EFFECTS OF ACIDIC PRECIPITATION ON THE WATER QUALITY OF STREAMS IN THE LAUREL HILL AREA, SOMERSET COUNTY, PENNSYLVANIA, 1983-86

By James L. Barker and Emitt C. Witt III

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CONVERSION FACTORS AND ABBREVIATIONS

For the convenience of readers who may prefer inch-pound units rather than the metric (International System) units in this report, the following conversion factors may be used:

<u>Multiply Metric Unit</u>	<u>By</u>	<u>To Obtain Inch-Pound Unit</u>
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
hectare (ha)	2.471	acre
square kilometer (km²)	0.3861	square mile (mi²)
cubic meter per second (m ³ /s)	35.31	cubic foot per second (ft ³ /s)
liter per second (L/s)	15.85	gallons per minute (gal/min)
liter per second (L/s)	0.0353	cubic foot per second (ft ³ /s)
megagram (Mg)	1.102	ton, short
degree Celsius (°C)	°F = 1.8 x °C + 32	degree Fahrenheit (°F)
kilogram per hectare (kg/ha)	1.12	pounds per acre (lbs/acre)

Other Abbreviations

microsiemens per centimeter at 25 degrees Celsius (μ S/cm) microequivalents per liter (μ eq/L) milliequivalents per liter (meq/L) milligrams per liter (mg/L) water year (wy)

<u>Sea level</u>: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called "Sea Level Datum of 1929". EFFECTS OF ACIDIC PRECIPITATION ON THE WATER QUALITY OF STREAMS IN THE LAUREL HILL AREA, SOMERSET COUNTY, PENNSYLVANIA, 1983-86

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ABSTRACT

Five headwater streams in the Laurel Hill area in southwestern Pennsylvania were investigated from September 1983 through February 1986 to determine possible effects of acidic precipitation on water quality. Precipitation in the Laurel Hill area is among the most acidic in the Nation, with a mean volume-weighted pH of 4.06. Sulfate is the dominant acid-forming anion, averaging 3.6 milligrams per liter or about 50 kilograms per hectare in wet deposition alone. Nitrate averages about 2 milligrams per liter or 7 kilograms per hectare in the study area.

Stream chemistry in the five streams is quite variable and apparently is influenced to a large degree by the bedrock geology and by small amounts of alkaline material in watershed soils. Three of the five streams with no or little acid-neutralizing capacity presently are devoid of fish because of low pH and elevated aluminum concentrations. Aluminum concentrations increase in the other two streams during rainfall and snowmelt despite comparatively higher base flow and acid-neutralizing capacities.

Comparison of the chemistry of streamflow during 14 storm events at South Fork Bens Creek and North Fork Bens Creek reveals similar chemical responses when discharge suddenly increases. Concentrations of dissolved metals and sulfate increased during stormflow and snowmelt runoff, whereas concentrations of base cations, silica, and chloride decreased. Nitrate concentrations were not affected by rainfall runoff but tended to increase with snowmelt runoff.

INTRODUCTION

<u>Background</u>

In response to the Acid Precipitation Act of 1980, surface-water monitoring studies have been conducted jointly by the U.S. Geological Survey and the U.S. Environmental Protection Agency (USEPA) in areas of the country sensitive to acidification from atmospheric deposition. These studies are a major activity of the Aquatic Effects Task Group of the National Acid Precipitation Assessment Program (NAPAP).

The Aquatic Effects Task Group has established a network of long-term monitoring stations at lakes and streams across the country to correlate changes in deposition and surface-water quality. It is intended that such a network will improve the ability to detect and measure changes in stream chemistry over time. As part of the network, five headwater streams on the eastern slope of Laurel Hill in Somerset County, Pennsylvania, were selected to document the effects of acidic atmospheric loading on a watershed system and to compare them with the effects observed in other parts of the country. Quantification of the effects of the current loading rate on these and other sensitive areas is expected to provide information necessary for regulatory agencies to formulate guidelines for acceptable atmospheric loading rates of acidic materials.

The Laurel Hill area was selected because the precipitation there has mean volume-weighted pH of 4.06, which is about 35 times more acidic than "pure rain" (pH, 5.6). In addition, Laurel Hill soils are formed principally in materials weathered from noncarbonate sedimentary rocks that are highly sensitive to acidification.

A study of 61 headwater streams in the Laurel Hill area by Sharpe and others (1983) shows that 10 streams, or 16 percent, lacked fish. The acidic condition and lack of fish are attributed to acid deposition. The researchers found that all streams devoid of fish had low pH, low acid-neutralizing capacity, and elevated concentrations of dissolved aluminum.

Purpose and Scope

This report describes results of an investigation to quantify the effects of present atmospheric-deposition levels on the water quality of streams within the Allegheny Mountains of southwestern Pennsylvania. The scope of this report is limited to the presentation and discussion of physical and chemical data collected from October 1983 through February 1986 at five firstand second-order watersheds of less than 10.4 km² (square kilometers). Discussions of the following are included: (1) precipitation quantity and chemical quality; (2) pre- and post-episodic observations of stream constituents; (3) dissolved-constituent response during episodic discharge; and (4) yearly chemical budgets for sulfate, nitrate, base cations, and chloride. All runoff data are listed at the end of the report. Monthly water-quality data for the five study streams and daily discharge data for the two primary streams are published in U.S. Geological Survey Water-Data Reports PA-84-3 and PA-85-3 (U.S. Geological Survey, 1985-86) and are not reproduced in this report.

Regional Characteristics

The study area is on the eastern slope of the Laurel Hill area of the Allegheny Mountains in northwest Somerset County, Pennsylvania near Johnstown in Cambria County (fig. 1). Five headwater streams with low acid-neutralizing capacity were included in the study. Two primary streams--South Fork Bens Creek and North Fork Bens Creek--and three satellite streams--North Branch Quemahoning Creek, Garys Run, and Cole Run--were sampled monthly to obtain background chemistry data. The two primary streams were also sampled for the dose/response phase of the study.

All five watersheds are within the mixed mesophytic forest region of Pennsylvania, but the watersheds also contain forest types dominated by beechmaple, northern hardwood, and oak-chestnut. There is much local species diversification because of differences in soil depth, soil moisture, elevation, and microclimate. The area was logged in the late 1880's and early 1900's, and the present-day forest is mostly second- and third-growth timber. Other cultural effects in all five basins have been minimal except for the construction of two small retention dams and an installation of a test well on South Fork Bens Creek. The watersheds have never been mined for coal.

