation coefficients were calculated for the data collected beginning in 1980 to reduce some of the analytical method-related effects on the data set.

Temporal trends in stream discharge and water-quality constituents were calculated by using the computer program, Estimate Trend (ESTREND), which was written by Schertz and others (1991). ESTREND is a monotonic trend procedure that 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 (less than values). The seasonal Kendall test for censored data was used when more than 5 percent of the observations were censored. In cases where a large number of detected values fell between multiple reporting limits, as often occurred for the nitrite plus nitrate concentrations, the Tobit test was used to calculate the trend. Trends were calculated by using unadjusted concentrations and flow-adjusted concentrations. Removal of flow-related variability in the water-quality data not only improved the power of the statistical test but decreased the possibility that the observed trends were an artifact of natural hydrologic variability (Hirsch and others, 1982; Schertz and others, 1991, 1994). Automated procedures are provided in ESTREND to adjust concentrations for flow-related variability. Flow adjustment was not made if the concentration-discharge model was not significant at the 90-percent confidence level (significance level $\alpha = 0.10$) (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. Three 4-month seasons were used for the Rock Creek and Beaver Creek trend tests, and two 6-month seasons were used for the Kings Creek trend test. Trends were considered statistically significant at the 99-percent confidence level ($\alpha = 0.01$). The ESTREND procedure also computes a trend slope, which represents the median rate of change in discharge or concentrations for the selected period of record. A locally weighted scatterplot smoothing technique (LOWESS), which graphically smooths the pattern of the data over time (Schertz and others, 1991), was applied on the time-series plots only in cases where the trend in the unadjusted concentrations was statistically significant. The entire period of record for a station was used, if possible, for the trend test because of the large data requirements for trend testing.

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 nearly 200 stations nationwide that provides long-term records of weekly precipitation chemistry. Sampling, analytical, and quality-assurance protocols for the NADP network are summarized in Peden (1983). Annual volume-weighted mean (VWM) concentrations for the NADP stations presented in this report were obtained at URL http://nadp.sws.uiuc.edu/.

In addition to the historical water-quality records and NADP data, synoptic samples were collected in the HBN basins during the late 1980's (Halfmoon Creek HBN Basin only) and the early 1990's from several main-stem sites or major tributary streams, lakes, or springs in each basin. This supplementary study was conducted 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 generally 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, specific conductance, pH, 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. 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. (Fishman and Friedman, 1989). Chemical data for the synoptic samples also are stored in NWIS.

ENVIRONMENTAL CHARACTERISTICS AND WATER QUALITY OF HYDROLOGIC BENCHMARK NETWORK STATIONS

A series of U.S. Geological Survey Circular reports describe the environmental characteristics and water quality at all of the HBN stations in the United States. Each report of the series is assigned a single circular series number beginning with Circular 1173 and followed by a letter. The titles of the reports in this circular series are: Environmental Characteristics and Water Quality of Hydrologic Benchmark Network Stations in the Eastern United States, 1963–95 (Circular 1173–A), Environmental Characteristics and Water Quality of Hydrologic Benchmark Network Stations in the Midwestern United States, 1963–95 (Circular 1173–B), Environmental Characteristics and Water Quality of Hydrologic Benchmark Network Stations in the West-Central United States, 1963–95 (this report, Circular 1173–C), and Environmental Characteristics and Water Quality of Hydrologic Benchmark Network Stations in the Western United States, 1963–95 (Circular 1173–D).

Halfmoon Creek near Malta, Colorado (07083000)

Site Characteristics and Land Use

The Halfmoon Creek HBN Basin is in the Southern Rocky Mountains physiographic province (Fenneman, 1946) in central Colorado (fig. 2). Halfmoon Creek drains 61 km^2 of rugged, mountainous terrain of the Sawatch Range. Elevations in the basin range from 2,969 to 4,399 m. The basin drains parts of Mount Elbert and Mount Massive, which are the second and third highest peaks, respectively, in the conterminous United States. The HBN station is about 6.9 km southwest of Malta, Colo., at a latitude of 39°10'20" and a longitude of 106°23'19". The ecoregion of the basin is classified as the Southern Rocky Mountain Steppe-Open Woodland-Coniferous Forest-Alpine Meadow Province (Bailey, 1995). The basin contains forested montane and subalpine zones. The northern slopes of the basin are heavily forested, whereas the south-facing slopes have sparse vegetation (W.A. Swensen, U.S. Geological Survey, written commun., 1997). Timber species in the lower part of the basin include lodgepole pine, Engelmann spruce, and fir. The upper basin (above 3,600 m) is alpine tundra.

Halfmoon Creek is a perennial stream that drains into Lake Fork, which is tributary to the Arkansas River. Several small natural lakes and ponds are located in the basin. The hydrology is largely controlled by melting of the annual snowpack, and mean monthly discharge ranges from about 0.10 m^3/s in February to 3.6 m^3/s in June (Crowfoot and others, 1996a). Variations in precipitation and temperature occur in the basin primarily because of the range in elevation. Average annual precipitation at the Leadville weather station in Lake County (about 10 km northeast of the HBN station) is about 32 cm. The weather station is at about the same elevation (about 3,000 m) as the HBN station. Annual precipitation at higher elevations in the basin is closer to 100 cm (Cobb and Biesecker, 1971) and is predominantly in the form of snow. Average annual runoff is about 40 cm (Crowfoot and others, 1996a). The climate of the area is characterized by cold winters and mild summers. Mean monthly temperatures at the weather station during the period 1976–95 ranged from –8.9°C in January to 12.2°C in July (National Climatic Data Center, 1996).

The geology of the upper basin is dominated by metamorphic rocks of Precambrian age, including biotite gneiss, schist, and migmatite (Van Loenen, 1985). The biotite gneiss is the most abundant rock type. Schist is next most abundant and contains varying amounts of sillimanite, garnet, hornblende, and muscovite. The remaining rock types, in order of decreasing abundance, are migmatite; quartz-rich, feldspathic gneiss; and calc-silicate gneiss. Small amounts of pegmatite also are present. Small intrusive masses of rhyolitic composition and small dikes of similar composition cut across the gneiss. Mineral deposits occur in brecciated zones of the intrusive rock. Some small vein deposits have high mineral-resource potential for gold, silver, lead, and zinc (Van Loenen and others, 1989). Talus from landslides and avalanche debris accumulate below steep ridges, whereas glacial material is deposited in the lower basin. Glacial deposits contain boulder till and gravel in moraines and outwash. The soil on glacial deposits on the mountains (slopes from 3 to 35 percent) generally is gravelly, sandy loam (U.S. Department of Agriculture, 1975a).

The Halfmoon Creek Basin lies entirely within Lake County and the San Isabel National Forest. The northern part of the basin lies within the Mount Massive Wilderness Area. Access to the lower part

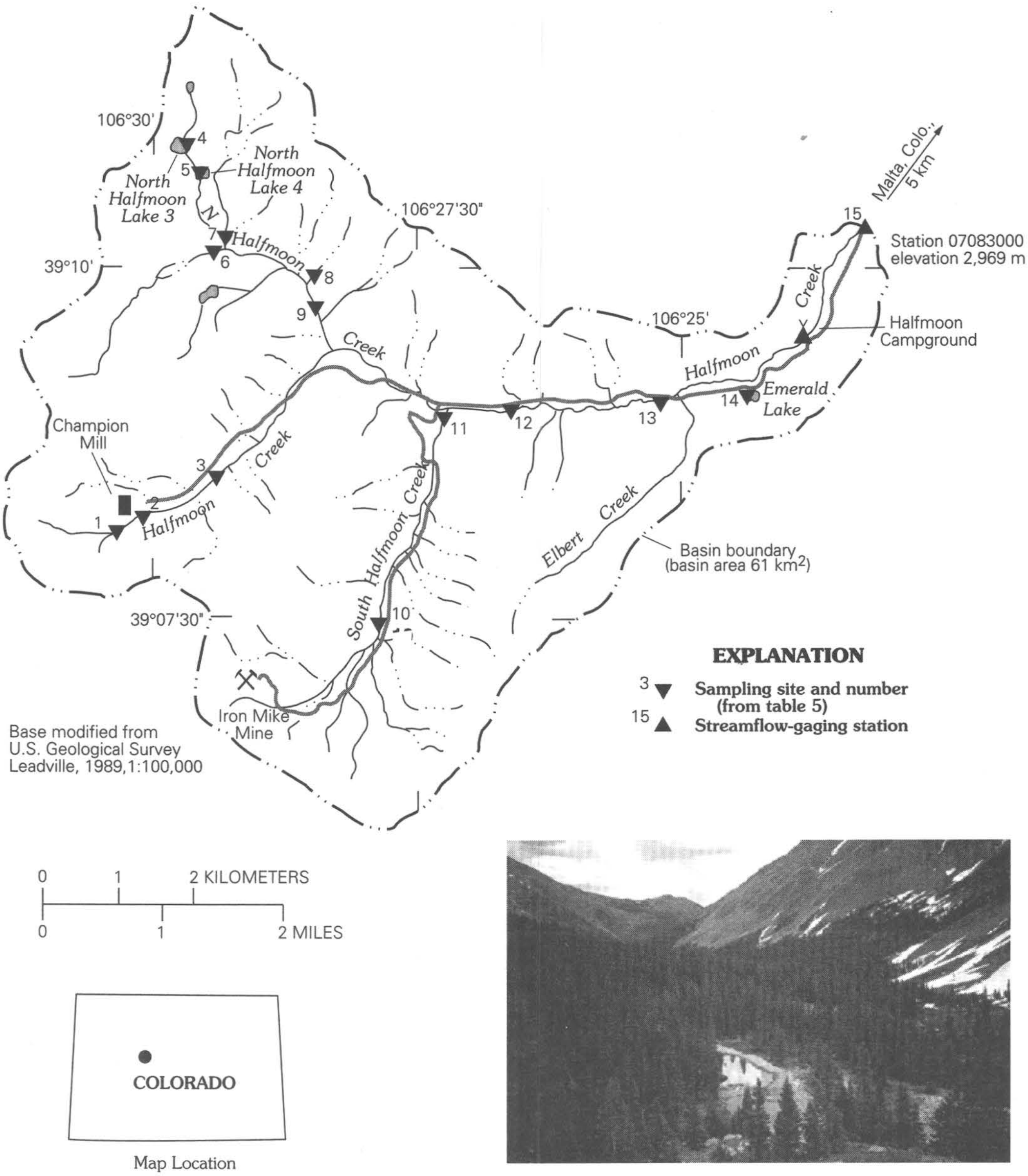


Figure 2. Map showing study area in Halfmoon Creek Basin and photograph of the landscape of the basin.

of the basin is by way of an improved, light-duty road. Access farther up the main stem of the drainage and some of the main tributaries is by four-wheel-drive roads and trails. Access may be restricted across private property, and mechanized vehicles are not allowed within the Mount Massive Wilderness Area. Access to the HBN station during the winter, as well as to the rest of the basin, is limited to snowmobiles, skis, or snowshoes. Recreational use in the basin is high, particularly in the summer. Activities include hiking, fishing, and camping. A U.S. Forest Service campground is upstream from the station, and the Mount Massive and Mount Elbert trailheads are both accessible from the basin. Several small, abandoned mines and an inactive mill are in the basin. Historically, small vein deposits of silver, gold, lead, and zinc yielded economic quantities of these metals from Halfmoon Creek Basin. Mining activity in Halfmoon

Creek Basin, however, was less than in other drainages in the upper Arkansas River Basin. Other potential influences on water quality in the basin include grazing (U.S. Geological Survey, 1993, p. 200), a few residences, and past forest fires (Cobb and Biesecker, 1971).

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for the Halfmoon Creek HBN station includes 256 water-quality samples that were collected from July 1965 to August 1995. Sampling frequency is described on the basis of water year, which begins on October 1 and ends on September 30. Sampling frequency increased from 2 samples in 1965 to 12 samples in 1967 and remained at 10–12 samples per year from 1967 to 1980. Sampling frequency was variable during the period 1981–90 when between three to nine samples were collected annually. During the early 1990's, sampling frequency generally was bimonthly. Samples were analyzed at USGS district water-quality laboratories until the early 1970's. After 1973, with the creation of the USGS Central Laboratory System, all samples were analyzed at the water-quality laboratory (now called NWQL) in Arvada, Colo. The period of record for discharge is from water year 1946 to current year (2000). Daily water temperature was recorded from May 1967 to September 1982.

Data quality was checked using ion balances and time-series plots. Calculated ion balances for samples with complete major-ion analyses are shown in figure 3. About 90 percent of the samples had ion balances within the ±6 percent range, indicating that the major-ion analytical results were of good quality and that unmeasured constituents, such as organic anions, nutrients, and trace metals, do not contribute substantially to the ionic composition of Halfmoon Creek. Time-series plots of ion concentrations were inspected for evidence of influences that are related to analytical method changes (fig. 3). Calcium, magnesium, potassium, and sodium generally have more scatter in the early part of the record. The scatter for potassium, and to a lesser extent magnesium, coincides with the water-quality laboratory location change around 1973. A decrease in scatter for calcium after 1983 coincides with a change in the analytical method for these analytes from atomic adsorption (AA) spectroscopy to inductively coupled plasma (ICP) spectroscopy (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 82.18, 1982). The reason for the decrease in scatter of sodium could not be isolated because it occurred around 1980, a few years before the method change. The decrease in scatter of sulfate concentrations after 1982 corresponds with the change from a methylthymol blue procedure to a turbidimetric titration method (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 83.07, 1983). The further decrease in the scatter of sulfate concentrations after 1990 corresponds with the change from turbidimetric titration to an ion-exchange chromatography analytical method (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 90.04, 1989; U.S. Geological Survey Office of Water Quality Technical Memorandum No. 90.13, 1990). Changes also were made in meters and electrodes used for field pH determinations during the study period. When changes in methods or instrumentation result in improved precision or elimination of measurement bias, time-series data can exhibit less scatter or a directional shift, respectively. The time-series data, therefore, may reflect the method or instrument change rather than an environmental change.

The median and range of major-ion concentrations in stream water collected at the Halfmoon Creek HBN station and VWM concentrations in wet precipitation measured at the Manitou NADP station are presented in table 2. The NADP station is about 130 km east and south of the HBN station. Precipitation chemistry at the NADP station was dilute and acidic with a VWM pH of 4.9 during the period of record, 1978–95. The dominant cations in precipitation were hydrogen, which contributed 28 percent of the total cation concentration, and calcium and ammonium, which each contributed 26 percent. Sulfate and nitrate were the dominant anions in precipitation, contributing 48 and 46 percent, respectively, of the total anion concentration. A high proportion of nitrate in precipitation in the Rocky Mountains has been attributed to exhaust from cars and other vehicles in urban areas and agricultural activity in the Great Plains States (National Atmospheric Deposition Program/National Trends Network, 1997). Precipitation chemistry at a USGS study site in Halfmoon Creek Basin near the gaging station was slightly more dilute and less acidic with a VWM pH of about 5.1 during the period 1989–94 (A.J. Ranalli, U.S. Geological Survey, written commun., 1997).

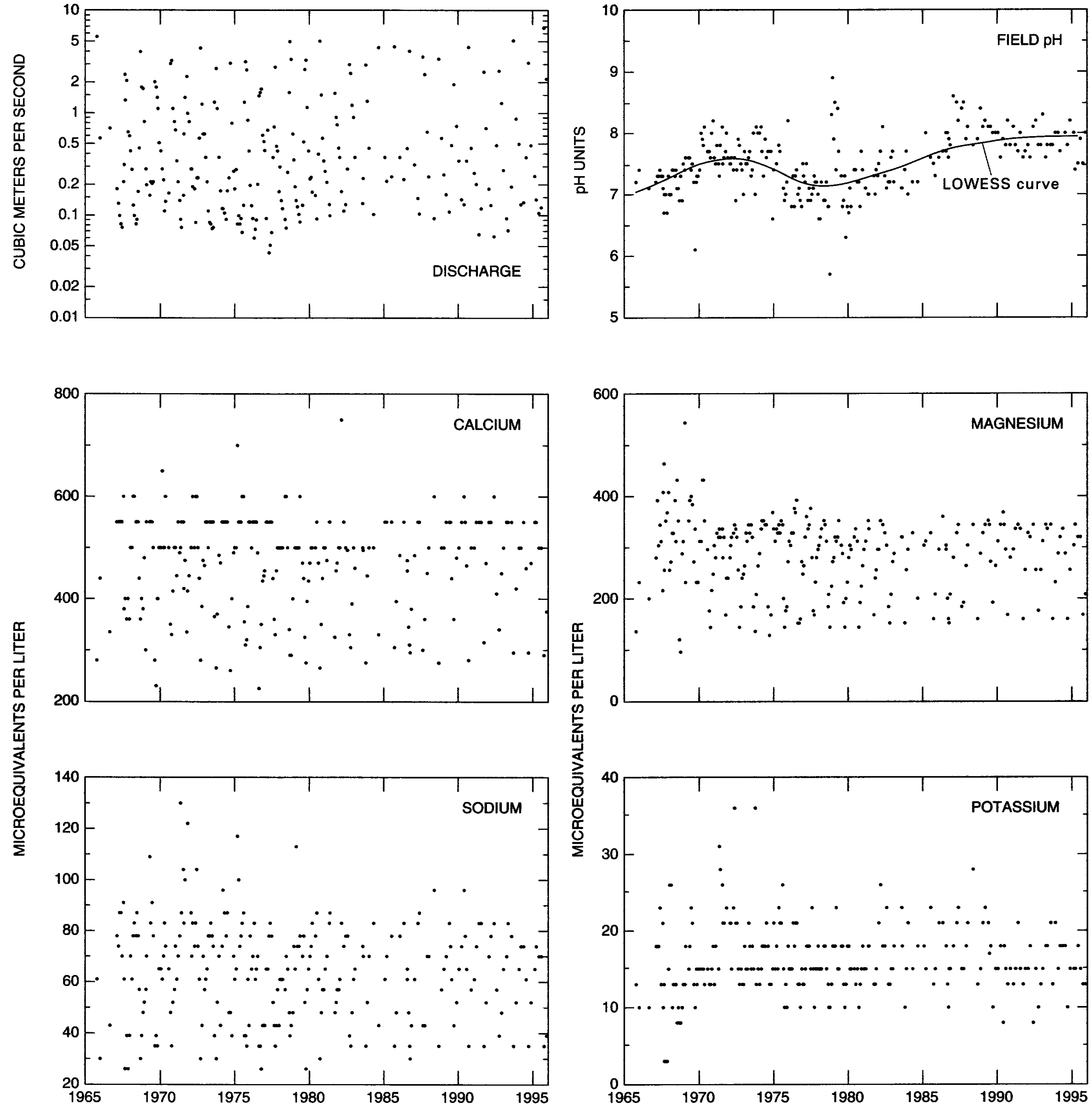


Figure 3. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Halfmoon Creek near Malta, Colorado.

Stream water in Halfmoon Creek is a calcium bicarbonate type. The sum of ion concentrations ranged from about 830 to about 2,500 µeq/L. Alkalinity ranged from 320 to 980 µeq/L, and bicarbonate is the primary contributor to alkalinity at this station. Calcium (57 percent) and magnesium (34 percent) accounted for the largest part of the median cation concentration. Bicarbonate accounted for 85 percent of the median anion concentration. The dominance of calcium, magnesium, and bicarbonate reflect the weathering of calc-silicate gneiss, which was formed, in part, by the metamorphism of limestone

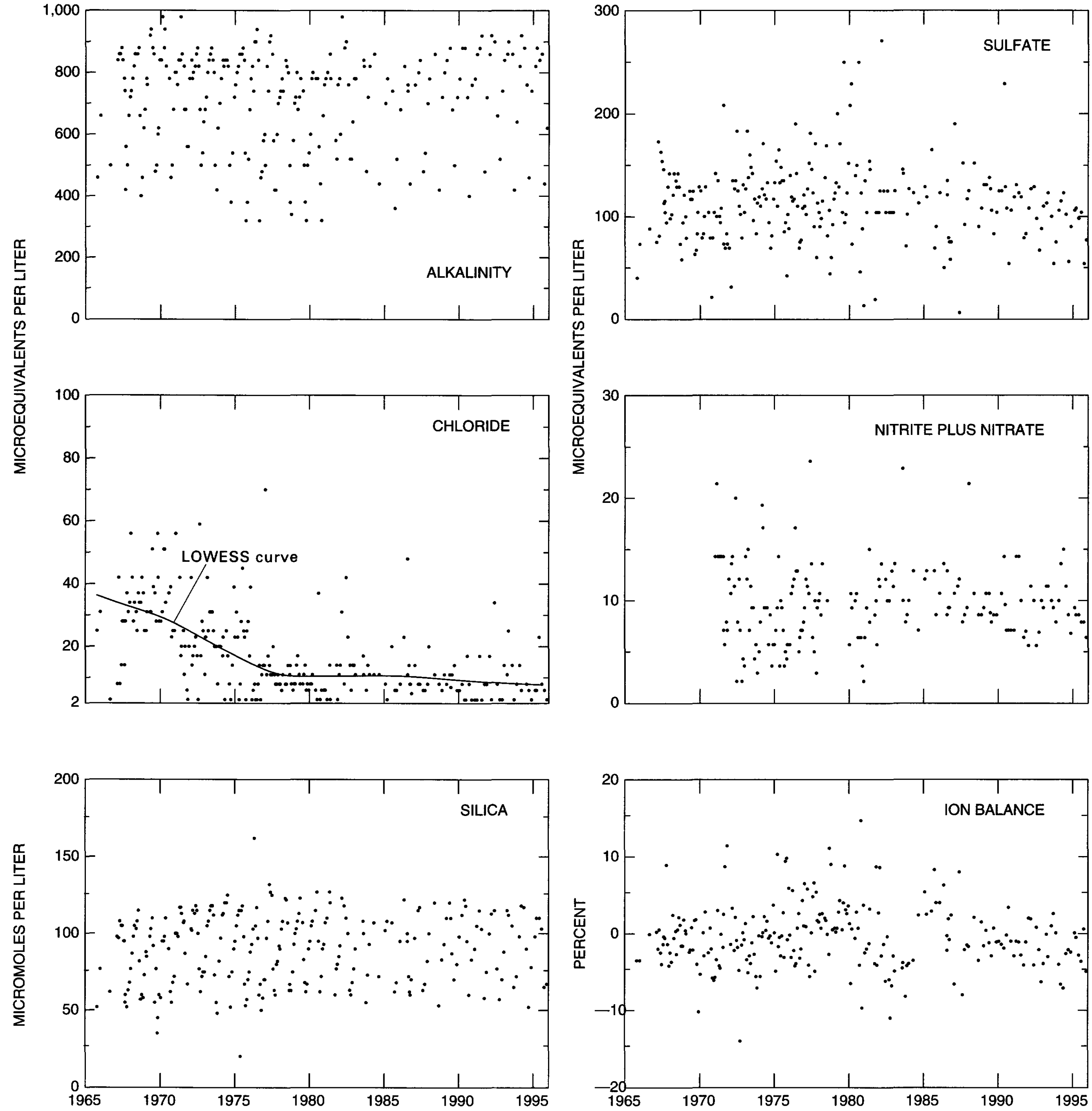


Figure 3. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Halfmoon Creek near Malta, Colorado—Continued.

or dolomite. Streams in basins with high annual runoff and geologic settings that contain metamorphic rocks, particularly schist and gneiss, tend to have low dissolved-solids concentrations (Biesecker and Leifeste, 1975). Specific conductance (43 to 107 µS/cm) is an indicator of the low dissolved solids at this station. Annual precipitation and runoff data indicate that evapotranspiration can account for about a twofold increase in stream-water concentrations compared to precipitation. About 40 percent of the median sulfate and chloride concentrations in the stream water can be accounted for by wet

Table 2. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ions measured in water-quality samples from Halfmoon Creek, Colorado, 1965–95, and volume-weighted mean concentrations in wet precipitation collected at the Manitou Station, Colorado, 1978–95

[Parameters in units of microequivalents per liter, except for 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; spec. cond., specific conductance; --, not reported; <, less than]

Parameter	Stream water						Precipitation VWM
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge	0.04	0.13	0.28	0.88	6.8	247	--
Spec. cond., field	43	65	86	95	107	226	--
pH, field	5.7	7.2	7.5	7.8	8.9	245	4.9[a]
Calcium	220	400	500	550	750	254	12
Magnesium	96	230	300	340	540	256	3.2
Sodium	26	48	65	78	130	253	4.4
Potassium	3.0	13	15	18	36	251	1.3
Ammonium	<.7	.7	1.4	4.3	16	100	12
Alkalinity, laboratory	320	580	760	840	980	251	--
Sulfate	6.2	90	110	130	270	253	22
Chloride	<2.8	8.5	14	25	70	254	2.9
Nitrite plus nitrate	2.1	7.1	9.3	12	24	183	21[b]
Silica	20	70	95	110	160	254	--

[a] Laboratory pH.
[b] Nitrate only.

precipitation. This indicates that sulfate and chloride sources may exist in the basin. The precipitation contribution of sulfate is a conservative estimate, however, because dry deposition is not included and it can be an important source. Sulfide minerals typically associated with mineralized rock zones have been mapped in the upper basin, and other minerals in igneous rocks can contribute small amounts of chloride to water (Hem, 1992, p. 118). The pH of the stream water generally remains near neutral to slightly alkaline. Concentrations of ammonium and nitrate were lower in the stream water than in the precipitation, indicating that nitrogen is retained by the biomass in the basin.

Correlations among dissolved constituents and discharge were determined for Halfmoon Creek (table 3). Base cations and anions were inversely correlated with discharge. These results are consistent with a hydrologic system where base-flow chemistry that is dominated by ground water is diluted during periods of increased discharge, particularly during annual snowmelt runoff. Ion concentrations in ground water tend to be greater than in surficial sources because the contact time with rocks and minerals is longer. Among the solutes, strong, positive correlations existed among base cations, particularly calcium and magnesium (rho value = 0.938), calcium and sodium (rho value = 0.880), and sodium and magnesium (rho value = 0.924). The relations of calcium, magnesium, and sodium with silica were strong and positively correlated (0.907, 0.949, and 0.941, respectively). Positive correlations among the base cations and alkalinity also were apparent (calcium, rho value = 0.878; magnesium, rho value = 0.898; and sodium, rho value = 0.847). Likewise, a strong correlation between alkalinity and silica was determined (rho value = 0.859). These relations reflect the weathering of feldspathic and calc-silicate minerals in the metamorphic rocks.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents for Halfmoon Creek from 1965 through 1995 are presented in table 4. A statistically significant ($\alpha = 0.01$) downward trend for dissolved chloride and a significant upward trend in pH were detected in both unadjusted and flow-adjusted concentrations. A statistically significant upward trend for dissolved silica was detected in the flow-adjusted concentrations. The results of the flow-adjusted tests indicate the changes

Table 3. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ions, Halfmoon Creek, Colorado, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; SiO_2, silica; --, not applicable]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	0.006	--	--	--	--	--	--	--	--
Ca	–.881	0.082	--	--	--	--	--	--	--
Mg	–.930	.044	0.938	--	--	--	--	--	--
Na	–.927	–.059	.880	0.924	--	--	--	--	--
K	–.523	.015	.536	.591	0.593	--	--	--	--
Alk	–.893	.092	.878	.898	.847	0.487	--	--	--
SO_4	–.556	–.094	.590	.625	.620	.448	0.461	--	--
Cl	–.236	–.071	.170	.263	.247	.433	.230	0.217	--
SiO_2	–.940	–.043	.907	.949	.941	.584	.859	.628	0.219

in hydrogen, chloride, and silica concentrations probably were not driven by changes in stream discharge. The upward trend in pH contrasts with the significant downward trend ($\alpha = 0.01$) in stream-water pH at this station that was observed for the period from the mid-1960's to 1981 (Smith and Alexander, 1983). Likewise, a significant downward trend ($\alpha = 0.01$) in alkalinity determined during the same period is no longer detected. Lewis and Grant (1980) reported decreasing pH and increasing nitrate concentrations in precipitation along the nearby Rocky Mountain Front Range for the period 1975–78. Kling and Grant (1984) correlated decreasing pH and alkalinity with increasing elevation in lakes in the nearby Front Range. The trend of increasing pH, however, is consistent with a more recent study (Lynch and others, 1995), which found increasing pH in precipitation at the Manitou NADP station for the period 1980–92. The downward trend in chloride concentrations is consistent with decreasing chloride concentrations in precipitation at the Manitou station. Some negative bias, however, may have been introduced in the stream-water chloride concentrations from the change in analytical methods for chloride from colorimetric during the 1970's to a ferric thiocyanate to automated segmented flow method during the 1980's, to ion exchange chromatography around 1990 (H.D. Ardourel, U.S. Geological Survey, written commun., 1997). The reason for the upward trend in flow-adjusted silica concentrations could not be determined.

Table 4. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major-ion concentrations, Halfmoon Creek, Colorado, 1965 through 1995

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

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	0.00	0.956	--	--
pH	.03	<.001	0.03	<0.001
Calcium	<.01	.092	.7	.013
Magnesium	<.01	.599	.4	.201
Sodium	<.01	.574	.05	.609
Potassium	<.01	.650	.02	.489
Alkalinity	.8	.126	.8	.212
Sulfate	<.01	.962	.09	.733
Chloride	–.6	<.001	–.6	<.001
Nitrite plus nitrate	.03	.318	.05	.153
Silica	.3	.013	.3	.004

Synoptic Water-Quality Data

Results of surface-water synoptic sampling conducted during 1988, 1989, and 1990 in the Halfmoon Creek Basin are presented in table 5, and locations of the sampling sites are shown in figure 2. Discharge at the HBN station (site 15) during the four sampling events was 0.63 m^3/s (July 1988), 0.17 m^3/s (November 1988), 0.19 m^3/s (March 1989), and 0.10 m^3/s (March 1990) compared to the mean monthly discharge of 2.4, 0.21, and 0.10 m^3/s for the months of July, November, and March, respectively (Crowfoot and others, 1996a).

Table 5. Physical properties and major-ion concentrations in surface-water samples collected at sites in the Halfmoon Creek Basin, Colorado, 1988 through 1990

[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; SiO_2, silica; concentrations in microequivalents per liter, except silica is in micromoles per liter; --, not measured; <, less than; criteria used in selection of sampling sites: BG = bedrock geology, TRIB = major tributary, LU = land use]

Site number	Site identification number	Sample date	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	SiO_2	Criteria
1	390806106302200	07/26/88	0.034	76	7.2	430	240	42	7.4	520	190	1.4	4.4	57	LU
		10/31/88	--	98	--	600	270	48	8.5	490	380	3.7	16	58	
2	390816106295700	10/31/88	--	104	7.8	560	360	50	10	670	270	3.9	13	62	LU
		03/22/89	<.001	127	8.0	750	380	74	12	710	440	8.5	14	72	
3	390830106292400	07/26/88	.10	75	7.5	430	250	40	9	570	130	2	4.5	55	LU
		10/31/88	--	94	7.9	550	310	52	10	640	220	5.1	13	62	
		03/22/89	.005	113	8.0	650	340	74	12	760	140	5.6	15	68	
		03/20/90	.004	116	7.6	700	380	78	14	830	290	2.8	21	73	
4	391050106294300	07/25/88	.003	28	--	160	72	23	3.8	220	29	2.5	--	32	BG
5	391039106293400	07/25/88	.001	27	--	160	70	22	3.3	220	27	1.7	--	28	BG
6	391010106292200	07/25/88	.099	38	--	220	120	26	5.4	310	46	2	3.9	42	TRIB
7	391011106291900	07/25/88	.085	35	--	220	80	29	6.7	280	38	2.8	6.9	42	TRIB
8	390955106283200	07/25/88	.003	53	--	300	160	65	11	420	63	4.8	18	82	TRIB
9	390945106282800	07/25/88	.24	40	--	240	110	29	6.4	330	44	2.3	4.6	45	BG
		11/01/88	--	58	7.7	360	180	43	9	440	73	5.9	16	62	
		03/23/89	.012	59	7.9	320	180	48	8.7	440	77	4.8	15	65	
		03/21/90	.033	58	7.7	340	180	48	9.5	460	73	<.3	18	68	
10	390724106275100	07/26/88	.097	79	7.6	490	220	52	14	660	98	3.9	5.9	67	LU
11	390901106271200	07/26/88	.17	93	7.9	550	300	57	15	790	100	3.4	8.6	75	TRIB
		11/01/88	--	108	8.0	650	370	61	18	910	130	6.2	14	78	
		03/22/89	.01	113	8.2	700	390	70	18	960	150	5.6	16	82	
		03/21/90	.025	116	8.1	700	380	70	18	990	140	<.3	21	85	
12	390901106263600	07/26/88	.50	70	7.8	400	220	41	10	580	77	2.8	6.8	62	BG
		11/01/88	--	91	7.9	500	310	57	15	740	110	6.2	14	73	
		03/22/89	.054	96	8.1	550	330	61	15	780	120	5.6	16	77	
		03/21/90	.052	97	7.9	550	330	61	16	820	130	5.1	18	82	
13	390905106250700	07/26/88	.58	72	7.8	410	240	43	11	600	81	3.1	7.1	65	BG
		11/01/88	--	96	7.8	550	350	61	16	790	120	5.9	10	85	
		03/23/89	.067	99	8.1	550	350	74	16	850	130	6.5	11	110	
		03/21/90	.063	102	7.7	550	350	74	17	880	120	2.8	14	93	
14	390906106242000	06/26/88	--	35	--	180	110	48	10	300	30	4.2	1.5	72	BG
15	07083000	07/26/88	.63	79	8.0	420	260	52	12	620	82	4.2	6.2	24	
		11/01/88	.17	95	7.9	500	340	65	16	810	120	7.6	8.2	30	
		03/22/89	.19	99	8.1	550	350	78	17	800	120	7.1	9.2	35	
		03/21/90	.10	100	7.8	550	350	78	18	840	130	.3	9.6	37	

The water type of samples from all sites in the basin was calcium bicarbonate. The sum of ions in tributary streams ranged from about 660 (site 7, July 1988) to about 2,400 µeq/L (site 2, March 1989). The sum of ions at the HBN station (site 15) ranged from about 1,500 (July 1988) to about 2,000 µeq/L (March 1990). Concentrations of most dissolved constituents measured during synoptic sampling of the tributaries were within the range of dissolved-constituent concentrations measured at the HBN station for the record period 1965–95 (table 2). Concentrations of dissolved sulfate at sites 1, 2, and 3 exceeded the historical maximums for the HBN station. Ion concentrations were generally more dilute in the three lake sites: North Halfmoon Lake No. 3 (site 4), North Halfmoon Lake No. 4 (site 5), and Emerald Lake (site 14); ion concentrations in the lakes ranged from 500 (site 5) to 680 μeq/L (site 14). Several constituents measured in the lake samples were less than the minimum concentration detected at the HBN station during 1965–95.

Concentrations of most major ions (including calcium, magnesium, sodium, bicarbonate, and sulfate) were lower in stream water of North Halfmoon Creek and its tributaries (sites 6–9) compared to Halfmoon Creek and South Halfmoon Creek. The elevated sulfate concentrations in samples that were collected from the upper Halfmoon Creek drainage (sites 1, 2, and 3) coincide with the mineralized zone identified as having high mineral-resource potential. Placer mining for low-grade gold has occurred along upper Halfmoon Creek (Van Loenen and others, 1989). Increased sulfate concentrations are associated with the oxidation of iron-sulfide minerals, particularly pyrite, which commonly are associated with precious metal deposits (Deer and others, 1966, p. 448). Mining operations expose sulfide minerals to air and water, increasing the potential for oxidation (Hem, 1992, p. 111). The sulfate concentration at site 10 (98 μeq/L), below a historical mine site on South Halfmoon Creek, however, was less than the median sulfate at the HBN station. The South Halfmoon Creek drainage is outside the high mineral-resource potential zone. In all drainages, the stream waters were near neutral to moderately alkaline (pH = 7.2 to 8.2) during the synoptic study.

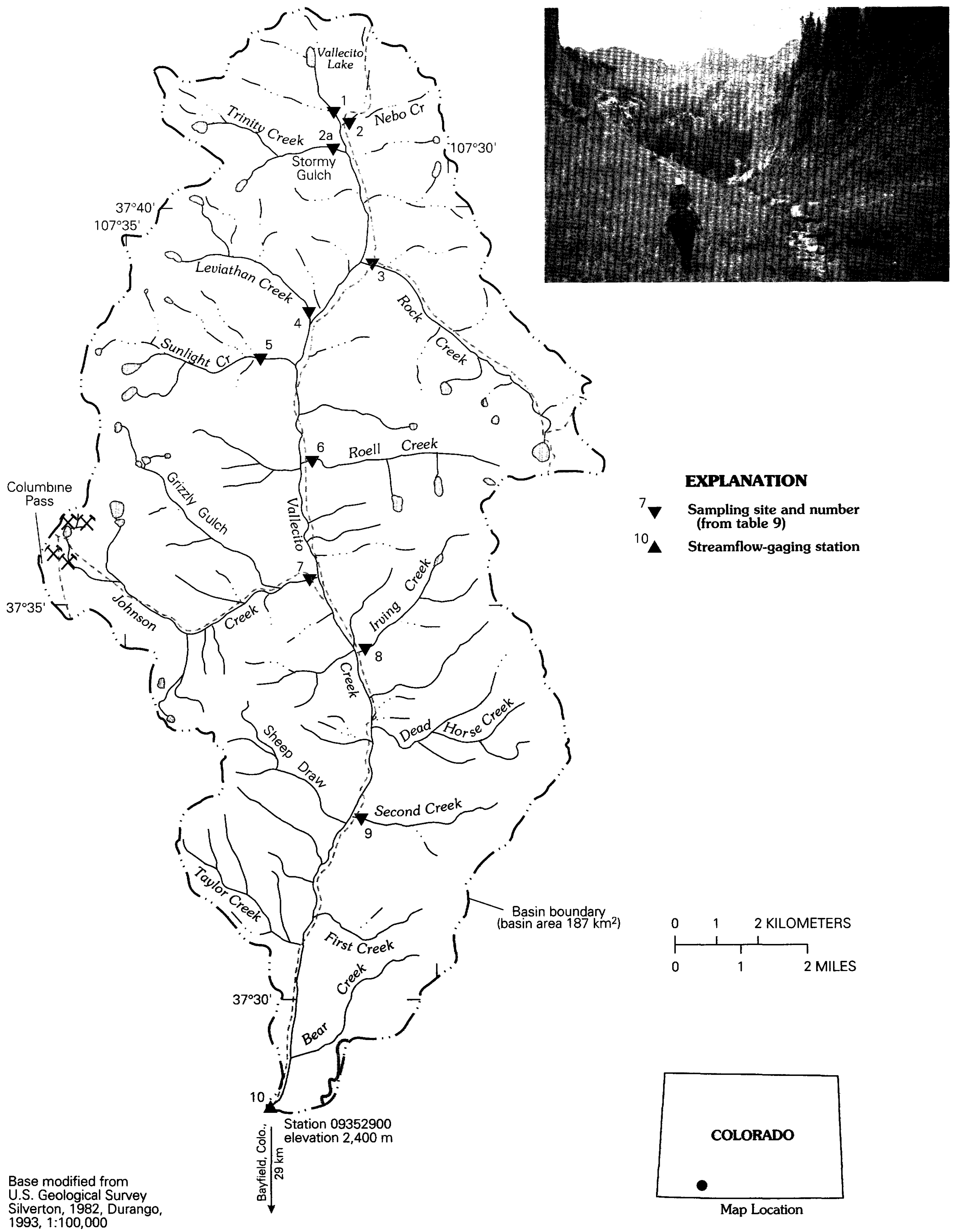
Vallecito Creek near Bayfield, Colorado (09352900)

Site Characteristics and Land Use

The Vallecito Creek HBN Basin is in the Southern Rocky Mountains physiographic province (Fenneman, 1946) in southwestern Colorado (fig. 4). Vallecito Creek drains about 187 km^2 of high-elevation, mountainous terrain in the San Juan Mountains. The HBN station, at a latitude of 37°28'39" and a longitude of 107°32'35", is 29 km north of the town of Bayfield, Colo., and 11 km north of Vallecito Dam. Elevations in the basin range from about 2,400 m at the HBN station to about 4,290 m. The average slope of the reach is 33 m/km (Cobb and Biesecker, 1971). The ecoregion of the basin is classified as the Southern Rocky Mountain Steppe-Open Woodland-Coniferous Forest-Alpine Meadow Province (Bailey, 1995). The basin is mostly forested and dominated by Engelmann spruce and fir forest, with scattered aspen groves. The forest grades into alpine tundra in the upper basin (above 3,600 m). Vallecito Creek is tributary to the Los Pinos River, which drains into the San Juan River in the Colorado River Basin.

Vallecito Creek is a perennial stream that originates at high altitude within the drainage at Vallecito Lake. The creek flows southward, draining several high mountain lakes and streams and ending in Vallecito Reservoir. On the western side of the basin, Vallecito Creek drains the eastern slope of the Needles Mountains. The basin has a snowmelt-dominated hydrograph with mean monthly discharges that range from 0.57 m^3/s in February to 15 m^3/s in June (Crowfoot and others, 1996b). The climate of the basin is variable and is generally related to the large changes in elevation. Climatic data are recorded at the Vallecito Dam weather station in the lower basin, about 13 km southwest of the HBN station. The Vallecito Dam weather station receives an average of 67 cm of precipitation annually, whereas annual precipitation in the upper basin is about 130 cm. About 80 percent of the precipitation in the upper basin occurs as snow (Cobb and Biesecker, 1971), and the average annual runoff is about 70 cm (Crowfoot and others, 1996b). Mean monthly temperatures at the weather station ranged from –5.9°C in January to 17.6°C in July during the period of record, 1948–95 (National Climatic Data Center, 1996). Average temperatures in the upper basin would be less, as temperatures decrease with increasing elevation.

The geology of the basin is characterized primarily by metamorphic and igneous rocks of Precambrian age. The upper part of the basin is underlain mainly by the Uncompahgre Formation, which consists of slate, phyllite, schist, quartzite, and conglomerate (Barker, 1969, p, A6). The southern two-thirds of the basin is split nearly in the middle by a north-south-trending contact that is characterized by an intrusive brecciated zone. On the west side of the contact is the Eolus Granite, which is composed mainly of quartz monzonite and granite (Gonzales, 1988, p. 60). On the east side of the contact are the Irving Formation and the Vallecito Conglomerate. The Irving Formation contains a variety of metamorphosed igneous and sedimentary rocks; lithologies include



Base modified from
U.S. Geological Survey
Silverton, 1982, Durango,
1993, 1:100,000

Figure 4. Map showing study area in Vallecito Creek Basin and photograph of the headwaters of Vallecito Creek, looking downstream into the basin.

mafic to felsic volcanic and associated volcaniclastic sedimentary rocks, and mafic intrusive rocks (Gonzales, 1988, p. 37). The Vallecito Conglomerate, which is named for the quartz-rich conglomerate exposed in the canyon of Vallecito Creek, is a thick succession of interbedded pebble-to-cobble conglomerate, sandstone, and subordinate siltstone (Gonzales, 1988, p. 59). The geology in the extreme southeast part of the basin, particularly in the Second Creek drainage, consists of undifferentiated rocks of Paleozoic age that overlie the Vallecito Formation (Gonzales, 1988, p. 61). Rocks of Paleozoic age include the Ignacio Quartzite of Cambrian age, the Elbert Formation and the Ouray Limestone of Devonian age, the Leadville Limestone of Mississippian age, and the Molas and Hermosa Formations of Pennsylvanian age (Gonzales, 1988, p. 61). Small sections of unconsolidated deposits of Cenozoic age are present along Vallecito Creek (Cross and Larsen, 1935, pl. 1).

The Vallecito Creek HBN station is in La Plata County. The Vallecito Creek Basin lies entirely within the San Juan National Forest and most of the basin is within the Weminuche Wilderness Area. The only road in the basin skirts the lower part of the basin for about 1 km. Access to the rest of the basin is by foot or horseback on pack trails, as mechanized vehicles are not permitted in the wilderness area. During the winter, access is limited to snowshoes and skis. Because almost all of the Vallecito Creek Basin is preserved as a wilderness area, recreational activities, such as hiking, backpacking, fishing, and hunting trips, are the predominant land use. Winter activities are limited owing to the high avalanche danger in the area (D.W. Grey, U.S. Geological Survey, oral commun., 1997). Historically, a small amount of mining took place in scattered areas throughout the basin, with a concentrated effort near the Columbine Pass area in the Johnson Creek subbasin.

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for the Vallecito Creek HBN station includes 234 water-quality samples that were collected from March 1963 to September 1995. Sampling frequency is described on the basis of water year, which begins on October 1 and ends on September 30. Sampling frequency was highly variable between 1963 and 1972; no samples were collected in 1965 and 1969, and 17 samples were collected in 1972. Sampling frequency generally was between 11 to 17 samples per year during 1971 to 1982. During the mid- to late 1980's and early 1990's, sampling generally was quarterly. Samples were analyzed at USGS district water-quality laboratories until the early 1970's. After 1973, with the creation of the USGS Central Laboratory System, all samples were analyzed at the water-quality laboratory (now called NWQL) in Arvada, Colo. The period of record for discharge is from water year 1963 to current year (2000). Daily water temperature was recorded from November 1962 to September 1982.

Data quality was checked using ion balances and time-series plots. Calculated ion balances for samples with complete major-ion analyses are shown in figure 5. More than 90 percent of the samples had ion balances within the ±10 percent range, indicating that the major-ion analytical results were of good quality and that unmeasured constituents, such as organic anions, nutrients, and trace metals, generally do not contribute substantially to the ionic composition of Vallecito Creek. Time-series plots of ion concentrations were inspected for evidence of influences that are related to analytical method changes (fig. 5). Magnesium and sodium show a similar pattern of having more scatter in the early part of the record and a decrease in scatter after 1983. This decrease coincides with a change in the analytical method for these analytes from AA spectroscopy to ICP spectroscopy (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 82.18, 1982). The decrease in scatter of sulfate concentrations after 1982 corresponds with the change from a methylthymol blue procedure to a turbidimetric titration method (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 83.07, 1983). The further decrease in the scatter of sulfate concentrations after 1990 corresponds with the change from turbidimetric titration to an ion-exchange chromatography analytical method (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 90.04–T, 1989; U.S. Geological Survey Office of Water Quality Technical Memorandum No. 90.13, 1990). Distinct temporal patterns also are evident in the field pH determinations. Changes were made in meters and electrodes used for field pH determinations during the study period. When changes in methods or instrumentation result in improved precision or elimination of measurement bias, time-series data can exhibit less scatter or a directional shift, respectively. The time-series data, therefore, may reflect the method or instrument change rather than an environmental change.