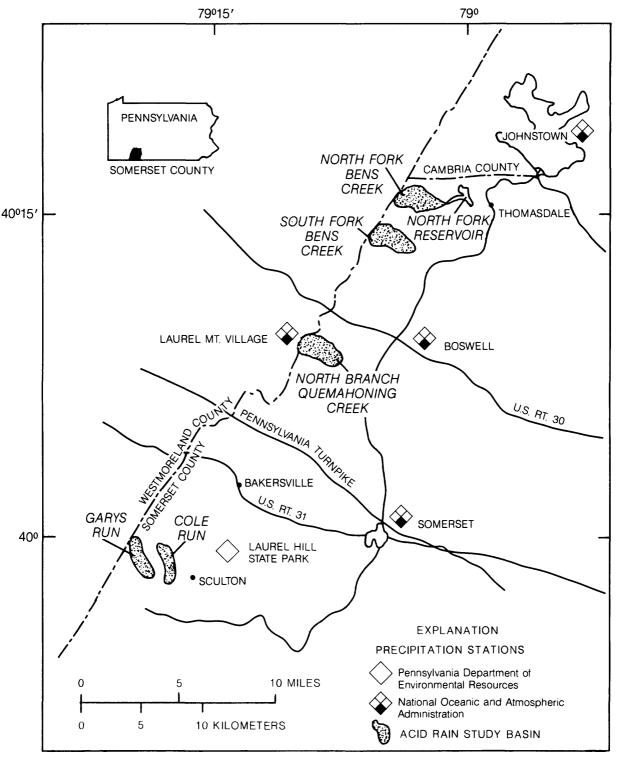


Figure 1.--Location of study basins and precipitation stations.

Climate and Air Quality

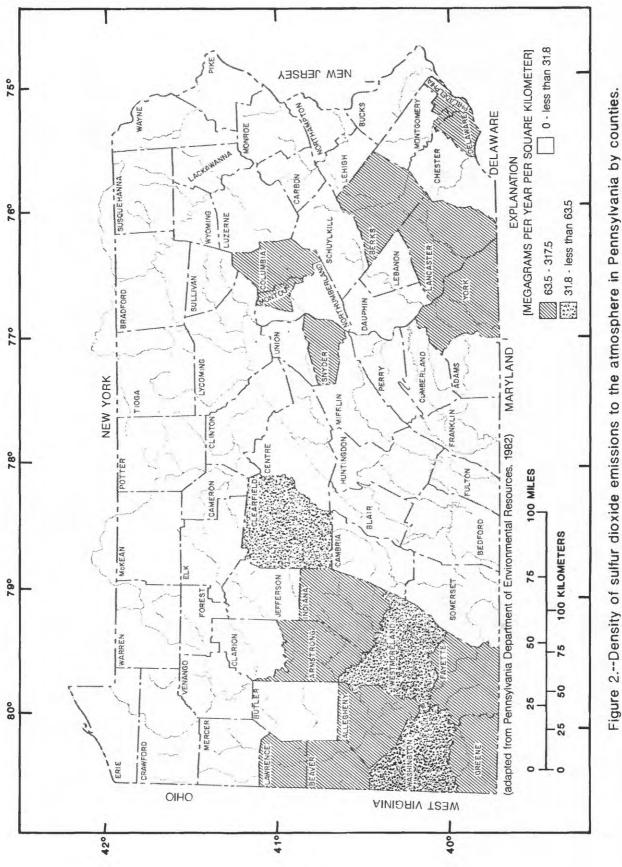
The climate of Laurel Hill is a continental type, but temperatures are more variable and precipitation more frequent than in other parts of the State. The average annual precipitation is 1,350 mm (millimeters), and precipitation is distributed evenly throughout the year. The average annual snowfall is 1,680 mm/yr (millimeters per year), and 510 mm/yr or more in a single storm is not uncommon. Summer thunderstorms occur on about 35 days per year and produce frequent, brief showers of 13 mm or more (U.S. Department of Agriculture, 1983).

National Oceanic and Atmospheric Administration (NOAA) meterological stations relevant to the study area are at Johnstown, Boswell, Laurel Mt. Village, and Somerset (fig. 1). Data for freeze periods were collected at Laurel Mt. Village, about 11.3 km (kilometers) south of the South Fork Bens Creek study area. The period of ice for the 1984 water year¹ was December 21 to February 15, and for the 1985 water year it was January 15-23 and February 5-13.

Most weather and, therefore, atmospheric chemicals and particulate matter in the study area are transported from regions west and southwest of Somerset County. Figure 2 shows emission densities of sulfur dioxide in Pennsylvania counties (Pennsylvania Department of Environmental Resources, 1982). Sulfur dioxide is emitted in the counties to the west and southwest of Somerset County. Therefore, rainfall in the study area would be expected to have elevated sulfate concentrations during most times.

A contour map of the volume-weighted annual mean pH of wet deposition, generated from data collected during 1985 (fig. 3), shows that Laurel Hill is within the area of the nation's most acidic wet deposition. The pH of the wet deposition collected in the South Fork Bens Creek watershed during 1983-85 had a mean of about 4.06, which is significantly lower than the value of 4.22 reported by Likens (1976). Similar pH values have been reported by the Pennsylvania State University/Pennsylvania Department of Environmental Resources (PSU/PaDER) for the precipitation at Laurel Hill State Park, about 29 km southwest of the Bens Creek study area. Data show that pH during January through December 1984 had a mean of 4.15 and ranged from 3.70 to 5.13 (Lynch, J.A., Pennsylvania State University, written commun., 1985).

¹Water year is the period October 1 through September 30 and is designated by the calendar year in which it ends.



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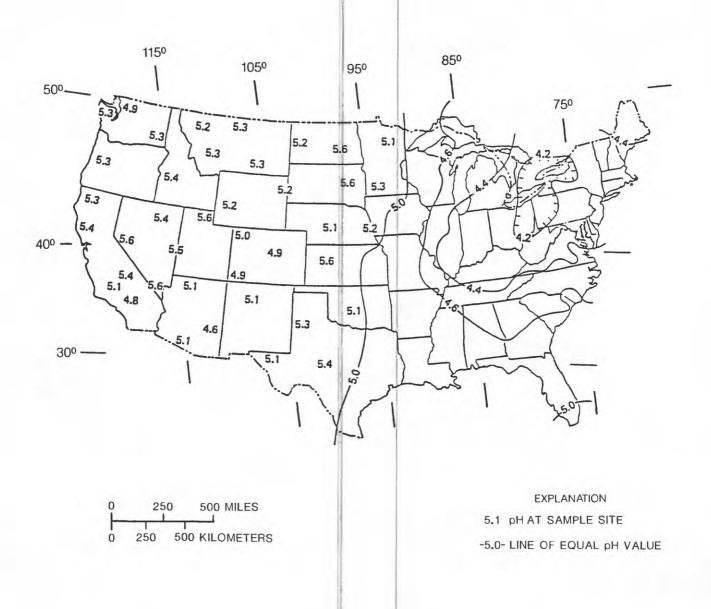


Figure 3.--pH of wet deposition (annual volume-weighted average) in the United States. Based on National Acid Precipitation Assessment Program and National Trends Network data (modified from U.S. Geological Survey 1985, fig. D-1).

Geology

Laurel Hill lies within the Allegheny Mountain section of the Appalachian Plateau physiographic province. It is an anticlinal mountain that is oriented in a northeast-southwest direction; its strike or ridge line slopes slightly to the southwest, and its dip across the rock layers is about 5°30' near the crest of the ridge (DeWalle and others, 1982).

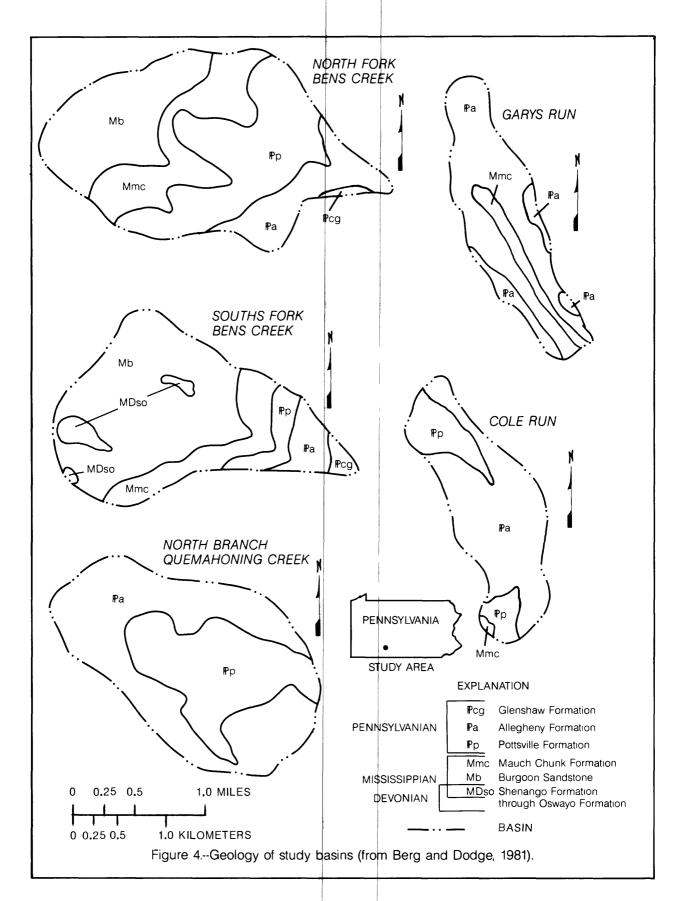
Sedimentary rocks of Pennsylvanian and Mississippian ages are exposed on Laurel Hill. Figure 4 shows the geology of each of the study basins. The Pennsylvanian age rocks, from youngest to oldest, are the Allegheny and the Pottsville Groups. The Mississippian and Devonian rocks, from youngest to oldest, are the Mauch Chunk Formation, the Loyalhanna Limestone, the Burgoon Sandstone, and the Shenango through Oswayo Formations, undivided. The Loyalhanna Limestone is highly compressed and discontinuous in the northern part of Somerset County (Flint, 1965). The Burgoon through Oswayo rocks are equivalent to the Pocono Group.

Exposed Mississippian-age rocks are older in the northern part of the anticlinal ridge (fig. 5A) than in the southern part (fig. 5B) because of differential erosion of the ridge top. The extent of exposure of the various rock units is important because the Loyalhanna Limestone, which may possibly underlie the Mauch Chunk Formation, is a source of base cations that increase stream pH and buffering capacity. On the other hand, the Allegheny Formation is a source of hydrogen ions that increase acidity in streams.

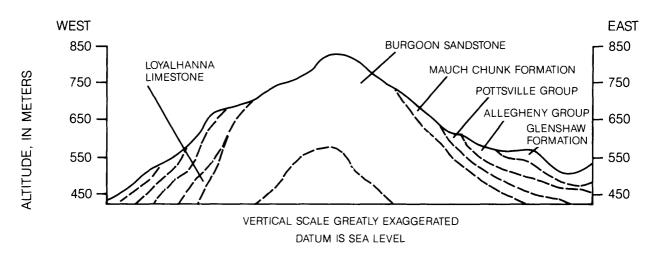
The percentages of the rock formations within the study basins are listed in table 1. The degree of acidification of surface water is linked to the geology and exposure of rock types in the watershed. Therefore, the local variation in geology may limit the transfer value of information on sensitivity of watersheds to acidification. The importance of basin hydrogeology to the sensitivity to acidification and the presence of trout populations on Laurel Hill has been extensively investigated by DeWalle and others (1987) and Sharpe and others (1987).