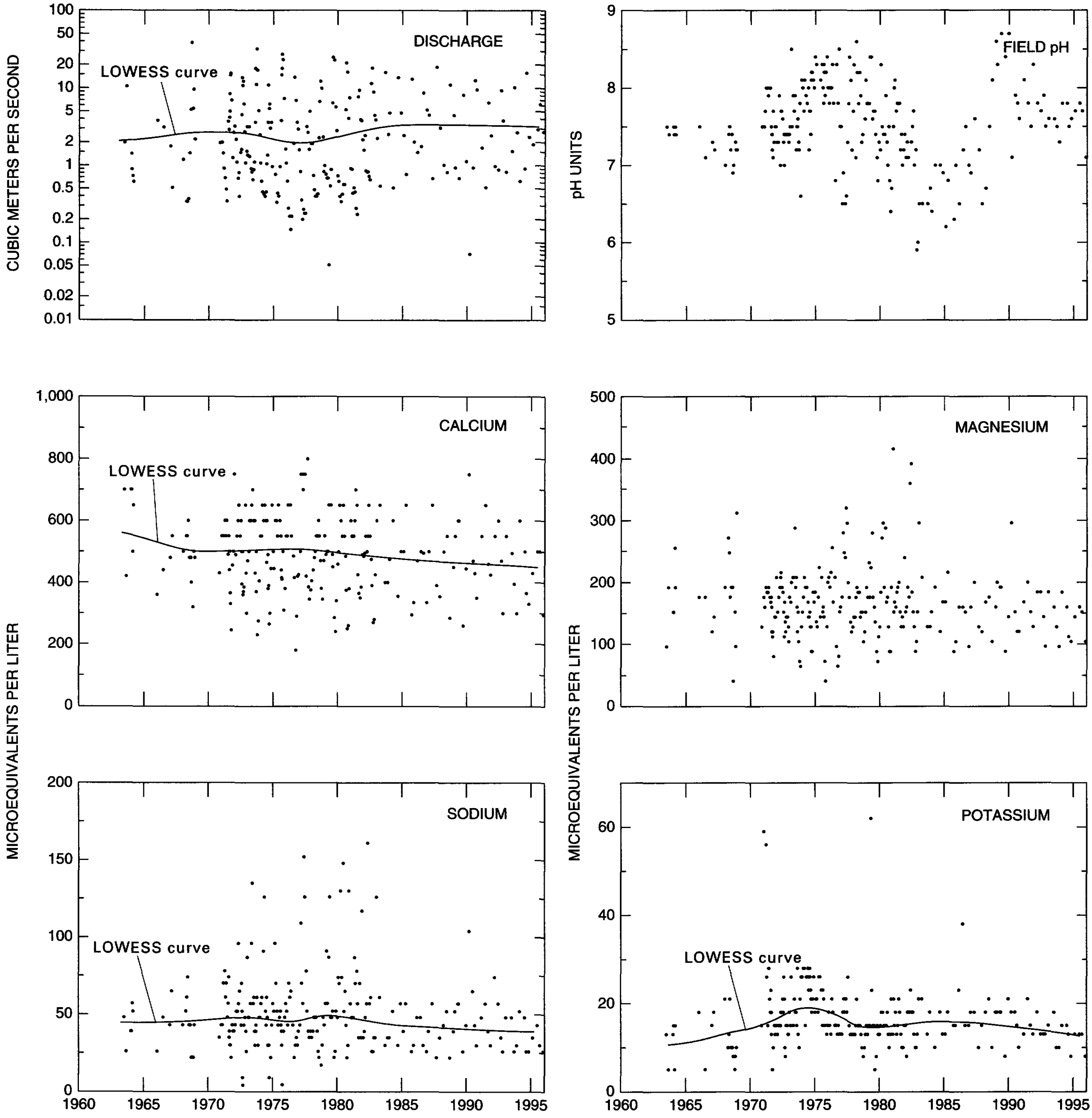


Figure 5. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Vallecito Creek near Bayfield, Colorado.

The median and range of major-ion concentrations in stream water collected at the Vallecito Creek HBN station and VWM concentrations in wet precipitation measured at the Molas Pass NADP station are presented in table 6. The NADP station is about 35 km northwest of the HBN station. Precipitation chemistry at the NADP station was dilute and slightly acidic with a VWM pH of 5.0 during the period of record, 1986–95. The dominant cation in precipitation was calcium, which contributed about 41 percent of the total cation concentration. The dominant anions in precipitation were sulfate and nitrate, which contributed 47 and 43 percent of the total anion concentration, respectively. Possible sources of the nitrogen

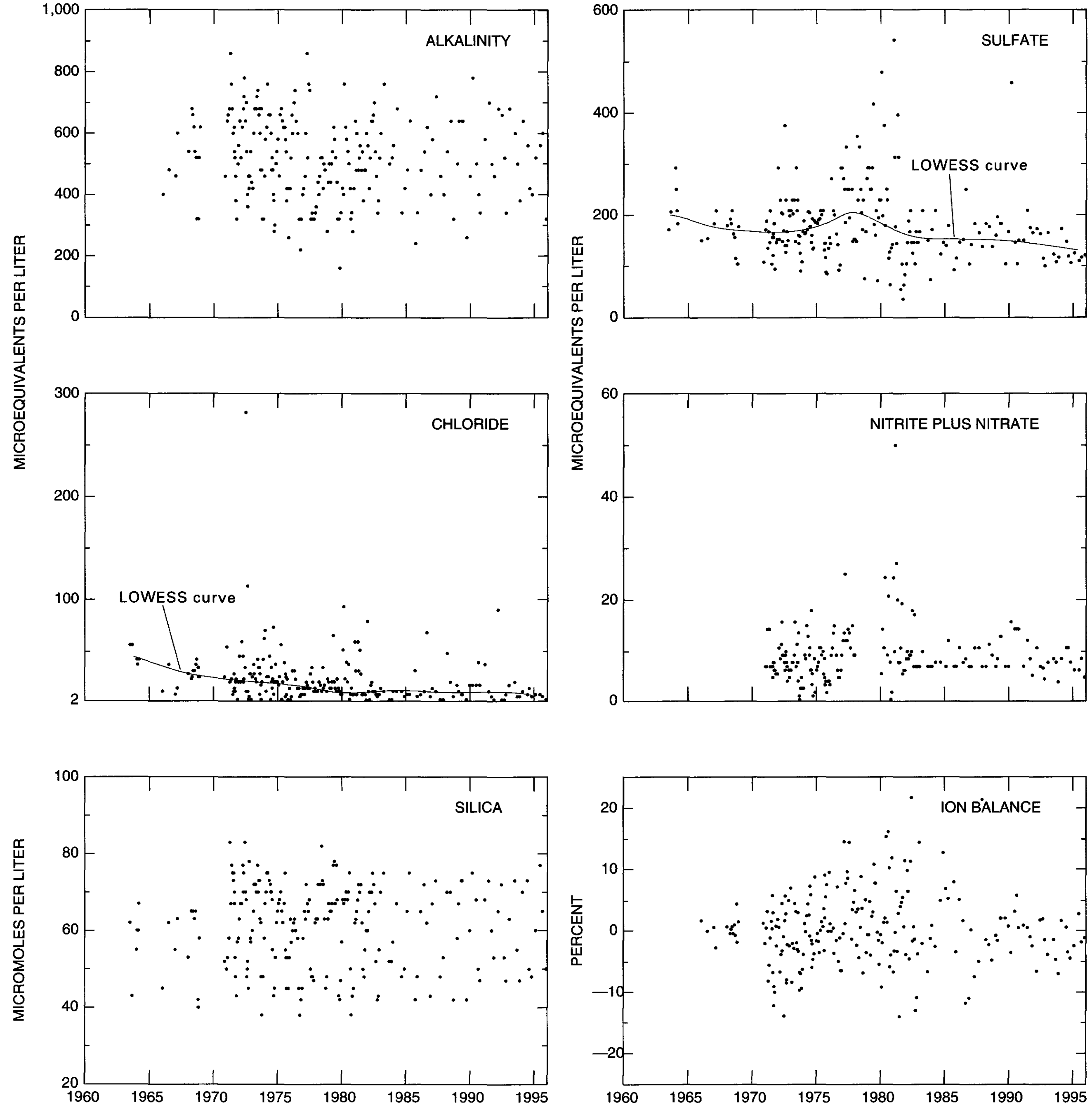


Figure 5. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Vallecito Creek near Bayfield, Colorado—Continued.

species and sulfate in precipitation are smelters, agriculture, and vehicles (National Acid Precipitation Assessment Program, 1993).

Stream water in Vallecito Creek is a slightly alkaline, calcium bicarbonate type. The sum of ion concentrations ranged from about 600 to about 2,400 µeq/L. Alkalinity ranged from 160 to 860 µeq/L, and bicarbonate was the primary contributor to alkalinity at this station. Calcium accounted for 69 percent of the median cation concentration, and bicarbonate accounted for 73 percent of median anion concentration. Streams in basins with high annual runoff and geologic settings that contain metamorphic rocks, particularly schist and gneiss, tend to have low dissolved-solids

Table 6. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ions measured in water-quality samples from Vallecito Creek, Colorado, 1963–95, and volume-weighted mean concentrations in wet precipitation collected at the Molas Pass Station, Colorado, 1986–95

[Parameters in units of microequivalents per liter, except for 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; spec. cond., specific conductance; --, not reported; <, less than]

Parameter	Stream water						Precipitation VWM
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge	0.05	0.74	1.9	5.2	39	231	--
Spec. cond., field	33	60	74	85	146	228	--
pH, field	5.9	7.2	7.5	7.9	8.7	226	5.0[a]
Calcium	180	400	500	600	800	233	14
Magnesium	40	130	160	190	420	234	2.0
Sodium	4.4	35	48	57	160	231	3.0
Potassium	5.1	13	15	18	62	232	.61
Ammonium	<.7	.9	2.1	5.0	12	74	4.6
Alkalinity, laboratory	160	420	520	620	860	226	--
Sulfate	35	140	170	210	540	230	12
Chloride	<2.8	8.5	16	28	280	230	2.4
Nitrite plus nitrate	<.7	6.4	7.9	11	50	185	11[b]
Silica	38	52	63	70	83	231	--

[a] Laboratory pH.

[b] Nitrate only.

concentrations (Biesecker and Leifeste, 1975). Specific conductance (33 to 146 µS/cm) is an indicator of the low dissolved solids at this station. Annual precipitation and runoff data indicated that evapotranspiration can account for less than a twofold increase in stream-water concentrations compared to precipitation. Wet precipitation contributes about 14 percent of the median sulfate concentration in Vallecito Creek, indicating that sulfate also is contributed from sources in the basin or is contributed from dry deposition. The pH of the stream water generally remained near neutral. Median concentrations of ammonium and nitrate are lower in the stream water than in the precipitation, indicating that some nitrogen is retained by the biomass in the basin.

Correlations among dissolved constituents and discharge were determined for Vallecito Creek (table 7). Base cations and anions were inversely correlated with discharge. These results are consistent with a hydrologic system where base-flow chemistry that is dominated by ground water is diluted during periods of increased discharge, particularly during annual snowmelt runoff. Ion concentrations in ground water tend to be greater than in surficial sources because the contact time with rocks and minerals is longer. Among the cations, the strongest positive correlations were between calcium and magnesium (rho = 0.918) and magnesium and sodium (rho = 0.867). Calcium and magnesium also were strongly correlated with alkalinity (rho values = 0.836 and 0.807, respectively) and silica (rho values = 0.873 and 0.807, respectively). These relations are consistent with a geologic setting that is rich in calc-silicate minerals.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents for Vallecito Creek are presented in table 8. A statistically significant upward trend for discharge was detected (p-value = 0.006) from 1970 to 1995. The trend in discharge only is representative of instantaneous measurements made during water-quality sampling and may not correspond with a trend in the continuous discharge record. Positive departures from average precipitation did occur during some years in the latter part of the period of record (Crowfoot and others, 1996b). Statistically significant downward trends were detected for unadjusted concentrations of calcium, sodium, potassium, sulfate, and chloride. Trends in calcium, sodium, and sulfate were not statistically significant in flow-adjusted concentrations. This indicates that the unadjusted trends probably were driven by the upward trend in discharge as these ions all showed inverse correlations with discharge. A downward trend in alkalinity at this station detected during the study by Smith and Alexander (1983) for the period from the mid-1960's to 1981 was not significant for the

Table 7. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ions, Vallecito Creek, Colorado, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; SiO_2, silica; --, not applicable]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	−0.263	--	--	--	--	--	--	--	--
Ca	−.800	0.267	--	--	--	--	--	--	--
Mg	−.731	.158	0.918	--	--	--	--	--	--
Na	−.680	.172	.762	0.867	--	--	--	--	--
K	−.439	.036	.544	.570	0.578	--	--	--	--
Alk	−.624	.176	.836	.807	.614	0.492	--	--	--
SO_4	−.659	.231	.711	.648	.536	.348	0.521	--	--
Cl	−.436	.227	.471	.394	.382	.396	.329	0.471	--
SiO_2	−.722	.239	.873	.807	.702	.589	.766	.545	0.357

period 1970–95. The downward trends for potassium and chloride were retained after flow adjustment. Potassium and chloride trends in stream water are consistent with decreasing concentrations of potassium and chloride in precipitation. Precipitation trends of potassium and chloride were observed at five NADP stations in Colorado by Lynch and others (1995) for the period 1980–92; however, the Molas Pass NADP station was not part of their study. After accounting for evapotranspiration, precipitation contributes about 25 percent of the median chloride concentration in stream water, but only about 8 percent of the median potassium concentration. Alternatively, trends in potassium and chloride may be caused by changes in analytical methods that occurred during the period of record.

Table 8. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major-ion concentrations, Vallecito Creek, Colorado, 1970 through 1995

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

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	1.00	0.006	--	--
pH	<.01	.79	<0.01	0.649
Calcium	−3	.003	−2.0	.034
Magnesium	−.8	.038	−.4	.280
Sodium	−.5	<.001	−.3	.071
Potassium	−.3	<.001	−.2	<.001
Alkalinity	−1	.320	.2	.908
Sulfate	−2	<.001	−1	.011
Chloride	−.5	<.001	−.5	.002
Nitrite plus nitrate	<.01	.839	.01	.644
Silica	<.01	.727	.01	.954

Synoptic Water-Quality Data

Results of surface-water synoptic sampling conducted July 25–27 and August 17, 1990, in the Vallecito Creek Basin are presented in table 9, and locations of the sampling sites are shown in figure 4. Discharge at the HBN station (site 10) was 2.5 m^3/s, which is less than the mean monthly discharge of 7.1 m^3/s for the month of July (Crowfoot and others, 1996b). Concentrations of dissolved constituents measured in the tributary creeks in the upper basin were generally less than the minimum concentrations of constituents measured at the HBN station for the period 1963–95 (table 6). The sum of ions ranged from about 160 µeq/L on Roell Creek (site 6) to 3,700 µeq/L on Second Creek (site 9); the sum of ions was 1,100 µeq/L at the HBN station (site 10). The percent difference of cations and anions for all samples except site 3 ranged from 0.7 to 5.4 percent, indicating that unmeasured ions did not contribute substantially to the ionic composition of the tributary waters. Site 3 had a cation deficit of 13 percent. This may indicate that unmeasured cations, possibly iron, may contribute to the ion composition of the water. An iron precipitate was observed on the streambed at this site.

The water type in three of the upper tributary creeks (sites 2, 2a, and 4) and the upper main stem (site 1) was calcium sulfate. The water type of Rock Creek (site 3) was magnesium sulfate. Streams with these water types generally have little buffering capacity. An abandoned mine, which was identified just upstream from the Rock Creek site (site 3), possibly contributed to the low pH (4.8) and low alkalinity (less than 10 µeq/L) measured at that site. The water type in the lower parts of the basin (sites 5,

Table 9. Physical properties and major-ion concentrations in surface-water samples collected at sites in the Vallecito Creek Basin, July 25–27 and August 17, 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; SiO_2, silica; concentrations in microequivalents per liter, except silica is in micromoles per liter; --, not measured; <, less than; criteria used in selection of sampling sites: BG = bedrock geology, TRIB = major tributary, LU = land use]

Site number	Site identification number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	SiO_2	Criteria
1	374105107314000	<0.03	20	6.6	90	66	8.7	4.4	10	138	2.5	5.7	27	BG
2	374103107313400	<.03	18	6.9	75	38	13	5.4	53	83	2.3	3.6	55	BG
2a	374038107413400	<.2	15	7.0	75	35	<8.7	2.3	50	67	2.5	4.3	32	BG
3	373915107311200	<.1	58	4.8	140	200	13	5.1	<10	480	2.8	1.4	53	LU
4	373835107320800	--	18	6.6	100	39	13	4.1	52	100	3.1	5.7	38	TRIB
5	373800107322500	--	20	7.6	130	29	17	12	120	52	2.3	3.6	33	BG, TRIB
6	373650107321400	--	9	6.9	55	17	<8.7	4.4	39	25	3.4	12	25	BG, TRIB
7	373521107320200	--	30	7.3	220	50	30	8.5	200	65	4.5	8.6	48	TRIB, LU
8	373423107311700	--	59	7.4	440	65	26	20	410	127	4.8	16	37	BG, TRIB
9	373219107312500	--	158	8.4	1,200	520	26	17	1,800	48	40	7.1	50	BG, TRIB
10	09352900	2.5	54	7.6	380	130	30	13	410	140	4.8	5.0	52	

6, 7, 8, 9, and 10) changes to calcium bicarbonate, owing to the changes of the rock types from the upper to the lower basin. The rock types of the upper basin are dominated by metamorphic slate, phyllite, and quartzite, whereas rock types in the lower basin are predominantly granite and metavolcanics. Second Creek (site 9), which drains Paleozoic rocks, including limestone, had larger concentrations of calcium, magnesium, and alkalinity than other sites—more than three times larger than the concentration at the HBN station. Bicarbonate contributed a large percentage of the anion concentration at site 9 (about 95 percent); this resulted in alkaline stream water (pH = 8.4). The buffering capacity of Vallecito Creek increased from slightly acidic (pH = 6.6) in the upper basin (site 1) to slightly alkaline (pH = 7.6) downstream (site 10).

Kings Creek near Manhattan, Kansas (06879650)

Site Characteristics and Land Use

The Kings Creek HBN Basin is in the Central Lowland physiographic province (Fenneman, 1946) in eastern Kansas. The ecoregion of the basin is classified as the Prairie Parkland (Temperate) Province, with alternating prairie and deciduous forest (Bailey, 1995). Kings Creek drains 10.6 km^2 of grassy terrain in the Flint Hills (fig. 6). The HBN station is 10 km south of Manhattan, Kans., at a latitude of 39°06'07" and a longitude of 96°35'42". The topography is gently rolling with basin elevations ranging from 335 to about 442 m. The slope of the main channel is 17m/km. Kings Creek is tributary to McDowell Creek, which drains into the Kansas River.

Kings Creek is an intermittent stream with sustained flows generally occurring in the spring. Average annual precipitation at the Manhattan, Kans., weather station is about 84 cm, which mostly falls in the form of rain during spring and early summer (National Climatic Data Center, 1996). Streamflow generally ceases during late summer, and the stream may remain dry during the fall. Flow in ephemeral headwater channels occurs only immediately following rainfall events. Mean monthly discharges range from less than 0.01 m^3/s in September to 0.23 m^3/s in May, and average annual runoff is about 20 cm (Putnam and others, 1996). The Kings Creek Basin is characterized by warm to hot summers and cold winters. Mean monthly temperature extremes at the weather station ranged from −1.8°C in January to 26.6°C in July during the period 1900–95 (National Climatic Data Center, 1996).

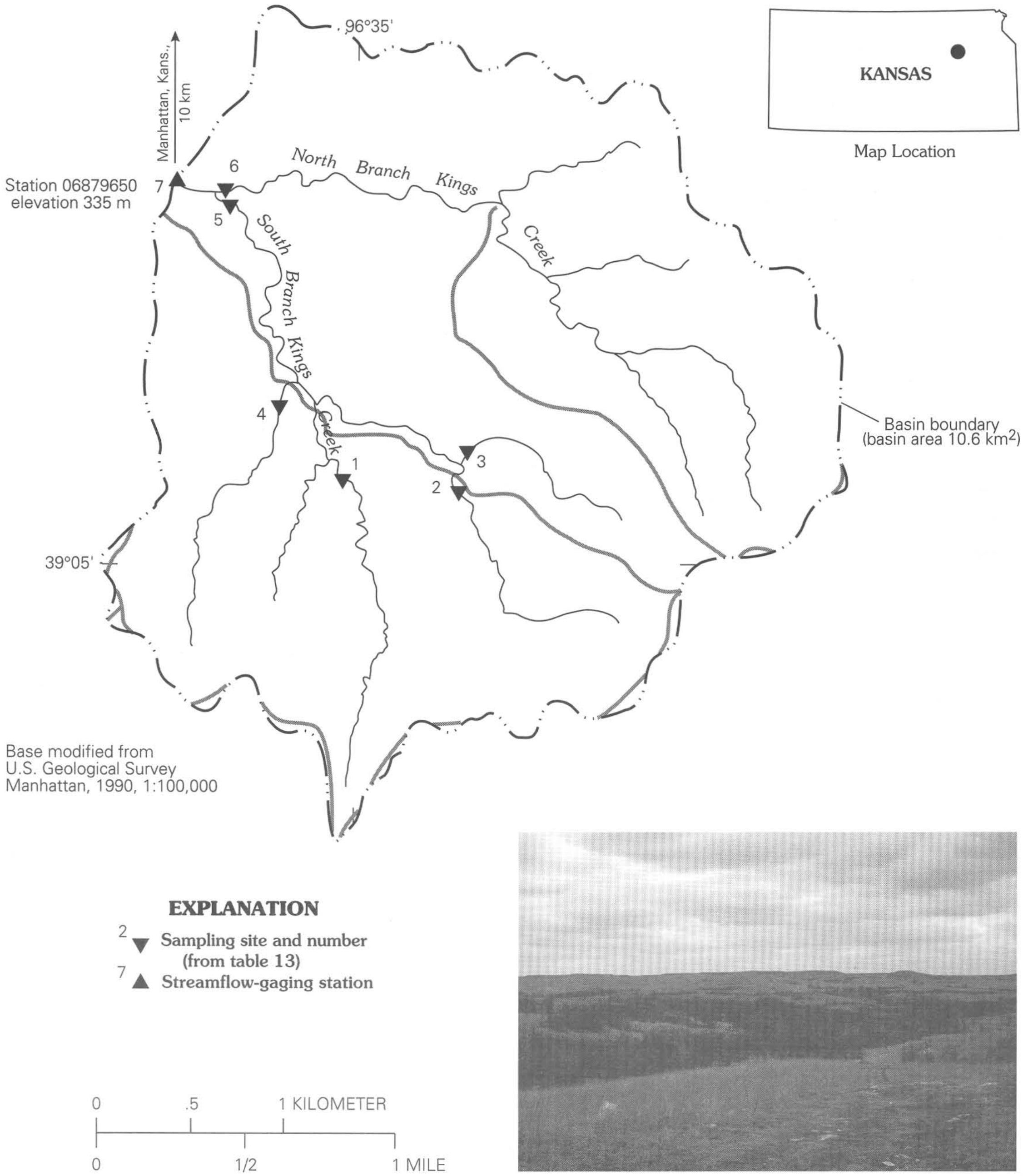


Figure 6. Map showing study area in Kings Creek Basin and photograph of the landscape of the basin.

The Kings Creek Basin is contained within the Konza Prairie Research Natural Area and is the only HBN Basin that exclusively drains pristine, native tallgrass prairie. The grass species are big bluestem, indian grass, switchgrass, little bluestem, Kentucky bluegrass, and Junegrass. The grasses have never been plowed because of the rocky soils and steep topography (Knapp and others, 1998). The prairie contains many species of herbaceous plants other than grasses, including heath aster, dotted gayfeather, ironweed, and several goldenrods. Annual burnings are set by land managers to control woody vegetation. The burning pattern varies in the basin; less frequently burned areas have a greater plant diversity, whereas burned areas tend to have a greater dominance of warm-season grasses. Woody vegetation in the unburned areas include sumac, dogwood, and eastern red cedar. Strips of forest along stream channels are composed of oak species, hackberry, and American elm.

The Kings Creek Basin lies within the Flint Hills Upland. The formation of prairie grasslands probably is associated with the Miocene uplift of the Rocky Mountains (Knapp and others, 1998), which caused a rain shadow to develop to the east, favoring drought-tolerant grasses over trees. The basin is underlain by sedimentary rocks of Paleozoic age (Jewett, 1941). Shales and limestones of the upper Council Grove Group of Permian age are in the uplands, whereas shales and limestones of the lower Council Grove Group are exposed in the alluvial valleys (Jewett, 1941). Alternating layers of more resistant flint- and chert-bearing limestone and less resistant shales give the terrain a benched appearance. Limestone units are exposed on steep-sided hills above valleys (Knapp and others, 1998). Ridges are flat and have shallow, rocky soils. Upland soils are silty clay loams, which are well drained, moderately deep to shallow, and sloping to moderately steep (U.S. Department of Agriculture, 1975b). Near the channel, soils are deep and stratified with silty, clay loams with low slopes of 0–6 percent; limestone and chert fragments are present in the subsoils.

The Kings Creek Basin lies within Riley County and is entirely within the Konza Prairie Research Natural Area, which was established in 1972 as a research facility. The land was originally acquired by The Nature Conservancy and is leased to Kansas State University, Division of Biology, for research purposes (Knapp and others, 1998). The Konza Prairie was selected as a research site for the Long Term Ecological Research Program of the National Science Foundation in 1981. Permission to access the site is obtained by contacting the Konza Prairie Office at Kansas State University in Manhattan. A light-duty service road provides access to some of the Kings Creek tributaries. Foot trails also provide access to the basin. Land-use activities are designed and controlled in the Kings Creek Basin. The land-management plan is designed to study the effect of fire and grazing on prairie plants and animals. The burn schedule is variable in the basin; sections are burned on a 1-, 2-, 4-, or 20-year cycle. Grazing divisions in the basin include grazed and ungrazed sections; both types of grazing divisions have burn schedules. Grazing in the South Branch Kings Creek drainage is by native bison, which were reintroduced to the prairie in 1987. Grazing by experimental cattle herds is allowed in other parts of the Konza research area, outside the Kings Creek Basin.

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for the Kings Creek HBN station includes 72 water-quality samples that were collected from April 1980 to July 1995. Sampling frequency is described on the basis of water year, which begins on October 1 and ends on September 30. Annual sampling frequency was variable over the 15-year period. The median number of annual samples that were collected was three; only one sample was collected in 1994. The highest sampling frequencies were in 1989 and 1990 when 9 and 12 samples were collected, respectively. In 1989 and 1990, multiple sampling events were conducted during storm runoff as part of the USGS National Water-Quality Assessment Program, and those samples were used to supplement the HBN data set. All samples were analyzed at the NWQL in Arvada, Colo. The period of record for discharge is from water year 1979 to current year (2000).

Data quality was checked using ion balances and time-series plots. Calculated ion balances for samples with complete major-ion analyses are shown in figure 7. More than 90 percent of the samples had ion balances within the ±10 percent range, indicating that the major-ion analytical results generally were of good quality and that unmeasured constituents, such as organic anions, nutrients, and trace metals, generally do not contribute substantially to the ion composition of the stream water. Time-series plots of ion concentrations were inspected for data quality (fig. 7). The increase in scatter in the chemical data during 1989 and 1990 was the result of samples that were collected during storm runoff periods, which also is reflected in the scatter in the discharge data for that same period (fig. 7).

The median and range of major-ion concentrations in the stream water collected at the Kings Creek HBN station and VWM concentrations in wet precipitation measured at the Konza Prairie NADP station are presented in table 10. The NADP station is about 1.5 km west of the HBN station. Precipitation chemistry at the NADP station was dilute and slightly acidic with VWM pH of 5.0 during the period of record, 1982–95. The dominant cation in precipitation was ammonium, which contributed about 37 percent of the total cation concentration; calcium contributed 31 percent and hydrogen contributed 19 percent. The dominant anions in precipitation were sulfate and nitrate, which contributed 54 and 40 percent, respectively. This was the highest VWM sulfate concentration (27 μeq/L) recorded for the NADP stations used in this study. Sulfate concentrations in precipitation tend to be higher in the Midwest and Ohio Valley, reflecting the sulfur emission source in these areas. Ammonium and nitrate tend to be higher in precipitation chemistry where livestock and fertilizer applications are common (National Atmospheric Deposition Program/National Trends Network, 1997). The dry deposition of nitrogen is not included in the wet deposition value but is important in tallgrass prairies and has been estimated to be 25 to 50 percent of the total atmospheric input (Gilliam, 1987).

Stream water in Kings Creek is a calcium bicarbonate type. The sum of ion concentrations ranged from about 4,300 to about 14,000 μeq/L. Alkalinity ranged from 1,900 to 6,200 μeq/L, and bicarbonate was the primary contributor to alkalinity at this station. The major cation, calcium, contributed 73 percent of median cation concentration in stream water. The major anion, bicarbonate, contributed 87 percent of the median anion concentration. The ion composition of the stream water reflects the weathering of the underlying limestone bedrock. Median concentrations of ammonium and nitrate were lower in the stream water than in the precipitation, indicating that nitrogen generally is retained by the prairie biomass. Nitrogen generally is a limiting nutrient in tallgrass prairies (Gilliam, 1987). Mean annual transport of nutrients from Kings Creek was very low compared to other streams in the lower Kansas River Basin (Helgesen, 1996); nitrate concentrations were low enough to limit algal growth during the summer (McArthur and others, 1985).

Correlations among dissolved constituents and discharge were determined for Kings Creek (table 11). The base cations and anions, except dissolved potassium, showed inverse relations with discharge. These results are consistent with a hydrologic system where base-flow chemistry that is dominated by ground water is diluted during periods of increased discharge, particularly rainfall events. Ion concentrations in ground water tend to be greater than in surficial sources because the contact time with rocks and minerals is longer. The time-series plots for base cations, except potassium, and base anions (fig. 7) show the inverse relation when compared to the discharge time-series plot during the 1989 and 1990 storm-event sampling. The behavior of potassium is more similar to plant nutrients and sediment. Exportation of nitrogen from the basin was reported to increase during storm events (McArthur and others, 1985), and sediment also shows a flow-driven relation during storm events (Knapp and others, 1998). The strongest ion correlation was between calcium and magnesium (rho value = 0.907), which is typical of a carbonate-dominated geologic environment.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents for Kings Creek from 1982 through 1995 are presented in table 12. The only statistically significant trend ($\alpha = 0.01$) was decreasing sodium for flow-adjusted concentrations. Except for the 1989 and 1990 storm-event sampling, sodium concentrations were generally constant until about 1992, after which they begin to decline. The time-series plot indicates that most discharge measurements made during 1993–95 were higher than the median discharge, and sodium did show an inverse correlation with discharge. However, the flow-adjustment should remove the

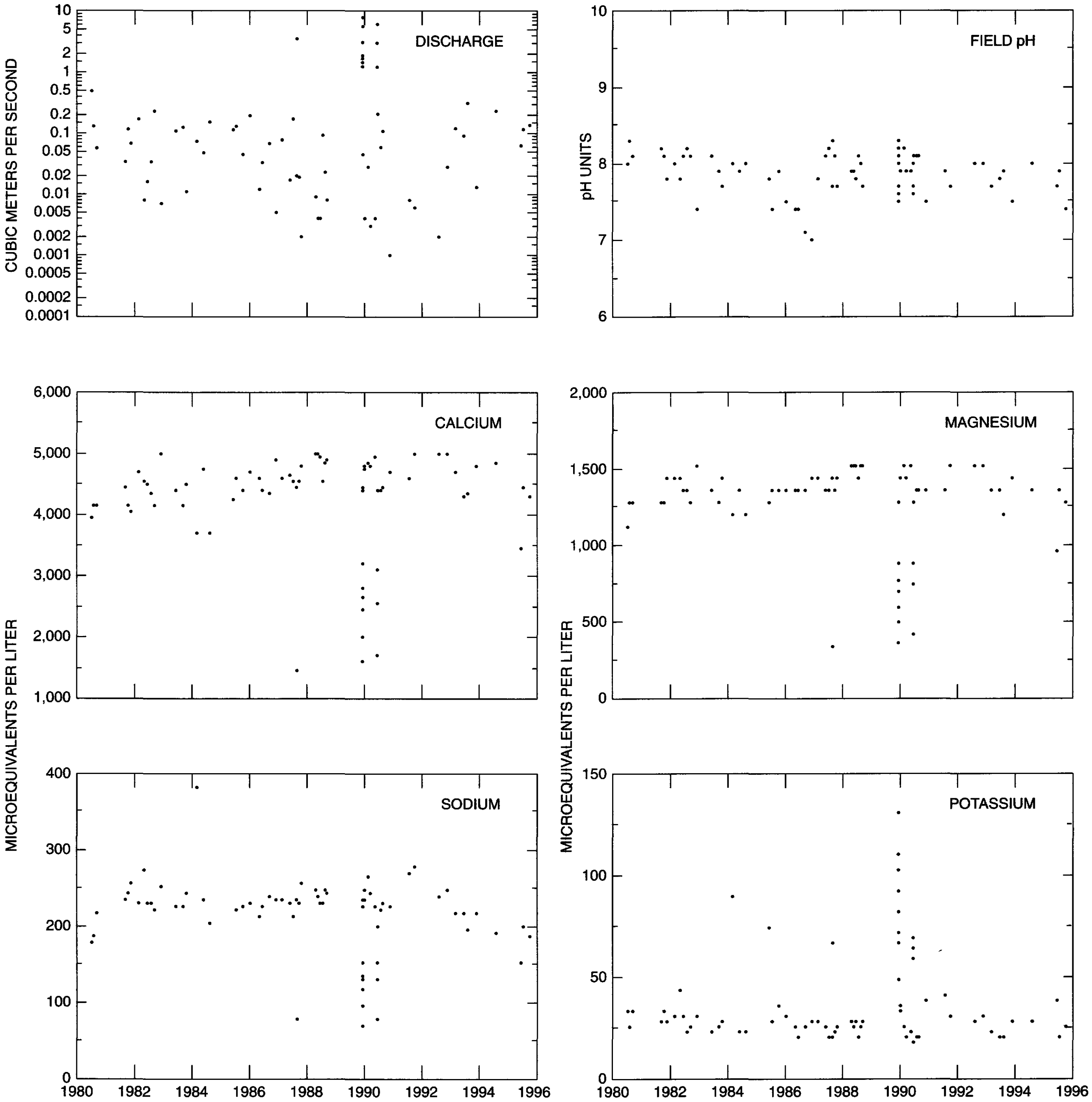


Figure 7. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Kings Creek near Manhattan, Kansas.

bias introduced by discharge. The downward sodium trend is consistent with the decrease in sodium detected in precipitation by Lynch and others (1995). For the period 1980–92, decreasing sodium concentrations were detected at 53 of 58 NADP stations throughout the country. Statistically significant downward trends ($\alpha = 0.05$) were reported at 28 of the 53 stations with decreasing sodium concentrations; many of these were in the regional area that includes Kansas.

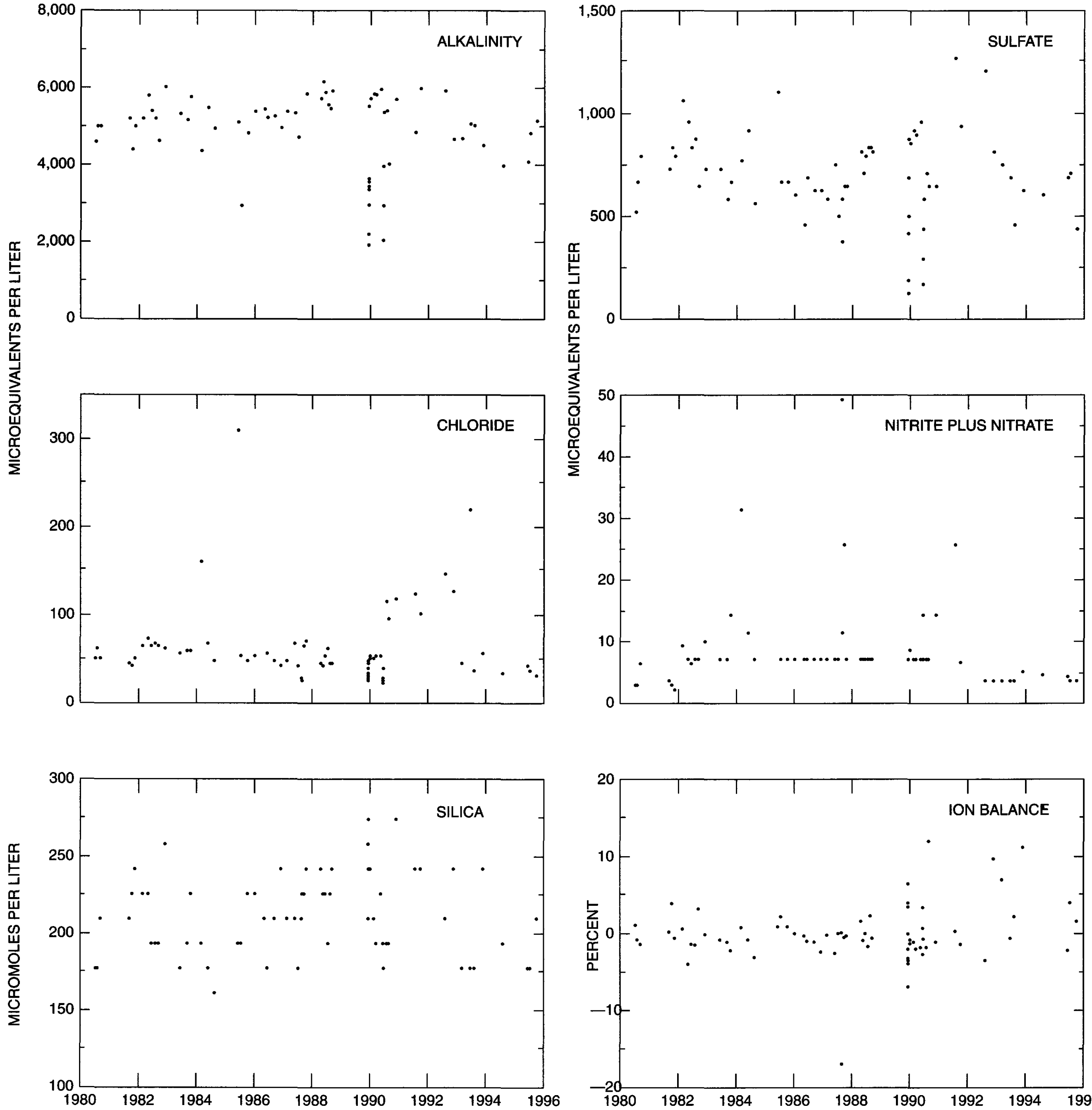


Figure 7. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Kings Creek near Manhattan, Kansas—Continued.

Synoptic Water-Quality Data

Results of a surface-water synoptic sampling conducted April 5, 1993, in the Kings Creek Basin are presented in table 13, and locations of the sampling sites are shown in figure 6. Discharge at the HBN station (site 7) was 0.48 m^3/s, which is higher than the mean monthly discharge of 0.16 m^3/s for the month of April (Putnam and others, 1996). Concentrations of dissolved constituents of tributaries generally were near or less than the median concentrations at the

Table 10. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ions measured in water-quality samples from Kings Creek, Kansas, 1980–95, and volume-weighted mean concentrations in wet precipitation collected at the Konza Prairie Station, Kansas, 1982–95

[Parameters in units of microequivalents per liter, except for 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; spec. cond., specific conductance; --, not reported; <, less than]

Parameter	Stream water						Precipitation VWM
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge	<0.001	0.01	0.07	0.17	7.9	72	--
Spec. cond., field	180	481	540	576	618	67	--
pH, field	7.0	7.7	7.9	8.1	8.3	72	5.0[a]
Calcium	1,400	4,200	4,400	4,800	5,000	72	16
Magnesium	340	1,300	1,400	1,400	1,500	72	2.5
Sodium	70	200	230	240	380	72	3.5
Potassium	18	23	28	38	130	72	.8
Ammonium	<.7	<.7	2.1	2.9	7.1	60	19
Alkalinity, laboratory	1,900	4,600	5,200	5,500	6,200	70	--
Sulfate	120	580	690	830	1,300	72	27
Chloride	22	41	51	65	310	72	3.4
Nitrite plus nitrate	2.1	6.4	7.1	7.1	49	65	20[b]
Silica	160	190	210	240	270	72	--

[a] Laboratory pH.

[b] Nitrate only.

Table 11. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ions, Kings Creek, Kansas, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; SiO_2, silica; --, not applicable]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	0.176	--	--	--	--	--	--	--	--
Ca	-.782	-0.164	--	--	--	--	--	--	--
Mg	-.804	-.187	0.907	--	--	--	--	--	--
Na	-.758	-.050	.682	0.774	--	--	--	--	--
K	.238	-.041	-.346	-.402	-0.164	--	--	--	--
Alk	-.784	-.051	.711	.742	.661	-0.362	--	--	--
SO_4	-.638	.159	.570	.610	.726	-.102	0.590	--	--
Cl	-.551	.047	.439	.480	.588	-.228	.441	0.626	--
SiO_2	-.274	-.085	.206	.205	.255	.566	.125	.053	-0.072

HBN station for the period 1980–95 (table 10). The sum of ions in the basin varied little, ranging from about 11,000 µeq/L on South Branch Kings Creek (site 1) to about 12,000 µeq/L on North Branch Kings Creek (site 6). The water chemistry in all the tributaries was similar to that at the HBN station and was a calcium bicarbonate type. The percent difference of cations and anions ranged from 0.2 to 1.2 percent, which indicates that unmeasured constituents, such as organic ions, nutrients, and trace metals, do not substantially contribute to the ionic composition of the basin waters.

The low variability of the water quality at the sampling sites is due to the small size of the Kings Creek Basin and the homogeneity of the geology and soils. The subbasins do have different burn and grazing practices. The North Branch Kings Creek (site 6) drains an area that is ungrazed, whereas the other tributaries drain areas grazed by bison. Samples from the ungrazed area have slightly higher concentrations of some of the base cations and anions, including sodium, sulfate, and chloride. The naming of the tributary (Appendix A) represents the burn schedule—for example, N20B is burned on a 20-year cycle. The effects of burning practices are difficult to assess with only one synoptic sample in each cycle. Some slight variation in nitrate exists—1.8 µeq/L for the 20-year cycle subbasin and less than 0.4 µeq/L in the 2- and 4-year cycle subbasins. However, all the nitrate concentrations were low. A study of soil-water chemistry found that burning does not appear to substantially alter soil-water nitrogen (Knapp and others, 1998).

Researchers have reported on other factors that affected nitrogen concentrations in prairie stream waters of the Konza Prairie Research Natural Area. Seasonal fluctuations were studied by McArthur and others (1985). They reported less nitrogen is exported from the basin during the summer growing season compared to fall or spring. Nitrate concentrations also responded to diurnal variations; the lowest concentrations tended to occur during daylight hours, corresponding to photosynthetic activity (McArthur and others, 1985). Tate (1990) reported that changes in flow characteristics influenced nitrate concentrations in the basin; nitrate concentrations were higher when the intermittent channels began to flow, then decreased as flow continued.

Table 12. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major-ion concentrations, Kings Creek, Kansas, 1982 through 1995

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

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	0.01	0.701	--	--
pH	–.02	.055	–0.02	0.124
Calcium	8	.728	7	.698
Magnesium	<.01	.670	–2	.635
Sodium	–2	.056	–2	.007
Potassium	<.01	.824	.08	.698
Alkalinity	–50	.016	–70	.016
Sulfate	–7	.318	–5	.211
Chloride	–.4	.897	([b])	--
Nitrite plus nitrate	–.2[a]	.086	--	--
Silica	<.01	.999	.4	.635

[a] Trend test for highly censored data was used.

[b] Concentration-flow model not significant at $\alpha = 0.10$.

Table 13. Physical properties and major-ion concentrations in surface-water samples collected at sites in the Kings Creek Basin, April 5, 1993

[Site locations shown in fig. 6; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO$_4$, sulfate; Cl, chloride; NO$_3$, nitrate; SiO$_2$, silica; concentrations in microequivalents per liter, except silica is in micromoles per liter; --, not measured; <, less than; criteria used in selection of sampling sites: LU = land use]

Site number	Site identification number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO$_4$	Cl	NO$_3$	SiO$_2$	Criteria
1	390515096350300	0.08	489	8.2	4,200	1,200	160	18	5,200	290	25	<0.4	170	LU
2	390513096343700	.04	538	8.1	4,300	1,100	160	21	5,400	290	23	1.6	170	LU
3	390519096343500	.01	493	8.2	4,000	1,000	170	24	5,000	290	28	1.8	170	LU
4	390529096351700	--	521	8.1	4,600	1,200	160	18	5,400	330	31	<.4	170	LU
5	390604096352900	.22	539	8.2	4,200	1,200	170	20	5,300	350	31	<.4	170	LU
6	390606096352900	.16	543	8.2	4,400	1,300	210	23	5,300	500	45	.7	180	LU
7	06879650	.48	543	8.1	4,400	1,300	190	21	5,300	460	37	1.2	180	

Rock Creek below Horse Creek near International Boundary, Montana (06169500)

Site Characteristics and Land Use

The Rock Creek HBN Basin is a sparsely populated basin in the Great Plains physiographic province (Fenneman, 1946) in northeastern Montana and southern Saskatchewan (fig. 8). The Rock Creek HBN station is about 3 km south of the Canadian boundary at latitude of 48°58'10" and a longitude of 106°50'20". At the station, Rock Creek drains 850 km^2 of gently rolling grasslands, flat valleys, and moderately defined drainage systems. The basin has little relief, with elevations that range from 760 to 980 m. The ecoregion of the basin is classified as the Great Plains-Palouse Dry Steppe Province (Bailey, 1995). Vegetative cover in the basin is predominantly prairie grass and scattered sagebrush; cottonwood trees and shrubs grow in some riparian areas. Rock Creek is tributary to the Milk River.

Streams in the Rock Creek Basin mostly are ephemeral or intermittent, including Rock Creek. Rock Creek typically goes dry at times in the late summer and early fall and may not flow during the winter owing to freezing conditions. Snowmelt produces runoff each year during the spring, and thunderstorms produce runoff in most streams during the summer. Thunderstorm activity typically causes increased discharge within a couple days (M.R. Johnson, U.S. Geological Survey, oral commun., 1997). The mean monthly discharges range from 0.01 m^3/s in January to 2.5 m^3/s in April (Shields and others, 1996). Average annual precipitation at the Opheim 10N weather station (about 34 km southeast of the site) is 29 cm. June is the wettest month, and February is the driest (Parrett and Hull, 1989, p. 2). Average annual runoff is less than 2 cm (Shields and others, 1996). The climate of the basin is typically continental where winters are cold and dry, and summers are hot and moderately dry. Mean monthly temperatures ranged from −13.5°C in January to 18.8°C in July during the period of record, 1959–95 (National Climatic Data Center, 1996).

The basin is underlain by gently dipping sedimentary rocks of Mesozoic age and unconsolidated deposits of Cenozoic age (Whitaker and Pearson, 1972, pl. 1). The rocks of Mesozoic age include undifferentiated Cretaceous formations: Frenchman, Whitemud, and Eastend Formations and the Bearpaw Shale (Whitaker and Pearson, 1972, pl. 1). The Frenchman, Whitemud, and Eastend Formations are generally interbedded sands, silts, and clay with locally carbonaceous zones (Whitaker and Pearson, 1972, pl. 1). The Bearpaw Shale of Late Cretaceous age is a noncalcareous, silty marine shale containing numerous bentonite beds and concretionary zones (Colton and others, 1989). Two formations of Tertiary age, Wood Mountain Formation and Ravenscrag Formation (Whitaker and Pearson, 1972), are in the northern part of the basin. The Wood Mountain Formation is composed of alluvial sand and gravel deposits locally conglomerated with carbonaceous cement and is preserved as an erosional remnant capping uplands (Whitaker and Pearson, 1972, pl. 1). The Ravenscrag Formation is a lignite-bearing, alluvial plain sediment. The area later was covered by continental glaciation from the Keewatin ice sheet. Most surficial deposits are of Quaternary age, either Pleistocene till, Holocene alluvium and colluvium, or Holocene alluvium. The soils in the area are deep, nearly level to strongly sloping soils formed in glacial till on uplands (U.S. Department of Agriculture, 1984b). Soils along the alluvial valleys are level to gently sloping with variable soil characteristics. Generally, they are moderately to well drained, but they are subject to flooding. The soil type is stratified loam to clay; soils high in clay tend to be alkaline.

The HBN station lies within Valley County, Mont.; however, most of the basin is within the Canadian Province of Saskatchewan. The Canadian part of the basin is designated as the Provincial Grasslands Park. Some of the land in the U.S. part of the basin is privately owned and some is administered by the Bureau of Land Management. Access is by way of a few light-duty roads and several unimproved roads. Access may be restricted across private holdings. Land use in the basin primarily is cattle grazing, with some hay and small grain production. Recreational use is limited to hunting in the fall. There are several minor diversions on Rock Creek and the tributary streams for irrigation and stock ponds.

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for the Rock Creek HBN station includes 91 water-quality samples that were collected from March 1977 to August 1995. Sampling frequency is described on the basis of water year, which begins on October 1 and ends on September 30.