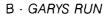
Basin	Shenango Formation	Burgoon Sandstone	Mauch Chunk Formation	Pottsville Formation	Allegheny Formation	Glenshaw Formation	Total
South Fork Bens Cr. North Fork Bens Cr. North Branch		62 29	14 22	12 33 34	6 15 66	3 1	100 100 100
Quemahoning Cr. Cole Run Garys Run			1 12	23 79	76 9		100 100

Table 1.--Bedrock geology of study basins as a percentage of basin area



A - NORTH FORK BENS CREEK





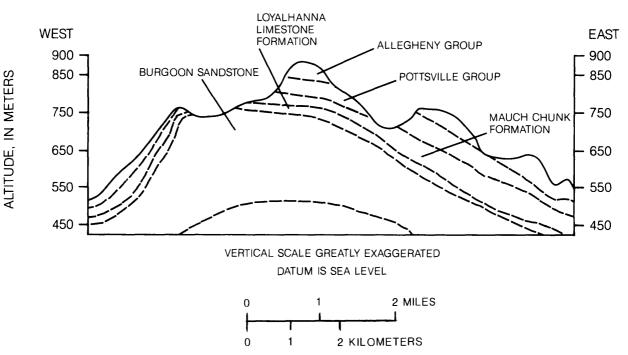


Figure 5.--Generalized geologic sections of Laurel Hill anticline in the vicinity of: A. North Fork Bens Creek; B. Garys Run.

Four soil series--Hazleton, Rayne-Gilpin, Cookport, and Ernest--are the dominant soils in the study watersheds. These soils are silt loams to very stony silt loams that are typically acidic (pH 3.6 to 5.5)¹, moderately deep, and well drained (U.S. Department of Agriculture, 1983). Detailed soil maps for each of the five watersheds and general information as to soil use, management, physical and chemical properties, and factors of soil formation are contained in the Soil Survey of Somerset County, Pennsylvania, (U.S. Department of Agriculture, 1983).

Soils

Site Descriptions

North Fork Bens Creek, South Fork Bens Creek, North Branch Quemahoning Creek, Garys Run, and Cole Run were selected for monthly chemical sampling to obtain background data on temporal variability of streams in the area. Two streams--South Fork Bens Creek and North Fork Bens Creek--were selected as primary sites and as such received additional sampling during storm and snowmelt runoff to determine the effects of rapidly changing streamflows.

North Fork Bens Creek at North Fork Reservoir

The site is located at lat 40°15′58"N., long 79°01′01"W. in northwestern Somerset County and is at the inlet to North Fork Reservoir 12.1 km southwest of Johnstown (fig. 1). The sampling site is on a second-order stream, which has a drainage area of 8.94 km². The watershed, at an elevation of 407 to 833 m (meters) above sea level, is nearly all forested and under the ownership and protection of the Greater Johnstown Municipal Authority.

Beginning with the autumn of 1984, this site was included in the dose/response phase of the study and designated a primary site, along with the South Fork Bens Creek site. As such, the two watersheds had the same types of equipment for continuously recording stage, automatically sampling the stream, and recording rain.

The upper half of the watershed is underlain by the Mississippian sandstones of the Burgoon Sandstone and Mauch Chunk Formation and the lower half by the Pennsylvanian sandstones of the Pottsville and Glenshaw Formations. The Loyalhanna Limestone, which is about 15 m thick in southern Somerset County, shows regional thinning trending northeastward to almost a complete disappearance at the approximate latitude of the Bens Creek watershed (Flint, 1965). The watershed contains no coal mines but at least one exploratory gas well. Soils are predominantly Hazleton, Ernest, and Rayne-Gilpin loams.

¹Soil pH is determined in the laboratory from an equilibrium solution of soil sample and distilled water at atmospheric pressure and temperature.

South Fork Bens Creek near Thomasdale

This primary site is located at lat $40^{\circ}13'41"N.$, long $79^{\circ}02'49"W.$ and is 12.6 km southwest of Johnstown (fig. 1). The sampling site is in a forested area on a second-order stream. The watershed has a drainage area of 8.50 km² and is at an elevation of between 505 and 884 m. Flow is regulated partially by two small dams having a combined capacity of 32,929.5 m³ (cubic meters). Daily diversion of about 1,037 m³ is metered by the Conemaugh Township Municipal Authority.

The upper 79 percent of the watershed is underlain by the Mississipian sandstones of the Burgoon Sandstone and Mauch Chunk Formation, and the lower 21 percent by Pennsylvanian sandstones of the Pottsville and Allegheny Formations. Basin soils consist primarily of shallow Hazleton very stony, sandy loam in the uplands and Cookport loam in the foothills.

Water quality of the South Fork Bens Creek was affected by artesian flow from a test well drilled by the Municipal Authority into the Burgoon Sandstone at about the center of the basin. Test well drilling began on October 10, 1984, and was completed as a 203 mm diameter hole, 54 m deep, with 11 m of bottom grouted casing. The total flow yield of the well was measured at 75 L/s (liters per second), (R. Casselberry, Meiser and Earl, Hydrogeologists, written commun., 1985). The well continued flowing at a rate of about 2.5 L/s until January 10, 1985, when it was capped. During the time water was flowing from the well, it had the effect of raising the stream pH, alkalinity, and specific conductance. The resulting effect on the stream water quality was such that the interpretive value of the stream was compromised and the study emphasis was transferred to North Fork Bens Creek in October 1984.

Grab samples of the overflow from the "test" well indicated the water quality generally is excellent, (R. Casselberry, Meiser and Earl, Hydrogeologists, written commun., 1985). A private laboratory analysis of an unfiltered sample collected on December 13, 1984, showed the following:

ΗΗα	7.8
Total suspended solids	1 mg/L
Iron.	$1 \frac{mg/L}{1}$
Manganese	0.2 mg/L
Aluminum	0.2 mg/L
Alkalinity to pH 4.5	56 mg/L as CaCO3
Acidity to pH 8.2	negative
Sulfate.	6 mg/L
Specific conductance	$\mu S/cm$
Calcium.	17 mg/L
Magnesium	2.7 mg/L
Hardness (Ca. Mg. Fe. Mn. A1)	56 mg/L as CaCO3
Total solids	66 mg/L
Fluoride	0.2 mg/L
Nitrogen ammonia	0.1 mg/L
Arsenic	$< 2 \mu g/L$
Cadmium	0.01 mg/L
Chromium	0.08 mg/L
Lead	0.12 mg/L
Mercury	$<2 \mu g/L$
Selenium	$< 2 \mu g/L$
Silver	0.02 mg/L
Barium	0.20 mg/L

¹Filtered analysis produced a dissolved-iron concentration of 0.13 mg/L.

North Branch Quemahoning Creek at Roytown

This satellite site is located at lat $40^{\circ}06'38"N.$, long $79^{\circ}08'41"W.$ in northwestern Somerset County and is about 19 km northwest of Somerset and 8 km north of Bakersville (fig. 1). This and all selected satellite sites were sampled monthly for major ions, dissolved metals, temperature, pH, specific conductance, alkalinity, and streamflow. The sampling site is on a secondorder stream in a watershed that is almost entirely forested. The drainage area is 6.89 km².

The watershed is underlain entirely by Pennsylvanian sandstones of the Pottsville and Allegheny Formations. Soils series developed on the material consists of the Hazleton and Cookport sandy and silt loams.

Garys Run near Barronvale

This satellite site is located at lat 39°58'25"N., long 79°17'51"W. in west-central Somerset County and is about 20.1 km southwest of Somerset and 4.8 km north of Sculton (fig. 1). The sampling site is on a first order stream; the drainage area is 3.16 km^2 . The watershed is entirely on state forest lands and is forest covered except for about 0.80 km² that was recently disturbed by clear-cut logging. The logged area does not affect stream quality except during periods of overland runoff.

Basin soils are predominantly of the Ernest and Rayne-Gilpin Series of sandy loams. Pennsylvanian sandstones of the Pottsville and Allegheny Formations dominate the geology. About 12 percent of the parent material is Mississippian sandstone of the Mauch Chunk Formation.

Cole Run near Barronvale

This satellite site is located at lat $39^{\circ}58'00"N.$, long $79^{\circ}17'25"W.$ in west central Somerset County and is about 17.4 km southwest of Somerset and 3.2 km north of Sculton (fig. 1). The sampling site is on a first order stream; the drainage area is 4.30 km². The watershed is completely forest covered and is within state forest boundaries.

The bedrock geology is nearly all Pennsylvanian sandstone of the Pottsville and Allegheny Formations. Although many soil series are represented, the Cookport, Hazleton, Ernest, and Rayne-Gilpin Series predominate.

12

METHODS OF STUDY

Data Collection

Methods of data collection, sample handling, and sample preservation were in accordance with the "Working Protocol" established in 1982 and revised in March 1985 by the ad hoc committee for Aquatic Effects Task Group E and the USEPA long-term surface water monitoring program.

Base flow was sampled monthly at each stream by collecting a grab sample at the centroid of flow. At the two primary sites, storm events were sampled using an automatic water sampler that was activated by a rise in stream stage. The automatic sampler was programmed to collect as many as 24 discrete samples at variable time intervals so that the rise, peak, and recession of the streamflow would be represented.

Precipitation was measured and recorded at the South Fork and the North Fork Bens Creek sites by weighing-bucket gages. All precipitation measurements were referenced to an adjacent National Weather Service standard rain gage. Weekly and episodic wet deposition samples were collected for chemical analysis by a wet/dry collector in accordance with methods described in the National Atmospheric Deposition Program Instruction Manual (Bigelow, 1982).

Water stage in South Fork and North Fork Bens Creeks was monitored continuously by a gas-purge servomanometer attached to chart and digital recorders. Relations of stage to discharge were developed using standard U.S. Geological Survey methods (Rantz and others, 1982) for the primary stations. Instantaneous streamflow was measured at the three satellite sites at the time of chemical sampling.

Sample Treatment and Analysis

Stream, wet deposition, and QA/QC (quality assurance/quality control) samples were passed through filters of several different pore sizes during the course of the study. In the beginning of the project $0.45 \ \mu m$ (micrometer) porosity nitrocellulose filters were used. Following a period of experimental filtering with $0.2 \ \mu m$ and $0.1 \ \mu m$ porosity between August and November 1984, all analyses for dissolved ions were filtered through $0.1 \ \mu m$ polycarbonate filters and stored at 4.0 °C (degrees Celsius) until analysis for dissolved ions. In addition, samples for cation analysis were acidified with $1 \ N$ ultrapure nitric acid to pH 2 or less prior to storing. Samples for dissolved organic carbon (DOC) were passed through $0.4 \ \mu m$ silver filters and chilled at 4.0 °C until analysis. Filtered samples were packed in ice and shipped to the U.S. Geological Survey Central Laboratory in Arvada, Colorado, for analyses using methods described in table 2 for low-ionic-strength solutions.

Values for several properties of streamflow and precipitation were measured in the field as samples were being collected. The properties and methods of field analysis are listed in table 3.

Table 2.--Laboratory analytical methods used for surface-water and wet-deposition samples

[Reporting level in milligrams per liter except as noted]

Chemical constituent	Analytical method	Limit of detection
Acidity as [H ⁺]	Electrometric titration	0.01
Acid neutralizing capacity	Electrometric titration (second	
	derivative method)	. 5
Aluminum, dissolved	Atomic-absorption spectroscopy	.05
Calcium, dissolved	Atomic-absorption spectroscopy	.005
Hardness, dissolved	Complexometric	1
Bromide, dissolved	Ion chromatography	.01
Chloride, dissolved	Ion chromatography	.01
Fluoride, dissolved	Ion chromatography	.01
Nitrate, dissolved	Ion chromatography	.01
Sulfate, dissolved	Ion chromatography	.01
Iron, dissolved	Atomic-absorption spectroscopy	2
Magnesium, dissolved	Atomic-absorption spectroscopy	.01
Manganese, dissolved	Atomic-absorption spectroscopy	0.2
pH	Electrometric titration	.1 units
Potassium, dissolved	Atomic-absorption spectroscopy	.01
Silica, dissolved	Atomic-absorption spectroscopy	.01
Sodium, dissolved 1 µS/cm	Atomic-absorption spectroscopy	.01
Carbon, organic, dissolved	Wet oxidation	.1
Nitrogen ammonia as N, dissolved	Block digest plus colorimetry	.001
Phosphate ortho - P, dissolved	Colorimetry, phosphomolybdate	.001

Table 3.--Field analytical methods used for surface-water and wet-deposition samples

Constituent	Analytical method
Acidity	Gran method (Gran, 1952)
Acid-neutralizing capacity, total as CaCO,	Gran method (Gran, 1952)
Temperature	Thermometer NBS*
Specific conductance	Wheatstone bridge
pH	Combination electrode
Discharge	Current meter (Rantz, 1982)

Quality Assurance

Quality assurance was an integral part of the sampling program throughout the study. Initially, quality assurance was done randomly, but became part of the monthly and storm event sampling program in February 1985 with the issuance of the USEPA QA/QC guidelines contained in the "Working Protocol" for the long-term monitoring program.