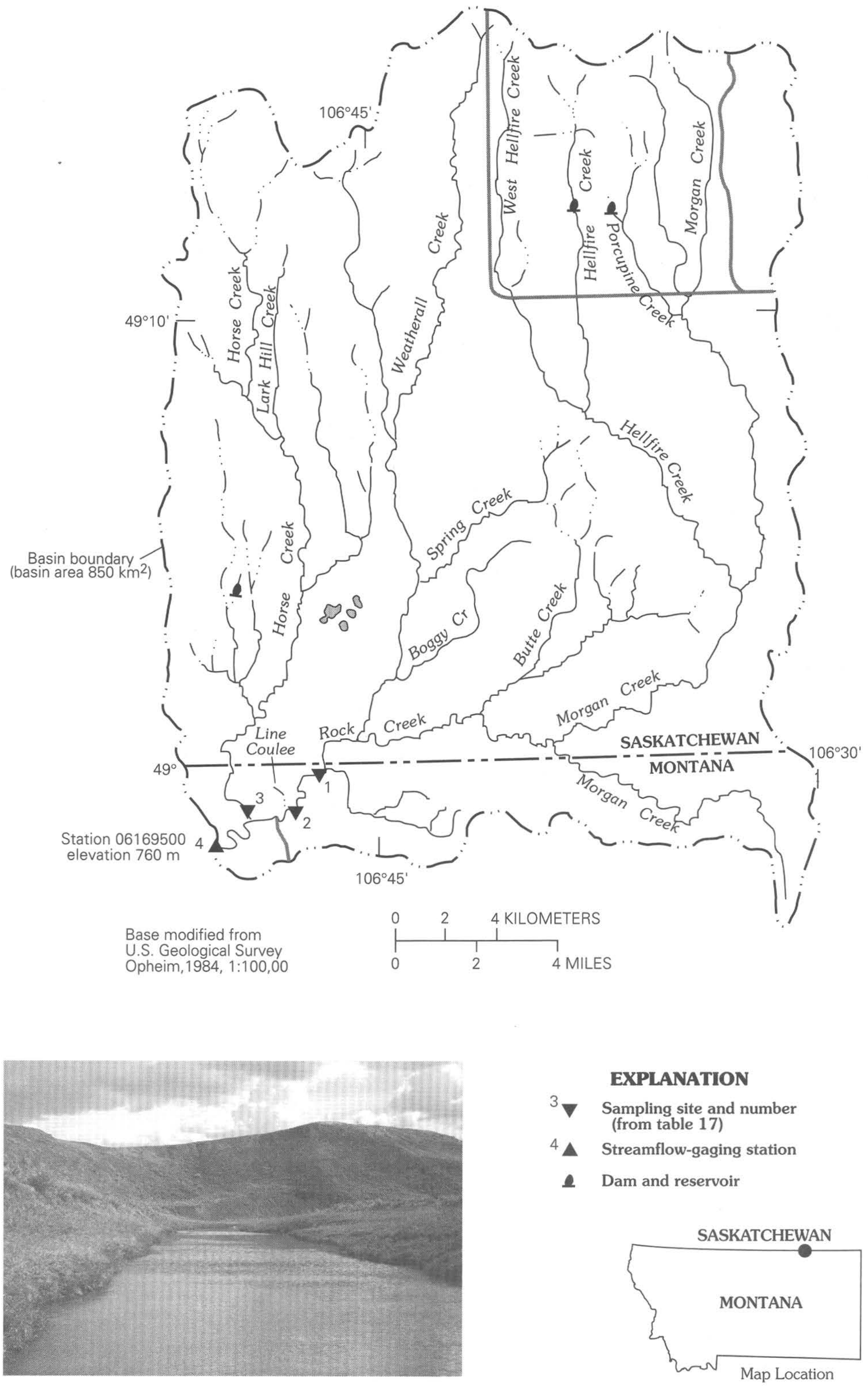


Figure 8. Map showing study area in Rock Creek Basin and photograph of Rock Creek.

Sampling frequency was at its peak during 1979–82 when an average of 10 samples were collected per year. The typical sampling frequency for this site, with the exception of the 1979–82 period, was about three samples per year. Samples were analyzed at the USGS NWQL in Arvada, Colo. The period of record for discharge is from water year 1916 to 1926, and from 1956 to current year (2000).

Data quality was checked using ion balances and time-series plots. Calculated ion balances for samples with complete major-ion analyses are shown in figure 9. All but two of the samples had an ionic balance within ±5 percent, indicating that the major-ion analytical results were of good quality and that unmeasured constituents, such as organic anions, nutrients, and trace metals, do not contribute substantially to the ionic

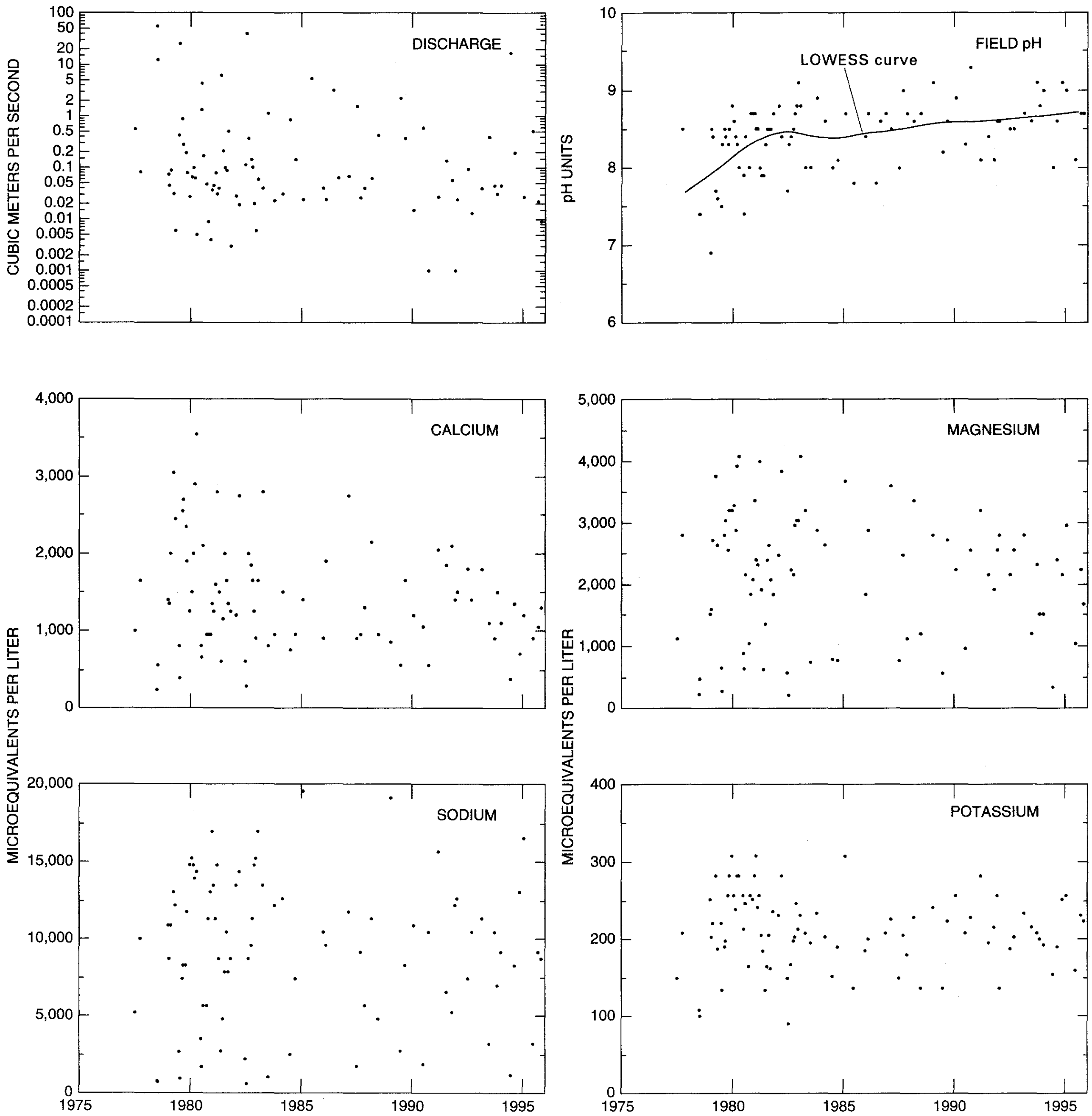


Figure 9. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Rock Creek below Horse Creek near International Boundary, Montana.

composition of Rock Creek. Time-series plots of ion concentrations were inspected for evidence of influences that are related to analytical method or sampling changes (fig. 9). The influence of analytical method changes should be less at this site because of the higher concentrations of dissolved constituents in samples collected from Rock Creek. Higher scatter exists in data for several of the constituents around the period of 1979–82. The constituents include calcium, magnesium, silica, and chloride. The increased scatter is the likely result of the higher sampling frequency of 10 samples per year compared to the lower sampling frequency of three samples in later years. A higher sampling frequency results in samples that are representative of a wider range of environmental conditions, and thus, a wider range in chemical concentrations.

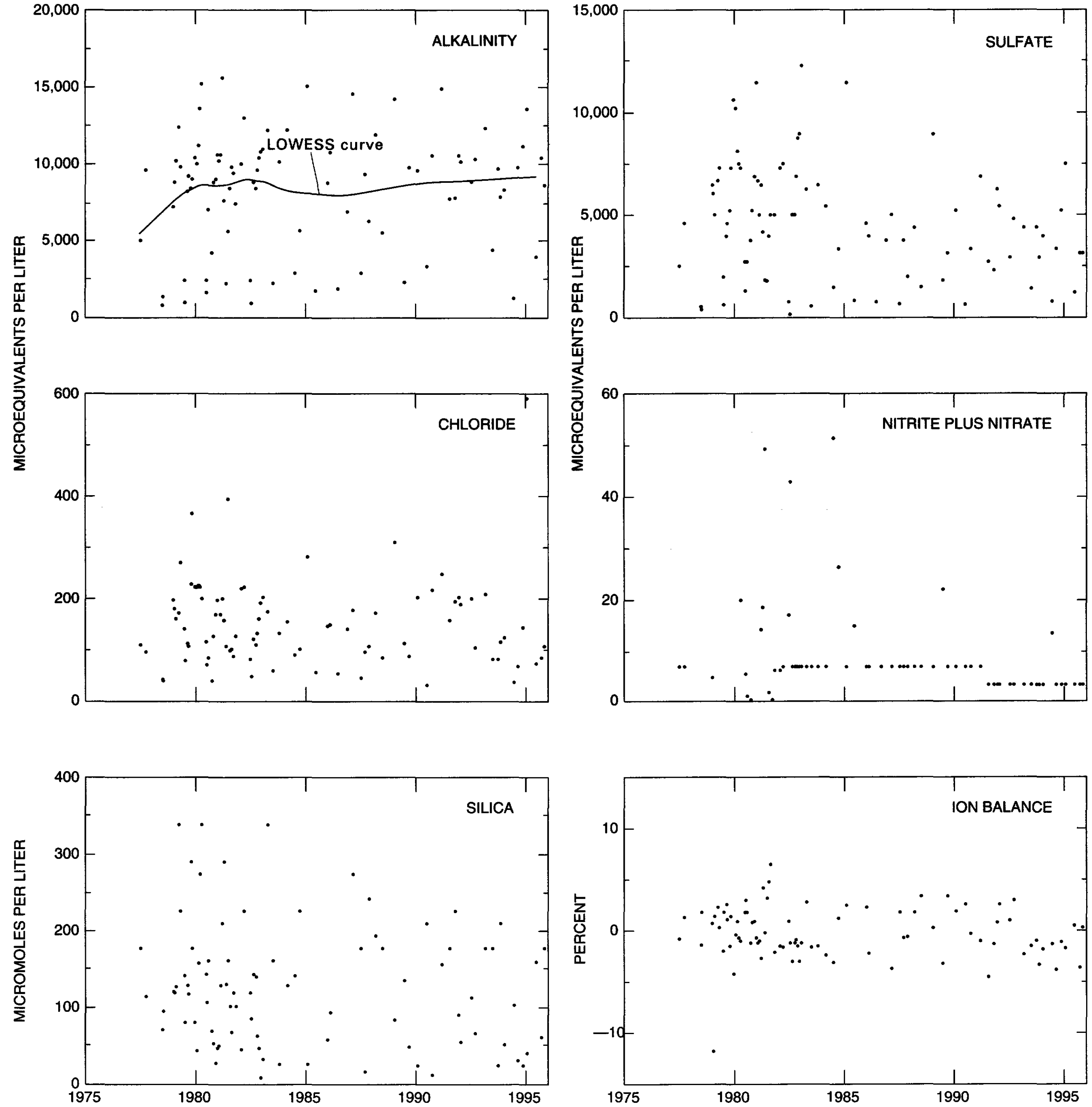


Figure 9. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Rock Creek below Horse Creek near International Boundary, Montana—Continued.

The reason for the higher scatter of nitrate data up to about 1985 could not be isolated. The step-pattern observed in the nitrate data around 1992 reflects a change to a lower minimum laboratory reporting level. Changes were made in meters and electrodes used for field pH determinations during the study period. When changes in methods or instrumentation result in improved precision or elimination of measurement bias, time-series data can exhibit less scatter or a directional shift, respectively. The time-series data, therefore, may reflect the method or instrument change rather than an environmental change.

The median and range of major-ion concentrations in stream water collected at the Rock Creek HBN station and VWM concentrations in wet precipitation measured at the Give Out Morgan NADP station are presented in table 14. The NADP station is 190 km southeast of the HBN station. Precipitation chemistry at the NADP station was dilute and slightly acidic with a VWM pH of 5.3 from 1982 to 1995. The dominant cations in precipitation were ammonium, 34 percent, and calcium, 32 percent. The dominant anions in precipitation were sulfate, 55 percent, and nitrate, 37 percent. A high proportion of nitrate in precipitation in some western areas has been attributed to exhaust from cars and other vehicles in urban areas and agricultural activity in the Great Plains States (National Atmospheric Deposition Program/National Trends Network, 1997).

The stream water at the Rock Creek HBN station is a sodium bicarbonate type. The sum of ion concentrations ranged from about 2,300 to about 49,000 μeq/L. Alkalinity ranged from 780 to 16,000 μeq/L. Bicarbonate was the primary contributor to alkalinity at this station and accounted for 66 percent of the median anion concentration. Sodium accounted for 72 percent of median cation concentration in stream water. Wide ranges of sodium can occur in natural waters because high concentrations of dissolved sodium can be reached before any precipitate is formed (Hem, 1992, p. 101). Potassium concentrations were high, which probably reflects the weathering of the clay materials in the basin (Deer and others, 1966). Ion concentrations, with the exception of ammonia and nitrite plus nitrate, are much greater in the stream water than in the precipitation, indicating that the input of most ions into the streams is from sources within the basin. In arid regions, when precipitation and runoff are insufficient to redissolve salts, salt residues accumulate in the soil or on exposed streambeds. Streams in basins with low average annual runoff and geologic

Table 14. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ions measured in water-quality samples from Rock Creek, Montana, 1977–95, and volume-weighted mean concentrations in wet precipitation collected at the Give Out Morgan Station, Montana, 1982–95

[Parameters in units of microequivalents per liter, except for 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; spec. cond., specific conductance; --, not reported; <, less than]

Parameter	Stream water						Precipitation
	Minimum	First quartile	Median	Third quartile	Maximum	n	VWM
Discharge	<0.001	0.03	0.06	0.37	56	91	--
Spec. cond., field	90	750	1,220	1,560	2,380	91	--
pH, field	6.9	8.1	8.5	8.7	9.3	90	5.3[a]
Calcium	240	950	1,400	1,800	3,600	87	15
Magnesium	210	1,200	2,300	2,900	4,100	87	5.7
Sodium	570	5,700	10,000	13,000	20,000	87	4.0
Potassium	90	190	210	250	310	89	1.5
Ammonium	<.7	1.4	4.3	7.9	36	60	16
Alkalinity, laboratory	780	5,600	9,000	11,000	16,000	90	--
Sulfate	140	2,500	4,400	6,500	12,000	89	21
Chloride	31	90	130	200	590	89	3.1
Nitrite plus nitrate	<.7	<.7	<7.1	7.1	51	72	14[b]
Silica	8.2	58	120	180	340	87	--

[a] Laboratory pH.
[b] Nitrate only.

Table 15. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ions, Rock Creek, Montana, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; SiO_2, silica; --, not applicable]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	–0.639	--	--	--	--	--	--	--	--
Ca	–.173	–0.048	--	--	--	--	--	--	--
Mg	–.540	.379	0.668	--	--	--	--	--	--
Na	–.702	.485	.435	0.881	--	--	--	--	--
K	–.570	.316	.331	.620	0.714	--	--	--	--
Alk	–.649	.455	.569	.927	.906	0.664	--	--	--
SO_4	–.652	.473	.431	.835	.969	.689	0.832	--	--
Cl	–.577	.343	.449	.691	.777	.602	.739	0.754	--
SiO_2	.346	–.624	.394	–.173	–.329	–.164	–.162	–.350	–0.064

settings that contain fine-grained sediments generally are characterized by high dissolved-solids concentrations (Biesecker and Leifeste, 1975). Specific conductance (median = 1,220 µS/cm) is an indicator of the high dissolved solids at this station. Annual precipitation and runoff data indicate that evapotranspiration can account for about a twentyfold increase in stream-water concentrations compared to precipitation. The median sodium concentration is 2,500 times greater in the stream than in the precipitation chemistry. This indicates that sodium is widely abundant in the soils and geologic materials in the basin. In contrast, median concentrations of ammonium and nitrate are lower in Rock Creek than in the precipitation and indicate that some nitrogen is retained by the biomass in the basin.

Correlations among dissolved constituents and stream discharge were determined for Rock Creek (table 15). Base cations and anions were inversely correlated with discharge. These results are consistent with a hydrologic system where base-flow chemistry that is dominated by ground water is diluted during periods of increased discharge. Ion concentrations in ground water tend to be greater than in surficial sources because the contact time with rocks and minerals is longer. The correlations with discharge, however, were not always strong. Some increases in discharge may be associated with temporary increases in dissolved-solids concentrations because salts that have accumulated in the soil are flushed out during the initial phases of melting of snow, thawing of frozen ground, or rainfall events. The strongest correlation among cations was between magnesium and sodium (rho value = 0.881). The strongest solute correlation was between sodium and sulfate (rho value = 0.969). Strong correlations also were found between sodium and alkalinity (rho value = 0.906), magnesium and alkalinity (rho value = 0.927), magnesium and sulfate (rho value = 0.835), and sodium and chloride (rho value = 0.777). These data reflect an abundance of various mineral salts in the basin.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents for Rock Creek during the period of 1978 through 1995 are presented in table 16. Statistically significant upward trends ($\alpha = 0.01$) were detected in pH and alkalinity for unadjusted concentrations. The alkalinity trend was no longer detected once the concentrations were adjusted for discharge, indicating that the trend was likely a function of streamflow conditions rather than changing water-quality conditions in the basin. The upward trend in pH remained after flow adjustment. A significant downward trend in sulfate concentrations also was detected in the flow-adjusted data. These trends in stream-water chemistry correspond with trends detected by Lynch and others (1995) for precipitation chemistry at an NADP station in western Montana during the period 1980–92. Lins (1987) reported that monthly sulfur-dioxide emissions in Montana decreased by 47 percent between 1975 and 1984. After accounting for evapotranspiration, stream-water sulfate concentrations were about 10 times greater than precipitation sulfate contributions, making it difficult to attribute stream-water trends only to changes in precipitation chemistry. The sulfate concentrations may have been slightly affected by sulfate method changes in 1982, which corresponds with the change from a methylthymol blue procedure to a turbidimetric titration method (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 83.07, 1983), and 1990, which corresponds with the change from turbidimetric titration to an ion-exchange chromatography analytical method (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 90.04, 1989; U.S. Geological Survey Office of Water Quality Technical Memorandum No. 90.13, 1990). The method changes, however, were more likely to have a higher impact on water with low sulfate concentrations.

Table 16. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major-ion concentrations, Rock Creek, Montana, 1978–95

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

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	–0.09	0.088	--	--
pH	.04	<.001	0.02	0.001
Calcium	<.01	.748	–4	.671
Magnesium	20	.365	–8	.339
Sodium	30	.471	–100	.151
Potassium	<.01	.840	–.4	.688
Alkalinity	100	.003	40	.369
Sulfate	–40	.130	–100	.005
Chloride	–.8	.662	–2	.234
Nitrite plus nitrate	.1[a]	.565	--	--
Silica	<.01	.999	([b])	--

[a] Trend test for highly censored data was used.

[b] Concentration-flow model not significant at $\alpha = 0.10$.

Synoptic Water-Quality Data

Results of a surface-water synoptic sampling conducted June 9 and 10, 1993, in the Rock Creek Basin are shown in table 17, and locations of the sampling sites are shown in figure 8. All sampling sites are south of the international border, in the southwestern part of the basin, and may not be representative of waters in the upper basin. Discharge at the HBN station (site 4) was 0.020 m^3/s, which is less than the historical mean monthly discharge of 0.34 m^3/s for the month of June (Shields and others, 1996). The discharge measured is more typical of streamflow conditions that occur in winter than in June.

The water type of the main-stem sites (sites 1, 2, and 4) and Horse Creek tributary (site 3) was sodium bicarbonate. Concentrations of dissolved constituents for the three main-stem sites (sites 1, 2, and 4) and one tributary (site 3) generally were within the range of historical values recorded at the HBN station for the period 1977–95 (table 14). The sum of ions ranged from about 15,000 μeq/L on Horse Creek (site 3) to about 31,000 μeq/L at the HBN station (site 4). Sodium carbonate salts contribute less to the ion composition of the water of Horse Creek than Rock Creek, as indicated by the percentages of contributions from major ions. Sodium constituted about 60 percent of cation concentration in the Horse Creek sample compared to about 73 percent in the Rock Creek samples. Bicarbonate constituted about 58 percent of the anion concentration in the Horse Creek sample compared to about 73 percent in the samples from Rock Creek. After adjusting for the effects of evapotranspiration, precipitation only contributes part of the salt-forming anions. Sulfate contributions from

Table 17. Physical properties and major-ion concentrations in surface-water samples collected at sites in the Rock Creek Basin, June 9 and 10, 1993

[Site locations shown in fig. 8; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; SiO_2, silica; concentrations in microequivalents per liter, except silica is in micromoles per liter; --, not measured; <, less than; criteria used in selection of sampling sites: TRIB = major tributary]

Site number	Site identification number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	SiO_2	Criteria
1	485949106463900	0.022	1,260	8.9	1,100	2,500	10,000	200	10,000	3,800	76	<0.4	8.5	TRIB
2	485858106473500	.020	1,330	9.0	950	2,700	11,000	230	11,000	4,200	79	<.4	13	TRIB
3	485856106492600	.020	713	8.5	1,400	1,200	4,300	280	4,400	3,100	60	.5	9.3	TRIB
4	06169500	.020	1,430	8.9	1,100	2,600	11,000	240	12,000	4,400	120	2.1	28	

precipitation ranged from about 10 percent (site 4) to about 13 percent (site 3). This indicates that sources for sulfate occur in both Horse Creek and Rock Creek drainages. Chloride contributions from precipitation range from about 53 percent (site 4) to nearly 100 percent (site 3). Discharge and lower ion concentrations in Horse Creek did not appear to have any dilution effects on Rock Creek as ion concentrations increased between sites 2 and 4. Precipitation chemistry probably can account for nitrate concentrations at all four synoptic sites.

Swiftcurrent Creek at Many Glacier, Montana (05014500)

Site Characteristics and Land Use

The Swiftcurrent Creek HBN Basin lies within the Northern Rocky Mountain physiographic province (Fenneman, 1946) in northern Montana (fig. 10). The HBN station is at the outlet of Swiftcurrent Lake in Glacier National Park, about 18 km southwest of Babb, Mont., at a latitude of 48°47'57" and a longitude

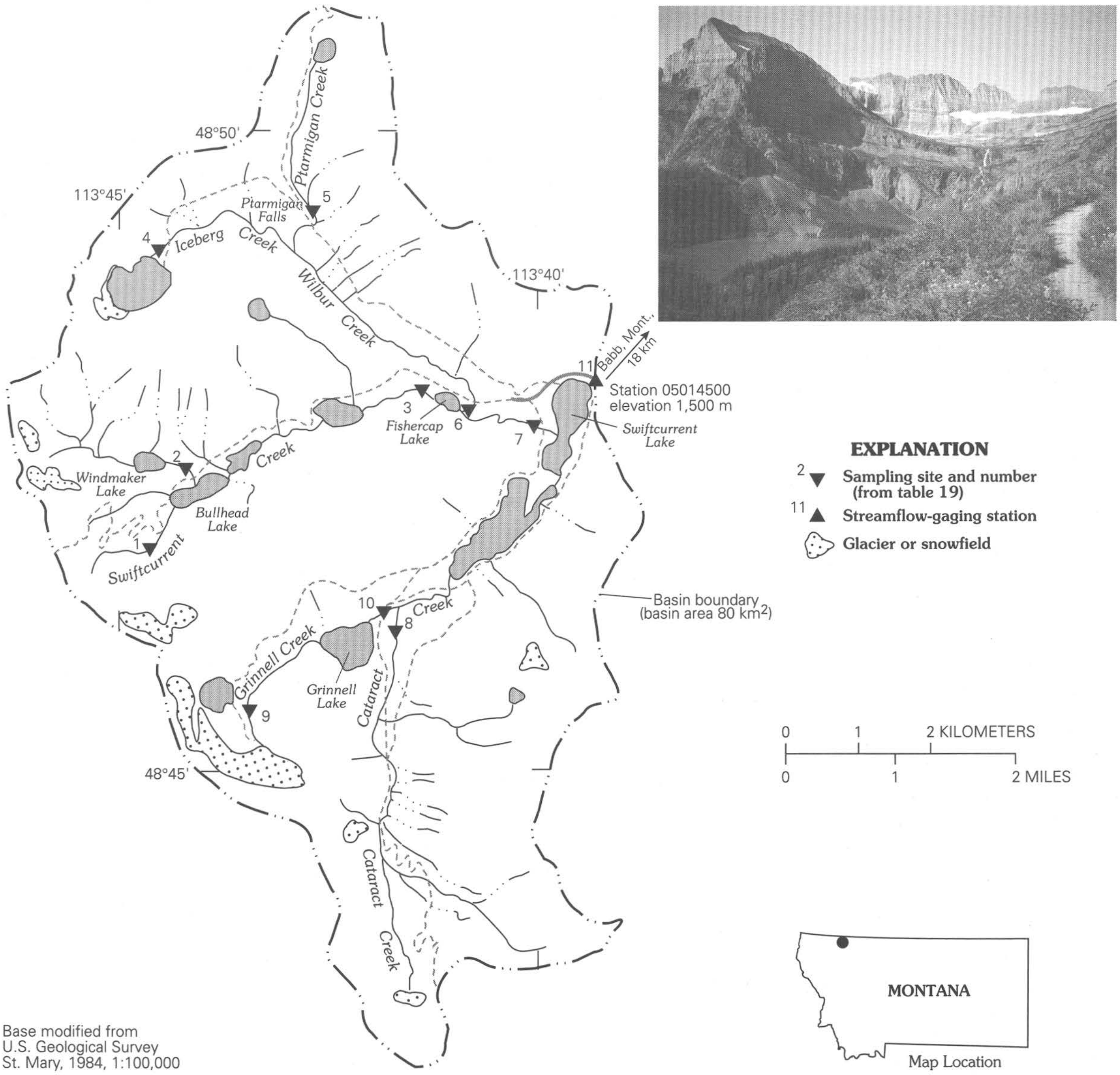


Figure 10. Map showing study area in Swiftcurrent Creek Basin and photograph of the Grinnell Creek Basin.

of 113°39'21". Swiftcurrent Creek at the HBN station drains 80 km^2 of rugged, mountainous terrain on the east side of the Rocky Mountains, entirely within Glacier National Park. Vertical rock exposures make for abrupt changes in basin topography; elevations range from 1,500 to 3,000 m. The ecoregion of the basin is classified as the Northern Rocky Mountain Forest-Steppe–Coniferous Forest–Alpine Meadow Province (Bailey, 1995). The vegetation in the Swiftcurrent Creek Basin changes with elevation. At lower elevations, forests of spruce and fir trees, aspen, and various shrubs cover the basin. At higher elevations, the vegetation grades into alpine tundra. The grass cover is sparse owing to the poorly developed soils and bare rock cover. Swiftcurrent Creek is tributary to the St. Mary River, which drains to the Saskatchewan River Basin.

Swiftcurrent Creek is a perennial, high-gradient mountain stream; several small glaciers near the Continental Divide form the headwaters of the stream. The basin has a snowmelt-dominated hydrograph; mean monthly discharges on Swiftcurrent Creek ranged from 0.75 m^3/s in February to 14 m^3/s in June (Shields and others, 1996). Average annual precipitation increases in the basin with increasing elevation. Average annual precipitation at the Many Glacier weather station is about 100 cm; higher elevations may receive closer to 200 cm. Precipitation falls predominantly in the form of snow. Average annual runoff is about 160 cm (Shields and others, 1996). The winters are cold and summers mild; mean monthly temperatures ranged from about −10.7°C in January to 14.8°C in July at the Many Glacier station during the period 1967–95 (National Climatic Data Center, 1996). Temperatures in the basin decrease with increasing elevation.

The Swiftcurrent HBN Basin drains a westward-dipping sequence of argillite, quartzite, and calcareous rocks of Precambrian age. The younger rocks in the sequence are exposed in the upper basin, whereas the older rocks are near the HBN station. The bedrock is very resistant to weathering and supplies little sediment to the stream. In the upper basin, Precambrian argillites are varicolored from dark green, gray, pink, to brick red. A series of greenish-gray mafic lava flow deposits lie in the upper basin, near the Continental Divide. Older, interbedded argillites, dolomites, stromatolitic limestones, and quartz arenites are present in the lower part of the basin (Earhart and others, 1990). Tectonic forces thrusted sediments upward from west to east. The eastern limb of the Akamina Syncline is the predominant structural feature in the basin. Unconsolidated materials on slopes are composed of locally derived, unsorted, angular gravel-sized clasts in a matrix of unsorted sand, silt, and clay (Carrara, 1990). Unsorted, subrounded to subangular, bouldery rubble on the valley floor was deposited as ground moraine by alpine glaciers.

The Swiftcurrent Creek HBN Basin lies entirely within the boundaries of Glacier National Park. The access to the HBN station is by paved road. Just beyond the HBN station, park facilities are clustered along Swiftcurrent Lake. The rest of the basin, including Grinnell Lake, Bullhead Lake, and Iceberg Lake, is accessible only by hiking trail. Between December and April, the road to the station usually is impassable owing to snow and generally is closed at the Many Glacier park entrance. During this time, the HBN station is most accessible by skis, snowshoes, or mountain bike (N.A. Midtlyng, U.S. Geological Survey, oral commun., 1997). The basin is essentially undeveloped except for park facilities, including a few hotels, campground, and ranger station, which are typically open from Memorial Day to Labor Day. The water supply for the facilities is withdrawn from the basin upstream from the HBN station; sewage disposal is downstream from the station. Recreational use of Glacier National Park is high. About 157,400 people used the park's backcountry during the summer season of 1988 (Coen, 1992). More than 95 percent of the backcountry users were day hikers. Other activities in the basin include fishing, backcountry camping, and some cross-country skiing. Several large lakes, which interrupt the steep stream gradients, lie in the basin. Wildlife is diverse and abundant in the park, including bighorn sheep, mountain goats, black and grizzly bear, whitetail and mule deer, moose, and wolves.

Historical Water-Quality Data

Samples for chemical analyses have not been collected routinely at the Swiftcurrent Creek HBN station. The data set analyzed for this report includes 83 measurements of instantaneous discharge and 82 measurements of specific conductance for the period October 1963 to July 1994 (table 18). The entire period of record for discharge at the Swiftcurrent Creek HBN station is from 1959 to 1997. Median values and ranges of discharge and specific conductance are shown in table 18. Discharge ranged from 0.19 to 40 m^3/s, with a median discharge of

3.1 m^3/s. The range of specific conductance for the period was 70 to 131 µS/cm, with a median value of 104 µS/cm. Specific conductance can be used as an indicator of the dissolved solids (Hem, 1992, p. 165). Based on the range of specific-conductance values, dissolved solids generally are low at this site. Streams in basins with high annual runoff tend to have low dissolved-solids concentrations (Biesecker and Leifeste, 1975). Specific conductance had an inverse relation with discharge. The Spearman rank correlation coefficient was –0.674.

Synoptic Water-Quality Data

Results of a surface-water synoptic sampling conducted August 1–3, 1992, in the Swiftcurrent Creek Basin are presented in table 19, and locations of the sampling sites are shown in figure 10. Discharge at the HBN station (site 11) was 2.9 m^3/s compared to the mean monthly discharge of 3.3 m^3/s for the month of August (Shields and others, 1996). The water at the HBN station (site 11) was a calcium bicarbonate type. Bicarbonate was the primary contributor to alkalinity at this station. The sum of ions for the HBN station was 2,100 µeq/L. The specific conductance was 102 µS/cm, compared to the median of 104 µS/cm for the period of record, 1964–94. Therefore, the synoptic sample should indicate typical water-quality composition at the HBN station. The dominant cation, calcium, contributed 67 percent of the total cation concentration in stream water; magnesium contributed 31 percent. Bicarbonate contributed 95 percent of the total anion concentration. The predominance of calcium and bicarbonate indicates that carbonate rocks in the basin contribute to the ion composition of the stream water. The weathering of dolomites and clay minerals in underlying argillites

Table 18. Minimum, first quartile, median, third quartile, and maximum values of physical properties measured at Swiftcurrent Creek, Montana, 1964–94

[Discharge in cubic meters per second; specific conductance in microsiemens per centimeter at 25 degrees Celsius; n, number of measurements]

Parameter	Stream water					
	Minimum	First quartile	Median	Third quartile	Maximum	n
Discharge	0.19	1.4	3.1	8.2	40	83
Specific conductance, field	70	97	104	111	131	82

Table 19. Physical properties and major-ion concentrations in surface-water samples collected at sites in the Swiftcurrent Creek Basin, August 1–3, 1992

[Site locations shown in fig. 10; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; SiO_2, silica; concentrations in microequivalents per liter, except silica is in micromoles per liter; --, not measured; <, less than; criteria used in selection of sampling sites: BG = bedrock geology, TRIB = major tributary, LU = land use]

Site number	Site identification number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	SiO_2	Criteria
1	484649113443200	0.22	75	8.0	600	160	13	2.0	730	33	<0.3	4.3	20	BG
2	484717113440800	.23	106	8.3	800	260	13	3.3	1,000	29	<.3	.7	25	TRIB
3	484754113411700	--	107	8.2	750	300	17	2.8	1,000	21	37	.6	23	TRIB
4	484903113443500	.14	84	8.2	550	250	13	2.8	750	56	<.3	3.6	17	BG
5	484920113424000	.06	175	8.2	1,000	700	35	7.4	1,500	48	<.3	8.6	52	TRIB
6	484753113404500	.28	120	8.2	600	160	8.7	4.6	1,100	19	<.3	.7	20	TRIB
7	484739113395800	.94	110	8.3	750	330	22	3.3	1,000	35	<.3	1.9	28	LU
8	484604113414500	.064	125	8.2	800	410	17	4.1	1,200	23	<.3	8.6	37	TRIB
9	484528113432600	--	49	7.9	360	120	8.7	2.3	430	19	2.8	<.7	12	BG
10	484614113415500	1.5	114	8.2	550	240	13	2.8	800	38	<.3	3.6	22	TRIB
11	05014500	2.9	102	8.8	700	330	17	3.1	980	48	.3	<.7	27	

is a source for magnesium in the basin (Coen, 1992). Sulfate and chloride concentrations generally were low and were comparable to precipitation chemistry at NADP stations in Montana. The percent difference of cations and anions was about 1 percent, indicating that unmeasured ions do not substantially contribute to the ionic content of Swiftcurrent Creek. Nitrate concentrations in the samples were less than nitrate concentrations in precipitation chemistry for NADP stations in Montana, indicating atmospheric inputs probably account for the nitrate measured in the stream water.

The water at the remaining synoptic sites (sites 1–10) also is an alkaline, calcium bicarbonate type. The sum of ions in tributaries in the basin ranged from 940 μeq/L in upper Grinnell Creek (site 9) to 3,300 μeq/L in Ptarmigan Creek (site 5). Water quality in the tributaries is a function of drainage size and underlying bedrock. The specific conductance in upper Grinnell Creek (49 μS/cm) was less than the minimum specific conductance (70 μS/cm) measured at the HBN station for the period of record, 1964–94. Site 1 and site 4 also had low specific conductance (75 and 84 μS/cm, respectively). The small drainage area and extensive exposures of resistant bedrock at these sites probably accounts for their low dissolved solids. The highest specific conductance was at site 5 on Ptarmigan Creek (175 μS/cm); that value exceeds the maximum specific conductance of 131 μS/cm measured at the HBN station for the period of record.

Dismal River near Thedford, Nebraska (06775900)

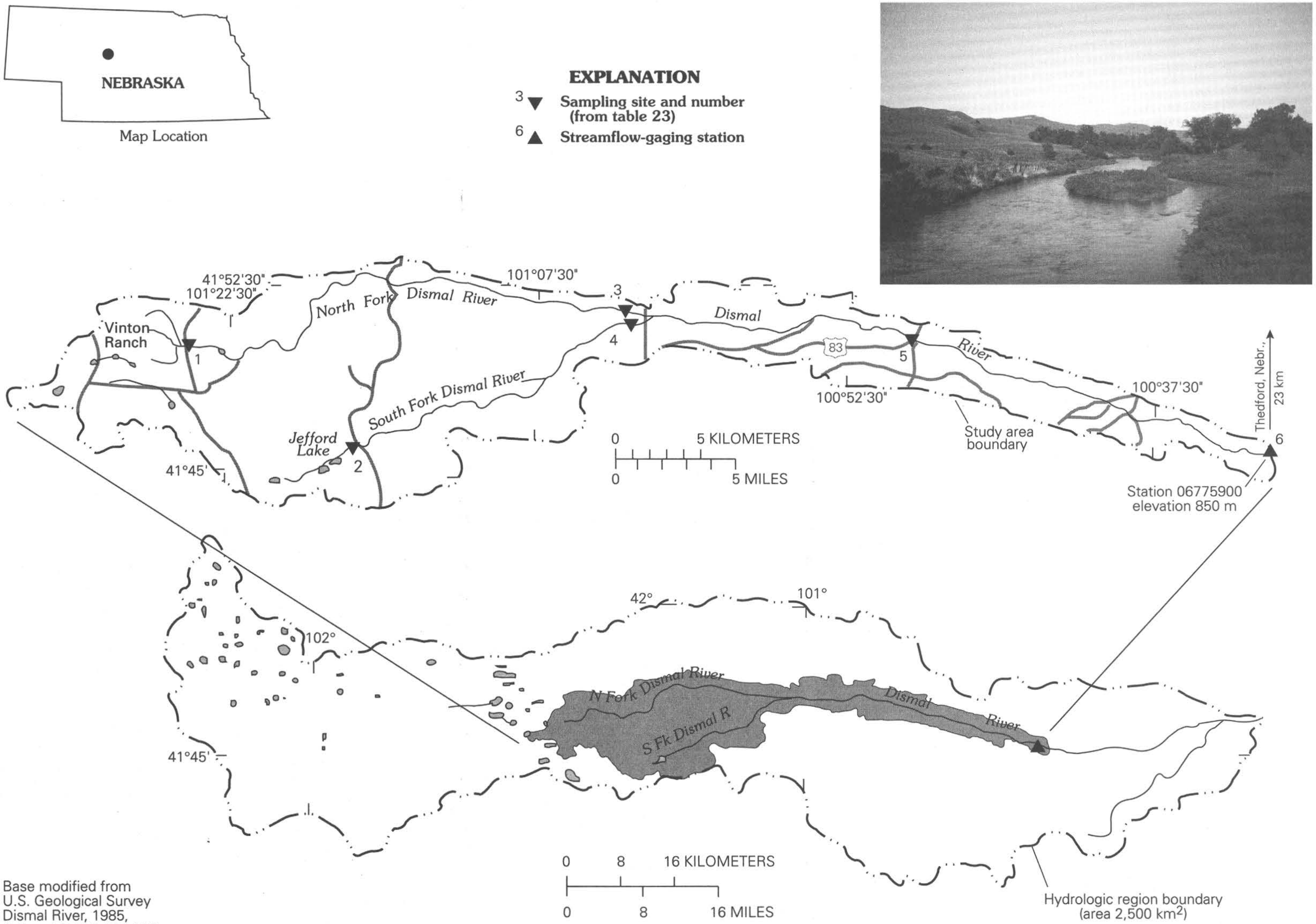
Site Characteristics and Land Use

The Dismal River HBN Basin is in the High Plains Section of the Great Plains physiographic province (Fenneman, 1946) in north-central Nebraska (fig. 11). The ecoregion of the basin is classified as the Great Plains Steppe Province (Bailey, 1995). The HBN station is 23 km south of Thedford, Nebr., at a latitude of 41°46'45" and a longitude of 100°31'30". The Dismal River drains about 2,500 km^2 of grass-stabilized sand dunes in the Sand Hills region. The river is deeply entrenched into interdunal valleys, and only about 80 km^2 close to the channel actually contribute directly to surface runoff in the river (Boohar and others, 1996). Several lakes lie in the upper basin but are outside the contributing drainage area. Basin elevations range from about 850 to about 1,200 m. The slope of the main stream is only about 1 m/km. The Dismal River is tributary to the Middle Loup River that, after the confluence with the North Loup River, forms the Loup River and drains into the Platte River.

Infiltration rates in the sand are high, allowing little surface runoff. Flow in the Dismal River is due almost entirely to ground-water discharge through seeps, springs, and boiling springs (Cornwell, 1990). Boiling sand springs result from vertical ground-water conduits (Guhman and Pederson, 1992). Conduits up to 10 m in diameter and 44 m deep are developed in alluvium. Flow characteristics are nearly uniform throughout the year, and mean monthly discharges only range from 5.4 m^3/s in August to 5.9 m^3/s in April (Boohar and others, 1996). Average annual precipitation at the Halsey 2W weather station, about 27 km southeast of the HBN station, is about 54 cm. Most of the precipitation falls during brief thunderstorms in spring and summer. The climate is characterized by cold winters to warm summers; mean monthly temperatures ranged from −5.4°C in January to 23.7°C in July during the period 1903–89 (National Climatic Data Center, 1996).

The vegetation of the Dismal River Basin is typical of the Sand Hills prairie. Whereas the Sand Hills prairie is less diverse than some grassland areas, it is unusually diverse for having such sandy soils. The Sand Hills prairie contains tallgrass species, shortgrass species, sedges, and forbs. The most widespread plant community, the bunchgrass community, is characteristic of the dunes (Bleed and Flowerday, 1990). The most common bunchgrass, little bluestem, is the State grass of Nebraska. Deciduous trees grow along the banks of the streams, and some windbreak trees have been planted. Interdunal valleys may contain meadow and marsh plant communities.

Several geologic processes have operated in the Sand Hills region (Ahlbrandt and others, 1980). Cretaceous chalk, limestones, and shales underlie the Sand Hills region about 150 to 400 m below the surface. The near-surface geology of the Dismal River Basin consists of unconsolidated eolian and alluvial materials and consolidated eolian and alluvial



Base modified from
U.S. Geological Survey
Dismal River, 1985,
Arthur, 1985, 1:100,000

Figure 11. Map showing study area in Dismal River Basin and hydrologic region boundary and photograph of the Dismal River downstream from the streamflow-gaging station.

materials. Cenozoic consolidated strata overlying the Cretaceous shales and underlying the Sand Hills are divided into two types. The older, homogeneous, lower units are the White River Group of Oligocene age and the Arikaree Group of Miocene age. These units consist of fine-grained sediments with abundant volcanically derived material of mostly eolian origin. Overlying the older units is the Ogallala Group of Miocene age, which is heterogeneous and generally coarser grained than the White River Group and the Arikaree Group. The Ogallala Group was deposited during an episode of stream erosion. The source of the sediments is believed to be the Rocky Mountains in Colorado and Wyoming (Bleed and Flowerday, 1990). The ion composition of some of the boiling springs indicates that some of the deeper springs may originate in the Ogallala aquifer (Gilbert and Pederson, 1988). Overlying the consolidated strata are alluvial silt, sand, and gravel deposits of Pliocene age. Some of the boiling springs may have water sources in the Pliocene deposits (Guhman and Pederson, 1992). The eolian sands around the Dismal River probably are between 3,000 and 8,000 years old and about 40 m thick. The Dismal River Valley is thought to be less than 1,500 years old (Bleed and Flowerday, 1990). Soils formed on both gentle and steep slopes are windblown sands that generally are deep and very permeable. The windblown materials form dune structures. Surface layers are typically grayish-brown, loose, fine sands about 10 cm thick. The underlying materials are pale brown, loose, fine sands up to 150 cm thick. Soils contain little organic matter (Bleed and Flowerday, 1990).

The Dismal River HBN station is in Thomas County. Land ownership within the Dismal River Basin is entirely private upstream from the HBN station (Will Boyer, Upper Loup Natural Resources District, written commun., 1996). Just downstream from the station, the Nebraska National Forest borders the north side of the river for about 26 km. The station is accessed from U.S. Highway 83. Other roads in the basin generally are unimproved four-wheel-drive roads. The basin is accessible year round, weather permitting. Land cover is essentially 100 percent rangeland; grazing by cattle is the predominant land use and has continued throughout the study period. There are private residences in the basin; a slight increase in the residential population may have occurred since 1960. A small part of the upper basin is subirrigated rangeland that is used occasionally for hay production (Will Boyer, Upper Loup Natural Resources District, written commun., 1996). Recreational use of the Dismal River includes canoeing, camping, and fishing. One golf course is developed on the high sandy hills.

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for the Dismal River HBN station includes 166 water-quality samples that were collected from December 1966 to August 1995. Sampling frequency is described on the basis of water year, which begins on October 1 and ends on September 30. Sampling frequency was monthly during the early part of the record, 1968–70. Sampling frequency generally was bimonthly during the period 1971–82. For the rest of the period, sampling frequency generally was quarterly. Samples were analyzed at USGS district water-quality laboratories until the early 1970's. After 1973, with the creation of the USGS Central Laboratory System, all samples were analyzed at the water-quality laboratory (now called NWQL) in Arvada, Colo. The period of record for discharge is from water year 1967 to current year (2000).

Data quality was checked using ion balances and time-series plots. Calculated ion balances for samples with complete major-ion analyses are shown in figure 12. About 95 percent of the samples had ion balances within the ±5 percent range, indicating that the major-ion analytical results generally were of good quality and that unmeasured constituents, such as organic anions, nutrients, and trace metals, do not contribute substantially to the ion composition of the stream water. Time-series plots of ion concentrations were inspected for evidence of influences that are related to analytical method changes (fig. 12). Magnesium and sodium show a similar pattern of having more scatter in the early part of the record and a decrease in scatter after 1983. This decrease coincides with a change in the analytical method for these analytes from AA spectroscopy to ICP spectroscopy (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 82.18, 1982). The decrease in scatter of dissolved sulfate after 1982 corresponds with the change from a methylthymol blue procedure to a turbidimetric titration method (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 83.07, 1983). The further decrease in the scatter of dissolved sulfate concentrations after 1990 corresponds with the change from turbidimetric titration to an ion-exchange chromatography analytical method (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 90.04, 1989; U.S. Geological Survey Office of Water Quality Technical Memorandum No. 90.13, 1990). Several temporal trends also were evident in the field pH values. Changes in field meters and electrodes used for field pH determinations also occurred during the study period. When changes in methods or instrumentation result in improved precision or elimination of measurement bias, time-series data can exhibit less scatter or a directional shift, respectively. The time-series data, therefore, may reflect the method or instrument change rather than an environmental change.

The median and range of major-ion concentrations in the stream water collected at the Dismal River HBN station and VWM concentrations in wet precipitation measured at the North Platte Agriculture Experimental Station NADP station are presented in table 20. The precipitation station is about 84 km southwest of the HBN station. Precipitation chemistry at the NADP station was dilute and slightly acidic with VWM pH of 5.6 during the period of record, 1985–95. The dominant cation in precipitation was ammonium, which contributed about 56 percent of cation concentration. This concentration and percentage were higher than at most NADP stations near HBN sites. The dominant anions in precipitation were sulfate and nitrate, which contributed 47 and 46 percent, respectively, of the total anion concentration. Ammonium concentrations in precipitation are highest across the middle part of the United States (National Atmospheric Deposition Program/National Trends Network, 1996), in agricultural areas where nitrogen sources, including livestock waste and fertilizer applications, are widespread. However, precipitation only contributes about 6 percent of the annual nitrogen input to central Nebraska basins compared to about 93 percent from waste and fertilizer sources (Boyd, 1996).