The QA/QC program consisted of replicate samples, filtration blanks, and container blanks to be taken at one primary stream site each time that site is sampled. In addition, replicates were to be obtained on two secondary streams three times yearly under low, intermediate, and high flow conditions. Audit or spiked samples were provided three times per year by an independent contractor to USEPA to determine interlaboratory bias and comparability among projects.

Precision data were generated by analyzing samples in duplicate. Differences between the two values were multiplied by 0.89 to approximate the standard deviation (Aquatic Effects Task Group, 1985). The standard deviation divided by the mean of the duplicate values and multiplied by 100 yielded the relative standard deviation (RSD), in percent.

Filtration and container blanks were prepared in the field and submitted to the laboratory to be analyzed with the routine samples. The blanks were analyzed to determine the adequacy of the filtration manipulation, the cleanliness of the linear-polyethylene dissolved-ion sample container, and purity of the deionized water (tables 4-6). Precision observations for chloride, phosphate, nitrate, and sulfate had average RSD values less than the objective precision value. Average RSD values for all other constituents were above the precision objectives. Filtration blanks generally confirmed the acceptability of the membrane procedure for dissolved constituents. Although few observations were less than detection limits, nearly all concentrations were within expected and acceptable ranges. The mean concentrations of sulfate, aluminum, iron, and manganese are of marginal utility because of one or two relatively high values that raised the mean. Container blanks confirmed the adequacy of the container and purity of the deionized water. Audit sample results are incomplete and not reported here but are available from the USEPA, Environmental Research Laboratory, Corvallis, Oregon.

Constituent	Number of replicate analyses	RSI	-	of alues ent)	Average RSD (percent)	Intralab relative precision goal² (percent)
Aluminum	9	3.6	to	33	16.4	10
Calcium	9	0	to	18	8.7	5
Magnesium	9	0	to	73	16.6	5
Sodium	9	0	to	62	7.8	5
Potassium	9	0	to	62	14	5
Fluoride	9	0	to	101	26.8	5
Chloride	9	0	to	3	1.1	5
Phosphate	9	0	to	19	2.1	10
Nitrate	9	0	to	23	4.8	10
Sulfate	9	0	to	10	2	5

Table 4.--Results of laboratory precision observations for replicates

 1 RSD = relative standard deviation--

RSD (in percent) = $\frac{\text{Standard Deviation}}{\text{Mean}} \times 100$

²Intralab relative precision goal is the precision at concentrations about 10 times instrument detection limits.

Table 5.--Results of analyses of container blanks for filtered and dissolved constituents in deionized water

> [mg/L, milligrams per liter; μ/L , micrograms per liter; <, less than]

	umber of bservations	Number of observations less than detection limit	Range of values	Estimated average concentration ¹
Calcium (mg/L)	9	0	0.010 to 0.900	0.280
Magnesium (mg/L	.) 9	0	.009 to .200	.060
Sodium (mg/L)	9	3	<.050 to .400	.160
Potassium (mg/L	.) 9	0	.010 to .170	.070
Fluoride (mg/L)	9	3	<.010 to .100	.040
Chloride (mg/L)	9	1	<.010 to .540	. 230
Phosphate (mg/L	.) 9	7	<.001 to .004	<.001
Nitrate (mg/L)	9	6	<.001 to .020	<.010
Sulfate (mg/L)	9	0	.090 to 1.600	. 510
Aluminum ($\mu g/L$)	9	2	<1.000 to 20	11
Iron $(\mu g/L)$	9	6	<2.000 to 6.900	2.600
Manganese (µg/L	.) 9	7	<1.000 to 2.600	1.200

¹Estimate may be low because of use of a single value for less-than (<) values.

Dissolved constituent	Number of observations	Number of observations less than detection limit	Range	of values
pH (units)	2		5.60	to 5.80
Alkalinity (mg/L as				
calcium carbonate)	2	0		2
Specific conductance	2	0		1
(µS/cm)				
Calcium (mg/L)	2	2	<.02	to <.03
Magnesium (mg/L)	2	1	<.01	to .04
Sodium (mg/L)	2	2	<.2	
Potassium (mg/L)	2	0	.02	to .04
Chloride (mg/L)	2	1	.02	to <.2
Sulfate (mg/L)	2	1	.1	to <.2
Silica (mg/L)	2	2		0
Nitrate (mg/L)	1	1	<.05	
Phosphorus (mg/L)	2	2	<.01	to <.06
Iron (µg/L)	2	1	<3	to 5
Manganese (µg/L)	2	2		<1
Aluminum (μ g/L)	2	1	<10	to 20
Acidity (H ⁺)	2	1	<.1	to .3
Bromide (mg/L)	2	2	<.01	to .1
Fluoride (mg/L)	2	1	<.01	to .03

Table 6.--Results of analysis of container blanks for dissolved constituents in deionized water

at 25 degrees Celsius]

[mg/L, milligrams per liter; μ g/L, micrograms per liter; <, less than; --, no detection limit; μ S/cm, microsiemens per centimeter

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Data Interpretation

The annual chemical budget or net flux for the major constituents was calculated for the 1984 and 1985 water year at North Fork Bens Creek and for the 1984 water year at South Fork Bens Creek. The 1985 chemical budgets for South Fork were not calculated because of the chemical changes as a result of the artesian flow of well water into the stream as described earlier. The 1984 chemical budgets for the North Fork were estimated from the South Fork precipitation data and streamflow-correlation analyses.

Because of the problems inherent in calculating mass balance over a 1year period, using conservative materials, a method described by Galloway and others (1983) to calculate net flux as a running sum was used. The term "Running Net Flux" (RNF) is defined as

$$n$$

$$RNF = \Sigma (I - 0)$$

$$i = 1$$
(1)
(1)

where i is the time in weeks of observation, n is the number of weeks, I is the atmospheric deposition (input) of the element and 0. is the stream discharge (output) of the element. The net flux, then, is equal to the weekly difference in the inputs and outputs of a constituent.

The running net flux (RNF) was then related to annual flux by the calculation of the "Retention Index" (RI), defined by Galloway and others (1983) as the ratio of the RNF value to the annual sum of input for each constituent. Mathematically,

$$RI = \frac{RNF}{n}$$
(2)
$$\sum_{i=1}^{n} (inputs)_{i}$$

The values of RI can range from 1 to $-\phi$. When RI = 1, the input was completely retained in the watershed. When RI = 0, input equaled output, and when RI = -1, input was 1/2 output.