Stream water in the Dismal River is a buffered, calcium bicarbonate type. The sum of ion concentrations ranged from about 3,400 to about 4,200 μeq/L. Alkalinity ranged from 1,400 to 1,900 μeq/L, and bicarbonate was the primary contributor to alkalinity at this station. The major cation, calcium, contributed 63 percent of the total cation concentration in stream water; bicarbonate, the major anion, contributed 89 percent of the median anion concentration. The small range in ion concentrations results from the constant ground-water source for stream discharge. The effects of evapotranspiration on the contributions of ions from precipitation using annual runoff data are difficult to determine owing to the large difference between total drainage area compared to the contributing drainage area. The concentrations of dissolved silica were higher at this station than at other HBN stations. The high quartz and feldspar content of the soil and underlying materials is the source of the silica. The range of nitrite plus nitrate concentrations (11 to 48 μeq/L) is much lower than in other Nebraska streams (Boyd, 1996) as little of the land use is cropland where nitrogen fertilizers are applied.

Correlations among dissolved constituents and discharge were determined for the Dismal River (table 21). The base cations and anions showed weak and mixed, positive and inverse relations with discharge; rho values range from –0.335 (silica) to 0.322 (pH). The discharge is not highly variable in this basin, and most of the water is derived from ground water. Surficial runoff containing low dissolved solids does not typically occur in the basin, and dilution effects from precipitation are not observed in the ion-discharge relations. Positive, but weak, correlations existed among base ions. The strongest correlation was between calcium and magnesium (rho value = 0.489). The weak relations in stream water may reflect contributions from varying ground-water sources (Gilbert and Pederson, 1988).

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents for the Dismal River from 1967 through 1995 are presented in table 22. A significant upward trend was observed in discharge. The trend in discharge is only representative of instantaneous measurements made during water-quality sampling and may not correspond with a trend in the continuous discharge record. The only significant trends ($\alpha = 0.01$) observed in the chemical data were a downward trend in unadjusted sulfate concentrations

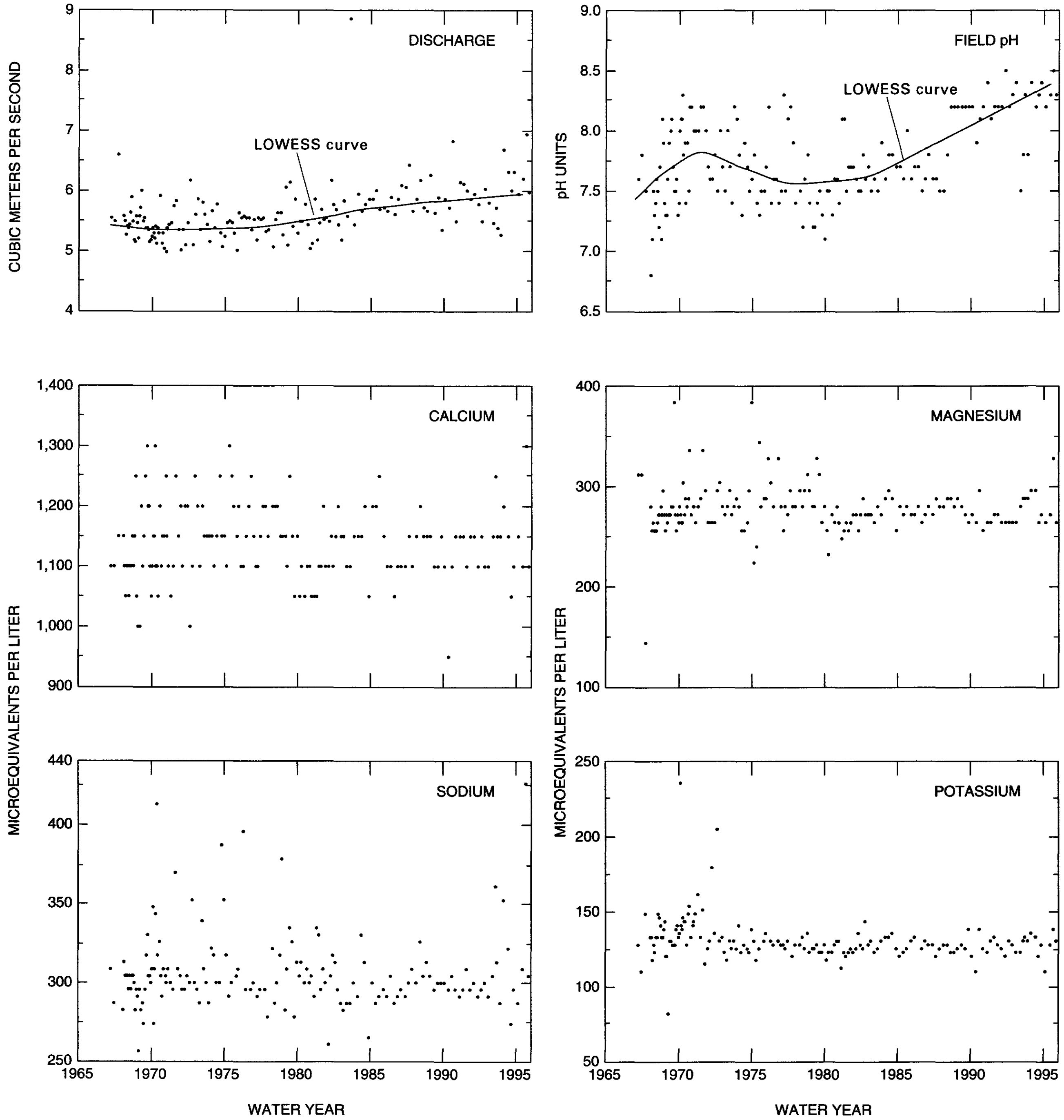


Figure 12. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Dismal River near Thedford, Nebraska.

and upward trends in unadjusted and flow-adjusted pH. The flow-adjustment model was not significant and did not calculate trends for most of the chemical constituents. This is probably because of the small range of discharges at this HBN station produced by the ground-water dominated flows. The increase in pH and decrease in sulfate concentrations reverses the trends determined by Smith and Alexander (1983) at this station. For the study period from the late 1960's to 1981, significant increases ($\alpha = 0.01$) were observed in

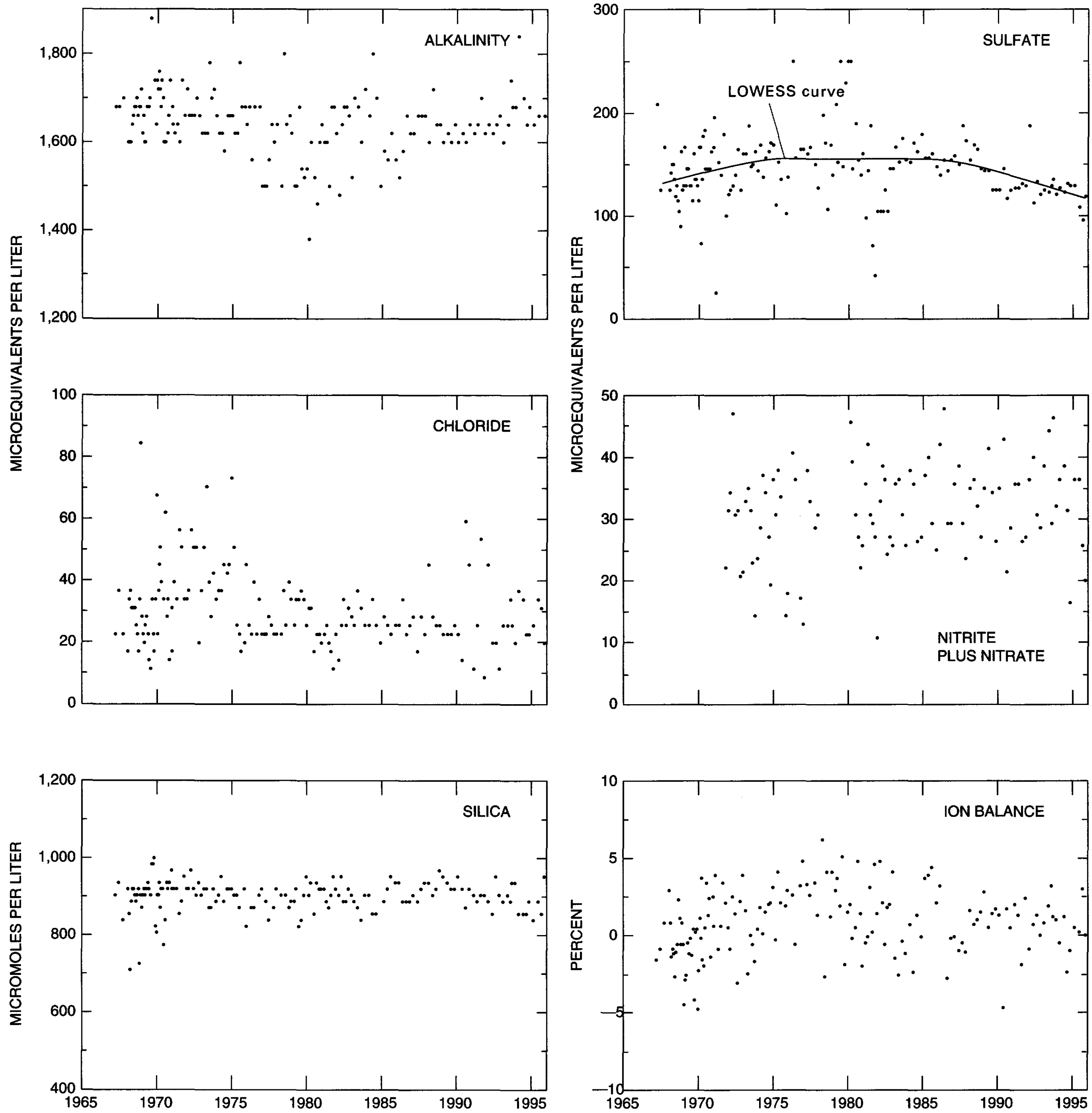


Figure 12. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Dismal River near Thedford, Nebraska—Continued.

sulfate, and a corresponding significant decrease was observed in pH and alkalinity. Sulfur-dioxide emissions in Nebraska increased by 38 percent during the period 1975–84 (Lins, 1987). Significant decreases in emissions, however, were observed in most of the other Midwestern and Northeastern States for this period. Concentrations of sulfate, hydrogen, and nitrate decreased in precipitation chemistry at a Nebraska NADP station for the period 1980–92 (Lynch and others, 1995).

Table 20. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ions measured in water-quality samples from the Dismal River, Nebraska, 1967–95, and volume-weighted mean concentrations in wet precipitation collected at the North Platte Agriculture Experimental Station, Nebraska, 1985–95

[Parameters in units of microequivalents per liter, except for 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; spec. cond., specific conductance; --, not reported; <, less than]

Parameter	Stream water						Precipitation VWM
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge	5.0	5.4	5.6	5.8	8.9	165	--
Spec. cond., field	148	174	178	182	218	166	--
pH, field	6.8	7.5	7.7	8.1	8.5	165	5.6[a]
Calcium	950	1,100	1,200	1,200	1,300	165	12
Magnesium	140	260	270	290	380	164	1.9
Sodium	260	300	300	310	430	159	2.5
Potassium	82	130	130	130	240	159	1.0
Ammonium	<.7	<.7	1.4	3.6	14	66	25
Alkalinity, laboratory	1,400	1,600	1,600	1,700	1,900	164	--
Sulfate	25	130	150	160	250	160	18
Chloride	8.5	22	25	34	84	164	2.2
Nitrite plus nitrate	11	27	31	36	48	104	17[b]
Silica	710	890	900	920	1,000	158	--

[a] Laboratory pH.

[b] Nitrate only.

Table 21. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ions, Dismal River, Nebraska, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; SiO_2, silica; --, not applicable]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	0.322	--	--	--	--	--	--	--	--
Ca	.107	0.165	--	--	--	--	--	--	--
Mg	.248	.066	0.489	--	--	--	--	--	--
Na	–.013	.077	.211	.322	--	--	--	--	--
K	.055	.057	.355	.393	.232	--	--	--	--
Alk	.158	.249	.407	.326	.317	0.431	--	--	--
SO_4	–.074	–.450	–.025	.126	–.041	–.108	–0.210	--	--
Cl	.198	–.039	.298	.336	.327	.279	.206	0.169	--
SiO_2	–.335	–.055	.121	–.084	.044	.024	–.166	–.109	–0.258

Synoptic Water-Quality Data

Results of a surface-water synoptic sampling conducted August 17 and 18, 1992, in the Dismal River Basin are presented in table 23, and locations of the sampling sites are shown in figure 11. Discharge at the HBN station (site 6) was 5.9 m^3/s compared to the mean monthly discharge of 5.4 m^3/s for the month of August (Boohar and others, 1996). The largest increase in discharge occurred between the confluence of the North and South Forks (sites 3 and 4) and site 5. This reach of the Dismal River receives ground-water inputs from the boiling springs (Guhman and Pederson, 1992).

All sites in the basin had a water type of calcium bicarbonate. During the synoptic sampling, the sums of ions at all sites upstream from the HBN station (site 6) were higher than the sum of ions at the HBN station (3,400 µeq/L) and ranged from 3,500 µeq/L (site 5) to 6,700 µeq/L (site 1). The concentrations of major ions at most sites in the upper basin on both the North Fork (sites 1 and 3) and South Fork (site 2) were higher than typically were measured at the HBN station for the period of record, 1967–95 (table 20). Concentrations in samples that were collected at the site in the lower basin (site 5) and at the HBN station (site 6) were generally near median values for the period of record. Concentrations of ions in waters of the Sand Hills generally are lower than other waters in Nebraska. This is attributed to the alkaline waters and their lower potential to dissolve minerals from rocks (Bleed and Flowerday, 1990) and the lack of weatherable minerals in underlying sands. The highest pH (9.4) was measured at site 2 and is characteristic of the strongly alkaline waters in the Sand Hills region. Silica concentrations were high in all samples and account for a significant portion of the dissolved solids. The percentage of silica was as high as about 30 percent of the dissolved solids at site 6. Nitrate concentrations generally increased from upstream to downstream, from <0.4 µeq/L (site 2) to 27 µeq/L (site 6); however, the highest nitrate concentration was 31 µeq/L, measured at site 4. This indicates that land use may be affecting nitrate concentrations in the basin, although concentrations at all sites were still much lower than other streams in Nebraska (Boyd, 1996). The nature of sandy soils also may transport nitrate faster than it can be assimilated by the plant communities.

Table 22. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major-ion concentrations, Dismal River, Nebraska, 1967 through 1995

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

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	0.9	<0.001	--	--
pH	.02	<.001	0.01	<0.001
Calcium	<.01	.750	([a])	--
Magnesium	<.01	.361	([a])	--
Sodium	<.01	.396	([a])	--
Potassium	<.01	.080	–.01	.816
Alkalinity	<.01	.149	([a])	--
Sulfate	–1	.009	([a])	--
Chloride	–.1	.096	([a])	--
Nitrite plus nitrate	.1	.040	([a])	--
Silica	<.01	.054	–.3	.459

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

Table 23. Physical properties and major-ion concentrations in surface-water samples collected at sites in the Dismal River Basin, August 17 and 18, 1992

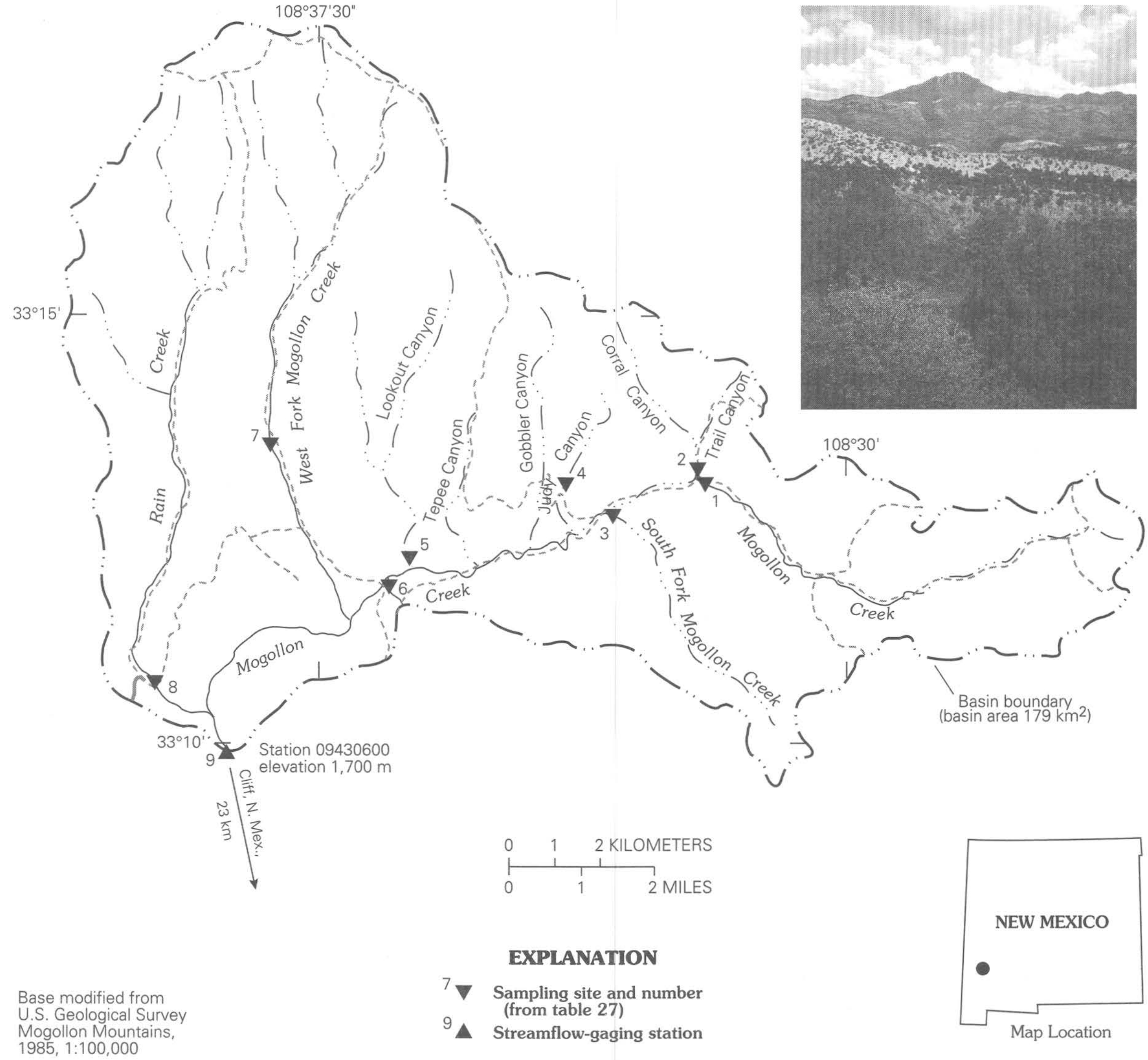
[Site locations shown in fig. 11.; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; SiO_2, silica; concentrations in microequivalents per liter, except silica is in micromoles per liter; --, not measured; <, less than; criteria used in selection of sampling sites: BG = bedrock geology, TRIB = major tributary]

Site number	Site identification number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	SiO_2	Criteria
1	414933101244300	0.01	320	7.9	1,900	620	700	130	3,300	25	34	0.4	730	BG
2	414532101165800	.02	247	9.4	1,100	580	870	64	2,500	8.3	28	<.4	800	BG
3	415112101021600	1.5	219	8.1	1,300	350	400	150	2,000	160	14	15	770	TRIB
4	415104101021600	1.1	182	8.0	1,100	270	360	150	1,700	110	23	31	680	TRIB
5	415042100492700	5.3	181	8.3	1,000	260	300	62	1,700	120	14	27	830	BG
6	06775900	5.9	175	8.2	1,000	250	280	120	1,600	120	17	27	1,000	TRIB

Mogollon Creek near Cliff, New Mexico (09430600)

Site Characteristics and Land Use

The Mogollon Creek HBN Basin is in the Mexican Highland Section of the Basin and Range physiographic province (Fenneman, 1946) in southwestern New Mexico (fig. 13). The HBN station is about 23 km north of the town of Cliff, N. Mex., at a latitude of 33°10'00" and a longitude of 108°38'57". Mogollon Creek drains about 179 km^2 of rugged, mountainous terrain of the Mogollon Mountains. Basin elevations range from 1,700 to 3,300 m. The slope of the stream is highly variable and ranges from about 190 m/km upstream from the streamflow-gaging station to less than 1 m/km at the station (Cobb and Biesecker, 1971). The ecoregion of the basin is classified as the Arizona-New Mexico Mountains Semi-Desert–Open Woodland–Coniferous Forest–Alpine Meadow Province (Bailey, 1995). Vegetative cover and density change with elevation in the basin. Pine and spruce are the predominant



Base modified from
U.S. Geological Survey
Mogollon Mountains,
1985, 1:100,000

Figure 13. Map showing study area in Mogollon Creek Basin and photograph of a mountain peak in the basin.

tree types at higher elevations, whereas juniper, cottonwood, and willow grow at lower elevations (Cobb and Biesecker, 1971). The cover is moderately dense at higher elevations and decreases with decreasing elevation. The upper part of the basin also contains ferns, moss, and damp meadows. Mogollon Creek is tributary to the Gila River.

Mogollon Creek is an intermittent stream that typically goes dry in the summer months. Discharge is dependent upon rainfall. Mean monthly discharge ranges from 0.10 m^3/s in June to 2.1 m^3/s in March (Ortiz and Lange, 1996). Average annual precipitation received at the Cliff weather station, about 15 km southeast of the site, is about 37 cm. About 10 percent of the precipitation falls as snow (Cobb and Biesecker, 1971). Average annual runoff is about 17 cm (Ortiz and Lange, 1996). Mean monthly temperatures ranged from 3.6°C in December to 24.4°C in July during the period 1948–95 (National Climatic Data Center, 1996).

The surficial geology of the basin is composed of a series of Tertiary-age extrusive or shallow intrusive volcanic units (Ratte´ and Gaskill, 1975). The area near the HBN station is underlain by a quartz latite of Oligocene age. The unit is described as compositionally zoned ash-flow tuff at least 600 m thick. Parts of the middle basin are underlain by latitic and andesitic lava flows. Other parts of the middle basin are underlain by rhyolite, which includes porphyritic lava flows with quartz and feldspar phenocrysts. In the upper basin of the Rain Creek and West Fork Mogollon Creek drainages (fig. 13) is a densely welded ash-flow tuff of Miocene or Oligocene age with quartz, sanidine, plagioclase, and biotite phenocrysts. In the eastern upper basin, the underlying rocks are banded rhyolite flows and domes of Miocene age. The Bursum Caldera is a prominent structural feature in the area. Some mineralization is associated with resurgent doming of the caldera, with faulting, or both. Fluorite deposits occur in the Rain Creek drainage, which is tributary to Mogollon Creek (Ratte´ and others, 1979).

The Mogollon Creek HBN station is in Grant County. The Mogollon Creek HBN Basin lies almost entirely within the Gila National Forest except for some private land near the station. Most of the National Forest land within the basin is within the Gila Wilderness Area, which was the first wilderness area designated in the United States (Ratte´ and Gaskill, 1975). A private, unimproved dirt road provides access to the HBN station. Pack trails access several tributaries in the drainage; wilderness area access is limited to foot trails and horseback. Recreational activity is limited, as access is limited by private holdings. Several prospect pits or open cuts from historical mining are in the Rain Creek drainage. Some cattle grazing occurs in the basin.

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for the Mogollon Creek HBN station includes 158 water-quality samples that were collected from February 1967 to September 1995. Sampling frequency is described on the basis of water year, which begins on October 1 and ends on September 30. Sampling frequency was highest during the early part of the record; 11 samples per year were collected during water years 1968–70. Sampling frequency decreased to three to six samples per year from 1972 through 1995. Samples were analyzed at the USGS New Mexico District water-quality laboratory until early 1970. From early 1970 through 1973, samples were analyzed at the USGS water-quality laboratory in Salt Lake City, Utah. After 1973, with the creation of the USGS Central Laboratory System, all samples were analyzed at the water-quality laboratory (now called NWQL) in Arvada, Colo. The period of record for discharge is from water year 1967 to current year (2000).

Data quality was checked using ion balances and time-series plots. Calculated ion balances for samples with complete major-ion analyses are shown in figure 14. More than 95 percent of the samples had ion balances within the ±10 percent range, indicating that the major-ion analytical results generally were of good quality and that unmeasured constituents, such as organic anions, nutrients, and trace metals, do not contribute substantially to the ion composition of the stream water. Time-series plots of ion concentrations were inspected for evidence of influences that are related to analytical method changes (fig. 14). The decrease in scatter of sulfate concentrations after 1982 corresponds with the change from a methylthymol blue procedure to a turbidimetric titration method (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 83.07, 1983). When changes in methods result in improved precision or

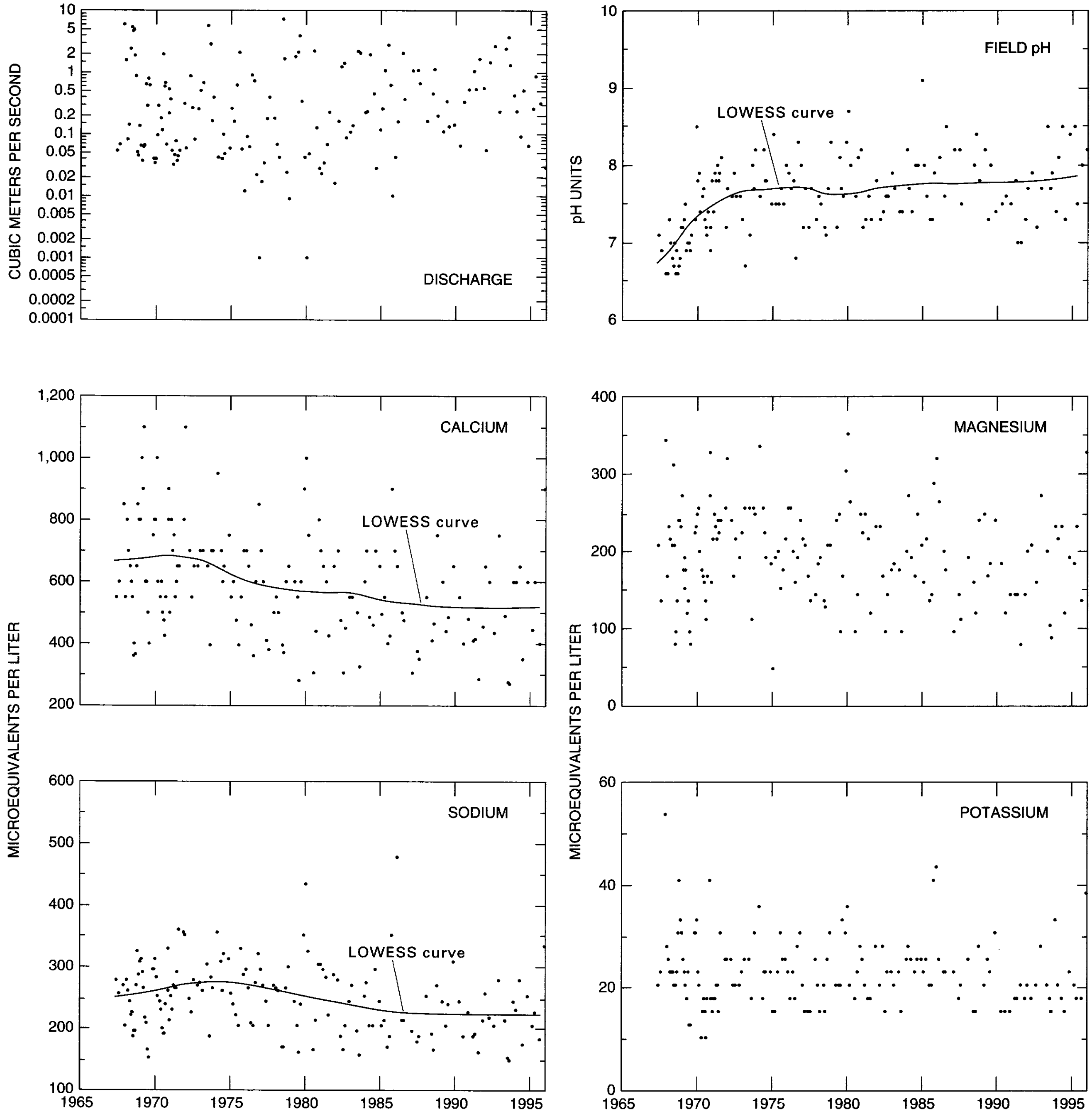


Figure 14. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Mogollon Creek near Cliff, New Mexico.

elimination of measurement bias, time-series data can exhibit less scatter or a directional shift, respectively. The time-series data, therefore, may reflect the method change rather than an environmental change. Field pH values increased sharply from 1967 to about 1972 and then began to level off.

The median and range of major-ion concentrations in the stream water collected at the Mogollon Creek HBN station and VWM concentrations in wet precipitation measured at the Gila Cliff Dwellings National Monument NADP station are presented in table 24. The NADP station is about

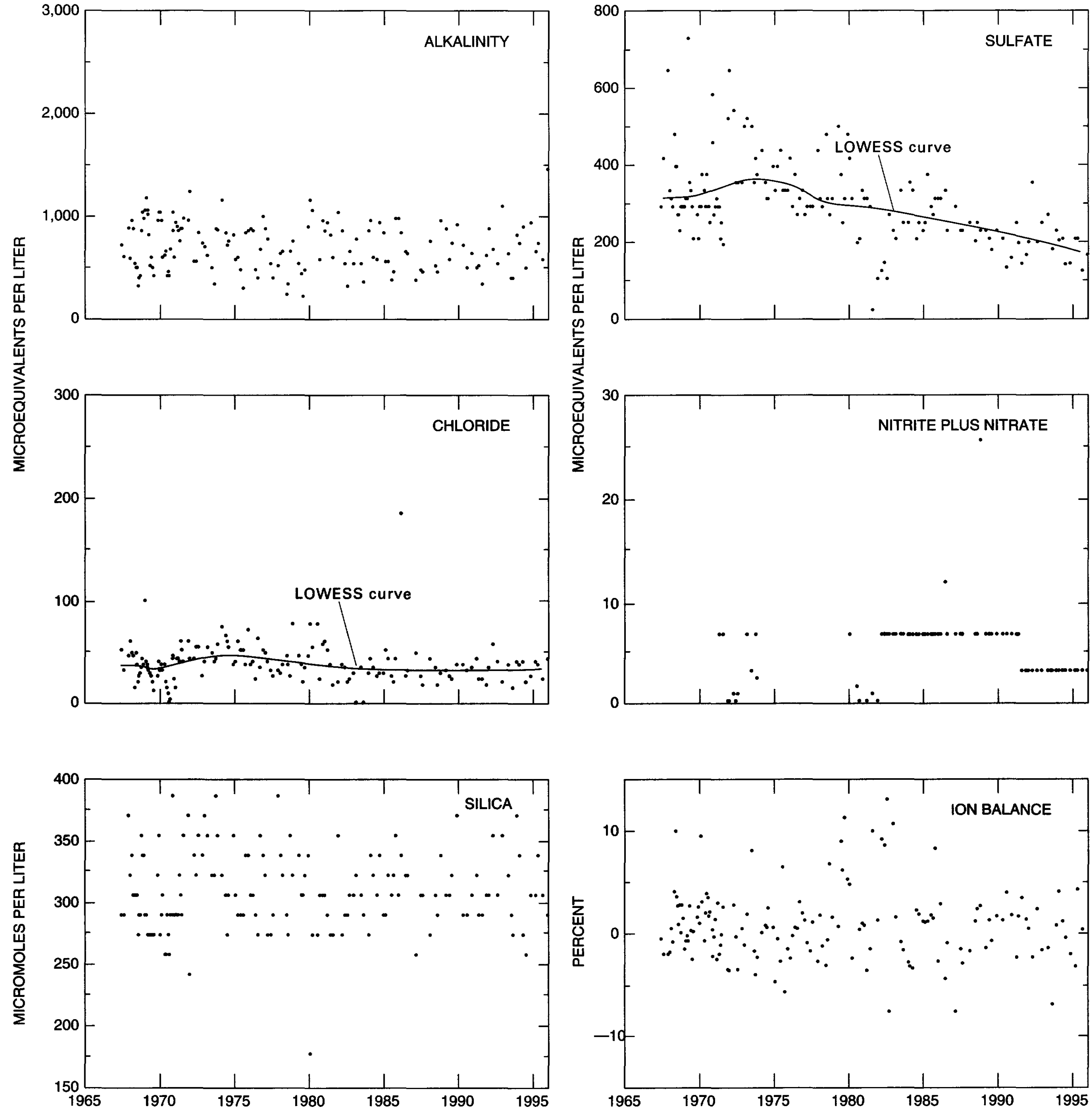


Figure 14. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Mogollon Creek near Cliff, New Mexico—Continued.

46 km northeast of the HBN station. Precipitation chemistry at the NADP station is dilute and acidic with VWM pH of 4.8 during the period of record, 1985–95. This was the lowest VWM pH for the NADP stations used in this report. The dominant cation in precipitation was hydrogen, which contributed 44 percent of the total cation concentration; calcium contributed 22 percent and ammonium contributed 16 percent. The dominant anion in precipitation was sulfate, which contributed 58 percent of the total anion concentration; nitrate contributed 31 percent.

Table 24. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ions measured in water-quality samples from Mogollon Creek, New Mexico, 1967–95, and volume-weighted mean concentrations in wet precipitation collected at the Gila Cliff Dwellings Station, New Mexico, 1985–95

[Parameters in units of microequivalents per liter, except for 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; spec. cond., specific conductance; --, not reported; <, less than]

Parameter	Stream water						Precipitation
	Minimum	First quartile	Median	Third quartile	Maximum	n	VWM
Discharge	<0.01	0.06	0.22	0.88	7.4	158	--
Spec. cond., field	47	82	108	122	176	158	--
pH, field	6.6	7.3	7.6	7.9	9.1	157	4.8[a]
Calcium	270	460	600	700	1,100	158	8.0
Magnesium	48	150	200	240	350	158	1.8
Sodium	150	200	250	280	480	157	3.8
Potassium	10	18	23	26	54	157	0.8
Ammonium	<.7	.7	1.4	4.3	11	64	5.8
Alkalinity, laboratory	220	520	680	880	1,500	158	--
Sulfate	23	230	290	350	730	157	21
Chloride	<2.8	28	39	48	190	157	3.9
Nitrite plus nitrate	<.7	<3.6	<7.1	7.1	26	83	11[b]
Silica	180	290	310	320	390	158	--

[a] Laboratory pH.
[b] Nitrate only.

Stream water in Mogollon Creek is a mildly alkaline, calcium bicarbonate type. The sum of ion concentrations ranged from about 1,000 to about 3,700 μeq/L. Alkalinity ranged from 220 to 1,500 μeq/L, and bicarbonate was the primary contributor to alkalinity at this station. The predominant cation in the stream water was calcium, which contributes 56 percent of the median cation concentration. Sodium was the second most abundant cation in the stream water. These constituents, plus high silica concentrations, typically are weathered from rocks of volcanic origin. The major anion, bicarbonate, contributed about 67 percent of median anion concentration. Annual precipitation and runoff data indicate that evapotranspiration can account for about a twofold increase in stream-water concentrations compared to precipitation. Sulfate and chloride also are input from materials within the basin as precipitation and can only account for about 14 and 20 percent, respectively, of the median concentrations of these constituents in stream water. Median concentrations of ammonium and nitrate were lower in the stream water than in the precipitation, indicating that nitrogen generally is retained by the biomass in the basin.

Correlations among dissolved constituents and discharge were determined for Mogollon Creek (table 25). The base cations and anions showed inverse relations with discharge. These results are consistent with a hydrologic system where baseflow chemistry that is dominated by ground water is diluted from precipitation runoff during periods of increased discharge. Ion concentrations in ground water tend to be greater than in surficial sources because the contact time with rocks and minerals is longer. Sulfate was poorly correlated (rho value = –0.047) with discharge, indicating that another process may be contributing to sulfate concentrations. Accumulations of sulfate salts in soils and subsequently flushing during precipitation may weaken the discharge-dilution relationship. Strong correlations existed among the base cations calcium, magnesium, and sodium. Rho values were 0.954 (calcium and magnesium), 0.933 (calcium and sodium), and 0.904 (magnesium and sodium). These cations also were strongly correlated with alkalinity, with rho values that ranged from 0.922 for magnesium and 0.938 for sodium.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents for Mogollon Creek during the period of record, 1967–95, are presented in table 26. Statistically significant downward trends ($\alpha = 0.01$) were observed for unadjusted concentrations of calcium, sodium, sulfate, and chloride. Downward trends remained after adjusting concentrations of calcium and sulfate for discharge variations. A statistically significant upward trend was observed for pH. No trend was observed for alkalinity. A downward trend in alkalinity was observed at this station by Smith and Alexander (1983) for the period from late 1960's to 1981. The downward trend for sulfate may be attributed to decreasing atmospheric sulfur dioxide concentrations following compliance with more stringent air-quality regulations and decreased production in nearby copper smelters (U.S. Geological Survey, 1993). Sulfur-dioxide emissions decreased by 33 percent in New Mexico during the period 1975–84 (Lins, 1987). The sulfate concentrations decreased around 1982 and 1990, however, when the analytical method changes for sulfate also occurred. Insufficient data existed for nitrate to calculate a trend. The scatter in the time-series plot for nitrate concentrations is a function of a change in the minimum reporting level for the laboratory method about 1991, rather than an environmental change.

Synoptic Water-Quality Data

Results of a surface-water synoptic sampling conducted August 27–30, 1991, in the Mogollon Creek Basin are presented in table 27, and locations of the sampling sites are shown in figure 13. Discharge at the HBN station (site 9) was 0.48 m^3/s compared to the mean monthly discharge of 0.44 m^3/s for the month of August (Ortiz and Lange, 1996). The water type in the basin is mixed. Percent contributions of the major cations—calcium, magnesium, and sodium—change within the basin. Calcium was the predominant cation at each site, but the percent contribution ranged from 41 percent (site 1) to 62 percent (site 8). The water type in the upper basin (sites 1 and 2) and on the West Fork Mogollon Creek tributary (site 7) was a calcium-sodium-magnesium bicarbonate. The percent magnesium was higher at sites 3, 4, and 6; the water type was a calcium-magnesium-sodium bicarbonate. The higher magnesium at these sites is coupled with higher bicarbonate concentrations. The water type at sites 5, 8, and 9 was calcium bicarbonate.

Table 25. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ions, Mogollon Creek, New Mexico, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; SiO_2, silica; --, not applicable]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	–0.313	--	--	--	--	--	--	--	--
Ca	–.736	0.272	--	--	--	--	--	--	--
Mg	–.665	.286	0.954	--	--	--	--	--	--
Na	–.822	.251	.933	0.904	--	--	--	--	--
K	–.460	.182	.647	.665	0.601	--	--	--	--
Alk	–.798	.310	.937	.922	.938	0.611	--	--	--
SO_4	–.047	.146	.358	.396	.248	.372	0.191	--	--
Cl	–.247	.207	.487	.542	.478	.327	.447	0.430	--
SiO_2	–.014	.009	.290	.370	.237	.367	.247	.232	–0.001

The total ions ranged from about 980 (site 1) to about 4,000 µeq/L (site 4); the concentration at the HBN station (site 9) was 1,700 µeq/L. In general, concentrations of dissolved constituents of tributaries generally were within the range of dissolved constituents at the HBN station for the period of record, 1967–95 (table 24), except for the unnamed tributary in Judy Canyon (site 4). The unnamed tributary in Judy Canyon contained higher concentrations of magnesium, alkalinity, and silica. The sample collected at the HBN station contained dissolved-constituent concentrations that were generally less than the median value for the period 1967–95 (table 24). Four of the tributary sites (sites 2, 3, 4, and 6) contained silica at a concentration greater than the maximum concentration detected at the HBN station during 1967–95 (table 24). The changes in stream chemistry reflect the different weathering rates of the different volcanic units; however, because of the heterogeneous geology in each drainage, it is difficult to isolate which lithologic units are controlling ion concentrations. All sites had silica concentrations that were high owing to the quartz-rich volcanic rocks in the basin. Concentrations of the major cation, calcium, and the major anion, bicarbonate, increased by twofold in Mogollon Creek between the upper sampling site (site 1) and the HBN station (site 9). The percent difference of cations and anions ranged from 0.1 to 7.8 percent, indicating that unmeasured ions did not substantially contribute to the ionic composition of the water. Nitrate concentrations were low in all basins and were characteristic of undeveloped areas (Mueller and others, 1995).

Table 26. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major-ion concentrations, Mogollon Creek, New Mexico, 1967 through 1995

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

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	0.1	0.115	--	--
pH	.01	.006	0.02	0.005
Calcium	–6	<.001	–3	.006
Magnesium	–.9	.08	–.1	.836
Sodium	–2	.001	–.9	.016
Potassium	<.01	.056	–.04	.590
Alkalinity	<.01	.922	2	.138
Sulfate	–7	<.001	–7	<.001
Chloride	–.5	.003	–.4	.024
Nitrite plus nitrate	([a])	--	--	--
Silica	<.01	.472	([b])	--

[a] Insufficient data to calculate trend.

[b] Concentration-flow model not significant at $\alpha = 0.10$.

Table 27. Physical properties and major-ion concentrations in surface-water samples collected at sites in the Mogollon Creek Basin, August 27–30, 1991

[Site locations shown in fig. 13; 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; SiO_2, silica; concentrations in microequivalents per liter, except silica is in micromoles per liter; --, not measured; <, less than; criteria used in selection of sampling sites: BG = bedrock geology, TRIB = major tributary, LU = land use]

Site number	Site identification number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	SiO_2	Criteria
1	331304108320700	--	54	7.4	220	96	180	38	260	160	28	<3.6	370	BG
2	331305108320800	--	66	7.4	260	96	240	28	400	150	34	<3.6	400	BG
3	331240108332500	<0.001	115	7.1	600	330	250	24	890	230	23	<.7	500	BG
4	331259108340000	<.002	211	7.4	900	690	380	21	1,600	330	37	<.7	550	BG
5	331203108361200	--	65	7.8	350	80	180	18	400	140	20	<3.6	300	BG
6	331153108363100	<.001	114	7.0	550	350	290	9.5	870	200	23	<.7	480	BG
7	331329108381100	--	101	7.3	550	220	230	20	760	160	25	<3.6	380	TRIB
8	331039108395200	--	77	7.7	470	100	170	12	550	140	16	<3.6	250	TRIB, LU
9	09430600	.48	80	8.0	490	140	240	18	620	140	23	<3.6	320	

Rio Mora near Tererro, New Mexico (08377900)

Site Characteristics and Land Use

The Rio Mora HBN Basin is in the Southern Rocky Mountains physiographic province (Fenneman, 1946) in northern New Mexico (fig. 15). The HBN station is 4.2 km north of Tererro, N. Mex., at a latitude of 35°46'38" and longitude of 105°39'27". Rio Mora drains about 138 km^2 of rugged, mountainous terrain in the Sangre De Cristo Range. Basin elevations range from about 2,400 to 3,900 m. Stream slope varies from about 19 m/km in open reaches to 57 m/km in canyon reaches.

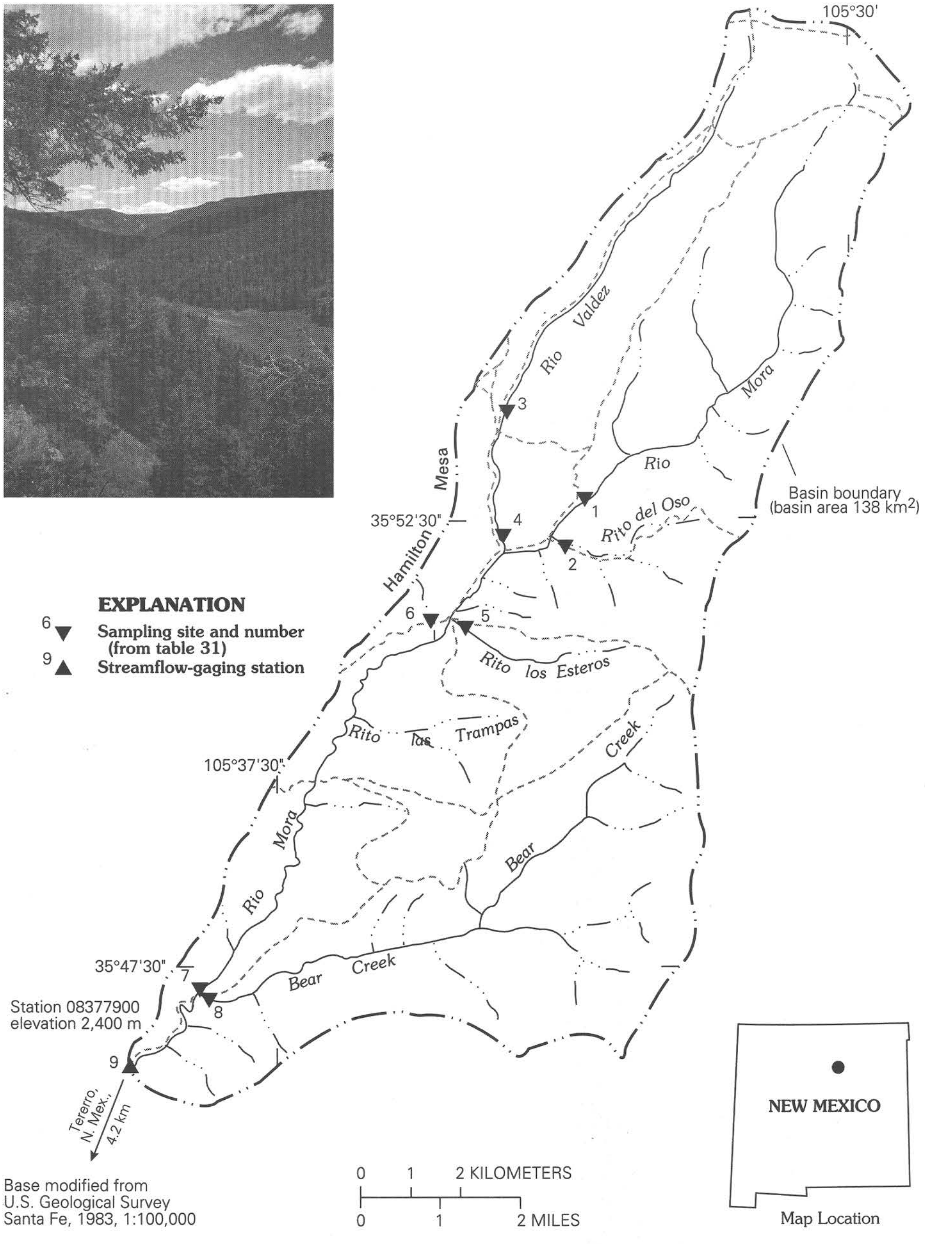


Figure 15. Map showing study area in Rio Mora Basin and photograph of the landscape in the upper part of the basin.

The ecoregion of the basin is classified as the Southern Rocky Mountain Steppe-Open Woodland-Coniferous Forest-Alpine Meadow Province (Bailey, 1995). Trees are the predominant vegetative cover; about 80 percent of the basin is covered by pine, spruce, and fir. Large aspen groves grow in some parts of the basin. The south slopes of the lower part of the basin are covered with scrub oak. High mountain meadows are common in the upper basin. The Rio Mora is tributary to the Pecos River.

The Rio Mora is a perennial stream with mean monthly discharges that range from 0.17 m^3/s in January to 3.6 m^3/s in May (Ortiz and Lange, 1996). Average annual precipitation at the Tererro weather station, which is at an elevation about 120 m lower than the HBN station, is 45 cm. Precipitation in the basin increases with increasing elevation. The snowpack usually accumulates from December to late February. Average annual runoff is about 20 cm (Ortiz and Lange, 1996). Mean monthly temperatures ranged from −2.2°C in January to 15.8°C in July during the period of record, 1948–61 (National Climatic Data Center, 1996).