Data interpretation for stormflow data involves general plots of constituents with runoff hydrographs. Correlation and regression analysis of some constituents from both individual events and entire data sets were computed using the computer package, Statistical Analysis Systems (1979). Values for chemical constituents interpreted by correlation and regression methods were transformed into logarithms because water quality data typically are not normally distributed.

Annual atmospheric loading was calculated from weekly net deposition volumes and concentration data. Volume-weighted mean seasonal concentrations (see table 9) were substituted for weekly precipitation not analyzed. Annual stream loads were calculated from flow duration curves and transport curves (Searcy, 1963; Porterfield, 1972) developed for each ion of interest. Concentration data are available for a range of monthly streamflows and for storm and snowmelt runoff events.

HYDROLOGIC INFORMATION USED IN ANALYSIS

Precipitation

Quantity

The annual precipitation at the South Fork Bens Creek gage was 1,482 mm and 1,049 mm for the 1984 and 1985 water years, respectively. The long-term average for the region is about 1,350 mm (National Oceanic and Atmospheric Administration, 1950-85). Heavy rains during the spring of 1984 were responsible for the annual precipitation being 9 percent above normal for that year. By comparison, the 1985 water year was 22 percent below normal; this deficiency was noticeable particularly during the latter part of the year. Figure 6 illustrates the weekly distribution of total precipitation for the period. Precipitation also was recorded at the North Fork Bens Creek watershed during the 1985 water year. Some records in October and November are missing, but the total for the year is estimated to be about 1,016 mm or within 3 percent of that measured at South Fork.

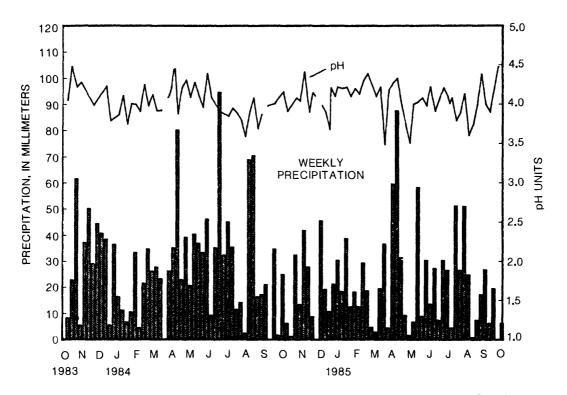
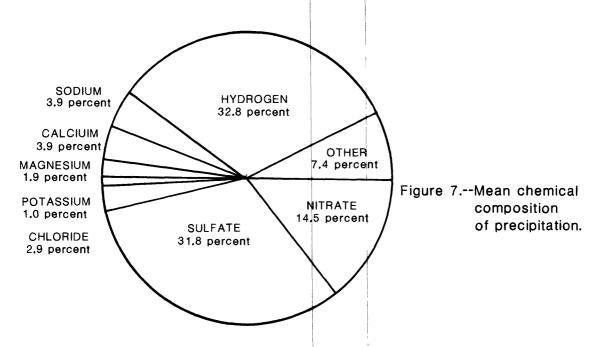


Figure 6.--Weekly precipitation and mean pH in South Fork Bens Creek watershed, 1984-85 water years.

Chemistry

Assessment of precipitation chemistry is based primarily on weekly and event samples of rain and snow collected at the South Fork Bens Creek site from September 1983 through February 1986 (table 7). As illustrated in figure 7, hydrogen and sulfate are the dominant ions in the composition of precipitation, averaging about 33 and 32 percent, respectively. These percentages are typical of precipitation in the northeastern United States. Nitrate, on the other hand, averaged about 15 percent of the total ionic composition: cations, 10 percent; and chloride, 3 percent.



The volume-weighted mean concentrations of the major ions in precipitation for the 1984-85 water years are presented in table 8 for comparison with concentrations at other atmospheric deposition monitoring sites in the northeast (Bowersox and DePena, 1980; Galloway and Likens, 1981; Shaffer and Galloway, 1982). The volume-weighted means are, in general, comparable to the values reported elsewhere, with some exceptions. Dissolved sodium, for example, was 6 to 19 times greater than that measured at other sites in the northeastern U.S. The average sulfate concentration measured in precipitation at South Fork Bens Creek was 3.6 mg/L (milligrams per liter), but only 2.8 mg/L at Shenandoah National Park in Virginia (Shaffer, 1982), 1.9 mg/L at Biscuit Brook in the Catskill Mountains of New York (P.S. Murdoch, U.S. Geological Survey, written commun., 1986), 3.8 mg/L at Leading Ridge near State College, Pennsylvania, and 2.4 mg/L at Laurel Hill State Park, Pennsylvania (James Lynch, Pennsylvania State University, written commun., 1985).

Dissolved nitrate, on the other hand, averaged 2.2 mg/L at South Fork Bens Creek compared with 1.5 mg/L at Shenandoah Park, Va. and 1.7 mg/L at Biscuit Brook, N.Y. The reasons for the wide variation in precipitation chemistry for some constituents has not been determined, but probably is related to the proximity of local influences such as the coal-fired generators and steel mills to the west and southwest of Laurel Hill. The pH of precipitation measured at South Fork Bens Creek is among the lowest of any monitored site in Pennsylvania and considerable lower (3.59 to 4.48) than many other sites in the northeastern U.S. for which long-term data are available. The volume-weighted average pH for the period 1984-85 was 4.06. Precipitation was slightly more acidic (pH = 4.00) during the growing season than during the dormant season (pH = 4.10). Figure 6 illustrates the weekly precipitation pH for the period of study at South Fork Bens Creek.

A Pearson correlation coefficient (r) and coefficient of determination (r^2) were calculated for the 1984 data to determine the degree of association between sulfate and pH and nitrate and pH in precipitation. The results of the statistical analysis indicate that a strong inverse relation exists between sulfate and pH, and between nitrate and pH (r values of -0.60 and -0.65, respectively).

Seasonal and annual input loads are summarized in table 9. Although the loading of most major ions was greatest during the November to April dormant season, 1984 sulfate and hydrogen-ion loads were highest during the May to October growing season. The data further suggest that, not only did sulfate and pH correlate, but also that sulfate in the form of sulfuric acid was primarily responsible for the highly acidic precipitation and that nitric acid also was a contributor, especially during the dormant season.