The Sangre De Cristo Range is an uplifted block of Precambrian plutonic and stratified metamorphic rocks partially overlain by sedimentary rocks of Paleozoic age (Moench and others, 1988; U.S. Geological Survey and others, 1980). Igneous and metamorphic rocks are exposed along the drainages. Intrusive igneous rocks of Precambrian age are predominantly biotite granite. The granites are pink or red, medium to coarse grained, with variable foliation. Mineral composition is 30–40 percent quartz, 60 percent microcline and oligoclase, and 5–10 percent biotite. Other plutonic rocks include dark, fine-grained, massive intrusive amphibolites, medium-gray, medium-grained tonalite, quartz diorite, and diabase. The metamorphic rocks of Precambrian age are dominated by white, pink, tan, or black quartzites with minor amounts of trace minerals, including magnetite, muscovite, tourmaline, chloritoid, and graphite. These quartzites are interbedded with two-mica, pelitic schist. Lower units contain white, gray, or tan quartzites composed of nearly 100 percent quartz. The geology of the Rio Mora Basin is dominated by rocks of Paleozoic age at higher elevations. Mississippian-age rocks are sandy, clastic, cross-bedded limestone, massive crystalline limestone, limestone breccia, and quartz-rich sandstone. Overlying these rocks are the Madera and Sandia Formations of Pennsylvanian age. The lower part of the Madera Formation contains fossiliferous marine limestone, dark-gray shale, and thin to thick sandstones. The Sandia Formation contains sandstone, conglomeratic sandstone, interbedded gray shale, sandy shale, and shaly limestone. Coarse alluvium has accumulated near the mouth of the basin.

The Rio Mora HBN station is in San Miguel County. The Rio Mora HBN Basin lies almost entirely within the Santa Fe National Forest except for a small, privately owned area near the HBN station. About 90 percent of the basin lies within the Pecos Wilderness Area. Access to the HBN station, during both summer and winter, is by an improved dirt road. An unimproved road continues upstream, past the HBN station. The rest of the basin is accessed primarily by a series of pack trails. Because most of the basin is within a designated wilderness area, access is restricted to foot trails and horseback. Recreation and grazing are the predominant land uses. Recreational activities in the basin include backcountry hiking, camping, hunting, and cross-country skiing.

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for the Rio Mora HBN station includes 201 water-quality samples that were collected from November 1962 to August 1995. Sampling frequency is described on the basis of water year, which begins on October 1 and ends on September 30. Sampling frequency was variable; 1 sample was collected in water year 1963 and between 5 to 14 samples were collected between water years 1964 to 1975. From 1976 to 1982, sampling frequency was bimonthly and was reduced to quarterly from 1983 to 1995. Samples were analyzed at the USGS New Mexico District water-quality laboratory until early 1970. From early 1970 through 1973, samples were analyzed at the USGS water-quality laboratory in Salt Lake City, Utah. After 1973, with the creation of the USGS Central Laboratory System, all samples were analyzed at the water-quality laboratory (now called NWQL) in Arvada, Colo. The period of record for discharge is from water year 1964 to current year (2000).

Data quality was checked using ion balances and time-series plots. Calculated ion balances for samples with complete major-ion analyses are shown in figure 16. More than 90 percent of the samples had ion balances within the ±5 percent range, indicating that the major-ion analytical results generally were of good quality and that unmeasured constituents, such as organic anions, nutrients, and trace metals, do not contribute substantially to the ion composition of the stream water. Time-series plots of ion concentrations were inspected for evidence of influences that are related to analytical method changes (fig. 16). A small decrease in scatter of sulfate concentrations after 1982 corresponds with the change from a methylthymol blue procedure to a turbidimetric titration method (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 83.07, 1983). Temporal patterns also were evident in the field pH measurements, particularly in the early part of the record. Changes were made in meters and electrodes used for field pH determinations during the study period. When changes in methods or instrumentation result in improved precision or elimination of measurement bias, time-series data can exhibit less scatter or a directional shift, respectively. The time-series data, therefore, may reflect the method or instrument change rather than an environmental change.

The median and range of major-ion concentrations in the stream water collected at the Rio Mora HBN station and the VWM concentrations in wet precipitation measured at the Bandelier National Monument NADP station are presented in table 28. The NADP station is about 68 km west of the HBN station. Precipitation chemistry at the NADP station is dilute and slightly acidic with a VWM pH of 5.0 during the period of record, 1982–95. The dominant cation in precipitation was calcium, which contributed about 32 percent of the total cation concentration; hydrogen contributed about 29 percent and ammonium contributed about 23 percent. Sulfate, the dominant anion in precipitation, contributed about 54 percent of the total anion concentration; nitrate contributed about 39 percent of the total anion concentration. A high proportion of nitrate in precipitation in the Rocky Mountains has been attributed to exhaust from cars and other vehicles in urban areas and agricultural activity in the Great Plains States (National Atmospheric Deposition Program/National Trends Network, 1997).

Stream water in the Rio Mora is a slightly alkaline, calcium bicarbonate type. The sum of ion concentrations ranged from about 700 to about 4,500 μeq/L. Alkalinity ranged from 260 to 1,900 μeq/L, and bicarbonate was the primary contributor to alkalinity at this station. Calcium, the major cation, accounted for about 79 percent of the median cation concentration in stream water; bicarbonate, the major anion, accounted for about 82 percent of the median anion concentration. The predominance of these two ions indicates that the weathering of carbonate rocks, particularly limestone, is important to stream chemistry. Annual precipitation and runoff data indicate that evapotranspiration can account for almost a threefold increase in stream-water concentrations compared to precipitation. After adjusting for evapotranspiration, sulfate and chloride concentrations in precipitation at the NADP station accounted for about 32 to 46 percent of the median stream-water concentrations, respectively. This is a conservative estimate of sulfate precipitation contributions, however, because dry deposition is not included. Median concentrations of ammonium and nitrate were lower in the stream water than in precipitation, indicating that nitrogen generally is retained by the biomass in the basin.

Correlations among dissolved constituents and discharge were determined for the Rio Mora (table 29). The base cations and anions showed inverse relations with discharge. These results are consistent with a hydrologic system where base-flow chemistry that is dominated by ground water is diluted during periods of increased discharge, including snowmelt runoff. Ion concentrations in ground water tend to be greater than in surficial sources because the contact time with rocks and minerals is longer. Strong correlations existed among the major carbonate ions. Carbonate rocks, including limestone, are common in the basin and are important in controlling the ion composition of the ground- and stream-water chemistry. The calcium-magnesium (rho value = 0.950) calcium-alkalinity correlations (rho value = 0.951) were the highest. The correlation between magnesium and alkalinity was 0.906. A strong correlation (rho value = 0.918) also exists between magnesium and sodium.

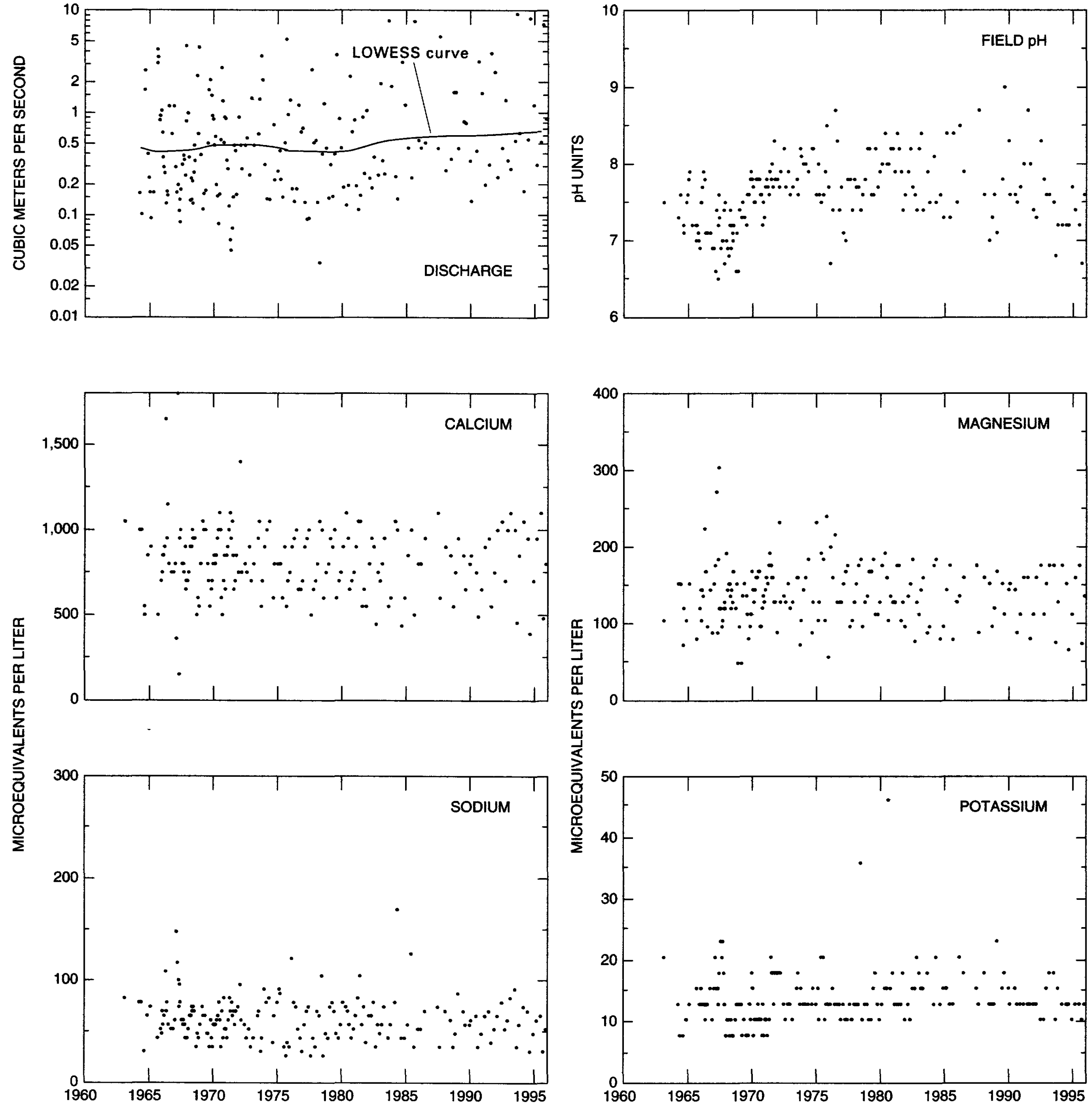


Figure 16. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Rio Mora near Tererro, New Mexico.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents for the Rio Mora from 1965 through 1995 are presented in table 30. Statistically significant upward trends ($\alpha = 0.01$) occurred in discharge. The trend in discharge is only representative of instantaneous measurements made during water-quality sampling and may not correspond with a trend in the continuous discharge record. Insufficient data existed for nitrate to calculate a trend. The scatter in the time-series plot for nitrate concentrations is a function of a change in the minimum reporting level for the laboratory method about 1991, rather than an environmental change.

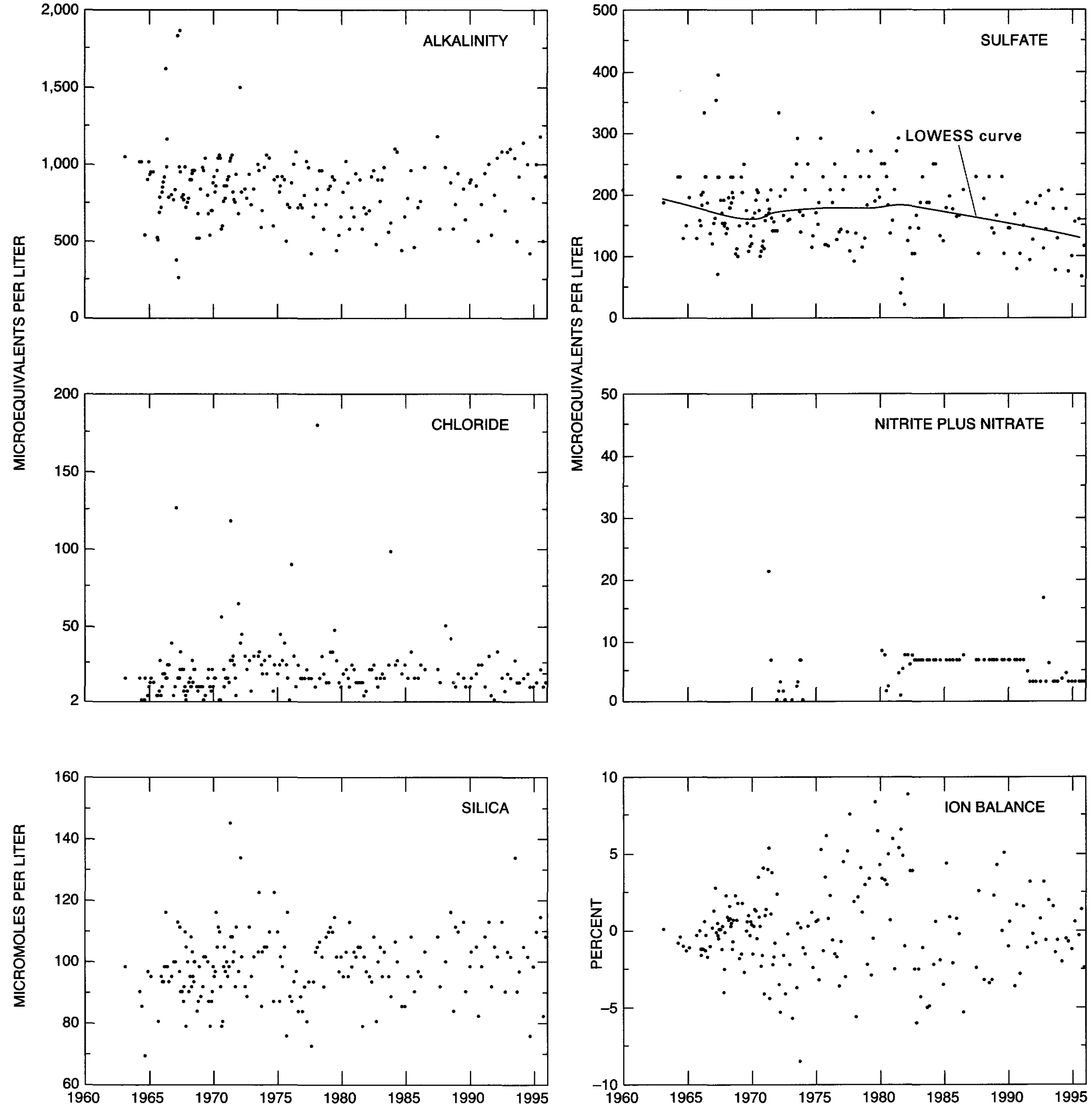


Figure 16. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Rio Mora near Tererro, New Mexico—Continued.

A statistically significant downward trend ($\alpha = 0.01$) occurred in unadjusted concentrations of sulfate. The sulfate trend was no longer detected after the concentrations were flow adjusted for variations in discharge. Trends in sulfate concentrations in New Mexico's surface waters have varied over the study period in other studies. Smith and Alexander (1983) observed an upward trend in flow-adjusted sulfate concentrations and a corresponding downward trend in alkalinity ($\alpha = 0.01$ to 0.10) for the period late 1960's to 1981 at this station. For the study period 1975–89, downward trends in sulfate were reported at

Table 28. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ions measured in water-quality samples from Rio Mora, New Mexico, 1963–95, and volume-weighted mean concentrations in wet precipitation collected at the Bandelier National Monument Station, New Mexico, 1982–95

[Parameters in units of microequivalents per liter, except for 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; spec. cond., specific conductance; --, not reported; <, less than]

Parameter	Stream water						Precipitation VWM
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge	0.03	0.19	0.42	0.91	9.3	200	--
Spec. cond., field	34	86	101	117	223	200	--
pH, field	6.5	7.3	7.6	7.9	9.0	201	5.0[a]
Calcium	150	700	800	950	1,800	195	11
Magnesium	48	110	140	160	300	195	1.8
Sodium	26	48	61	74	170	193	2.8
Potassium	7.7	10	13	15	46	191	.77
Ammonium	<.7	.7	2.1	4.3	18	66	8.0
Alkalinity, laboratory	260	720	860	960	1,900	201	--
Sulfate	21	140	170	210	400	193	18
Chloride	<2.8	11	17	25	180	199	2.6
Nitrite plus nitrate	<.7	<3.6	6.0	7.1	21	86	13[b]
Silica	69	92	98	100	150	192	--

[a] Laboratory pH.
[b] Nitrate only.

Table 29. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ions, Rio Mora, New Mexico, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; SiO_2, silica; --, not applicable]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	−0.135	--	--	--	--	--	--	--	--
Ca	−.771	0.070	--	--	--	--	--	--	--
Mg	−.805	.094	0.950	--	--	--	--	--	--
Na	−.792	.045	.872	0.918	--	--	--	--	--
K	−.121	.110	.101	.165	0.226	--	--	--	--
Alk	−.712	−.063	.951	.906	.814	0.118	--	--	--
SO_4	−.593	.188	.700	.681	.683	.269	0.590	--	--
Cl	−.230	−.020	.330	.387	.319	.247	.324	0.424	--
SiO_2	−.388	−.023	.683	.685	.631	.136	.708	.460	0.150

several surface-water stations in New Mexico (U.S. Geological Survey, 1993). The decrease was attributed to reductions in emissions from copper smelters. Lins (1987) reported that sulfur-dioxide emissions in New Mexico decreased by 33 percent for the period 1975–84. Lynch and others (1995) have reported corresponding decreases in precipitation sulfate concentrations for the period 1980–92.

Synoptic Water-Quality Data

Results of a surface-water synoptic sampling conducted June 18–20, 1991, in the Rio Mora Basin are presented in table 31, and locations of the sampling sites are shown in figure 15. Discharge at the HBN station (site 9) was 1.3 m^3/s compared to the mean monthly discharge of 2.5 m^3/s for the month of June (Ortiz and Lange, 1996). The sum of ions ranged from 700 (site1) to 2,700 μeq/L (site 6); the concentration at the HBN station (site 9) was 1,500 μeq/L. Concentrations of dissolved constituents were within the range of concentrations observed at the Rio Mora HBN station for the period of record, 1963–95 (table 28), except for sodium at the Rio Mora site upstream from the pack trail (site 1), which was less than any samples at the HBN station. The concentrations of constituents collected at the HBN station (site 9) during the synoptic sampling generally were less than the first-quartile values reported for the station (table 28). Concentrations of dissolved constituents, except sulfate and nitrate, increased in the downstream direction at sites on the Rio Mora (sites 1, 7, and 9). The water type of samples that were collected throughout the Rio Mora Basin was calcium bicarbonate. Sulfate concentrations were variable in the drainages and ranged from 46 (site 5) to 250 (site 3) μeq/L. The percent difference of cations and anions ranged from 2.4 to 7.4 percent, indicating that unmeasured ions do not substantially contribute to the ionic content of the water.

Table 30. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major-ion concentrations, Rio Mora, New Mexico, 1965 through 1995

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

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	0.3	0.004	--	--
pH	<.01	.749	([a])	--
Calcium	<.01	.503	1	0.317
Magnesium	<.01	.313	0.2	.436
Sodium	<.01	.661	.2	.224
Potassium	<.01	.094	([a])	--
Alkalinity	<.01	.525	3	.013
Sulfate	–1	.006	–.7	.039
Chloride	<.01	.227	([a])	--
Nitrite plus nitrate	([b])	--	--	--
Silica	.1	.080	.2	.012

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

[b] Insufficient data to calculate trend.

Table 31. Physical properties and major-ion concentrations in surface-water samples collected at sites in the Rio Mora Basin, June 18–20, 1991

[Site locations shown in fig. 15; 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; SiO_2, silica; concentrations in microequivalents per liter, except silica is in micromoles per liter; --, not measured; <, less than; criteria used in selection of sampling sites: BG = bedrock geology, TRIB = major tributary]

Site number	Site identification number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	SiO_2	Criteria
1	355241105333100	0.45	39	7.5	270	55	22	9.0	270	67	6.5	<0.7	75	BG
2	355216105335100	.05	92	7.8	700	160	74	13	790	200	8.7	<.7	140	BG
3	355329105343700	.18	71	7.8	600	88	26	9.7	530	250	6.2	<.7	73	BG
4	355215105323700	.26	73	7.8	600	100	26	10	560	130	6.5	1.4	77	TRIB
5	355120105350900	.09	92	7.9	750	120	44	11	770	46	8.7	<.7	93	BG
6	355127105352700		138	8.1	1,200	180	52	10	1,100	160	5.6	<3.6	110	BG
7	354725105383200	.91	65	7.8	500	88	35	10	490	230	7.3	<.7	85	TRIB
8	354724105383200	.19	133	8.1	1,100	150	52	12	1,100	75	8.5	<3.6	110	TRIB
9	08377900	1.3	81	7.9	650	110	39	11	620	100	8.5	<.7	92	

Tributaries contributing high concentrations of calcium and bicarbonate were Bear Creek (site 8) and the unnamed tributary below Hamilton Mesa (site 6). The tributary below Hamilton Mesa may contain higher concentrations of calcium (1,200 µeq/L) and bicarbonate (1,100 µeq/L) because it is the only subbasin draining almost entirely sedimentary rocks. The concentrations of calcium (1,100 µeq/L) and bicarbonate (1,100 µeq/L) at Bear Creek (site 8), which drains sedimentary, igneous, and metamorphic rocks, are more than double the concentrations at the nearby Rio Mora site (site 7) upstream from the mouth of Bear Creek. The influence of Bear Creek on water quality at the Rio Mora HBN station (site 9) is reflected in higher concentrations of calcium, magnesium, and alkalinity, and a lower sulfate concentration compared to the upstream site (site 7). Nitrate concentrations are low in all basins and are characteristic of undeveloped areas (Mueller and others, 1995).

Bear Den Creek near Mandaree, North Dakota (06332515)

Site Characteristics and Land Use

The Bear Den Creek HBN Basin is in the Missouri Plateau Section of the Great Plains physiographic province (Fenneman, 1946) in western North Dakota (fig. 17). The HBN station is about 8.8 km northwest of Mandaree, N. Dak., at a latitude of 47°47'14" and a longitude of 102°46'05". Bear Den Creek drains 192 km^2 of grass-covered hills and badlands that are gently rolling in the upper basin to steep land slopes in the lower basin. Basin elevations range from about 594 to 869 m. The ecoregion of the basin is classified as the Great Plains-Palouse Dry Steppe Province (Bailey, 1995). The Bear Den Creek Basin predominantly is covered with a fairly dense sod of native grass with small trees growing in some of the drainages. Part of the western basin is cultivated with grain crops. Bear Den Creek drains into Lake Sakakawea on the Missouri River.

Bear Den Creek is an intermittent stream. At times during the late summer and winter months, little or no flow occurs in the channel. Spring rains produce the highest flows in March and April. Mean monthly discharges range from 0.004 m^3/s in December to 1.0 m^3/s in March (Harkness and others, 1996). Average annual precipitation at the Keene weather station (17 km northwest of the HBN station) is 39 cm. Most of the precipitation falls as rain in the spring and early summer. Average annual runoff is about 3 cm (Harkness and others, 1996). The climate is characterized by cold winters and mild summers; mean monthly temperatures ranged from −12.3°C in January to 20.5°C in July during the period of record, 1959–95 (National Climatic Data Center, 1996).

The Bear Den Creek Basin is underlain by the Sentinel Butte Formation of Paleocene age. The formation contains interbedded brownish-gray and gray silt, clay, sand, and lignite (Carlson, 1985). The formation is characterized by bentonitic clay, petrified wood, and scoria. Lignite, a low-grade coal consisting of plant fragments and petrified wood, are from ancient swamps that formed along ancient streams flowing eastward from the Rocky Mountain uplift. The reddish layers of scoria-like material are composed of sediment that was baked by burning lignite (Bluemle, 1975). Flood-plain deposits are composed of brownish-gray silt and clay with minor amounts of sand and gravel.

The Bear Den Creek HBN station is in McKenzie County. The Bear Den Creek Basin is 75 percent privately owned, 20 percent is owned by the Fort Berthold Indian Reservation, 2 percent is State land, 2 percent is Federal land, and 1 percent other (Paul Deutsch, Natural Resources Conservation Service, written commun., 1996). Access to the HBN station is by a primitive road off a secondary highway on the Fort Berthold Indian Reservation. The basin is accessible year round, as weather permits. Primitive roads, improved roads, and primary access routes (typically suited for automobile travel) traverse parts of the upper basin. No roads exist in parts of the lower and eastern basin. Land use in the basin is predominantly agriculture, including pastures with cattle and horse grazing in the central and eastern parts and a small amount of cultivation in the western part. Rural residences and stock ponds are present in the basin. An oil and gas field and pipeline associated with oil production is located in the northwest part of the basin (Lawrence, 1987). Oil drilling was active during the 1970's and 1980's (L.L. Rutschke, U.S. Geological Survey, oral commun., 1997). Scoria gravel pits also are present in the basin.

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for the Bear Den Creek HBN station includes 236 water-quality samples that were collected from August 1966 to August 1995. Sampling frequency is described on the basis of water

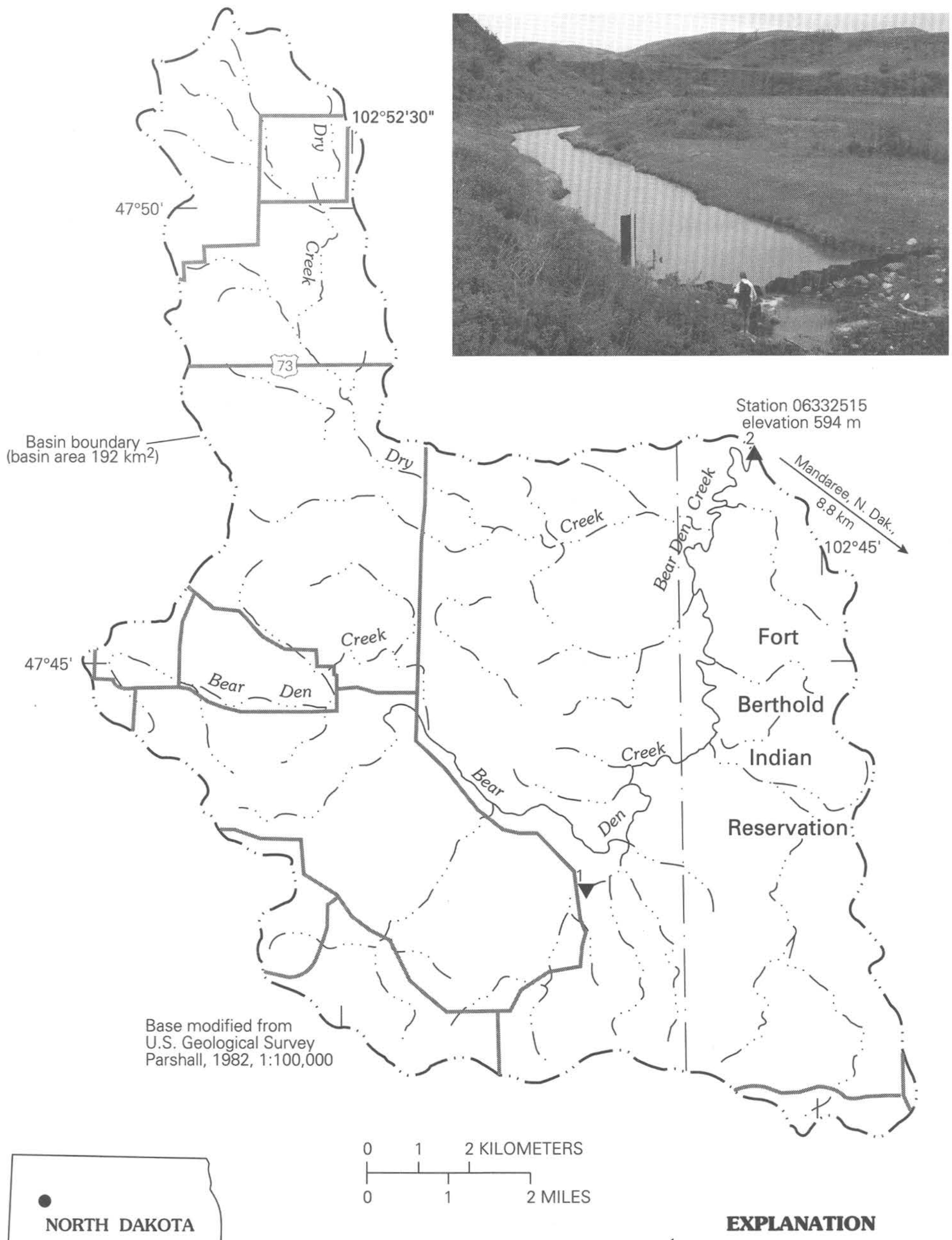


Figure 17. Map showing study area in Bear Den Creek Basin and photograph of the streamflow-gaging station.

year, which begins on October 1 and ends on September 30. Sampling frequency was variable during the period of record. The most complete data set exists for the period between 1968 and 1981 when 10–14 samples were collected annually. After 1981, sampling frequency decreased; five or six samples were collected in most water years. Samples were analyzed at USGS district water-quality laboratories until the early 1970's. After 1973, with the creation of the USGS Central Laboratory System, all samples were analyzed at the water-quality laboratory (now called NWQL) in Arvada, Colo. The period of record for discharge is from water year 1966 to current year (2000).

Data quality was checked using ion balances and time-series plots. Calculated ion balances for samples with complete major-ion analyses are shown in figure 18. More than 95 percent of the samples had ion balances within the ±5 percent range, indicating that the major-ion analytical results generally were of good quality and that unmeasured constituents, such as organic anions, nutrients, and trace metals, do not contribute substantially to the ion composition of the stream water. Time-series plots of ion concentrations were inspected for evidence of influences that are related to analytical method changes (fig. 18). The

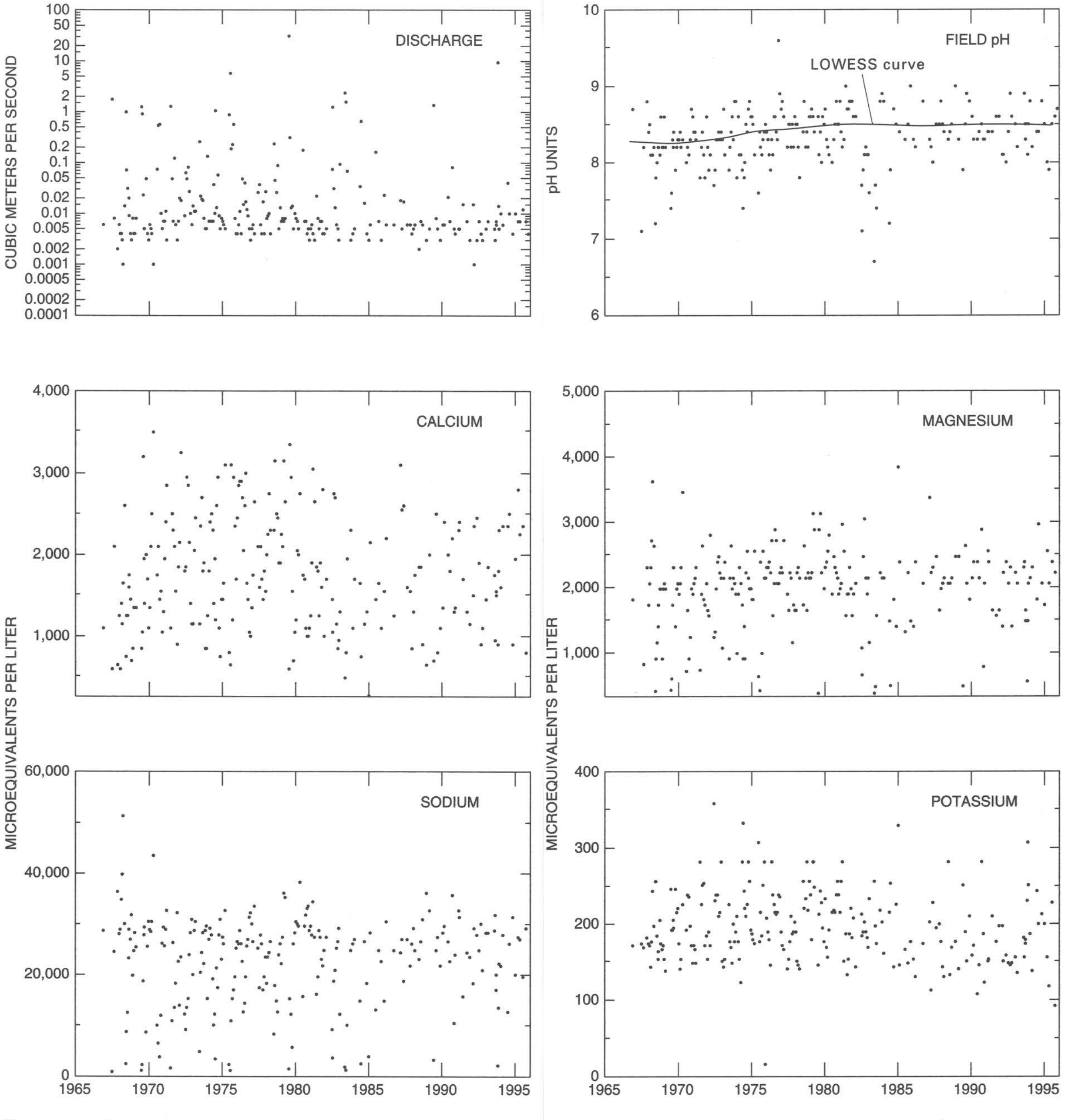


Figure 18. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Bear Den Creek near Mandaree, North Dakota.

decrease in scatter of cations may be related to more variation in discharge, which reflects greater sampling frequency in the early part of record. The method changes in 1982 and 1990 for sulfate are less apparent in the data scatter at this site probably owing to the large range of concentrations observed at this site. The positive bias introduced by the sulfate turbidimetric titration method between 1982 and 1989 probably is not substantial because the method bias occurred at low concentrations (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 90.04, 1989; U.S. Geological Survey Office of Water Quality

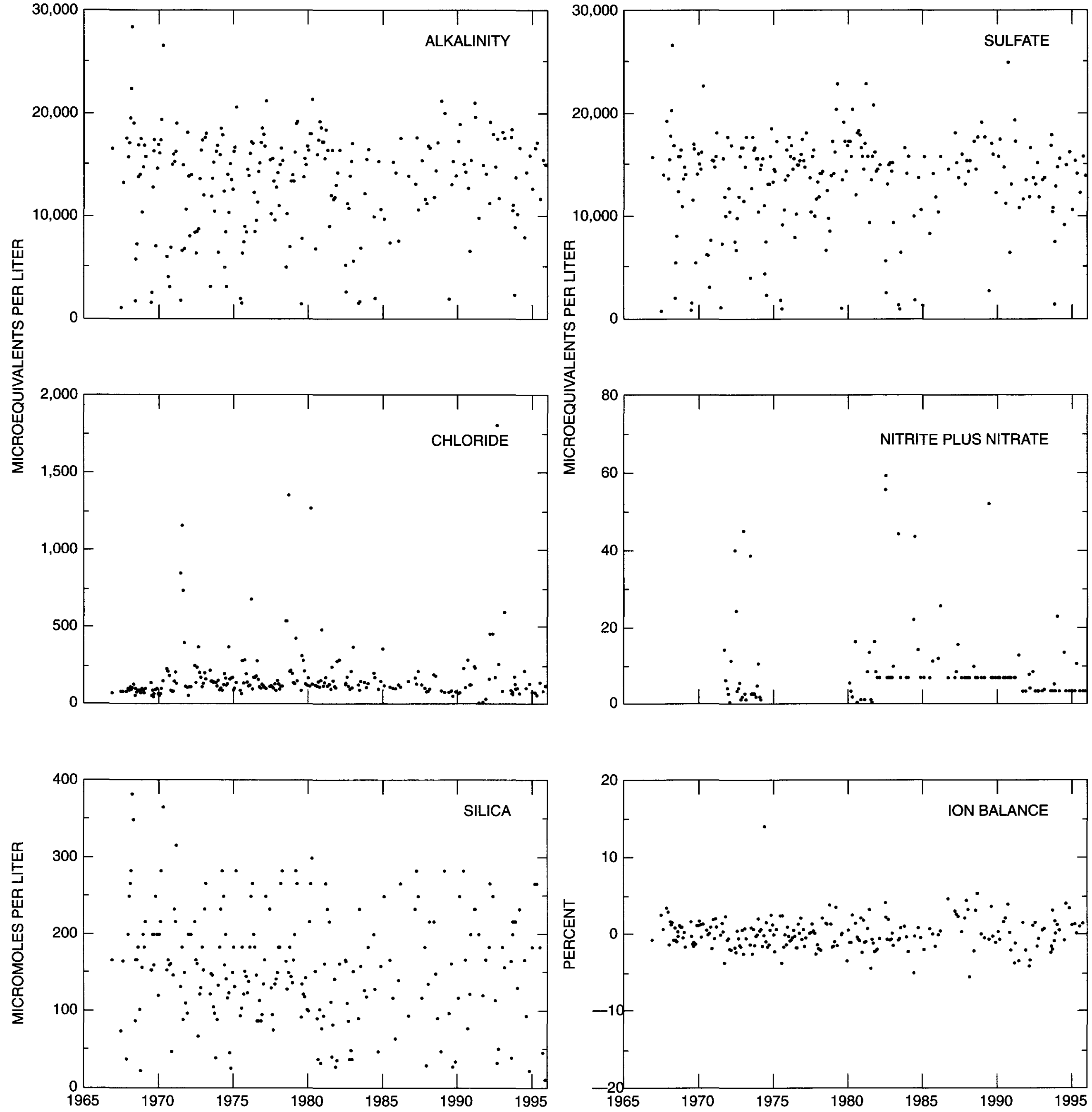


Figure 18. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Bear Den Creek near Mandaree, North Dakota—Continued.

Technical Memorandum No. 90.13, 1990). Changes also were made in meters and electrodes used for field pH determinations during the study period. When changes in methods or instrumentation result in improved precision or elimination of measurement bias, time-series data can exhibit less scatter or a directional shift, respectively. The time-series data, therefore, may reflect the method or instrument change rather than an environmental change.

The median and range of major-ion concentrations in the stream water collected at the Bear Den Creek HBN station and VWM concentrations in wet precipitation measured at the Theodore Roosevelt National Park NADP station are presented in table 32. The NADP station is about 59 km southwest of the HBN station. Precipitation chemistry at the NADP station is dilute and slightly acidic with VWM pH of 5.3 during the period of record, 1981–95. Ammonium, the dominant cation in precipitation, contributed 37 percent of the total cation concentration, followed by calcium, which contributed 30 percent of the total cation concentration. The dominant anion in precipitation was sulfate, which contributed 57 percent of the total anion concentration, followed by nitrate, which contributed 38 percent of the concentration. Contributions from nitrogen species were less at this site than in precipitation from eastern North Dakota, possibly because the area is farther from the intensive crop activities in the Midwest.

Stream water in Bear Den Creek is a sodium sulfate-bicarbonate type. The sum of ion concentrations ranged from about 3,800 to about 100,000 μeq/L. Alkalinity ranged from 1,000 to 28,000 μeq/L, and bicarbonate is the primary contributor to alkalinity at this station. The dominant cation in the stream water was sodium, which accounted for 86 percent of the median cation concentration. The sodium concentrations were over 10 times greater than the calcium or magnesium concentrations. Wide ranges of sodium can occur in natural waters because high concentrations of sodium can be reached before any precipitate is formed (Hem, 1992, p. 101). Potassium concentrations were high, which probably reflect the weathering of the clay materials in the basin (Deer and others, 1966). Dissolved solids at this HBN station were higher than any other station in the Hydrologic Benchmark Network. Streams in basins with low

Table 32. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ions measured in water-quality samples from Bear Den Creek, North Dakota, 1966–95, and volume-weighted mean concentrations in wet precipitation collected at the Theodore Roosevelt National Park Station, North Dakota, 1981–95

[Parameters in units of microequivalents per liter, except for 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; spec. cond., specific conductance; --, not reported; <, less than]

Parameter	Stream water						Precipitation VWM
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge	<0.001	0.005	0.007	0.02	31	236	--
Spec. cond., field	192	1,950	2,650	2,900	4,600	236	--
pH, field	6.7	8.2	8.4	8.6	9.6	233	5.3[a]
Calcium	270	1,200	1,700	2,300	3,500	235	12
Magnesium	340	1,600	2,100	2,300	3,800	234	4.0
Sodium	830	17,000	25,000	29,000	51,000	235	3.3
Potassium	15	160	190	230	360	235	.80
Ammonium	<.7	1.4	3.6	7.9	27	88	15
Alkalinity, laboratory	1,000	10,000	14,000	17,000	28,000	234	--
Sulfate	730	11,000	15,000	16,000	27,000	236	21
Chloride	2.8	93	120	170	1,800	235	2.2
Nitrite plus nitrate	<.7	<3.6	7.1	8.3	59	124	14[b]
Silica	10	110	160	200	380	235	--

[a] Laboratory pH.

[b] Nitrate only.

Table 33. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ions, Bear Den Creek, North Dakota, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; SiO_2, silica; --, not applicable]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	–0.410	--	--	--	--	--	--	--	--
Ca	.080	–0.301	--	--	--	--	--	--	--
Mg	–.295	.056	0.485	--	--	--	--	--	--
Na	–.538	.299	.107	0.667	--	--	--	--	--
K	.195	–.057	–.143	–.168	–0.291	--	--	--	--
Alk	–.637	.214	.135	.637	.903	–0.388	--	--	--
SO_4	–.431	.299	.250	.735	.869	–.121	0.717	--	--
Cl	.002	–.197	.111	.079	.027	.192	–.008	0.036	--
SiO_2	.124	–.508	.621	.181	–.076	–.167	.067	–.054	0.041

average annual runoff and geologic settings that contain fine-grained sediments generally are characterized by high dissolved-solids concentrations (Biesecker and Leifeste, 1975). Specific conductance (192 to 4,600 µS/cm) is an indicator of the high dissolved solids at this station. Annual precipitation and runoff data indicate that evapotranspiration can account for at least a tenfold increase in stream-water concentrations compared to precipitation. Sodium concentrations were about 7,600 times higher in the stream than in precipitation, indicating a large source for sodium in the materials in the basin. Chloride concentrations also were higher than can be accounted for by evaporation of precipitation alone. In arid regions, when precipitation and runoff are insufficient to redissolve salts, salt residues accumulate in the soil or on exposed streambeds. Median concentrations of bicarbonate and sulfate in stream water were 48 and 51 percent of the total anion concentration, respectively. The highest dissolved solids occurred during low-flow conditions; ground-water recharge from the fractured lignite beds generally is high in dissolved solids (Cobb and Biesecker, 1971). Median concentrations of ammonium and nitrate were lower in the stream water than in precipitation, indicating that nitrogen generally is retained by the biomass in the basin.

Correlations among dissolved constituents and discharge were determined for Bear Den Creek (table 33). The base cations and anions showed weak and mixed, positive and inverse relations with discharge. The average annual runoff is very low, which indicates that dilution of stream waters from precipitation is not a substantial process in the basin on an annual basis. Dilution from precipitation may be important, however, on an event basis. Some increases in discharge may be associated with temporary increases in dissolved-solids concentrations because salts that have accumulated in the soil are flushed out during the initial phases of the melting of snow, thawing of frozen ground, or rainfall events. Strong correlations were between sodium and alkalinity (rho value = 0.903) and sodium and sulfate (rho value = 0.869). Magnesium also was correlated with sodium, alkalinity, and sulfate. These relations, as well as the high concentrations of these constituents, indicate that dissolution of sodium- and magnesium-rich carbonate and sulfate salts contributes to the ion composition of the stream water.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents for Bear Den Creek from 1967 through 1995 are presented in table 34. The only statistically significant trend ($\alpha = 0.01$) was an increase in unadjusted pH values. The flow-adjusted model did not predict a significant trend in pH, indicating variations in discharge may be controlling the hydrogen concentrations. Other trends in regional precipitation chemistry may be difficult to detect at this HBN station because, even after accounting for evapotranspiration, precipitation concentrations of base cations and anions were very small compared to stream-water concentrations of these constituents.

Synoptic Water-Quality Data

Results of a surface-water synoptic sampling event conducted on June 6, 1993, in the Bear Den Creek Basin are presented in table 35, and locations of the sampling sites are shown in figure 17. Discharge at the HBN station (site 2) was 0.03 m^3/s, which is slightly less than the mean monthly discharge of 0.08 m^3/s for the month of June (Harkness and others, 1996). Bear Den Creek typically starts to go dry about this time of year. Although a rain event occurred 1 day prior to the synoptic sampling, most of the ephemeral tributaries were dry during the synoptic sampling. One unnamed tributary in the south part of the drainage was sampled, but it was not measurably flowing.

The sums of ions were 78,000 μeq/L at the unnamed tributary site (site 1) and 50,000 μeq/L at the HBN station (site 2). All analyzed constituents from the samples that were collected during the synoptic study were within the range recorded at the HBN station for the period of record, 1966–95 (table 32). The water type at the unnamed tributary (site 1) was sodium sulfate. The water type at the HBN station (site 2) was a sodium bicarbonate, although sulfate was a substantial component, contributing 48 percent of the total anion concentration. The composition of the water at site 1 indicates that dissolution of several salts contribute to the ion composition, including sodium carbonate, sodium sulfate, and sodium chloride. The chloride concentration at site 1 was more than 10 times the concentration at the HBN station. After adjusting for the effects of evapotranspiration, precipitation is estimated to contribute only about 5 percent of the chloride at site 1 compared to about 50 percent of the chloride at site 2. Sulfate contributions from precipitation were about 1 percent at site 1 and about 2 percent at site 2. This is a much smaller percentage than is typical of stations in the HBN program; precipitation is estimated to contribute at least 90 percent of the mean stream sulfate concentration at about one-half of the HBN stations around the country (Smith and Alexander, 1983). Precipitation chemistry can account for the nitrate concentrations in samples that were collected during the synoptic study.

Table 34. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major-ion concentrations, Bear Den Creek, North Dakota, 1967 through 1995

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

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	<0.01	0.064	--	--
pH	.01	.004	<0.01	0.091
Calcium	<.01	.767	–3	.704
Magnesium	9	.033	4	.263
Sodium	100	.145	–36	.454
Potassium	–1	.025	–.5	.277
Alkalinity	59	.072	–37	.075
Sulfate	11	.654	–32	.224
Chloride	–.9	.197	–.6	.441
Nitrite plus nitrate	.2[a]	.071	--	--
Silica	–1	.048	–1	.023

[a] Trend test for highly censored data was used.

Table 35. Physical properties and major-ion concentrations in surface-water samples collected at sites in the Bear Den Basin, June 6, 1993

[Site locations shown in fig. 17; 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; SiO_2, silica; concentrations in microequivalents per liter, except silica is in micromoles per liter; --, not measured; criteria used in selection of sampling sites: TRIB = major tributary]

Site number	Site identification number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	SiO_2	Criteria
1	474235102485100	--	3,650	8.3	2,200	2,800	33,000	250	16,000	23,000	480	0.4	140	TRIB
2	06332515	0.03	2,410	8.8	1,200	1,400	22,000	140	13,000	12,000	45	.4	100	

Beaver Creek near Finley, North Dakota (05064900)

Site Characteristics

The Beaver Creek HBN Basin lies in the Western Lake Section of the Central Lowland physiographic province (Fenneman, 1946) in eastern North Dakota (fig. 19). The HBN station is about 11 km northeast of Finley, N. Dak., at a latitude of 47°35'40" and a longitude of 97°42'18". Beaver Creek drains 415 km^2 of gently undulating terrain; basin elevations range from 360 to 460 m. The slope of the main channel is about 3 m/km. The basin is in the transition region between the Great Plains Steppe Province and

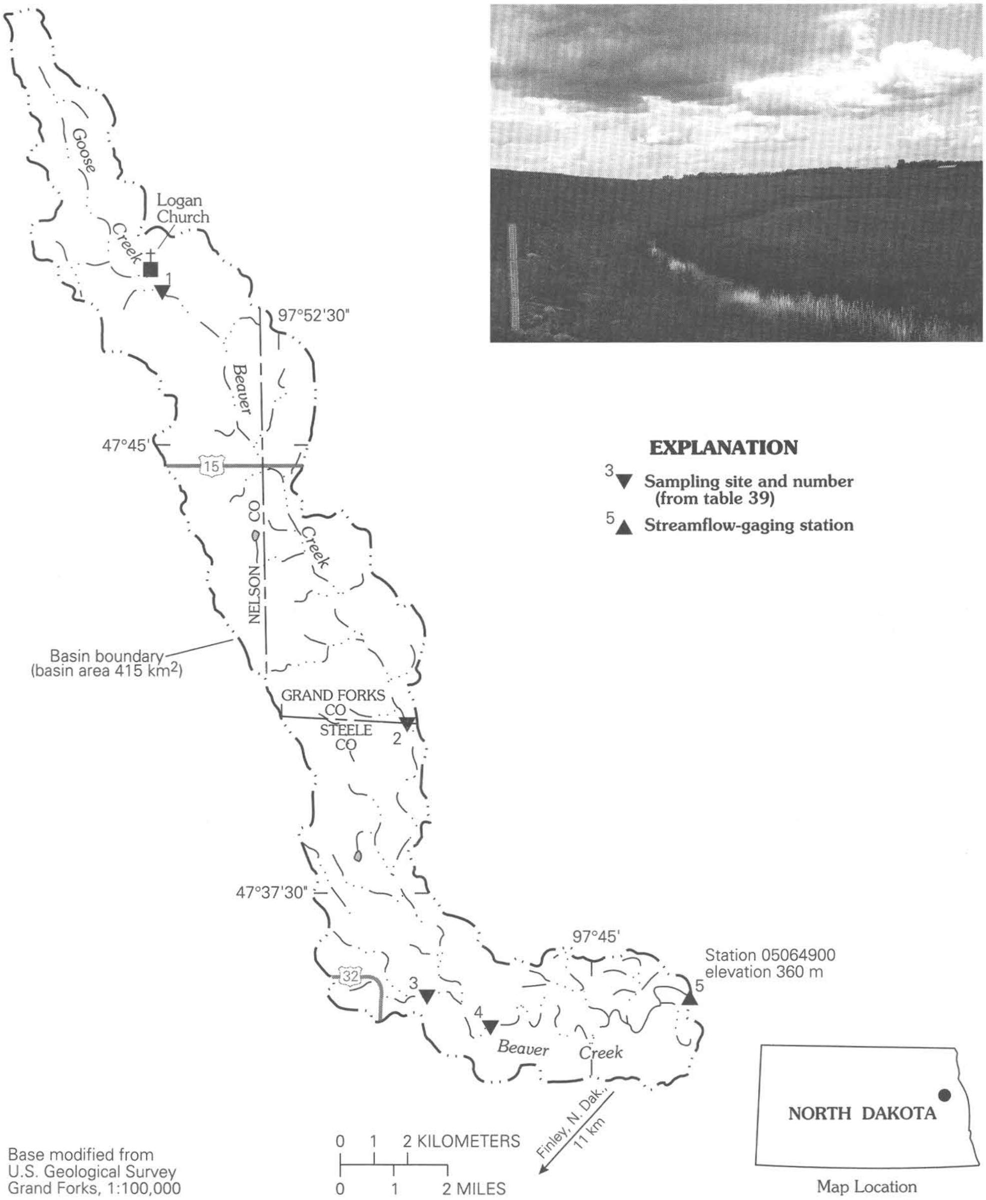


Figure 19. Map showing study area in Beaver Creek Basin and photograph upstream from the streamflow-gaging station.

the Prairie Parkland (Temperate) Province (Bailey, 1995). Most of the basin is under cultivation, although in some areas, prairie grasses are present in dense growth and represent the natural cover. Trees generally are limited to groves around farmsteads and windbreaks around fields. Beaver Creek is tributary to the Goose River, which is tributary to the Red River of the North.

Beaver Creek has intermittent flow, a meandering channel, and ponded sections. Since June 1987, flow has been regulated by a flood-control dam about 3 km upstream from the HBN station (Harkness and others, 1996). No flow typically occurs for several months during the winter each year when ice and snow may fill in the channel. Mean monthly discharges range from less than 0.002 m^3/s in January to 1.5 m^3/s in April (Harkness and others, 1996). Average annual precipitation at the Cooperstown weather station (about 48 km southwest of the HBN station) is 49 cm. Average annual runoff in the basin is about 2 cm (Harkness and others, 1996). The basin has cold winters and fairly mild summers. Mean monthly temperatures ranged from −14.8°C in January to 21.0°C in July during the period of record, 1934–95 (National Climatic Data Center, 1996).

Basin geology consists of a thick mantle of clay-rich glacial till with granitic cobbles and boulders. The glacial deposits are primarily ground moraine composed of glacial till and collapsed glacial sediment, eskers, and drumlins (Harris and Luther, 1991). Larger deposits may have resulted when the ice margin stabilized and more debris was deposited at the edge of the ice (Bluemle, 1988). The glacial deposits range from 15 to 46 m thick in most of the basin (Cobb and Biesecker, 1971). The underlying bedrock consists of shale. Soils generally are limy loam or clay loam (U.S. Department of Agriculture, 1997).

The Beaver Creek HBN station is in Steele County. Land ownership in the basin is predominantly private with the exception of rights-of-way along public roads. Light-duty, improved roads and secondary highways provide access to the Beaver Creek Basin year round. Access to the HBN station is by gravel road off the paved road. Snowmobiles are sometimes required off the main road during winter. The Beaver Creek Basin predominantly is agricultural; about 50 percent of the basin is pasture and rangeland, and about 50 percent is planted in crops such as wheat, barley, corn, and sunflowers (K.L. Boespflug, U.S. Geological Survey, oral commun., 1997). Pastures are grazed by cows, horses, and sheep. The basin also contains stock ponds, rural residences, and gravel pits. During the last 30 years, the basin has had a decrease in rural population, a decrease in rangeland, and an increase in the planting of low residue crops. Since 1985, land-use practices have been implemented to control cropland erosion within the basin, particularly along the stream corridor (Stuart Blotter, Natural Resources Conservation Service, written commun., 1996).

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for the Beaver Creek HBN station includes 132 water-quality samples that were collected from April 1965 to September 1995. Sampling frequency is described on the basis of water year, which begins on October 1 and ends on September 30. The sampling frequency was variable over the study period. During the period 1965–80, five samples were collected each year on average, but the range of samples that were collected in any given year was between one and nine. The sampling frequency decreased during the period 1981–95 to an average of three samples per year. Samples were analyzed at USGS district water-quality laboratories until the early 1970's. After 1973, with the creation of the USGS Central Laboratory System, all samples were analyzed at the water-quality laboratory (now called NWQL) in Arvada, Colo. The period of record for discharge is from water year 1965 to the current year (2000).

Data quality was checked using ion balances and time-series plots. Calculated ion balances for samples with complete major-ion analyses are shown in figure 20. More than 95 percent of the samples had ion balances within the ±5 percent range, indicating that the major-ion analytical results generally were of good quality and that unmeasured constituents, such as organic anions, nutrients, and trace metals, do not contribute substantially to the ion composition of the stream water. Time-series plots of ion concentrations were inspected for data quality (fig. 20). The time-series data generally do not reflect method changes for cations and sulfate, probably owing to the large range of concentrations observed at this station. A decrease in the ion balance is observed.

The median and range of dissolved-constituent concentrations in the stream water collected at the Beaver Creek HBN station and VWM concentrations in wet precipitation measured at the Icelandic State Park NADP station are presented in table 36. The NADP station is about 132 km northwest of the HBN station. Precipitation chemistry at the NADP station is dilute and slightly acidic with VWM pH of 5.4 during the period of record, 1983–95. The dominant cation in precipitation was ammonium, which contributed about 50 percent of the total cation concentration; calcium contributed 24 percent. The dominant anions in precipitation were sulfate and nitrate, contributing 50 and 44 percent of the total anion concentration, respectively. The ammonium contributed by precipitation was higher at this HBN station than at most sites. Ammonium concentrations increase where livestock waste and fertilizer applications are widespread (National Atmospheric Deposition Program/National Trends Network, 1997).

Stream water in Beaver Creek is a calcium-magnesium-sodium sulfate type. The sum of ion concentrations ranged from about 4,000 to about 68,000 µeq/L. Alkalinity ranged from 960 to 13,000 µeq/L, and bicarbonate is the primary contributor to alkalinity at this station. Calcium, the major cation, contributed about 40 percent of the median cation concentration in stream water. Magnesium and sodium each accounted for 29 percent of the median cation concentration. Potassium concentrations were high, which probably reflect the weathering of the clay materials in the basin (Deer and others, 1966). Sulfate contributed 53 percent and bicarbonate contributed 42 percent of the median anion concentration in stream water. Dissolved solids at this HBN station were higher than at most other stations in the Hydrologic Benchmark Network. Specific conductance (210 to 2,730 µS/cm) is an indicator of the high dissolved solids at this station. Streams in basins with low average annual runoff and geologic settings that contain fine-grained sediments generally are characterized by high dissolved-solids concentrations (Biesecker and Leifeste, 1975). Annual precipitation and runoff data indicate that evapotranspiration can account for about a twentyfold increase in stream-water dissolved-solids concentrations compared to precipitation (Harkness and others, 1996). Therefore, the maximum ammonium and nitrate concentrations can be accounted for by precipitation as well.

Correlations among dissolved constituents and discharge were determined for Beaver Creek (table 37). The base cations and anions all showed inverse but mostly weak correlations with discharge. The low annual runoff (less than 2 cm) indicates that dilution of stream waters from precipitation is not a substantial process in the basin on an annual basis, but it may be an important process during precipitation events. Strong, positive correlations existed among base cations calcium, magnesium, and sodium. Rho values were 0.946 (calcium and magnesium), 0.875 (calcium and sodium), and 0.958 (magnesium and sodium). Correlations among anions were positive, but not as strong as the cations. Strong correlations also occurred among base cations and the major anions of bicarbonate, sulfate, and chloride. The strongest correlation was between magnesium and sulfate (rho value = 0.964).

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents for Beaver Creek from 1968 through 1995 are presented in table 38. Statistically significant upward trends ($\alpha = 0.01$) existed for flow-adjusted concentrations of dissolved magnesium and sulfate. The absence of a trend in unadjusted concentrations helps eliminate changes in laboratory methods as a source of the trends. Smith and Alexander (1983) determined trends in sulfate, alkalinity, and pH were not statistically significant for this HBN station during the period from the mid-1960's to 1981, although sulfur-dioxide emissions increased by 55 percent in North Dakota during the period 1975–84 (Lins, 1987). Recent trends in precipitation at regional NADP stations show decreasing sulfate and magnesium

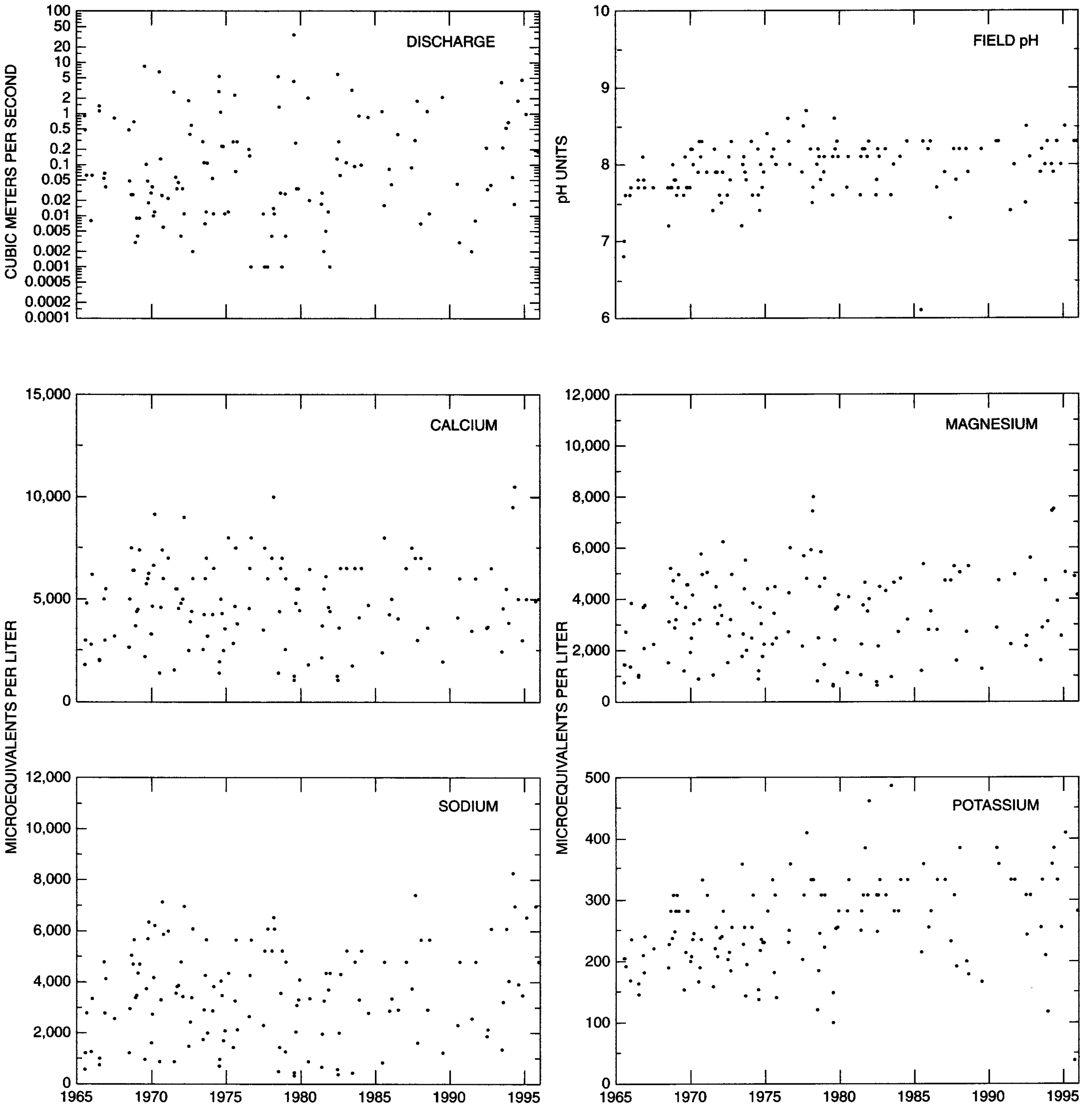


Figure 20. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Beaver Creek near Finley, North Dakota.

for the period 1980–92 (Lynch and others, 1995). However, after accounting for evapotranspiration, precipitation only accounts for about 6 percent of the stream-water sulfate. This may indicate that the source of the sulfate and magnesium is dissolution of magnesium-sulfate salts within the basin, as indicated by the strong correlation between magnesium and sulfate.

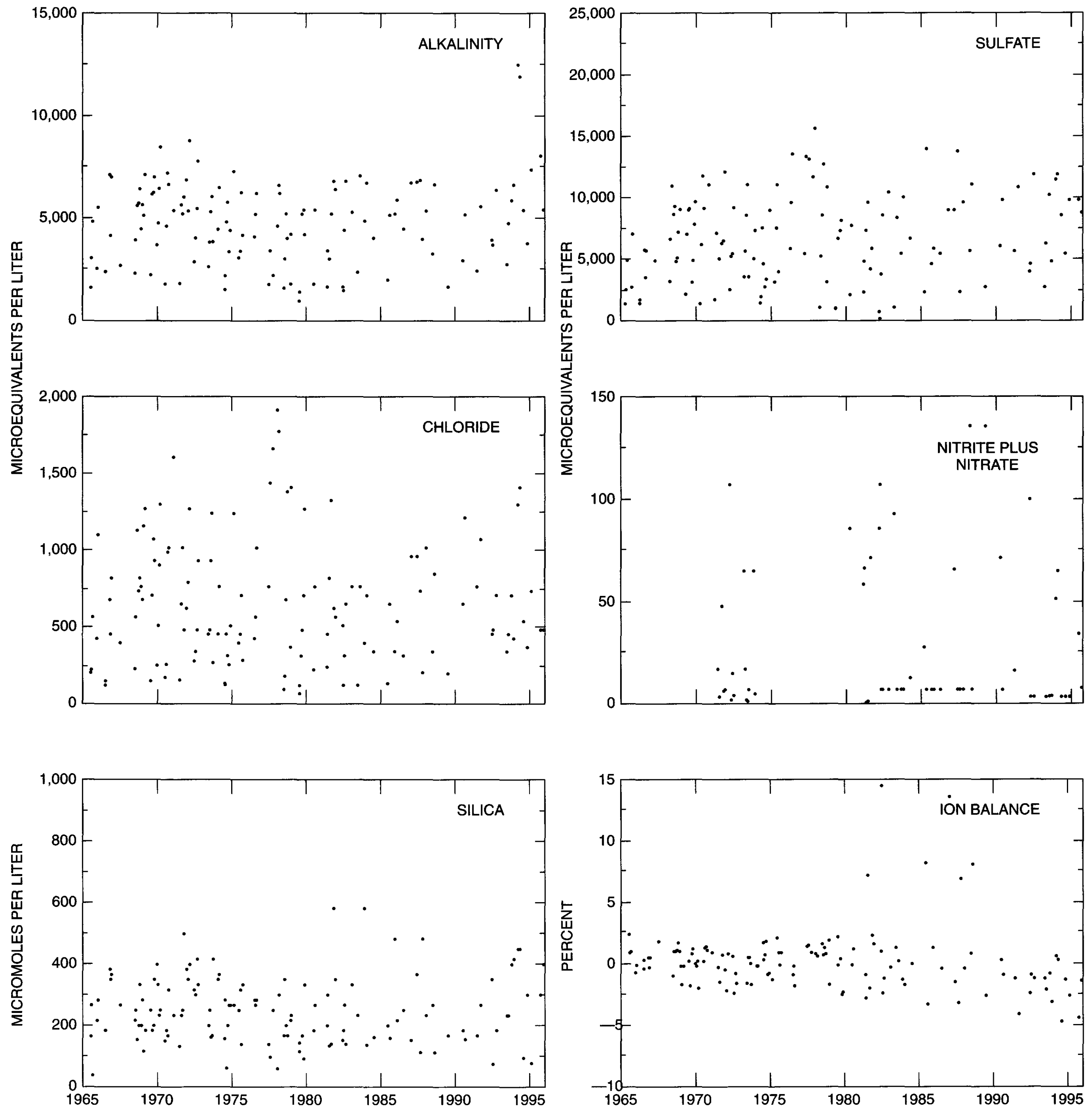


Figure 20. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Beaver Creek near Finley, North Dakota—Continued.

Synoptic Water-Quality Data

Results of a surface-water synoptic sampling conducted June 4 and 5, 1993, in the Beaver Creek Basin are presented in table 39, and locations of the sampling sites are shown in figure 19. Discharge at the HBN station (site 5) was 0.02 m^3/s, which is less than the mean monthly discharge of 0.15 m^3/s for the month of June (Harkness and others, 1996).

Table 36. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ions measured in water-quality samples from Beaver Creek, North Dakota, 1965–95, and volume-weighted mean concentrations in wet precipitation collected at the Icelandic State Park Station, North Dakota, 1983–95

[Parameters in units of microequivalents per liter, except for 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; spec. cond., specific conductance; --, not reported; <, less than]

Parameter	Stream water						Precipitation VWM
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge	<0.001	0.012	0.057	0.48	35	132	--
Spec. cond., field	210	759	1,090	1,440	2,730	132	--
pH, field	6.1	7.7	8.0	8.2	8.7	131	5.4[a]
Calcium	1,000	3,400	4,800	6,400	10,000	132	11
Magnesium	600	2,200	3,400	4,600	8,000	132	4.1
Sodium	310	2,000	3,400	4,800	8,300	132	2.7
Potassium	38	210	260	310	490	132	1.1
Ammonium	1.4	3.6	5.7	9.3	59	46	23
Alkalinity, laboratory	960	3,200	5,000	6,200	13,000	132	--
Sulfate	120	3,800	6,200	9,200	16,000	130	18
Chloride	65	340	560	920	1,900	132	2.3
Nitrite plus nitrate	<.7	4.1	7.1	58.5	140	63	16[b]
Silica	37	170	230	330	580	130	--

[a] Laboratory pH.

[b] Nitrate only.

Table 37. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ions, Beaver Creek, North Dakota, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; SiO_2, silica; --, not applicable]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	–0.123	--	--	--	--	--	--	--	--
Ca	–.534	0.239	--	--	--	--	--	--	--
Mg	–.491	.316	0.946	--	--	--	--	--	--
Na	–.384	.340	.875	0.958	--	--	--	--	--
K	–.406	.158	.403	.383	0.301	--	--	--	--
Alk	–.330	.251	.816	.856	.881	0.242	--	--	--
SO_4	–.449	.316	.921	.964	.929	.384	0.749	--	--
Cl	–.711	.123	.845	.826	.768	.481	.658	0.815	--
SiO_2	.101	–.190	–.026	–.032	.056	–.177	.190	.098	–0.114

The water type of samples that were collected in the basin was mixed. Water type at sites on the main stem (sites 1, 2, 4, and 5) was a calcium-sodium-magnesium sulfate. The water type of the unnamed tributary (site 3) was a calcium-sodium-magnesium sulfate-bicarbonate.

The sum of ions in the basin ranged from 33,000 µeq/L at the HBN station (site 5) to 46,000 µeq/L (site 2). The concentrations of ions sampled at the synoptic sites was generally between the third quartile and the maximum values reported at the HBN station during the period of 1965–95 (table 36). The high ion concentrations correspond to a low discharge, indicating that ground water is likely the source. After adjusting for the effects of evapotranspiration, precipitation is estimated to contribute only a small percentage of the salt-forming anions. Chloride contributions from precipitation ranged from about 6 percent (sites 3 and 5) to about 8 percent (site 2). Sulfate contributions from precipitation ranged from about 2 percent (site 2) to about 4 percent (sites 3 and 5). This is a much smaller percentage than is typical of most stations in the HBN; precipitation is estimated to contribute at least 90 percent of the mean stream sulfate concentration at about one-half of the HBN stations around the country (Smith and Alexander, 1983). Dissolved constituents generally were higher in the upper basin and decreased in a downstream direction. The decrease in ions at the station may be due to dilution from unsampled tributaries, although a corresponding increase in flow was not measured during the synoptic sampling. The percent difference of cations and anions ranged from 0.9 to 3.1 percent, indicating that unmeasured ions did not substantially contribute to the ionic content of the water. Concentrations of nitrate were lower in stream water than in precipitation, indicating that nitrogen generally is retained by the biomass in the basin.

Table 38. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major-ion concentrations, Beaver Creek, North Dakota, 1968 through 1995

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

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	<0.01	0.925	--	--
pH	<.01	.895	(b)	--
Calcium	20	.191	20	0.160
Magnesium	30	.014	40	.004
Sodium	50	.029	40	.036
Potassium	3	.057	3	.023
Alkalinity	40	.073	30	.113
Sulfate	90	.025	100	.007
Chloride	3	.632	5	.189
Nitrite plus nitrate	.4[a]	.625	--	--
Silica	1	.410	(b)	--

[a] Trend test for highly censored data was used.

[b] Concentration-flow model not significant at $\alpha = 0.10$.

Table 39. Physical properties and major-ion concentrations in surface-water samples collected at sites in the Beaver Creek Basin, June 4 and 5, 1993

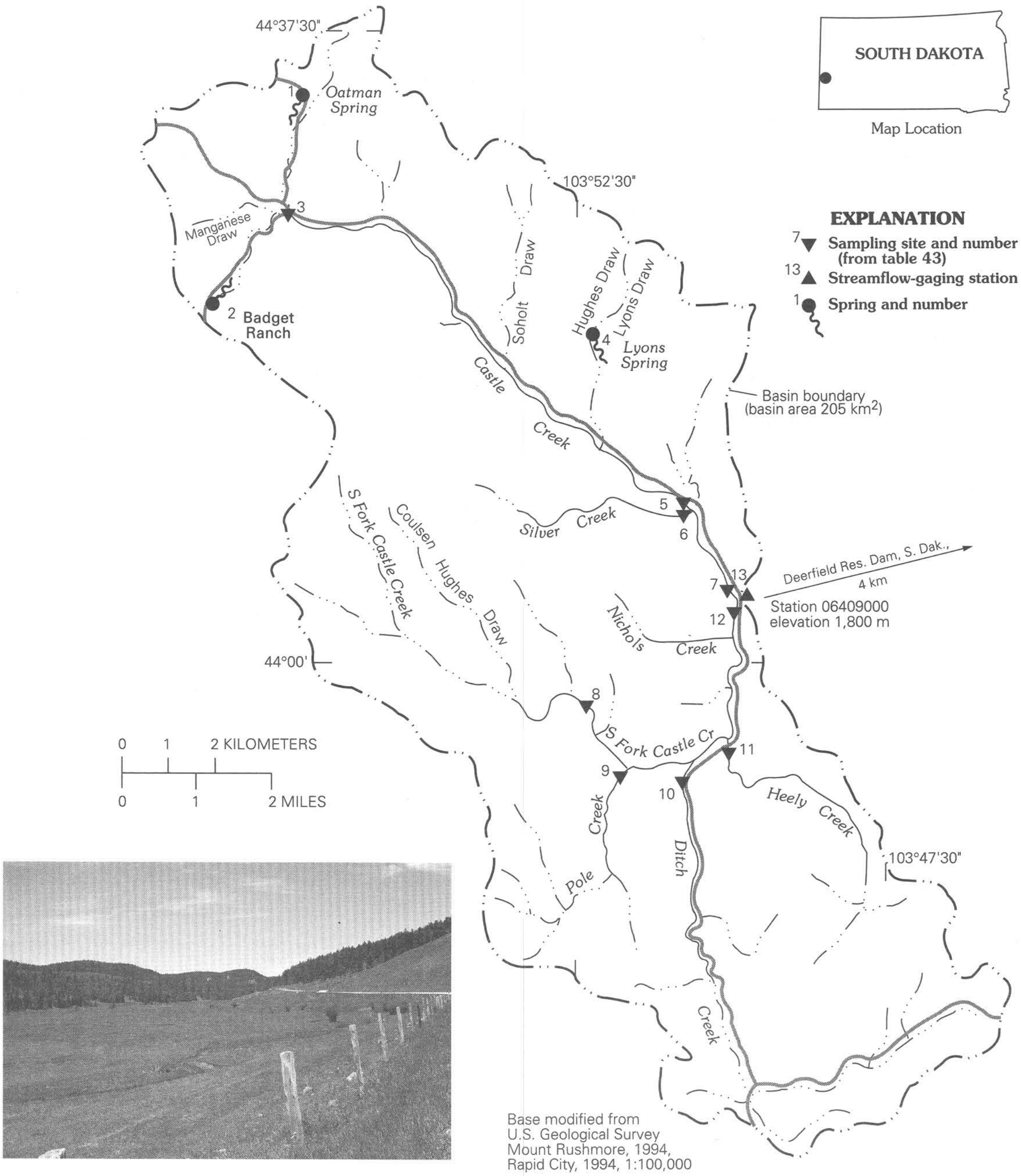
[Site locations shown in fig. 19; Q, discharge in cubic meters per second; SC, specific conductance in microsiemens per centimeter at 25 degrees Celsius; pH in standard units; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; NO_3, nitrate; SiO_2, silica; concentrations in microequivalents per liter, except silica is in micromoles per liter; --, not measured; <, less than; criteria used in selection of sampling sites: TRIB = major tributary, LU = land use]

Site number	Site identification number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	SiO_2	Criteria
1	474737097552700	--	1,910	8.0	8,500	6,200	7,400	490	8,200	14,000	560	<0.4	270	TRIB
2	474021097492800	0.01	1,960	8.1	8,500	5,800	7,800	330	7,800	15,000	540	5.4	320	LU
3	473546097485100	--	1,710	7.9	9,500	6,000	4,300	150	9,200	9,400	730	1.2	350	LU
4	473517097472900	.02	1,790	7.9	8,000	5,500	6,100	330	7,500	13,000	590	1.2	200	LU
5	05064900	.02	1,510	8.3	6,500	4,900	5,200	360	6,100	9,400	730	.4	110	

Castle Creek above Deerfield Reservoir, South Dakota (06409000)

Site Characteristics and Land Use

The Castle Creek HBN Basin is within the Black Hills Section of the Great Plains physiographic province (Fenneman, 1946) in southwestern South Dakota (fig. 21). The HBN station is about 4 km southwest of the dam on Deerfield Reservoir and about 23 km northwest of Hill City, S. Dak., at a latitude of 44°00'49" and a longitude of 103°49'48". Castle Creek drains 205 km^2 of dissected, mountainous terrain. Elevations in the basin range from about 1,800 to about 2,170 m. The average stream slope is about 15 m/km (S.K. Sando,



Base modified from
U.S. Geological Survey
Mount Rushmore, 1994,
Rapid City, 1994, 1:100,000

Figure 21. Map showing study area in Castle Creek Basin and photograph of Silver Creek.

U.S. Geological Survey, written commun., 1998). The ecoregion of the basin is classified as the Black Hills Coniferous Forest Province (Bailey, 1995). A moderately dense Ponderosa pine forest covers most of the basin, and spruce, aspen, willows, and smaller trees and brush grow in the valley areas. Some of the valley floors have been cleared for pastures. Castle Creek is tributary to Rapid Creek, which drains into the Cheyenne River.

Castle Creek is a perennial stream with a small range of mean monthly discharges from 0.23 m^3/s in January to 0.47 m^3/s in May (Burr and others, 1996). The average annual precipitation received at the Deerfield 3 SE weather station (5.4 km southeast of the HBN station) is 51 cm. The upper basin receives enough snow to sustain a snowpack through most of the winter (B.C. Engle, U.S. Geological Survey, written commun., 1997). Average annual runoff is about 5 cm (Burr and others, 1996). The area has cold winters and mild summers. Mean monthly temperatures ranged from –7.3°C in December to 15.5°C in July during the period 1981–95 (National Climatic Data Center, 1996).

The Black Hills are a dome-shaped uplift, dissected by streams. The central core rocks of the Black Hills underlie the area near the HBN station and are composed of Precambrian micaceous schist and phyllite. The upstream part of the Castle Creek HBN Basin drains predominantly Paleozoic carbonate rocks of the Limestone Plateau, including the Madison Limestone of Mississippian age, an important regional aquifer. Lithologic types are cliff-forming dolomitic limestones, dolomites, limestones, shale, and siltstone (DeWitt and others, 1986; DeWitt and others, 1989). Important characteristics of the Madison Limestone, locally known as the Pahasapa Limestone, are its karstic features, including numerous fractures, solution cavities, and springs. The caverns of Jewel Cave National Monument and Wind Cave National Park formed in the Madison Limestone, south and east of the Castle Creek HBN Basin. The Madison is a key factor in the surface-water hydrology of the Black Hills area. Many streams lose all or part of their flow to the sinkholes; resurgent springs are located farther downstream (Driscoll, 1992). The soils in the basin are silty, generally deep, well drained, and gently sloping to steep. Soils are formed in materials weathered from limestone (U.S. Department of Agriculture, 1990). There is very little alluvium in the stream valleys.

The Castle Creek HBN station is in Pennington County. The basin lies entirely within the Black Hills National Forest, although some of the land along the valley floors is privately owned. Much of the drainage area can be accessed by improved paved roads and light-duty gravel and dirt roads. Foot trails provide access to areas farther up the drainages. The HBN station can be accessed by vehicle during all seasons, weather permitting. Manmade features in the basin include a gravel pit, roads, trails, and a campground. An established Forest Service campground is in the Ditch Creek drainage. Timber harvest has occurred one or more times throughout the basin. Cattle and horses graze throughout the basin. Hay and oats are grown in the pastures along the valley bottoms. Recreational uses in the basin include four-wheel-drive vehicle use, fishing, hiking, hunting, and camping. Winter recreation in the upper basin includes skiing and snowmobiling. The basin sees substantial tourism because of its location within the popular Black Hills and its close proximity to Mount Rushmore National Monument. There is a gravel mine in the South Fork Castle Creek drainage, and Black Hills gold is mined lower in the Castle Creek drainage downstream from the HBN study area.

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for the Castle Creek HBN station includes 240 water-quality samples that were collected from December 1964 through August 1995. Sampling frequency is described on the basis of water year, which begins on October 1 and ends on September 30. Sampling frequency was quarterly from 1965 through 1967 and increased to 10–13 samples collected annually during the period 1968 to 1982. After 1982, samples generally were collected quarterly. Samples were analyzed at USGS district water-quality laboratories until the early 1970's. After 1973, with the creation of the USGS Central Laboratory System, all samples were analyzed at the water-quality laboratory (now called NWQL) in Arvada, Colo. The period of record for discharge is from water year 1948 to current year (2000). Daily water temperature was recorded from May 1964 to September 1984.

Data quality was checked using ion balances and time-series plots. Calculated ion balances for samples with complete major-ion analyses are shown in figure 22. More than 95 percent of the samples had

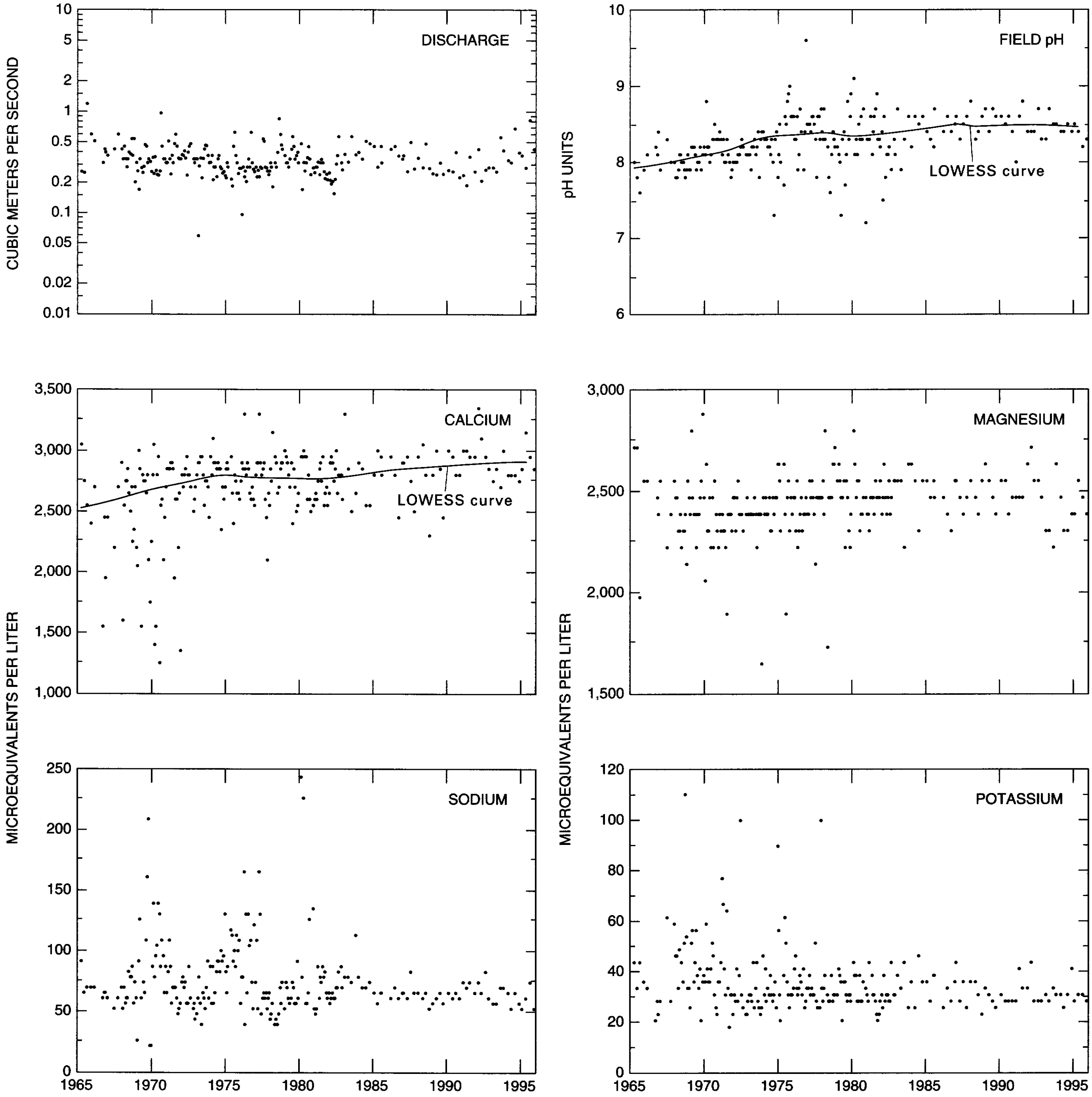


Figure 22. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Castle Creek above Deerfield Reservoir, near Hill City, South Dakota.

ion balances within the ±10 percent range, indicating that the major-ion analytical results were of good quality and that unmeasured constituents, such as organic anions, do not contribute much to the ionic composition of Castle Creek. Time-series plots of ion concentrations were inspected for evidence of influences that are related to analytical method changes (fig. 22). Calcium, magnesium, and sodium show a similar pattern of having more scatter in the early part of the record and a decrease in scatter after 1983. This decrease coincides with a change in the analytical method for these analytes

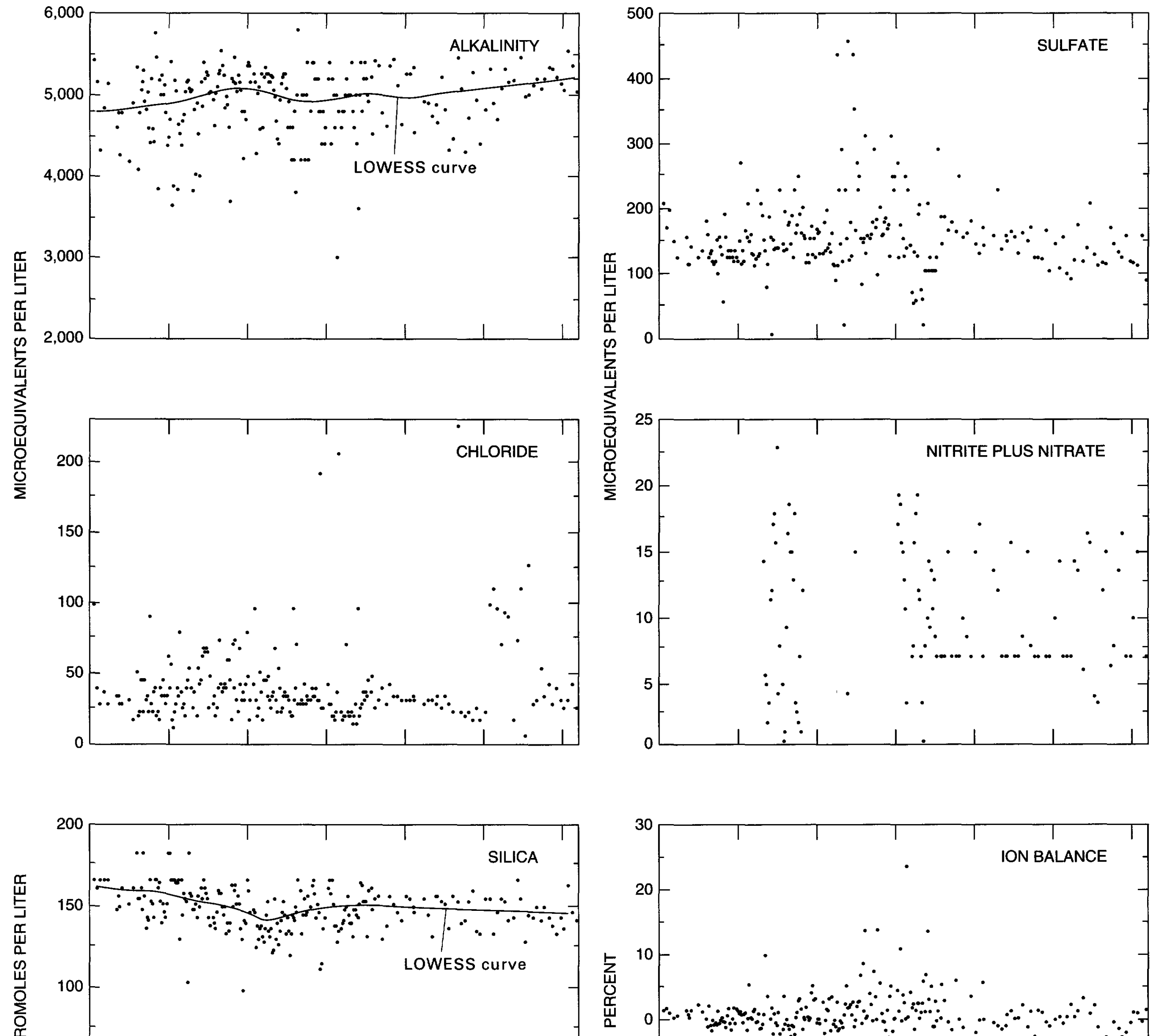


Figure 22. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Castle Creek above Deerfield Reservoir, near Hill City, South Dakota—Continued.

from AA spectroscopy to ICP spectroscopy (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 82.18, 1982). Several samples had high sulfate concentrations in the late 1970's. The decrease in scatter of sulfate concentrations after 1982 corresponds with the change from a methylthymol blue procedure to a turbidimetric titration method (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 83.07, 1983). Changes also were made in meters and electrodes used for field pH determinations during the study period. When changes in methods or instrumentation result in improved precision or elimination of measurement bias, time-series data can exhibit less scatter or a directional shift, respectively. The time-series data, therefore, may reflect the method or instrument change rather than an environmental change.

The median and range of major-ion concentrations in stream water collected at the Castle Creek HBN station and VWM concentrations in wet precipitation measured at the Newcastle, Wyo., NADP station are presented in table 40. The NADP station is about 43 km southwest of the HBN station. Precipitation chemistry at the NADP station was dilute and slightly acidic with VWM pH of 5.3 during the period of record, 1981–95. The dominant cation in precipitation was calcium, accounting for about 38 percent of the cation concentration. About 33 percent of the total cation concentration was contributed by ammonium. Sulfate and nitrate contributed about 51 and 42 percent, respectively, to the total anion concentration in precipitation.

Stream water in Castle Creek is an alkaline, calcium bicarbonate type. The sum of ion concentrations ranged from about 7,600 to about 12,000 μeq/L. Alkalinity ranged from 3,000 to 5,800 μeq/L, and bicarbonate was the primary contributor to alkalinity at this station. Dissolved calcium and magnesium contributed over 98 percent of the median cation concentration in stream water, and bicarbonate contributed 96 percent of the median anion concentration. The predominance of these constituents is typical of a geologic setting containing limestones and dolomites. Carbonate rocks generally are more soluble than silica-rich rocks, including sandstones, granite, and schists; greater solubility of rock increases dissolved-solids concentrations in streams (Biesecker and Leifeste, 1975). Specific conductance (304 to 715 μS/cm) is an indicator of dissolved solids at this station. Median concentrations of ammonium and nitrate were lower in the stream water than in the precipitation, indicating that nitrogen generally is retained by the biomass in the basin.

Correlations among dissolved constituents and discharge were determined for Castle Creek (table 41). Base cations and anions showed weak and mixed, positive and inverse correlations with stream discharge. The lack of strong correlations with discharge probably is due to the narrow range of discharge associated with the well-drained soils and the karstic nature of underlying

Table 40. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ions measured in water-quality samples from Castle Creek, South Dakota, 1965–95, and volume-weighted mean concentrations in wet precipitation collected at the New Castle Station, Wyoming, 1981–95

[Parameters in units of microequivalents per liter, except for 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; spec. cond., specific conductance; --, not reported; <, less than]

Parameter	Stream water						Precipitation VWM
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge	0.06	0.26	0.31	0.40	1.2	240	--
Spec. cond., field	304	439	467	485	715	239	--
pH, field	7.2	8.1	8.3	8.5	9.6	237	5.3[a]
Calcium	1,200	2,600	2,800	2,900	3,400	240	15
Magnesium	1,600	2,400	2,500	2,600	2,900	239	2.9
Sodium	22	61	65	83	240	237	3.0
Potassium	18	28	31	38	110	238	.87
Ammonium	<.7	.7	1.4	4.3	14	72	13
Alkalinity, laboratory	3,000	4,700	5,000	5,200	5,800	239	--
Sulfate	6.2	120	150	170	460	239	18
Chloride	5.6	25	34	42	230	236	2.5
Nitrite plus nitrate	<.7	7.1	8.6	15	23	114	15[b]
Silica	1.7	140	150	160	180	239	--

[a] Laboratory pH.
[b] Nitrate only.

Table 41. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ions, Castle Creek, South Dakota, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; SiO_2, silica; --, not applicable]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	–0.086	--	--	--	--	--	--	--	--
Ca	–.224	0.140	--	--	--	--	--	--	--
Mg	–.244	.138	0.404	--	--	--	--	--	--
Na	.011	.056	.068	0.084	--	--	--	--	--
K	.095	–.128	.115	–.058	0.278	--	--	--	--
Alk	–.208	–.004	.702	.307	.097	0.197	--	--	--
SO_4	.217	.153	.126	.081	.158	.100	0.039	--	--
Cl	.055	–.112	.113	–.057	.138	.172	.192	0.156	--
SiO_2	–.084	–.350	.299	.227	.024	.376	.270	–.053	0.088

carbonates, which allows precipitation to infiltrate quickly. The magnitude of the minimum values of calcium (1,200 μeq/L) and magnesium (1,600 μeq/L) compared to precipitation indicates that most of the cations in stream water are contributed from groundwater sources that have been in contact with geologic materials. The stream solutes also showed weak correlations with each other, except for calcium and alkalinity (rho value = 0.702). The fact that calcium and magnesium are not strongly correlated, nor magnesium and alkalinity, may indicate that the calcium-alkalinity relationship is controlled by the limestones rather than the dolomites.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents for Castle Creek from 1965 through 1995 are presented in table 42. Statistically significant upward trends ($\alpha = 0.01$) occurred in pH, calcium, and alkalinity. A significant downward trend in unadjusted silica concentrations was observed. After the statistical test was adjusted for discharge, only the upward trends remained in concentrations of calcium and alkalinity. This indicates that stream discharge may have been controlling the pH and silica trends, but not the calcium and alkalinity trends. Regional precipitation chemistry shows a widespread decline in calcium concentrations for the period 1980–92 (Lynch and others, 1995). The decrease in calcium in precipitation is not consistent with the upward trend in calcium in stream water. However, carbonate rock rather than precipitation is the predominant control on the calcium in the stream water. Variations in timber harvest is one land-use change that has occurred in the basin.

Table 42. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major-ion concentrations, Castle Creek, South Dakota, 1965 through 1995

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

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	–0.01	0.592	--	--
pH	.01	<.001	([b])	--
Calcium	10	<.001	9	<0.001
Magnesium	<.01	.018	3	.048
Sodium	<.01	.327	([b])	--
Potassium	–.2	.013	([b])	--
Alkalinity	10	.001	9	.003
Sulfate	–.6	.122	–0.4	.188
Chloride	<.01	.750	([b])	--
Nitrite plus nitrate[a]	<.01[a]	.306	--	--
Silica	–.3	.002	([b])	--

[a] Trend test for highly censored data was used.

[b] Concentration-flow model not significant at $\alpha = 0.10$.

An upward trend in flow-adjusted sulfate concentrations and increasing levels of sulfur-dioxide emissions were reported by Smith and Alexander (1983) for the mid- to late 1960's to 1981. Annual precipitation and runoff data for Castle Creek indicate that evapotranspiration can account for about a tenfold increase in stream-water concentrations compared to precipitation, which indicates precipitation is the primary contributor of sulfate in stream water. The lack of a trend for the period 1965–95 indicates that sulfate deposition may have decreased in the area since that study.

Synoptic Water-Quality Data

Results of a surface-water synoptic sampling conducted June 12–14, 1993, in the Castle Creek Basin are presented in table 43, and locations of the sampling sites are shown in figure 21. Discharge at the HBN station (site 13) was 0.96 m^3/s compared to the mean monthly discharge of 0.40 m^3/s for the month of June (Burr and others, 1996). The sum of ions ranged from 1,100 (site 2) to 11,000 μeq/L at several sites, including the HBN station (site 13). Concentrations of dissolved constituents in tributaries and springs generally were within the range of dissolved constituent concentrations for the Castle Creek HBN station (table 40) with the exception of site 2, which had a smaller concentration of calcium, magnesium, and bicarbonate than the minimum value recorded at the HBN station. Water in the basin is generally a calcium-magnesium bicarbonate or calcium bicarbonate type. Water sampled from the tributaries and springs were near neutral to alkaline. The percent difference of cations and anions ranged from 0.1 to 7.1 percent for all sites, indicating that unmeasured ions did not contribute substantially to the ionic composition of the water.

Two samples that were collected in the headwaters of the Castle Creek drainage were from springs (sites 1 and 2). The first location of sustained flow in the Castle Creek channel was noted at site 3. The concentrations of constituents were more dilute in Badget Ranch Spring (site 2). The exact location of the contact between the Madison Limestone and the Minnelusa Formation of Permian age is unknown in the area near this spring. The Minnelusa Formation includes sandstone, breccia, limestone, and shale. The geochemical composition of the Badget Ranch sample is more characteristic of a geologic environment containing silica-rich rocks like the Minnelusa Formation than a predominantly limestone environment. The different water quality at the two springs also could be the result of different residence time. Samples that were collected from areas draining metamorphosed tuffaceous shale tend to have higher concentrations of sodium and sulfate (sites 7, 11, 12, and 13). Precipitation chemistry can account for the nitrate concentrations in samples that were collected during the synoptic sampling.

Table 43. Physical properties and major-ion concentrations in surface-water samples collected at sites in the Castle Creek Basin, June 12–14, 1993

[Site locations shown in fig. 21; 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; SiO_2, silica; concentrations in microequivalents per liter, except silica is in micromoles per liter; --, not measured; <, less than; criteria used in selection of sampling sites: BG = bedrock geology, TRIB = major tributary]

Site number	Site identification number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	SiO_2	Criteria
1	440650103570000	--	458	7.8	3,800	1,500	52	44	5,000	25	<2.8	7.5	350	BG
2	440414103583000	--	50	7.2	380	100	52	49	480	8.3	17	2	230	BG
3	440521103571600	--	407	--	2,800	1,800	39	14	4,400	58	8.5	37	180	BG
4	440400103521100	--	476	8.3	2,800	2,500	52	22	5,300	56	14	6.4	150	BG
5	440156103504300	0.39	483	8.4	3,000	2,300	61	31	5,200	180	34	4.9	160	TRIB
6	440148103504100	.04	481	8.5	3,000	2,500	57	28	5,300	100	17	6.9	140	TRIB
7	440055103495900	.55	491	8.4	3,100	2,400	78	33	5,200	230	62	7.8	170	TRIB
8	435930103521900	.02	463	8.4	3,200	2,100	48	19	5,000	56	45	4.8	130	BG
9	435847103513900	.01	460	8.5	3,000	2,200	57	31	5,100	63	17	4.9	150	TRIB
10	435832103504400	.09	477	8.5	3,200	2,200	52	20	4,900	65	31	9.5	150	TRIB
11	435856103500000	.06	501	8.4	2,800	2,600	87	72	5,400	200	25	1.6	160	BG
12	440039103495100	.25	449	8.5	2,800	2,200	87	46	4,600	120	25	1.9	170	TRIB
13	06409000	.96	476	8.5	3,000	2,300	83	36	5,100	190	51	6	170	

Little Vermillion River near Salem, South Dakota (06478540)

Site Characteristics and Land Use

The Little Vermillion River HBN Basin lies in the Western Lake section of the Central Lowland physiographic province (Fenneman, 1946) in eastern South Dakota (fig. 23). The HBN station is about 8 km northeast of Salem, S. Dak., at a latitude of 43°47'39" and a longitude of 97°22'02". The Little Vermillion River drains about 204 km^2 of glaciated plain and is tributary to East Fork Vermillion River in the Lewis and Clark River Basin. The basin is rather flat, with elevations that range from 460 to 497 m, and has numerous shallow lakes. The slope of the main channel is about 1 m/km. The basin is in the transition region between the Great Plains Steppe Province and the Prairie Parkland (Temperate) Province (Bailey, 1995). About 90 percent of the basin is under cultivation, and the remaining area is covered with a moderately dense growth of prairie grass (Cobb and Biesecker, 1971). Trees are planted as shelterbelts around farmsteads.

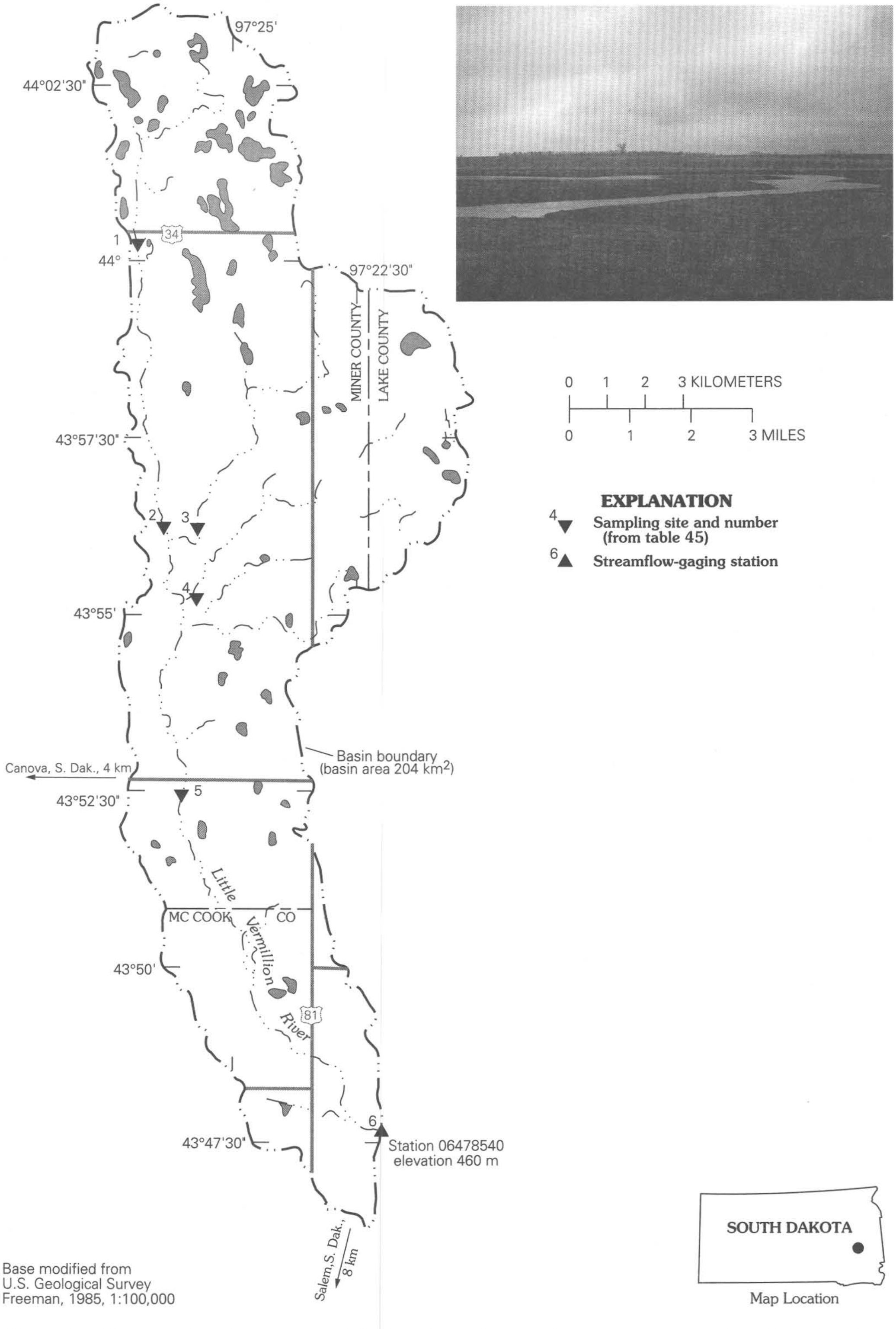
The Little Vermillion River is an intermittent stream. No flow occurs for many days each year, primarily during fall and winter. Mean monthly discharge ranges from 0.001 m^3/s in January to 0.51 m^3/s in July (Burr and others, 1996). Average annual precipitation at the Salem weather station, about 17 km southwest of the site, is 64 cm. Most of the precipitation occurs as rain in spring and summer. Average annual runoff is only about 3 cm (Burr and others, 1996). The mean monthly temperatures ranged from about –11.9°C in January to 24.0°C in August during the period of record, 1969–72 (National Climatic Data Center, 1996).

The surface of the Little Vermillion HBN Basin is mantled by deposits of Pleistocene age. Outwash and alluvium are near the stream channel. Glacial deposits of outwash, oxidized till, and unoxidized till show evidence of three intervals of glaciation (Schroeder, 1988). Glacial deposits are composed of silty, pebbly clays, sands, and gravel. Average thickness of these deposits is about 50 m. Bedrock geology underlying the glacial deposits includes Pierre Shale and Niobrara Formation of Jurassic age and the Sioux Quartzite of Proterozoic age (Darton, 1951, pl. 1). The Pierre Shale is dark gray with abundant bentonite. The Niobrara Formation is a light-brown to dark-brown speckled marl with some pyrite, gypsum, and shell fragments. The Sioux Quartzite is pink to red, massive orthoquartzite (Schroeder, 1988). Basin soils are described as well-drained to somewhat poorly drained, level to moderately sloping loamy soils (U.S. Department of Agriculture, 1980; 1984a).

The Little Vermillion River HBN Basin is in Miner and McCook Counties. Land ownership is private except for rights-of-way along public roads. Railroad tracks and a network of roads, including unimproved, improved, and highways, provide access to the basin year round. Nearly the entire basin is used for agriculture. Crops, including corn and soybeans, are grown on about 90 percent of the land, and the remaining area is used for grazing cattle. During the 1980's, much of the area occupied by row crops was returned to grassland under the Conservation Reserve Program (Darrell Campbell, Farm Service Agency, oral commun., 1997). In the 1990's, some of the set-aside grassland was returned to row crops (M.J. Burr, U.S. Geological Survey, oral commun., 1997). Rural residences and stock ponds are present throughout the basin, and several lakes lie in the upper basin where waterfowl production is managed. Gravel pits are constructed in the basin, primarily along the main channel of the Little Vermillion River (Koch and McGarvie, 1988).

Historical Water-Quality Data

Samples for chemical analyses have not been collected routinely at the Little Vermillion HBN station. The data set analyzed for this report for the Little Vermillion River HBN station includes 121 measurements of instantaneous discharge and 113 measurements of specific conductance for the period February 1976 to August 1995. The entire period of record for discharge is from 1966 to 1997. Median values and ranges of discharge and specific conductance are shown in table 44. Discharge ranged from less than 0.001 to 18 m^3/s with a median discharge of 0.34 m^3/s. The range of specific conductance for the period was 140 to 1,970 µS/cm, with a median value of 860 µS/cm. Specific conductance is an indicator of dissolved solids. Based on the range of specific-conductance values, dissolved solids generally are high at this site. Streams in basins with fine-grained sediments and low annual runoff tend to have high dissolved-solids concentrations (Biesecker and Leifeste, 1975). Specific conductance had an inverse relation with discharge. The Spearman rank correlation coefficient was –0.716 and was significant for an α of 0.01.



Base modified from
U.S. Geological Survey
Freeman, 1985, 1:100,000

Figure 23. Map showing study area in Little Vermillion River Basin and photograph of the Little Vermillion River in the upper basin.

Synoptic Water-Quality Data

Results of a surface-water synoptic sampling conducted April 8, 1993, in the Little Vermillion River Basin are presented in table 45, and locations of the sampling sites are shown in figure 23. Discharge at the HBN station (site 6) was 2.3 m^3/s compared to the mean monthly discharge of 0.46 m^3/s for the month of April (Burr and others, 1996). The water type at the Little Vermillion River HBN station is a calcium-magnesium sulfate type. The sum of ions at the HBN station is 20,000 µeq/L. The specific conductance of 958 µS/cm was higher than the median but less than the third quartile for the period of record, 1976–95. The dominant cations, calcium (43 percent) and magnesium (39 percent), contributed 82 percent of the total cation concentration. Potassium concentrations were high, which probably reflect the weathering of the clay materials in the basin (Deer and others, 1966). Sulfate contributed 64 percent and bicarbonate contributed 33 percent of total anion concentration. Bicarbonate was the primary contributor to alkalinity at this station. Annual precipitation and runoff data indicated that evapotranspiration can account for about a twentyfold increase in stream-water concentrations compared to precipitation. Sulfate and chloride concentrations were higher than can be accounted for by evapotranspiration of precipitation at the South Dakota NADP stations, indicating that there is a source for these constituents within the basin. The percent difference of cations and anions was about 2 percent, indicating that unmeasured ions do not substantially contribute to the ionic content of the Little Vermillion River.

The waters at the remaining synoptic sites (sites 1–5) are calcium-magnesium sulfate. The sum of ions in tributary and upper-basin main-stem sites ranged from about 17,000 µeq/L (site 4) to about 24,000 µeq/L (site 2). The specific conductance on the main stem (site 2) in the upper basin was

Table 44. Minimum, first quartile, median, third quartile, and maximum values of physical properties measured at the Little Vermillion River, South Dakota, 1976–95

[Discharge in cubic meters per second; specific conductance in microsiemens per centimeter at 25 degrees Celsius; n, number of stream samples; <, less than]

Parameter	Stream water					
	Minimum	First quartile	Median	Third quartile	Maximum	n
Discharge	<0.001	0.04	0.34	1.8	18	121
Specific conductance, field	140	520	860	1,180	1,970	113

Table 45. Physical properties and major-ion concentrations in surface-water samples collected at sites in the Little Vermillion River Basin, April 8, 1993

[Site locations shown in fig. 23; 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; SiO_2, silica; concentrations in microequivalents per liter, except silica is in micromoles per liter; --, not measured; <, less than; criteria used in selection of sampling sites: BG = bedrock geology, TRIB = major tributary, LU = land use]

Site number	Site identification number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	SiO_2	Criteria
1	440027097265200	--	1,020	7.8	4,500	4,300	1,600	510	3,400	7,300	310	<0.4	280	BG
2	435609097260800	--	1,120	7.9	4,800	4,900	2,000	510	3,000	8,100	420	54	250	TRIB
3	435609097253600	--	884	7.8	3,900	3,400	1,200	490	2,300	6,000	450	140	220	TRIB
4	435516097254000	--	840	7.9	3,800	3,300	1,000	410	2,400	5,800	370	61	220	TRIB
5	435238097254800	--	979	7.8	4,400	4,000	1,500	460	2,400	7,500	340	79	220	LU
6	06478540	2.3	958	7.9	4,200	3,800	1,300	440	3,300	6,500	340	6.8	160	

1,120 µS/cm, which was higher than the specific conductance measured downstream at sites 5 (979 µS/cm) and 6 (958 µS/cm). This sampling was conducted on the rising limb of the hydrograph, and this dilution effect is not typical of base-flow conditions for this station. Nitrate concentrations in samples that were collected from several synoptic sites (sites 2, 3, 4, and 5) were higher than concentrations in most of the other HBN basins and undeveloped sites in other studies (Mueller and others, 1995). This may indicate that there is a source for some nitrogen in the basin, possibly fertilizer or animal waste; however, evapotranspiration rates also are high in this basin.

Cache Creek near Jackson, Wyoming (13018300)

Site Characteristics and Land Use

The Cache Creek HBN Basin is in the Middle Rocky Mountains physiographic province (Fenneman, 1946) in western Wyoming (fig. 24). The HBN station is 3.9 km southeast of the town of Jackson, Wyo., at a latitude of 43°27'08" and a longitude of 110°42'12". Cache Creek drains about 27 km^2 of steep mountain and canyon terrain in the Gros Ventre Mountains. Basin elevations range from about 2,100 to about 3,100 m. The ecoregion of the basin is classified as the Southern

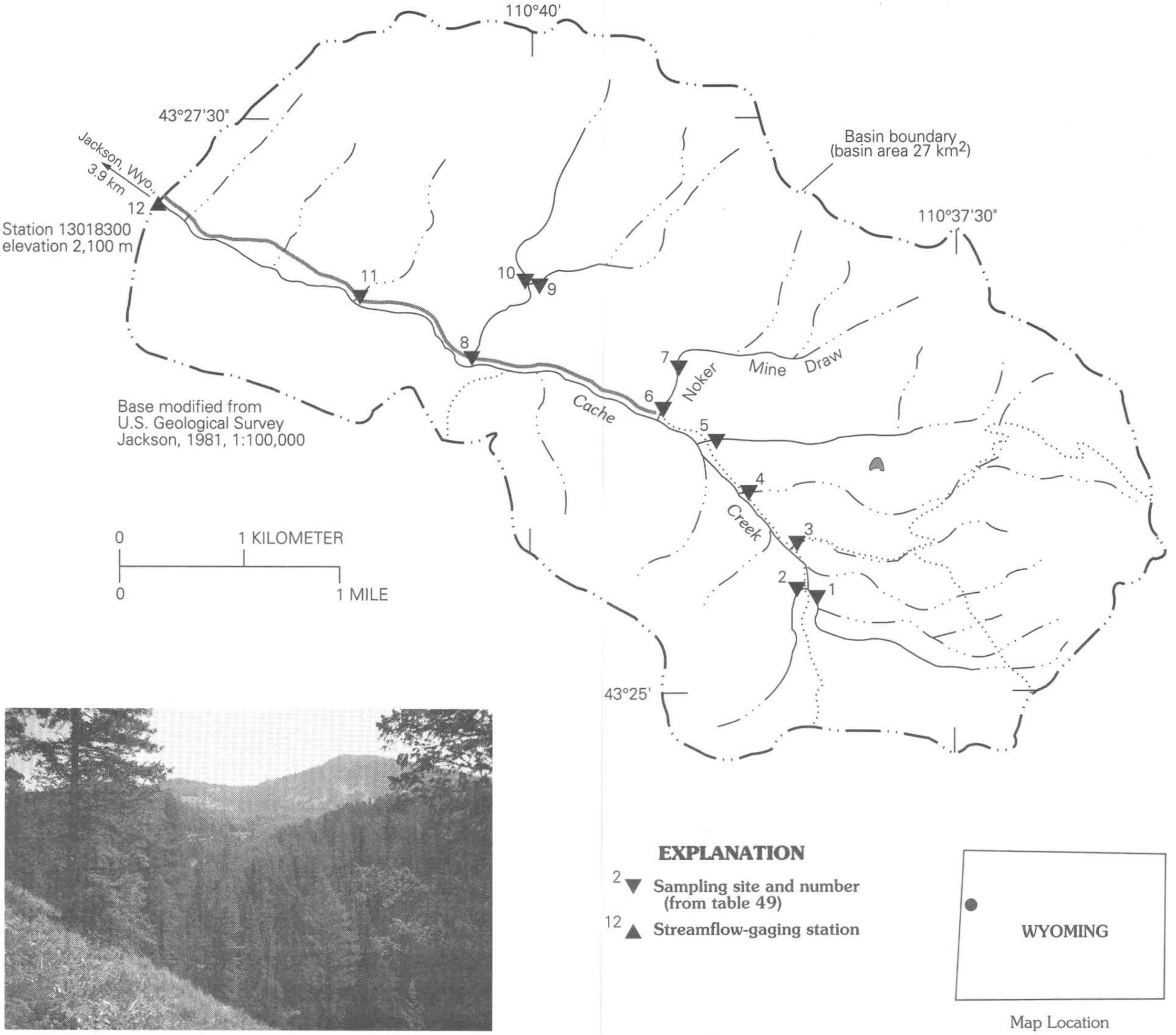


Figure 24. Map showing study area in Cache Creek Basin and photograph of the landscape of the basin.

Rocky Mountain Steppe-Open Woodland-Coniferous Forest-Alpine Meadow Province (Bailey, 1995). Timber covers about 80 percent of the north-facing slopes and 50 percent of the south-facing slopes. On the south-facing slopes, subalpine fir, lodgepole pine, and Engelmann spruce are the dominant timber species. Subalpine fir, Douglas fir, and lodgepole pine timber species dominate the north-facing slopes. Grass, forbs, and brush cover the remaining area up to timber line. Underbrush includes mountain big sagebrush, whortleberry, huckleberry, and pinegrass (Sandra Key, U.S. Forest Service, written commun., 1997). Cache Creek is tributary to Flat Creek, which is tributary to the Snake River.

Cache Creek is a perennial stream with a snowmelt-dominated hydrograph where mean monthly discharge ranges from 0.11 m^3/s during base flow in February to 1.4 m^3/s during snowmelt runoff in June (Smalley and others, 1996). Average annual precipitation is about 40 cm at the Jackson weather station, which is at a lower elevation than the HBN basin. Cobb and Biesecker (1971) reported about 76 cm of precipitation for the Cache Creek site, which mostly falls as snow. Average annual runoff is about 40 cm (Smalley and others, 1996). Mean monthly temperatures ranged from –9.2°C in January to 16.0°C in July during the period of record, 1948–95 (National Climatic Data Center, 1996). Average temperatures will be lower and average precipitation will be higher for the HBN basin because of the higher elevations.

The relief within the Cache Creek Basin is the result of uplifting by folding and faulting (Simons and others, 1988). Two thrust faults trend through the study area: the Cache Creek Thrust Fault and Jackson Thrust Fault. The underlying bedrock is composed of deformed sedimentary rocks (Goetze, 1981). Paleozoic rocks are in the upper drainages on the north side of the Cache Creek Thrust Fault. Paleozoic rocks from several periods are located in the basin: Cambrian shale and limestone; Ordovician dolomite; Devonian siltstone and shale; Mississippian limestone, shale, and sandstone; and Pennsylvanian and Permian sandstone, shale, limestone, and dolomite. Cretaceous units primarily are in the eastern part of the basin, including the Cody Shale, Bacon Ridge Sandstone, and the Sohare Formation. The Cody Shale is described as a dark, marine shale with glauconitic sandstones. The Bacon Ridge Sandstone is light-gray to tan, fine- to medium-grained, massive to thick-bedded sandstone. The Sohare Formation contains sandstone, shale, marlstone, and some beds of minable coal. Unconsolidated units cover a large part of the valley and slopes and include slope wash, landslide debris and slump blocks, talus deposits, and partly lithified limestone conglomerate. Soils in the basin are well drained with moderate to rapid permeabilities (Glenn, 1981). Two main soil types occupy the dissected forest slopes. The soil type on steep slopes (greater than 20 percent) are light-brown, sandy, gravelly loam, containing about 10 to 60 percent rock fragments. Clay content ranges from about 20 to 45 percent. The soils on gradual slopes (less than 20 percent) are grayish-brown to pale-brown, lime-loamy, mixed, silt loam. Rock fragment content is about 10 to 30 percent. Subsoils are well developed in this soil type (Glenn, 1981).

The Cache Creek Basin is in Teton County and lies entirely within the Bridger-Teton National Forest. The northern and eastern parts of the basin predominantly lie in the Gros Ventre Wilderness Area. One dirt road serves the lower part of the basin. Travel on the road is restricted to authorized use by the Forest Service, other agencies, and permitted outfitters. The upper part of the basin is reached by trail only. Access for the general public is by horses, hiking, and mountain biking in summer and is restricted to skiing, snowshoeing, and snowmobiles in the winter. Mechanized vehicles only are allowed in that portion of the basin outside the Gros Ventre Wilderness Area. Land use in the basin has changed over the years. Two small coal mines provided coal for local needs up to the mid-1930's. Prior to 1938, small-scale logging and cattle grazing occurred in the basin (Sandra Key, U.S. Forest Service, written commun., 1997). In 1942, the basin was closed to grazing and timber harvest for protection of the water supply from Cache Creek to the town of Jackson. Restoration in the basin during the 1960's included road closure, road and trail erosion control, and seeding of disturbed areas. Since the 1970's, recreation has been the predominant land use. Hiking, biking, and camping activity can be substantial during summer owing to the close proximity of the basin to the town of Jackson and Grand Teton and Yellowstone National Parks. Hunting is the dominant recreational use in the fall, and cross-country skiing and snowshoeing are popular winter recreational uses in the basin.

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for the Cache Creek HBN station includes 272 water-quality samples that were collected from July 1965 to August 1995. Sampling frequency is described on the basis of water year, which begins on October 1 and ends on September 30. Between 10–12 samples were collected per year for most of the period from 1966 through 1982. After 1982, sampling frequency was reduced, generally to a bimonthly schedule. Samples were analyzed at USGS district water-quality laboratories until the early 1970's. After 1973, with the creation of the USGS Central Laboratory System, all samples were analyzed at the water-quality laboratory (now called NWQL) in Arvada, Colo. The period of record for discharge is from June 1962 to current year (2000).

Data quality was checked using ion balances and time-series plots. Calculated ion balances for samples with complete major-ion analyses are shown in figure 25. More than 95 percent of the samples had ion balances within the ±5 percent range, indicating that the major-ion analytical results were of good

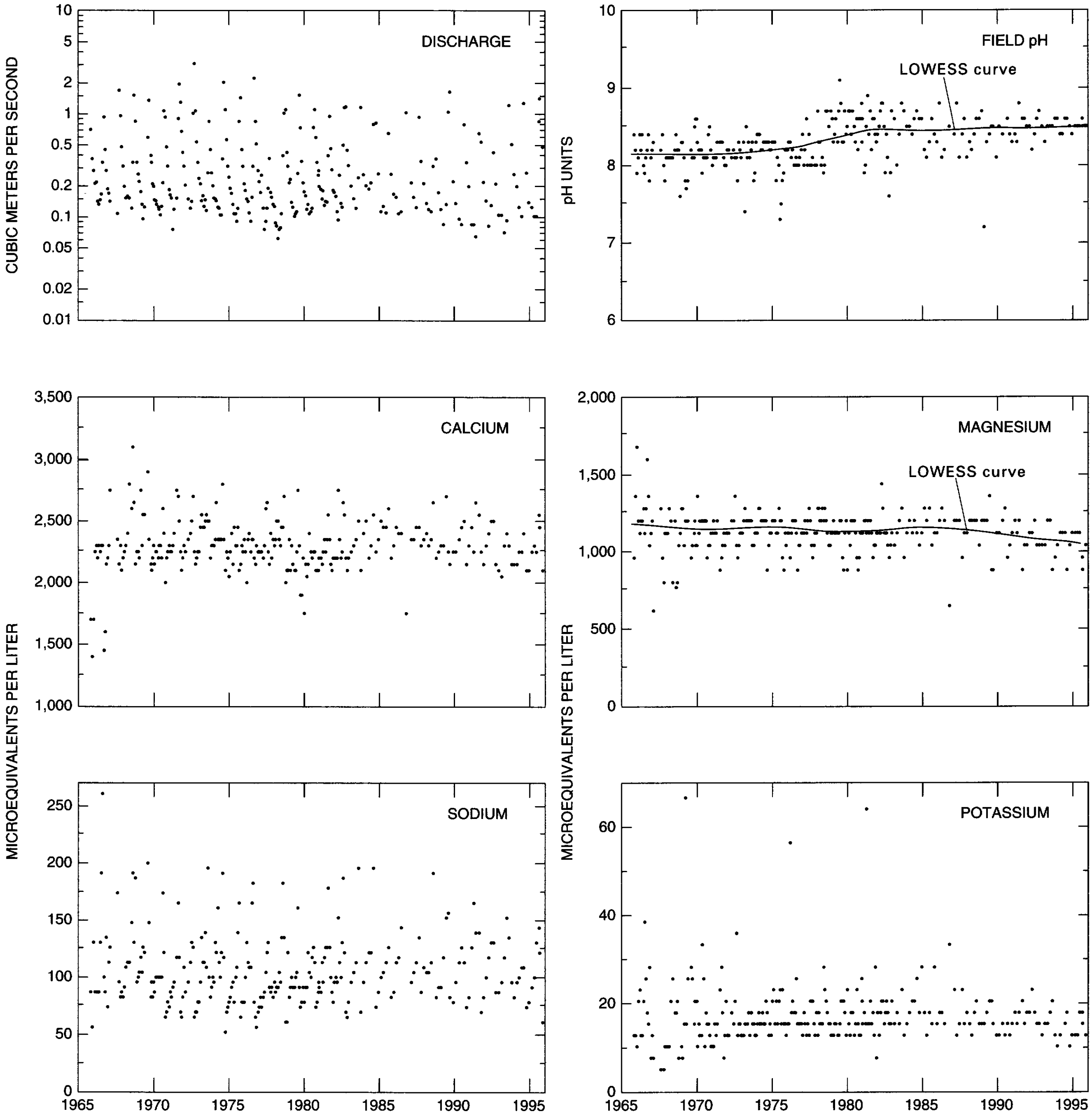


Figure 25. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Cache Creek near Jackson, Wyoming.

quality and that unmeasured constituents, such as organic ions, nutrients, and trace metals, do not contribute substantially to the ion composition of the water. Time-series plots of ion concentrations were inspected for data quality (fig. 25). Generally, there is more scatter for cations (calcium, magnesium, and sodium) in the early part of the record, but method-related causes were not isolated. Changes could be related to the decrease in sampling frequency. The method changes for sulfate in 1982 and 1990 also are not apparent in the scatter of the sulfate data at this site. The field pH values generally were lower prior to 1980. Changes were made in meters and electrodes used for field pH determinations during the study period.

The median and range of major-ion concentrations in the stream water collected at the Cache Creek HBN station and VWM concentrations in

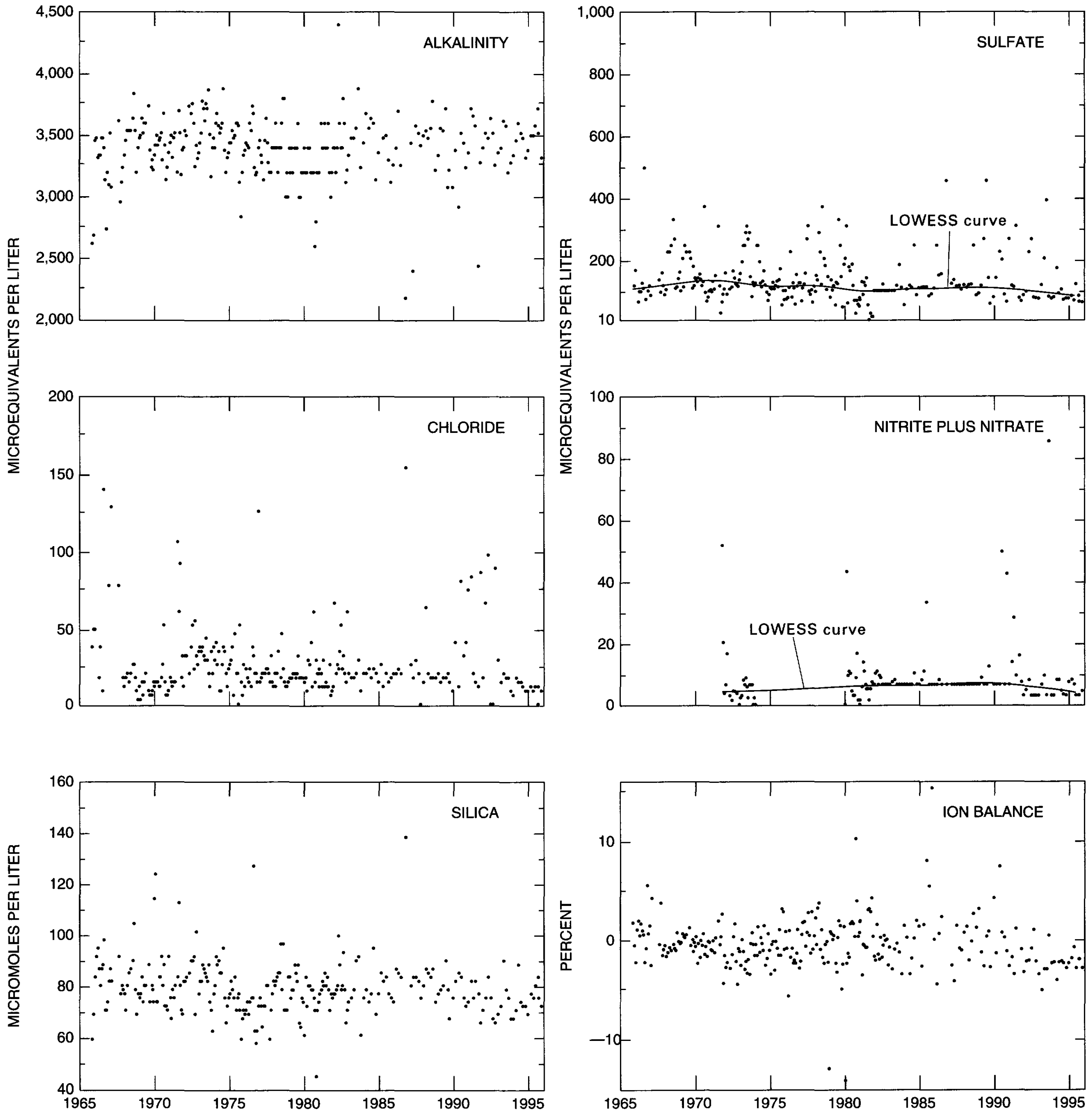


Figure 25. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Cache Creek near Jackson, Wyoming—Continued.

wet precipitation measured at the Gypsum Creek NADP station are presented in table 46. The NADP station is about 83 km southeast of the HBN station. Precipitation chemistry at the NADP station was dilute and slightly acidic with VWM pH of 5.3 over the 1985–95 period of record. The dominant cation in precipitation was calcium, which contributed 35 percent of the total cation concentration; ammonium contributed 24 percent and hydrogen contributed 19 percent. The dominant anions in precipitation were sulfate, which contributed 46 percent, and nitrate, which contributed 40 percent of the total anion concentration.

Stream water in Cache Creek is a fairly buffered, calcium bicarbonate type. The sum of ion concentrations ranged from about 5,900 to about 8,900 μeq/L. Alkalinity ranged from 2,200 to 4,400 μeq/L, and bicarbonate was the primary contributor to alkalinity at this station. Calcium and magnesium accounted for 97 percent of the median cation concentration in stream water; alkalinity accounted for 96 percent of the median anion concentration. These results indicate that carbonaceous rocks, including limestone and dolomite, are the primary contributors to the ion composition of the stream water. Concentrations of dissolved constituents were higher in Cache Creek, which drains sedimentary rocks, compared to other high mountain HBN sites that drain Precambrian igneous and metamorphic rocks. Annual precipitation and runoff data indicate that evapotranspiration can account for about a twofold increase in stream-water concentrations compared to precipitation (Smalley and others, 1996). Although chloride concentrations in stream water were small, precipitation chemistry can account for only about 30 percent. The sedimentary rocks in the basin are of marine origin and may contribute some of the chloride to stream water. Concentrations of ammonium and nitrate were lower in the stream water than in the precipitation, indicating that nitrogen generally is retained by the biomass in the basin.

Correlations among dissolved constituents and discharge were determined for Cache Creek (table 47). The base cations and anions, except potassium, showed inverse relations with discharge. However, these correlations were weak. Positive correlations occurred among dissolved constituents, but most of these correlations also were weak. The strongest correlation was between calcium and sodium (rho value = 0.721). The weak correlations may result from the large number of different geologic units and lithologies exposed in the basin and the different contributions from various drainages during runoff conditions.

Table 46. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major ions measured in water-quality samples from Cache Creek, Wyoming, 1965–95, and volume-weighted mean concentrations in wet precipitation collected at the Gypsum Creek Station, Wyoming, 1985–95

[Parameters in units of microequivalents per liter, except for 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; spec. cond., specific conductance; --, not reported; <, less than]

Parameter	Stream water						Precipitation VWM
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge	0.06	0.13	0.20	0.37	3.1	272	--
Spec. cond., field	220	300	315	334	450	269	--
pH, field	7.2	8.1	8.3	8.5	9.1	269	5.3[a]
Calcium	1,400	2,200	2,300	2,400	3,100	272	9.5
Magnesium	620	1,000	1,100	1,200	1,700	272	2.0
Sodium	52	87	100	120	260	272	3.4
Potassium	5.1	13	15	20	67	270	.52
Ammonium	<.7	1.4	2.1	4.3	12	98	6.4
Alkalinity, laboratory	2,200	3,200	3,400	3,500	4,400	272	--
Sulfate	10.4	94	120	160	500	272	11
Chloride	<2.8	14	22	31	150	271	3.3
Nitrite plus nitrate	<.7	<3.6	7.1	8.6	86	139	9.6[b]
Silica	45	74	79	84	140	272	--

[a] Laboratory pH.

[b] Nitrate only.

Table 47. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ions, Cache Creek, Wyoming, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; SiO_2, silica; --, not applicable]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	0.208	--	--	--	--	--	--	--	--
Ca	–.119	–0.008	--	--	--	--	--	--	--
Mg	–.696	–.125	0.424	--	--	--	--	--	--
Na	–.200	–.010	.721	0.308	--	--	--	--	--
K	.113	.065	.328	.096	0.418	--	--	--	--
Alk	–.369	–.114	.586	.516	.528	0.237	--	--	--
SO_4	–.490	–.182	.303	.525	.369	.260	0.358	--	--
Cl	–.114	–.063	.097	.192	.074	.283	.062	0.269	--
SiO_2	–.435	–.089	.581	.667	.619	.331	.483	.576	0.229

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents for Cache Creek from 1965 through 1995 are presented in table 48. Statistically significant upward trends ($\alpha = 0.01$) occurred for pH and nitrate for unadjusted concentrations. Statistically significant downward trends in magnesium and sulfate were determined in unadjusted concentrations. Flow adjusting for variations due to discharge removed the trends in pH; insufficient data existed to flow-adjust nitrate concentrations. The trend in unadjusted nitrate concentrations may be a function of a change in the minimum reporting level for the laboratory method rather than an environmental change, as seen in the linear step pattern in the time-series plot about 1982. The trends for sulfate and magnesium were retained after flow adjusting, indicating that they probably were not caused by variations in discharge. Smith and Alexander (1983) also detected a downward trend in sulfate concentrations for the period mid- to late 1960's to 1981 at this station. Lins (1987), however, reported an increase in sulfur-dioxide emissions of 24 percent in Wyoming for the period 1975–84. Most Western States, including Montana, New Mexico, Utah, Arizona, Nevada, California, Oregon, and Washington, had decreasing sulfur-dioxide emissions, indicating that regional emissions were lower overall. The magnesium and sulfate trends are consistent with trends in precipitation chemistry for the region that show decreasing sulfate and magnesium for the period 1980–92 (Lynch and others, 1995). However, it is unlikely that stream-water magnesium would be affected by precipitation chemistry owing to much higher magnesium concentration in the stream.

Table 48. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major-ion concentrations, Cache Creek, Wyoming, 1965 through 1995

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

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	–0.02	0.377	--	--
pH	.01	<.001	([b])	--
Calcium	–2	.033	–3	0.018
Magnesium	<.01	.009	–2	<.001
Sodium	<.01	.444	([b])	--
Potassium	<.01	.433	([b])	--
Alkalinity	–1	.276	–2	.071
Sulfate	–2	.008	–1	.006
Chloride	–.1	.192	([b])	--
Nitrite plus nitrate	.2[a]	<.001	--	--
Silica	–.2	.015	–.2	.016

[a] Trend test for highly censored data was used.

[b] Concentration-flow model not significant at $\alpha = 0.10$.

Synoptic Water-Quality Data

Results of a surface-water synoptic sampling conducted July 30 and 31, 1992, in the Cache Creek Basin are presented in table 49, and locations of the sampling sites are shown in figure 24. Discharge at the HBN station (site 12) was 0.13 m^3/s compared to the mean monthly discharge of 0.68 m^3/s for the month of July (Smalley and others, 1996). The water type of all samples that were collected from tributaries and

Table 49. Physical properties and major-ion concentrations in surface-water samples collected at sites in the Cache Creek Basin, July 30–31, 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; SiO_2, silica; concentrations in microequivalents per liter, except silica is in micromoles per liter; --, not measured; <, less than; criteria used in selection of sampling sites: BG = bedrock geology, TRIB = major tributary, LU = land use]

Site number	Site identification number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	SiO_2	Criteria
1	432526110382100	0.007	399	8.3	3,100	1,100	170	18	4,000	54	25	0.4	77	BG
2	432527110382500	.003	430	8.3	3,400	1,200	160	15	4,500	110	25	1.6	90	BG
3	432539110382700	<.001	452	8.2	3,100	1,300	350	18	4,400	83	25	1.6	100	TRIB
4	432552110384200	.07	260	8.4	1,800	800	22	14	2,600	110	17	4.9	57	LU
5	432606110385600	.01	347	8.4	2,600	960	78	17	3,300	77	20	1.0	73	TRIB
6	432615110391300	.03	303	8.5	2,000	1,100	52	15	3,100	67	20	3.0	72	LU
7	432625110390700	--	304	8.4	2,000	1,100	48	15	3,100	60	17	4.2	72	LU
8	432627110402200	.04	315	8.5	2,000	1,200	35	11	3,300	54	20	5.8	73	TRIB
9	432647110395800	--	313	8.3	2,000	1,200	35	11	3,200	56	20	8.0	70	BG
10	432647110400000	--	322	8.3	2,000	1,300	30	10	3,300	63	20	8.2	75	BG
11	432559110385700	<.001	475	8.4	3,300	960	870	24	4,600	29	28	.7	110	BG
12	13018300	.13	311	8.4	2,100	1,100	83	15	3,200	88	20	.6	73	

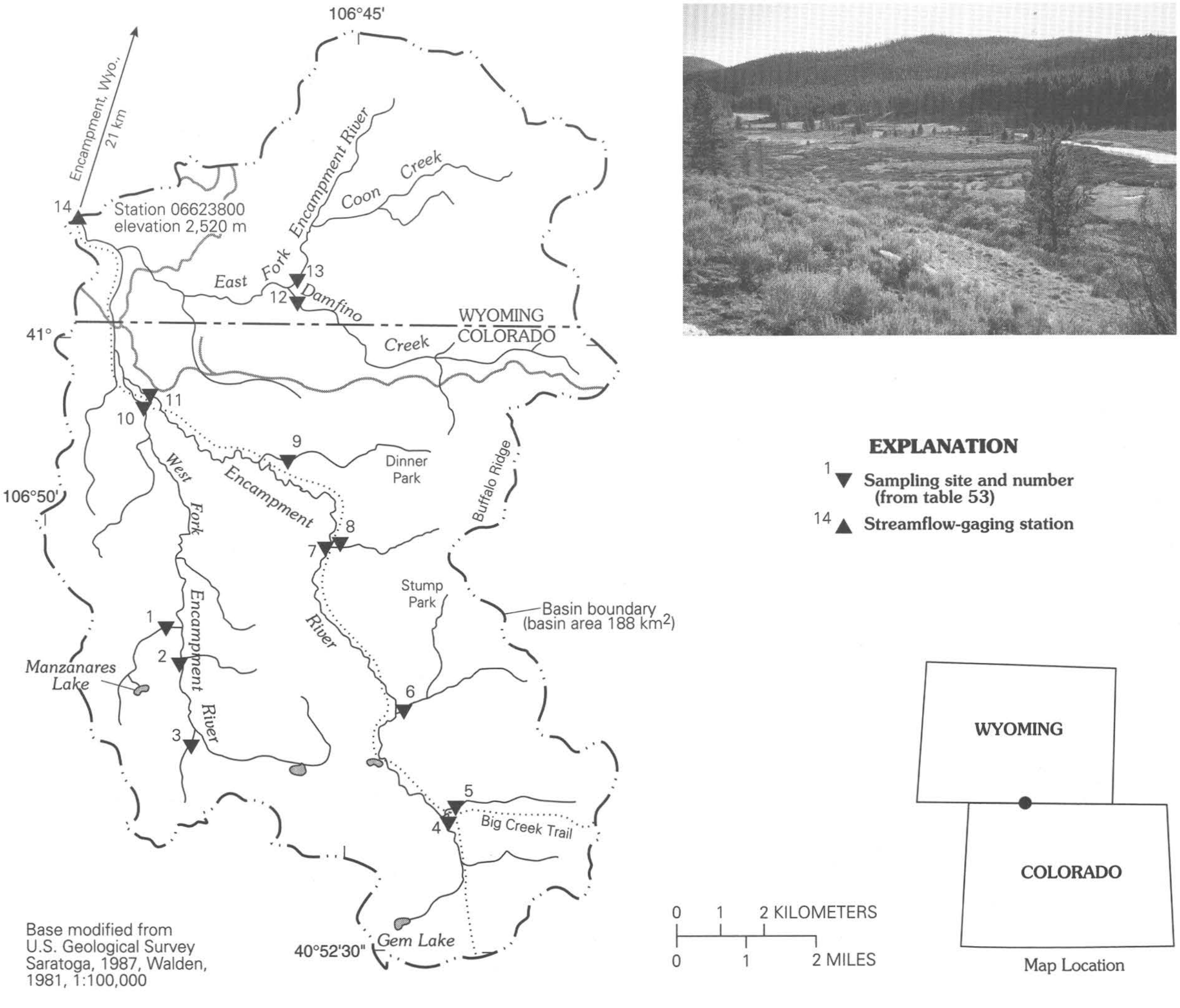
main-stem sites in the Cache Creek Basin was calcium bicarbonate. The sum of ions ranged from about 5,400 (site 4) to about 9,800 µeq/L (site 11); the ion concentration at the HBN station (site 12) was about 6,600 µeq/L. Concentrations of dissolved constituents at tributaries generally were within the range of dissolved constituents for the HBN station for the period 1965–95 (table 46). Quaternary deposits cover a large portion of drainage upstream from site 4 and may explain the higher discharge at this site. Quaternary deposits also make up a large part of the surficial geology upstream from site 11; however, stream discharge was low at site 11 during the synoptic sampling (less than 0.001 m^3/s). The parent materials of the Quaternary deposits account for the differences in the water chemistry at these sites (sites 4 and 11). Rocks in the upper basin of site 4 are Cambrian shale and limestone, whereas rocks in the upper basin of site 11 are Permian rocks containing phosphorite. The phosphorite rocks probably contribute to the high sodium concentration at site 11 (870 µeq/L). Cretaceous shales probably are the source of the elevated sodium concentrations at sites 1, 2, and 3. Sulfate concentrations were the highest in samples from sites 2 and 4. Site 4, which was sampled downstream from an abandoned coal mine, may have been affected by acid-mine drainage, as evidenced by iron staining on the streambed. The waters of these tributaries, however, were alkaline (pH values of 8.3 and 8.4, respectively). No difference was observed in the water quality at sites upstream (site 7) and downstream (site 6) from the mine on Noker Mine Draw. The percent difference of cations and anions in all samples ranged from 0.1 to 5.3 percent, indicating that unmeasured ions did not substantially contribute to the ionic composition of the water, but all were positive. Nitrate concentrations are low in all basins and are characteristic of undeveloped areas (Mueller and others, 1995).

Encampment River above Hog Park Creek near Encampment, Wyoming (06623800)

Site Characteristics and Land Use

The Encampment River HBN Basin is in the Southern Rocky Mountains physiographic province (Fenneman, 1946) in northern Colorado and southern Wyoming (fig. 26). The HBN station is 21 km south of Encampment, Wyo., at a latitude of 41°01'25" and a longitude of 106°49'27". The Encampment River drains 188 km^2 of mountainous terrain in the Park Range of northern Colorado and the Sierra Madres of southern Wyoming. Elevations in the basin range from 2, 520 to more than 3,470 m. The stream gradient of the main stream is about 19 m/km. The ecoregion of the basin is classified as the Southern Rocky Mountain Steppe-Open Woodland-Coniferous Forest-Alpine Meadow Province (Bailey, 1995). Over 90 percent of the area is covered by montane and subalpine forest types, including spruce and subalpine fir, lodgepole pine, and minor amounts of aspen (Jerry Schmidt, U.S. Forest Service, written commun., 1997). Vegetation of the alpine meadows and valleys includes grasses, wildflowers, and small shrubs. A small part of the basin is bare ground or rock, lying above timberline. The Encampment River is tributary to the North Platte River.

The Encampment River is a perennial stream with a snowmelt-dominated hydrograph. Mean monthly discharge ranges from 0.52 m^3/s during base flow in February to 17 m^3/s during snowmelt runoff in June (Smalley and others, 1996). Average annual precipitation at the Encampment weather station is about 37 cm. Precipitation increases in the basin with increasing elevation. At the higher



Base modified from U.S. Geological Survey Saratoga, 1987, Walden, 1981, 1:100,000

Figure 26. Map showing study area in Encampment River Basin and photograph of the East Fork Encampment River.

elevations, precipitation is about 76 cm, which mostly falls as snow during the period October through May (Cobb and Biesecker, 1971). Average annual runoff is about 50 cm. The climate of the basin is characterized by cold winters and mild summers. Mean monthly temperatures ranged from –5.8°C in January to about 17.2°C in July at the Encampment weather station during the period 1948–95 (National Climatic Data Center, 1996). Basin temperatures decrease with increasing elevation.

The geology of the basin is dominated by crystalline rocks. The rocks generally are resistant to erosion and form ledges and cliffs. Most of the area is underlain by intrusive and metamorphic rock types (Snyder, 1980; Houston and Graff, 1995). The Precambrian intrusive rocks are red to gray, massive, and range in composition from biotite granite to quartz monzonite to granodiorite. The metamorphic rocks include felsic gneiss and amphibolite metavolcanics that predominantly are faintly layered pink, gray, or green gneisses and are about 50 percent felsic and 50 percent mafic. Minerals in the metamorphic unit include quartz, feldspars, biotite, muscovite, magnetite, hornblende, garnet, sillimanite, and epidote. A small part of the southwestern part of the basin contains Permian or Triassic calcareous siltstone, shale, mudstone, and conglomerate. Precambrian metavolcanics and metasedimentary rocks are complexly folded and faulted (Snyder and others, 1987). Mineralization also occurred locally. Quaternary glacial till and remnant moraines lie within canyons and at the mouths of canyons.

The Encampment River HBN station is in the Medicine Bow-Routt National Forest. The headwaters lie within the Mount Zirkel Wilderness Area. The area near the HBN station also is designated as wilderness. About 99 percent of the land is federally owned. A small part of the East Fork Encampment Basin in Wyoming is State-owned and private land. Land cover is about 90 percent coniferous forest, 9 percent brush and grasses, and 1 percent roads and parking areas. Access to the HBN station is by light-duty road to within about 2 km of the site, then by hiking trail. Access has been improved by upgrading local gravel roads due to increased recreational use during the 1970's and 1980's. Four-wheel-drive roads and pack trails provide access to the tributary drainages during the summer. Access to the basin in winter is limited to snowmobiles, skis, and snowshoes. Mechanized vehicles are not allowed within the wilderness area.

Activities in the Encampment River HBN Basin that may affect water quality include logging operations, primarily at lower elevations, cattle grazing, and recreational use (Jerry Schmidt, U.S. Forest Service, written commun., 1997). Grazing was intense around the turn of the century and continued until the mid-1900's when animal numbers were reduced. Grazing by sheep continued until 1968, when the allotment was temporarily rested. In 1978, the allotment was reopened to cattle grazing. Timber harvest has occurred in many of the drainages outside the wilderness area from the early 1900's to present (2000). Timber harvest was minimal in the West Fork and East Fork Encampment River tributaries during the period 1960 to 1990. Timber harvest was allowed in these basins during 1990–96; a total of about 620 km^2 was harvested during this period. Best-management practices, including limiting clearcut size and tractor-logging harvesting, presently are used to minimize impact to forest resources. In the early 1900's, railroad ties were floated or "driven" down tributary creeks of the Encampment River (Young and others, 1994). The tie drives and stream clearing associated with the driving reduced channel complexity and decreased the amount of large woody debris in streams. Recreational use is mainly fishing, hiking, horseback riding, backpacking, and hunting. Some primitive camping takes place in the basin. One closed mine is in the upper East Fork drainage, but the site is dry with no visible drainage. Several mines that are in the immediate vicinity, but outside the drainage area, have produced minor amounts of ore (Snyder and others, 1987).

Historical Water-Quality Data and Time-Series Trends

The data set analyzed for the Encampment River HBN station includes 204 water-quality samples that were collected from October 1964 to September 1995. Sampling frequency is described on the basis of water year, which begins on October 1 and ends on September 30. Generally, about 8–10 samples were collected each year from 1968 through 1982. Sampling frequency was quarterly for most of the remaining sampling period. Samples were analyzed at USGS district water-quality laboratories until the early

1970's. After 1973, with the creation of the USGS Central Laboratory System, all samples were analyzed at the water-quality laboratory (now called NWQL) in Arvada, Colo. The period of record for discharge is from water year 1965 to current water year (2000).

Data quality was checked using ion balances and time-series plots. Calculated ion balances for samples with complete major-ion analyses are shown in figure 27. More than 90 percent of the samples had ion balances within the ±10 percent range, indicating that the major-ion analytical results generally were of good quality and that unmeasured constituents, such as organic anions, nutrients, and trace metals, generally do not contribute substantially to the ion composition of the stream water. Time-series plots of ion concentrations were inspected for data quality (fig. 27). Magnesium and sodium have slightly more scatter in the early part of the record and a decrease in scatter after 1983. This decrease coincides with a change in the analytical method for these analytes from AA spectroscopy to ICP spectroscopy (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 82.18, 1982). The decrease in scatter of sulfate concentrations after 1982 corresponds with the change from a methylthymol blue procedure to a turbidimetric titration method (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 83.07, 1983). The further decrease in the scatter of sulfate concentrations after 1990 corresponds with the change from turbidimetric titration to an ion-exchange chromatography analytical method (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 90.04, 1989; U.S. Geological Survey Office of Water Quality Technical Memorandum No. 90.13, 1990). Changes also were made in meters and electrodes used for field pH determinations during the study period. When changes in methods or instrumentation result in improved precision or elimination of measurement bias, time-series data can exhibit less scatter or a directional shift, respectively. The time-series data, therefore, may reflect the method or instrument change rather than an environmental change.

The median and range of major-ion concentrations in the stream water collected at the Encampment River HBN station and VWM concentrations in wet precipitation measured at the Nash Fork NADP station are presented in table 50. The NADP station is about 80 km northeast of the HBN station. Precipitation chemistry at the NADP station was dilute and slightly acidic with a VWM pH of 5.2 during the period of record, 1987–92. The dominant cation in precipitation was calcium, which contributed 33 percent of the total cation concentration; ammonium contributed 25 percent and hydrogen contributed 22 percent. The dominant anions in precipitation were sulfate, which contributed 47 percent, and nitrate, which contributed 44 percent of the total anion concentration. A high proportion of nitrate in precipitation in the Rocky Mountains has been attributed to exhaust from cars and other vehicles in urban areas and agricultural activity in the Great Plains States (National Atmospheric Deposition Program/National Trends Network, 1997).

Stream water in the Encampment River is a mildly alkaline, calcium bicarbonate type. The sum of ion concentrations ranged from about 510 to about 1,900 μeq/L. Alkalinity ranged from 140 to 720 μeq/L, and bicarbonate was the primary contributor to alkalinity at this station. The major cations in the stream water were calcium (62 percent), magnesium (19 percent), and sodium (16 percent). Bicarbonate, the major anion, contributed 86 percent of the median anion concentration. Dissolved solids generally are low at this site because granitic and gneissic bedrock is resistant to weathering. Annual precipitation and runoff data indicate that evapotranspiration can account for less than a twofold increase in stream-water concentrations compared to precipitation. About 38 percent of the median sulfate concentration can be attributed to precipitation after accounting for evapotranspiration. Similar to sulfate, only 39 percent of the median chloride concentration is attributable to precipitation. Igneous minerals, including hornblende, can contribute small amounts of chloride to stream water (Hem, 1992). Silica is a substantial component of the dissolved solids and is contributed by the feldspar- and quartz-rich rocks. Median concentrations of ammonium and nitrate were lower in the stream water than in the precipitation, indicating that nitrogen generally is retained by the biomass in the basin.

Correlations among dissolved constituents and discharge were determined for the Encampment River (table 51). The base cations and anions, except dissolved chloride, showed inverse relations with discharge. These results are consistent with a hydrologic system where base flow is diluted during periods of increased discharge, particularly annual

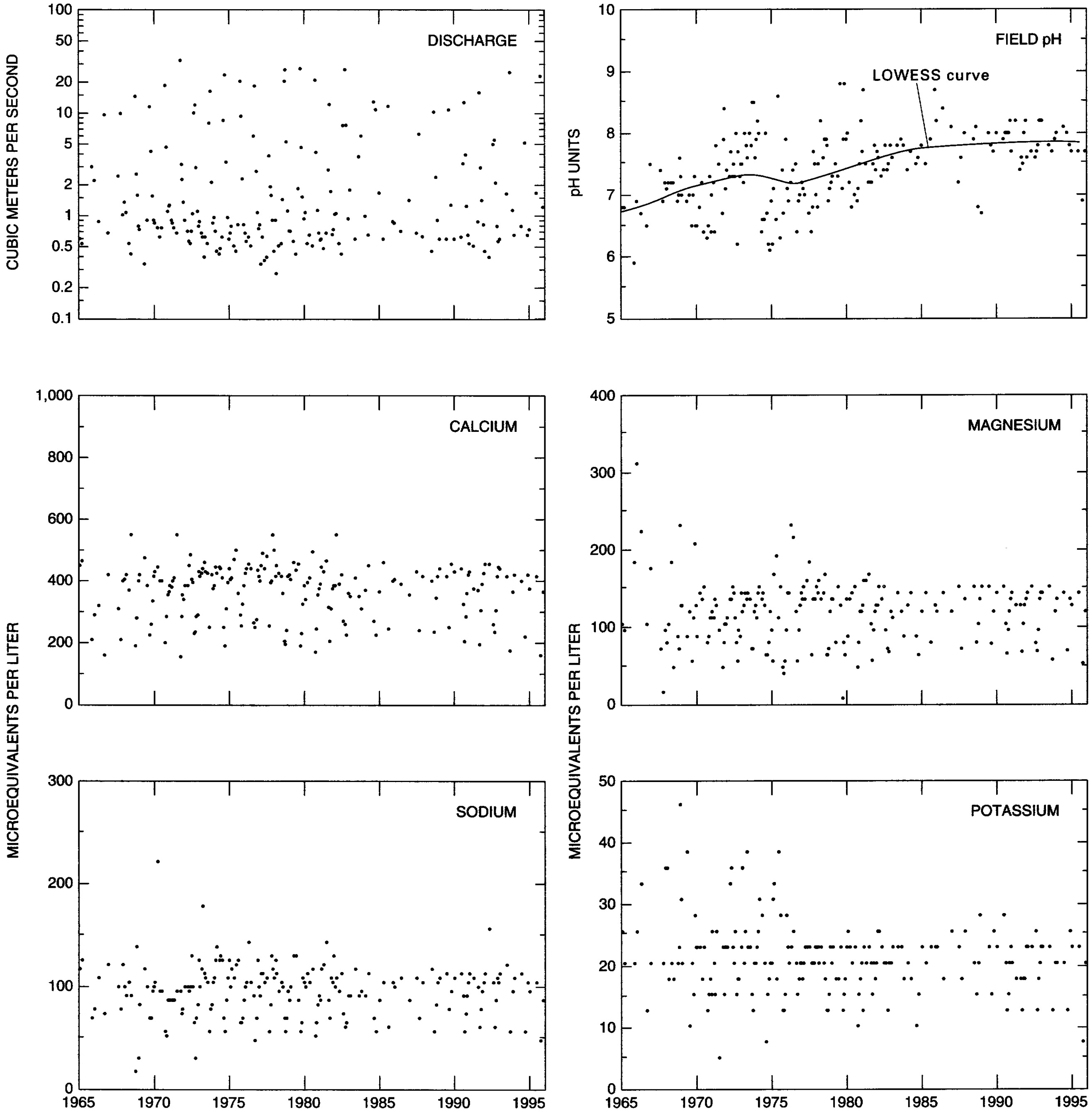


Figure 27. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Encampment River above Hog Park Creek near Encampment, Wyoming.

snowmelt runoff. Ion concentrations in ground water tend to be greater than in surficial sources because the contact time with rocks and minerals is longer. The consistency and strength of the relations of calcium (rho value = –0.849), sodium (–0.830), magnesium (–0.869), and silica (–0.864) with discharge indicate that the high concentrations of these constituents, which occur at low flow, reflect the ground-water chemistry. Strong correlations existed among the base cations calcium, magnesium, and sodium (rho value = 0.855 or greater). The strongest correlation was between calcium and magnesium

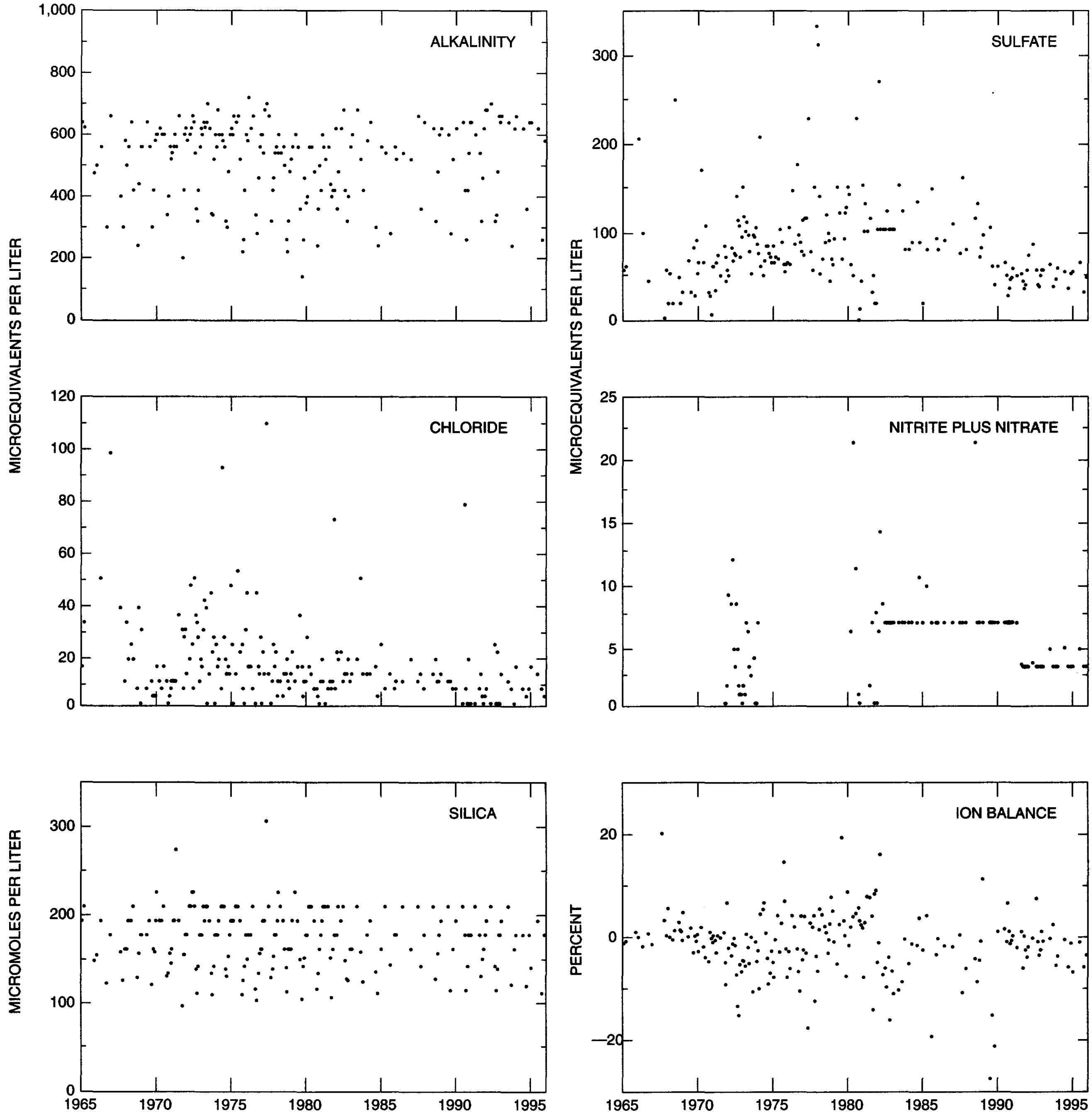


Figure 27. Temporal variation of discharge, field pH, major-ion concentrations, and ion balances, Encampment River above Hog Park Creek near Encampment, Wyoming—Continued.

(rho value = 0.935). Strong correlations also existed between the base cations and dissolved silica: calcium (rho value = 0.850); magnesium (rho value = 0.920); and sodium (rho value = 0.862). These relations reflect the weathering of felsic and mafic silicate minerals in the Precambrian rocks.

Results of the seasonal Kendall test for trends in discharge and major dissolved constituents for the Encampment River from 1965 through 1995 are presented in table 52. A statistically significant upward trend ($\alpha = 0.01$) for unadjusted pH was determined. The flow-adjusted test, however, did not confirm

Table 50. Minimum, first quartile, median, third quartile, and maximum values of physical properties and major-ions measured in water-quality samples from the Encampment River, 1965–95, and volume-weighted mean concentrations in wet precipitation collected at the Nash Fork Station, Wyoming, 1987–92

[Parameters in units of microequivalents per liter, except for 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; spec. cond., specific conductance; --, not reported; <, less than]

Parameter	Stream water						Precipitation VWM
	Minimum	First quartile	Median	Third quartile	Maximum	n	
Discharge	0.27	0.62	0.91	2.9	33	204	--
Spec. cond., field	17	50	62	69	140	203	--
pH, field	5.9	7.0	7.5	7.8	8.8	201	5.2[a]
Calcium	160	300	390	420	550	203	9.7
Magnesium	8.2	88	120	140	310	204	2.0
Sodium	17	83	100	110	220	203	3.5
Potassium	5.1	18	20	23	46	201	.48
Ammonium	<.7	<1.1	1.4	3.6	13	75	7.2
Alkalinity, laboratory	140	420	560	620	720	204	--
Sulfate	2.1	54	75	100	330	203	14
Chloride	<2.8	8.5	14	21	110	204	2.7
Nitrite plus nitrate	<.7	<3.6	6.4	7.1	21	107	13[b]
Silica	97	150	180	190	310	204	--

[a] Laboratory pH.
[b] Nitrate only.

Table 51. Spearman rank correlation coefficients (rho values) showing the relation among discharge, pH, and major ions, Encampment River, 1980 through 1995

[Q, discharge; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Alk, alkalinity; SO_4, sulfate; Cl, chloride; SiO_2, silica; --, not applicable]

	Q	pH	Ca	Mg	Na	K	Alk	SO_4	Cl
pH	–0.132	--	--	--	--	--	--	--	--
Ca	–.849	0.137	--	--	--	--	--	--	--
Mg	–.869	.110	0.935	--	--	--	--	--	--
Na	–.830	.125	.855	0.894	--	--	--	--	--
K	–.483	.209	.633	.571	0.576	--	--	--	--
Alk	–.777	.215	.782	.796	.738	0.512	--	--	--
SO_4	–.264	.044	.270	.328	.290	.359	0.099	--	--
Cl	.137	–.059	–.163	–.117	–.088	.168	–.177	0.353	--
SiO_2	–.864	.103	.850	.920	.862	.534	.699	.348	0.001

this trend. The large number of censored nitrate values resulted in insufficient data to calculate a trend for nitrate concentrations. The pattern in the scatter of nitrate concentrations in the time-series plot is a function of a change in the minimum reporting level for the laboratory method about 1991, rather than an environmental change. An upward trend in sulfate and a downward trend in alkalinity determined by Smith and Alexander (1983) at this station were no longer detected in the data. Precipitation-chemistry data have shown a decrease in sulfate concentrations in many regional NADP stations for the period 1980–92 (Lynch and others, 1995). No trend in stream-water sulfate was detected at this station, but concentrations were consistently low after about 1990.

Table 52. Results of the seasonal Kendall test for trends in discharge and unadjusted and flow-adjusted pH and major-ion concentrations, Encampment River, 1965 through 1995

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

Parameter	Unadjusted		Flow adjusted	
	Trend	p-value	Trend	p-value
Discharge	−0.12	0.411	--	--
pH	.03	<.001	([a])	--
Calcium	.6	.199	0.4	0.200
Magnesium	<.01	.651	−.02	.872
Sodium	<.01	.723	.06	.622
Potassium	<.01	.299	−.03	.255
Alkalinity	.9	.194	.7	.201
Sulfate	.09	.761	−.01	.970
Chloride	−.2	.040	([a])	--
Nitrite plus nitrate	([b])	--	--	--
Silica	<.01	.749	−.2	.221

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

[b] Insufficient data to calculate trend.

Synoptic Water-Quality Data

Results of a surface-water synoptic sampling conducted September 10–12, 1990, in the Encampment River Basin are presented in table 53, and locations of the sampling sites are shown in figure 26. Discharge at the HBN station (site 14) was 0.54 m^3/s compared to the mean monthly discharge of 0.90 m^3/s for the month of September (Smalley and others, 1996). The water type of all tributary and main-stem sites sampled in the basin was calcium bicarbonate. The sum of ion concentrations in tributaries ranged from about 620 (site 4) to about 5,000 μeq/L (site 3). The sum of ions concentration at the HBN station (site 14) was about 1,300 μeq/L; concentrations of major cations and anions were near the median concentrations for the period 1965–95 (table 50). Concentrations of ions in tributary water samples were within the range of ion concentrations for the HBN station (table 49), except for concentrations of certain constituents at sites 2 and 3. Concentrations of calcium, magnesium, bicarbonate, and

Table 53. Physical properties and major-ion concentrations in surface-water samples collected at sites in the Encampment River Basin, September 10–12, 1990

[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; SiO$_2$, silica; concentrations in microequivalents per liter, except silica is in micromoles per liter; --, not measured; <, less than; criteria used in selection of sampling sites: BG = bedrock geology, TRIB = major tributary, LU = land use]

Site number	Site identification number	Q	SC	pH	Ca	Mg	Na	K	Alk	SO$_4$	Cl	NO$_3$	SiO$_2$	Criteria
1	405627106475100	--	51	7.8	280	140	100	19	500	27	4.8	<0.7	200	BG
2	405603106474200	--	90	8.0	650	190	83	24	780	170	5.1	2.1	120	TRIB
3	405508106472800	--	198	8.3	1,800	510	140	22	1,800	770	5.6	<.7	120	BG
4	405409106431600	--	32	7.5	180	55	61	18	280	25	4.8	<.7	110	BG
5	405414106432000	--	31	7.6	170	55	74	18	280	31	4.2	<.7	150	BG
6	405528106440900	--	39	7.8	240	72	83	12	390	35	5.6	<.7	160	BG
7	405731106452000	--	63	7.9	440	110	78	28	660	44	6.5	1.4	140	TRIB
8	405731106451400	--	51	7.9	360	79	83	16	500	35	5.1	<.7	180	BG
9	405831106460100	--	50	7.9	300	130	110	16	490	35	5.9	<.7	220	BG
10	405916106482800	--	71	8.0	450	180	100	25	650	81	8.7	<.7	170	TRIB
11	405919106481500	--	67	8.0	450	140	87	26	640	48	7.3	<.7	160	LU
12	410039106460101	--	55	8.0	350	130	120	17	540	38	9.6	<.7	200	TRIB
13	410041106460101	--	38	7.8	220	88	96	14	360	38	7.0	<.7	180	TRIB
14	06623800	0.54	60	7.9	400	140	100	23	600	58	9.0	<.7	180	

sulfate in the sample collected at the unnamed south tributary to the West Fork Encampment River (site 3) were much higher (3 to 10 times) than the median concentrations of ions in samples from the HBN station. The geology in the upper basin upstream from site 3 includes an area draining sedimentary rocks containing siltstone, shales, mudstone, and conglomerate. Water in contact with fine-grained sedimentary deposits such as these tends to have higher dissolved solids than water in contact with the more resistant Precambrian igneous and metamorphic rocks that are predominant in the rest of the basin. Contributions from this unnamed south tributary (site 3) contribute to the elevated concentrations of constituents in the upper West Fork Encampment River (site 2), particularly calcium, which exceeds the maximum concentration at the HBN station. Low dissolved solids were reported for sites 4 and 5. Pleistocene till deposits dominate the surficial geology around those sites. Rocks in the basin upstream from sites 4 and 5 are Precambrian quartz monzonite. The percent difference of cations and anions in all synoptic samples ranged from 0.2 to 3.8 percent, indicating that unmeasured ions did not substantially contribute to the ionic content of the water. Nitrate concentrations were low in all basins and are characteristic of undeveloped areas (Mueller and others, 1995).

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APPENDIXES

APPENDIX A. SAMPLING-SITE INFORMATION

Table A–1. Sampling-Site Information

Site	Site-identification number	Site name
Halfmoon Creek near Malta, Colorado (07083000)		
1	390806106302200	Halfmoon Creek above Champion Mill
2	390816106295700	Halfmoon Creek below Champion Mill
3	390830106292400	Halfmoon Creek near Prospect Mine
4	391050106294300	North Halfmoon Lake number 3
5	391039106293400	North Halfmoon Lake number 4
6	391010106292200	North Halfmoon Creek above north branch of creek
7	391011106291900	north branch of North Halfmoon Creek below Halfmoon Lakes
8	390955106283200	third unnamed tributary to north Halfmoon Creek at mouth
9	390945106282800	North Halfmoon Creek 0.42 mile above Halfmoon Creek
10	390724106275100	South Halfmoon Creek near Iron Mike Mine
11	390901106271200	South Halfmoon Creek above Halfmoon Creek
12	390901106263600	Halfmoon Creek above Bog
13	390905106250700	Halfmoon Creek above Elbert Creek
14	390906106242000	Emerald Lake
15	07083000	Halfmoon Creek near Malta, Colorado
Vallecito Creek near Bayfield, Colorado (09352900)		
1	37410510731400	Vallecito Creek above Nebo Creek
2	374103107313400	Nebo Creek
2a	374038107413400	Stormy Gulch
3	373915107311200	Rock Creek
4	373835107320800	Leviathan Creek
5	373800107322500	Sunlight Creek
6	373650107321400	Roell Creek
7	373521107320200	Johnson Creek
8	373423107311700	Irving Creek
9	373219107312500	Second Creek
10	09352900	Vallecito Creek at near Bayfield, Colorado
Kings Creek near Manhattan, Kansas (06879650)		
1	390515096350300	Watershed N4D
2	390513096343700	Watershed N1B
3	390519096343500	Watershed N20B
4	390529096351700	Watershed N2B
5	390604096352900	South Branch Kings Creek
6	390606096352900	North Branch Kings Creek
7	06879650	Kings Creek near Manhattan, Kansas
Rock Creek below Horse Creek near International Boundary, Montana (06169500)		
1	485949106463900	Rock Creek below International Boundary
2	485858106473500	Rock Creek above Line Coulee
3	485856106492600	Horse Creek above confluence with Rock Creek
4	06169500	Rock Creek below Horse Creek near International Boundary, Montana
Swiftcurrent Creek at Many Glacier, Montana (05014500)		
1	484649113443200	Swiftcurrent Creek above Bullhead Lake
2	484717113440800	unnamed creek below Windmaker Lake
3	484754113411700	Swiftcurrent Creek above Fishercap Lake
4	484903113443500	Iceberg Creek

Table A–1. Sampling-Site Information—Continued

Site	Site-identification number	Site name
Swiftcurrent Creek at Many Glacier, Montana (05014500)—Continued		
5	484920113424000	Ptarmigan Creek above falls
6	484753113404500	Wilbur Creek above Fishercap Lake
7	484739113395800	Swiftcurrent Creek above Swiftcurrent Lake
8	484604113414500	Cataract Creek
9	484528113432600	upper Grinnell Creek
10	484614113415500	Grinnell Creek below Grinnell Lake
11	05014500	Swiftcurrent Creek at Many Glacier, Montana
Dismal River near Thedford, Nebraska (06775900)		
1	414933101244300	North Fork Dismal River near Vinton Ranch
2	414532101165800	South Fork Dismal River below Jefford Lake
3	415112101021600	North Fork Dismal River
4	415104101021600	South Fork Dismal River
5	415042100492700	Dismal River three miles above gage
6	06775900	Dismal River near Thedford, Nebraska
Mogollon Creek near Cliff, New Mexico (09430600)		
1	331304108320700	Mogollon Creek above Trail Canyon
2	331305108320800	unnamed tributary in Trail Canyon
3	331240108332500	South Fork Mogollon Creek
4	331259108340000	unnamed tributary in Judy Canyon
5	331203108361200	unnamed tributary in Lookout Canyon
6	331153108363100	unnamed tributary below Lookout Canyon
7	331329108381100	West Fork Mogollon Creek
8	331039108395200	Rain Creek
9	09430600	Mogollon Creek near Cliff, New Mexico
Rio Mora near Tererro, New Mexico (08377900)		
1	355241105333100	Rio Mora above pack trail
2	355216105335100	Rito del Oso
3	355329105343700	upper Rio Valdez
4	355215105323700	Rio Valdez
5	355120105350900	Rito Los Esteros
6	355127105352700	tributary below Hamilton Mesa
7	354725105383200	Rio Mora above Bear Creek
8	354724105383200	Bear Creek
9	08377900	Rio Mora near Tererro, New Mexico
Bear Den Creek near Mandaree, North Dakota (06332515)		
1	474235102485100	unnamed tributary south of middle Bear Den Creek
2	06332515	Bear Den Creek near Mandaree, North Dakota
Beaver Creek near Finley, North Dakota (05064900)		
1	474737097552700	Beaver Creek at Logan Church
2	474021097492800	Beaver Creek at Steele and Grand Forks County Boundary
3	473546097485100	unnamed tributary to Beaver Creek
4	473517097472900	Beaver Creek below unnamed tributary
5	05064900	Beaver Creek near Finley, North Dakota
Castle Creek above Deerfield Reservoir, South Dakota (06409000)		
1	440650103570000	Oatman Spring
2	440414103583000	spring near Badget Ranch
3	440521103571600	spring below Manganese Draw near Castle Creek headwaters
4	440400103521100	Lyons Spring
5	440156103504300	Castle Creek above Silver Creek

Table A–1. Sampling-Site Information—Continued

Site	Site-identification number	Site name
Castle Creek above Deerfield Reservoir, South Dakota (06409000)—Continued		
6	440148103504100	Silver Creek
7	440055103495900	Castle Creek above South Fork
8	435930103521900	South Fork Castle Creek above Pole Creek
9	435847103513900	Pole Creek
10	435832103504400	Ditch Creek
11	435856103500000	Heely Creek
12	440039103495100	South Fork Castle Creek
13	06409000	Castle Creek at gage
Little Vermillion River near Salem, South Dakota (06478540)		
1	440027097265200	upper west branch Little Vermillion River
2	435609097260800	west branch Little Vermillion River
3	435609097253600	upper east branch Little Vermillion River
4	435516097254000	lower east branch Little Vermillion River
5	435238097254800	Little Vermillion River at highway near Canova
6	06478540	Little Vermillion River near Salem, South Dakota
Cache Creek near Jackson, Wyoming (13018300)		
1	432526110382100	upper Cache Creek
2	432527110382500	unnamed tributary to upper Cache Creek
3	432539110382700	unnamed tributary to upper Cache Creek near pack trail
4	432552110384200	unnamed tributary to Cache Creek below coal mine
5	432606110385600	unnamed tributary to Cache Creek above Noker Mine Draw
6	432615110391300	Noker Mine Draw tributary near Cache Creek
7	432625110390700	Noker Mine Draw tributary above mine
8	432627110402200	unnamed tributary below Cache Creek Thrust Fault near Cache Creek
9	432647110395800	east branch of Noker Mine Draw tributary above mine
10	432647110400000	north branch of Noker Mine Draw tributary above mine
11	432559110385700	unnamed tributary one mile upstream of Cache Creek gage
12	13018300	Cache Creek near Jackson, Wyoming
Encampment River above Hog Park Creek near Encampment, Wyoming (06623800)		
1	405627106475100	unnamed tributary below Manzanares Lake
2	405603106474200	West Fork Encampment River four miles upstream from gage
3	405508106472800	unnamed south tributary to West Fork Encampment River
4	405409106431600	Encampment River below Gem Lake
5	405414106432000	unnamed tributary crossing Big Creek Trail
6	405528106440900	unnamed tributary below Stump Park
7	405731106452000	Encampment River above unnamed tributary below Buffalo Ridge
8	405731106451400	unnamed tributary below Buffalo Ridge
9	405831106460100	unnamed tributary below Dinner Park
10	405916106482800	West Fork Encampment River
11	405919106481500	Encampment River above West Fork Encampment River
12	410039106460101	Damfino Creek
13	410041106460101	East Fork Encampment River above Damfino Creek
14	06623800	Encampment River above Hog Park Creek near Encampment, Wyoming

APPENDIX B. SITE MAPS

Halfmoon Creek (07083000)

a. U.S. Geological Survey topographic maps:

Lake County, Colorado (1:50,000), 1975
Mount Elbert, Colorado (1:24,000), 1979
Mount Massive, Colorado (1:24,000), 1967, streamflow-gaging station
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c. Soil surveys:

U.S. Department of Agriculture, 1975, Soil survey of Chaffee-Lake area, Colorado: U.S. Department of Agriculture, Soil Conservation Service, 78 p.

d. Other maps:

Leadville, Colorado, 30' x 60' quadrangle, Bureau of Land Management, 1983, scale 1:100,000.

Vallecito Creek near Bayfield, Colorado (09352900)

a. U.S. Geological Survey Topographic Maps

Columbine Pass, Colorado (1:24,000), 1975
Emerald Lake, Colorado (1:24,000), 1973
La Plata County, Colorado (1:50,000), 1975
Rio Grande Pyramid, Colorado (1:24,000), 1975
Storm King Peak, Colorado (1:24,000), 1975
Vallecito Reservoir, Colorado (1:24,000), 1971, streamflow-gaging station

b. Geologic maps:

Cross, W., and Larsen, E.S., 1935, A brief review of the geology of the San Juan Region of southwestern Colorado: U.S. Geological Survey Bulletin 843, 138 p.

Gonzales, D.A., 1988, A geologic investigation of the early Proterozoic Irving Formation, southeastern Needle Mountains, Colorado: U.S. Geological Survey Open-File Report 88–660, 119 p.

Larsen, E.S., Jr., and Cross, W., 1956, Geology and petrology of the San Juan region, southwestern Colorado: U.S. Geological Survey Professional Paper 258, 303 p.

c. Soil Surveys

No soil survey available.

d. Other maps:

U.S. Geological Survey orthophotoquad, 7.5-minute series:

Columbine Pass, Colorado, 1975
Emerald Lake, Colorado, 1978
Rio Grande Pyramid, Colorado, 1976
Storm King Peak, Colorado, 1975
Vallecito Reservoir, Colorado, 1977

Kings Creek near Manhattan, Kansas (06879650)

a. U.S. Geological Survey topographic maps:

Manhattan, Kansas (1:100,000), 1990
Swede Creek, Kansas (1:24,000), 1982, streamflow-gaging station

b. Geologic maps:

Jewett, J.M., 1941, The geology of Riley and Geary Counties, Kansas: State Geological Survey of Kansas Bulletin 39.

c. Soil surveys:

U.S. Department of Agriculture, 1975, Soil survey of Riley County and part of Geary County, Kansas: U.S. Department of Agriculture, Soil Conservation Service, 71 p.

Rock Creek below Horse Creek near International Boundary, Montana (06169500)

a. U.S. Geological Survey topographic maps:

Coal Mine Creek East, Montana-Saskatchewan (1:24,000), 1976
Coal Mine Creek West, Montana-Saskatchewan (1:24,000), 1984
Lighthouse Hill, Montana-Saskatchewan (1:24,000), 1984, streamflow-gaging station

b. Geologic maps:

Colton, R.B., Whitaker, S.T., and Ehler, W.C., 1989, Geologic map of the Opheim 1° × 30' quadrangle, Valley and Daniels Counties, Montana: U.S. Geological Survey Open-File Report 89–319.

Whitaker, S.H., and Pearson, D.E., 1972, Geological map of Saskatchewan: Province of Saskatchewan Department of Mineral Resources and Saskatchewan Research Council, 1 pl.

c. Soil surveys:

U.S. Department of Agriculture, 1984, Soil survey of Valley County, Montana: U.S. Department of Agriculture, Soil Conservation Service, 102 p.

d. Other maps:

Opheim, Montana, 30' x 60' quadrangle, Bureau of Land Management, 1984, scale 1:100,000.

Horse Creek topographic map, Surveys and Mapping Branch, Department of Energy, Mines, and Resources, 1974, scale 1:50,000.

McCord topographic map, Surveys and Mapping Branch, Department of Energy, Mines, and Resources, 1975, scale 1:50,000.

Swiftcurrent Creek at Many Glacier Creek, Montana (05014500)

a. U.S. Geological Survey topographic maps:

Ahern Pass, Montana (1:24,000), 1968
Logan Pass, Montana (1:24,000), 1968
Many Glacier, Montana (1:24,000), 1968, streamflow-gaging station
Saint Mary, Montana-Alberta (1:100,000), 1981

b. Geologic maps:

Alpha, T.R., and Nelson, W.H., 1990, Geologic sketches of Many Glacier, Hidden Lake Pass, Comeau Pass, and Bears Hump Viewpoint, Waterton-Glacier International Peace Park, Alberta, Canada, and Montana, United States: U.S. Geological Survey Miscellaneous Investigation Series Map I–1508–E.

Carrara, P.E., 1990, Surficial geologic map of Glacier National Park, Montana: U.S. Geological Survey Miscellaneous Investigation Series Map I–1508–D.

Earhart, R.L., Raup, O.B., Whipple, J.W., Ison, A.L., and Davis, G.A., 1990, Geologic maps, cross section, and photographs of the central part of Glacier National Park, Montana: U.S. Geological Survey Miscellaneous Investigation Series Map I–1508–B.

James, H.L., 1982, Glacial features of the Upper Swiftcurrent Valley, Glacier National Park, Montana: Montana Bureau of Mines and Geology Geologic Map 27.

Ross, C.P., 1959, Geology of Glacier National Park and the Flathead region, northwestern Montana: U.S. Geological Survey Professional Paper 296.

c. Soil surveys:

No soil survey available.

Dismal River near Thedford, Nebraska (06775900)

a. U.S. Geological Survey topographic maps:

Dismal River, Nebraska (1:100,000), 1985
Jefford Lake, Nebraska (1:24,000), 1984
Rosebud Lake, Nebraska (1:24,000), 1985, streamflow-gaging station
Shimmins Lake, Nebraska (1:24,000), 1984
Shimmins Lake SE, Nebraska (1:24,000), 1984
Thedford SE, Nebraska (1:24,000), 1985
Thedford SW, Nebraska (1:24,000), 1985

b. Geologic maps:

Ahlbrandt, T.S., Fryberger, S.G., Hanley, J.H., and Bradbury, J.P., 1980, Geologic and paleoecologic studies of the Nebraska Sand Hills: U.S. Geological Survey Professional Paper 1120–A, B, C.

c. Soil surveys:

U.S. Department of Agriculture, Soil Survey of Thomas County, Soil Conservation Service (out of date).

Mogollon Creek near Cliff, New Mexico (09430600)

a. U.S. Geological Survey topographic maps:

Diablo Range, New Mexico (1:24,000), 1965
Grouse Mountain, New Mexico (1:24,000), 1965
Mogollon Baldy Peak, New Mexico (1:24,000), 1965
Mogollon Mountains, New Mexico (1:100,000), 1985
Rice Ranch, New Mexico (1:24,000), 1965, streamflow-gaging station
Shelley Peak, New Mexico (1:24,000), 1965

b. Geologic maps:

Ratte´, J.C., and Gaskill, D.L, 1975, Reconnaissance geologic map of the Gila Wilderness Study Area, Southwest New Mexico: U.S. Geological Survey Miscellaneous Investigation Series Map I–886, 2 pl., scale 1:62,500.

Ratte´, J.C., Gaskill, D.L., Eaton, G.P., Peterson, D.L., Stotelmeyer, R.B., and Meeves, H.C., 1979, Mineral resources of the Gila Primitive Area and Gila Wilderness, New Mexico: U.S. Geological Survey Bulletin 1451, 229 p.

c. Soil surveys:

No soil survey available.

d. Other maps:

Mogollon Mountains, New Mexico, 30' x 60' quadrangle, Bureau of Land Management, 1985, scale 1:100,000.

Gila National Forest Map, 1996, Southwestern Region, U.S. Department of Agriculture.

Rio Mora near Tererro, New Mexico (08377900)

a. U.S. Geological Survey topographic maps:

- Cowles, New Mexico (1:24,000), 1961, streamflow-gaging station
- Elk Mountain, New Mexico (1:24,000), 1963
- Gascon, New Mexico (1:24,000), 1965
- Pecos Falls, New Mexico (1:24,000), 1963

b. Geologic maps:

Moench, R.H., Grambling, J.A., and Robertson, J.M., 1988, Geologic map of the Pecos Wilderness, Santa Fe, San Miguel, Mora, Rio Arriba, and Taos Counties, New Mexico: U.S. Geological Survey Miscellaneous Field Studies Map MF–1921–B, 2 pl., scale 1:48,000.

U.S. Geological Survey, U.S. Bureau of Mines, New Mexico Bureau of Mines and Mineral Resources, 1980, Mineral resources of the Pecos Wilderness and adjacent areas, Santa Fe, San Miguel, Mora, Rio Arriba, and Taos Counties, New Mexico: U.S. Geological Survey Open-File Report 80–382, 103 p.

c. Soil surveys:

No soil survey available.

d. Other maps:

Santa Fe National Forest map, 1975, U.S. Department of Agriculture, scale 1 inch = 2 miles.

Santa Fe, New Mexico, 30' x 60' quadrangle, Bureau of Land Management, 1983, scale 1:100,000.

Bear Den Creek near Mandaree, North Dakota (06332515)

a. U.S. Geological Survey topographic maps:

- Blue Buttes, North Dakota (1:24,000), 1965, streamflow-gaging station
- Croff, North Dakota (1:24,000), 1959
- Figure 4 Ranch, North Dakota (1:24,000), 1970
- Johnsons Corner, North Dakota (1:24,000), 1965
- Mandaree, North Dakota (1:24,000), 1970
- Sanish SW, North Dakota (1:24,000), 1967

b. Geologic maps:

Bluemle, J.P., 1988, Guide to the geology of southeastern North Dakota, North Dakota Geological Survey Educational Series 18, 36 p.

Carlson, C.G., 1985, Geology of McKenzie County, North Dakota, North Dakota Geological Survey, Bulletin 80, pt 1.

c. Soil surveys:

No soil survey available.

d. Other maps:

Parshall, North Dakota, 30' x 60' quadrangle, Bureau of Land Management, 1982, scale 1:100,000

U.S. Department of Agriculture, 1986, Little Missouri National Grassland, North Dakota: U.S. Department of Agriculture, Forest Service, scale 1:126,720.

Beaver Creek near Finley, North Dakota (05064900)

a. U.S. Geological Survey topographic maps:

- Aneta, North Dakota (1:24,000), 1967
- Finley, North Dakota (1:24,000), 1967
- Finley NE, North Dakota (1:24,000), 1967
- Golden Lake, North Dakota (1:24,000), 1970, streamflow-gaging station
- Grand Forks, North Dakota-Minnesota (1:100,000), 1985
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b. Geologic maps:

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Harris, K.L., and Luther, M.R., 1991, Surface geology of the Goose River map area: North Dakota Geological Survey Atlas Series Map 14, sheet A1.

c. Soil surveys:

U.S. Department of Agriculture, 1997, Soil survey of Steele County, North Dakota: U.S. Department of Agriculture, Natural Resources Conservation Service, 214 p.

Castle Creek above Deerfield Reservoir, South Dakota (0640900)

a. U.S. Geological Survey topographic maps:

- Crooks Tower, South Dakota (1:24,000), 1956
- Crows Nest Peak, South Dakota (1:24,000), 1956
- Deerfield, South Dakota (1:24,000), 1979, streamflow-gaging station
- Ditch Creek, South Dakota (1:24,000), 1956
- Mount Rushmore, South Dakota (1:100,000), 1977
- Preacher Spring, South Dakota (1:24,000), 1956
- Rapid City, South Dakota (1:100,000), 1980

b. Geologic maps:

DeWitt, E., Redden, J.A., Busher, D., and Wilson, A.B., 1989, Geologic map of the Black Hills area, South Dakota and Wyoming: U.S. Geological Survey Miscellaneous Investigations Series Map I–1910, 1 pl., scale 1:250,000.

DeWitt, E., Redden, J.A., Wilson, A.B., Buscher, D., and Dersche J.S., 1986, Mineral resource potential and geology of the Black Hills National Forest, South Dakota and Wyoming: U.S. Geological Survey Bulletin 1580, 135 p.

c. Soil surveys:

U.S. Department of Agriculture, 1990, Soil survey of Custer and Pennington Counties, Black Hills parts, South Dakota: U.S. Department of Agriculture, Soil Conservation Service, 295 p.

d. Other maps:

Black Hills National Forest map, 1988, U.S. Department of Agriculture.

Little Vermillion River near Salem, South Dakota (06478540)

a. U.S. Geological Survey topographic maps:

Oldham SW, South Dakota (1:24,000), 1968
Canova East, South Dakota (1:24,000), 1971
Unityville, South Dakota (1:24,000), 1971
Winfred, South Dakota (1:24,000), 1971
Winfred SE, South Dakota (1:24,000), 1971, streamflow-gaging station

b. Geologic maps:

Darton, N.H., 1951, Geologic map of South Dakota: U.S. Geological Survey, 1 pl.

Schroeder, W., 1988, Geology and water resources of Miner County, South Dakota: Department of Water and Natural Resources, South Dakota Geological Survey Bulletin 31, 38 p.

c. Soil surveys:

U.S. Department of Agriculture, 1980, Soil survey of McCook County, South Dakota: U.S. Department of Agriculture, Soil Conservation Service.

———1984, Soil survey of Miner County, South Dakota: U.S. Department of Agriculture, Soil Conservation Service.

Cache Creek near Jackson, Wyoming (13018300)

a. U.S. Geological Survey topographic maps:

Cache Creek, Wyoming (1:24,000), 1965, streamflow-gaging station
Jackson, Wyoming (1:100,000), 1981
Turquoise Lake, Wyoming (1:24,000), 1965

b. Geologic maps:

Goetze, P.R., 1981, Regional geologic map for the Cache Creek-Bear Thrust environmental impact statement, Teton and Sublette Counties, Wyoming: U.S. Geological Survey Open-File Report 81–856, 1 pl.

Love, C.M., and Love, J.D., 1978, Geologic map of the Turquoise Lake quadrangle, Teton County, Wyoming: U.S. Geological Survey Open-File Report 78–481.

Love, J.D., and Love, C.M., 1978, Geologic map of the Cache Creek quadrangle, Teton County, Wyoming: U.S. Geological Survey Open-File Report 78–480.

Simons, F.S., Love, J.D., Keefer, W.R., Harwood, D.S., and Kulik, D.M., 1988, Mineral resources of the Gros Ventre Wilderness Study Area, Teton and Sublette Counties, Wyoming: U.S. Geological Survey Bulletin 1591, 65 p.

c. Soil surveys:

Glenn, W.R., 1981, Soil resource inventory order 3, Cache Creek-Little Granite Creek EIS area, Bridger-Teton National Forest: U.S. Geological Survey Open-File Report 81–855, Dern and Polk Resource Consultants, 51 p.

d. Other maps:

Bridger-Teton National Forest map, Buffalo and Jackson Ranger Districts, U.S. Department of Agriculture, scale 1:126,720.

Jackson, Wyoming 30' x 60' quadrangle, Bureau of Land Management, 1981, scale 1:100,000.

Kruger, P.W., 1981, Report on climate, air quality, and noise for the Cache Creek-Bear Thrust environmental impact statement: U.S. Geological Survey Open-File Report 81–859.

Encampment River above Hog Park Creek, near Encampment, Wyoming (06623800)

a. U.S. Geological Survey topographic maps:

Blackhall Mountain, Wyoming-Colorado (1:24,000), 1983
Davis Peak, Colorado (1:24,000), 1955
Dudley Creek, Wyoming-Colorado (1:24,000), 1983, streamflow-gaging station
Mount Zirkel, Colorado (1:24,000), 1955
Saratoga, Wyoming-Colorado (1:100,000), 1982
Walden, Wyoming-Colorado (1:100,000), 1981
West Fork Lake, Colorado (1:24,000), 1962

b. Geologic maps:

Houston, R.S., and Ebbett, B.E., 1977, Geologic map of the Sierra Madre and western Medicine Bow Mountains, southeastern Wyoming: U.S. Geological Survey Miscellaneous Field Studies Map MF–827, 1 sheet.

Houston, R.S., and Graff, P.J., 1995, Geologic map of Precambrian rocks of the Sierra Madre, Carbon County, Wyoming, and Jackson and Routt Counties, Colorado: U.S. Geological Survey Miscellaneous Investigations Series Map I–2452, 2 sheets.

Snyder, G.L., 1980, Geologic map of the northernmost Park Range and southernmost Sierra Madre, Jackson and Routt Counties, Colorado: U.S. Geological Survey Miscellaneous Investigations Series Map I–1113, scale 1:48,000.

Snyder, G.L., Patten, L.L., and Daniels, J.J., 1987, Mount Zirkel Wilderness and northern Park Range vicinity, Colorado: U.S. Geological Survey Bulletin 1554.

c. Soil surveys:

No soil survey available.

d. Other maps:

U.S. Geological Survey orthophotoquad, 7.5-minute series:

- Blackhall Mountain, Wyoming-Colorado, 1980
- Davis Peak, Colorado, 1983
- Dudley Creek, Wyoming-Colorado, 1980
- Mount Zirkel, Colorado, 1983
- West Fork Lake, Colorado, 1983

Routt National Forest map, Ranger Districts, 1996, U.S. Department of Agriculture.

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