	Manga- nese, dis- solved (µg/L)		88		₽₽	64	e O	15 4	งงปังง	© S l l l l l l l l l l l l l l l l l l l	ю	40
	Iron, dis- solved (μg/L)		9 11		6 6 6	10 27	10 35	42 60 18	1 18 7 7 3 3 8 6 7 7 7 8 8 7 7 7 7 8 8 7 7 7 7 8 8 7 7 8 7 7 8 7 7 8 7 7 8 7 7 8 7 7 8 7 7 8 7 7 7 8 7	13 18 19 19	14	12 8
	Alum- inum dis- solved (µg/L)		30		10 <10	70 20	40 40	5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	790 ¹ 10 3001 410	20 40 1101	20	120 ¹ 30
	Phos- phorus, ortho, dis- solved (mg/L)		<0.06 <.06		<0.06 <.06	6.06 <.06	.08.06	.06.06.06.06	× × • 06 • 06 • 06 • 06	× × • • • • • • • • • • • • • • • • • •	<.06	<.06 <.06
Liter;	Nitro- gen nitrate dis- solved (mg/L as N)		0.15		0.04	.12 .24		.21 .37 .10		10 15 04 15	.12	.16
ams per	Silica, dis- solved (mg/L)		00		~~	• •	00	000	00000	00000	0	00
degrees Celsius; mg/L, milligrams per liter; , indicates no data]	Bromide dis- solved (mg/L)	1983	<0.1 <.1	1984	<0.1 <.1	; ;	.13				<.1	<.1 <.1
us; mg/L, no data]	Flou- ride, dis- solved (mg/L)	eptember	<0.01 <.01	September	<0.01 <.01	0. 10.	.02	.03 .01 .01			.02	.03 <.01
es Celsi ndicates	Chlo- ride, dis- solved (mg/L)	982 to S	0.2		<0.2 <.2	6 .0	. 43 . 54	.62 .69 <.2	 	8.00 9.00 7.00 7.00	<.2	2 ⁷
at 25 degre than;, 1	Sulfate dis- solved (mg/L)	Quality Data, Water Year October 1982 to September	4.4 4.5	Water Year October 1983 to	1.6 2.3	2.7 4.6	4.7	3 4 5. 3 4 5. 3 4 5	1.5 2.6 2.6 2.6	5.3 3.7 1.8 1.8	6.2	6.2 4.5
meter at less th	Alka- linity lab (mg/L as CaCO ₃)	er Year	<1.0 <1.0	er Year	44	₽₽	44	244	40444	44444	1	44
per centimeter liter; <, less	Potas- sium dis- solved (mg/L)	ata, Wat	0.0 0		00	<u></u>	г. ⁶⁰ .	.37 .19	.06 .02 .05 .05 .05	03 05 05 05 07	.05	.06
osiemens p trams per 1	Sodium dis- solved (mg/L)	Mality D	е. . Э	Quality Data.	0.3 <.2	ง่ง่	0.4	r.4.0	8.8.9.8 V V V		<.2	55 V V
[μS/cm, micros μ8/L, microgre	Magne- sium dis- solved (mg/L)	Water (1.0 1.	Water (0 .1	-: - :	<.01 .06	.1 .09 .06	.06 .01 .01 .04	<pre></pre>	40.	.02
[μS/cr μ g/ L.	Calcium dis- solved (mg/L)		0 .2 0		0.1 .1	<u></u>	. 47	1.6 .76 .22	.15 .15 .17	74 09 46	.17	.17
	Acidity (mg/L as H ⁺)		11		0.1	1.2	<u>ю</u>	199		44441 44444	۲.	e.e.
	pH (stand- ard units)		3.98 4.08		4.48 4.22	4.01	3.98 4.12	3.92 3.92 4.12	44.44 44.24 2111885 311 311	4 4.09 4 4.28 4.39 4.39 4.39	3.91	3.85 3.95
	Spe- cific con- duct- ance ance (μS/cm)		44 39		15 29	45 50	48 29	60 50 30	25 24 24 24 24 24 24 24 24 24 24 24 24 24	60 48 60 18	58	65 44
	Time		0630 0930		1145 0930	0945 1035	1010 1045	1045 0945	0925 0835 1100 0915	0930 0930 0930 0915 0930	0690	- 0915 0915
	Date		SEPT 06-13 13-20		OCT 10-18 18-25	JAN 17-24 24-31	FEB 14-21 21-28	FEB 28- MAR 06 06-13 20-27	MAR 27- APR 03 03-05 05-10 10-17 17-24	APR 24- MAY 01 01-08 08-15 15-22 22-29	JUNE 12-19	JUNE 26- JULY 03 0915 03-10 0915
						22						

Table 7.--Chemical data for precipitation samples from South Fork Bens Creek near Thomasdale, 1983-86

Spe- cific	Spe- cific					Magne-		Potas-	Alka- linity		Chlo-	Flou-			Nitro- gen nitrate	Phos- phorus,	Alum-		Manga-
con- pH Calcium duct- (stand- Acidity dis- anca ard (meV. solved	pH (stand- Acidity ard (mm/1.	tand- Acidity d (me/l.		Calcium dis- solved		sium dis- solved	Sodium dis- solved	sium dis- solved	lab (mg/L	Sulfate dis- solved	ride, dis- solved	ride, dis- solvad	Bromide dis- solved	Silica, dis- solvad	dis- solved (me/l.	ortho, dis- solved	inum dis- solved	Iron, dis- solved	nese, dis- solved
cm) units) es H^+) (mg/L)	cm) units) es H^+) (mg/L)	units) es H^+) (mg/L)	(mg/L)			(mg/L)	(mg/L)	(mg/L)	caco ₃)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	as N)	(mg/L)	(µg/L)	(7/8/J)	(µg/l)
Mater Que	Hater	Water	Water	Water		Quelity	lity Date, W	Jater Yee	ir Octob	Water Year October 1983 to September 1984Continued	o Septemi	ber 1984	Continu	pe					
0900 52 3.89 0.2 0.07 0900 38 4.08 .1 .06 0900 77 3.69 .5 .15	3.89 0.2 0 4.08 1.1 3.69 .5	0.2 .1 .5	0	0.07 .06 .15		0.02 .01 .01	20.2 20.2 20.2	0.03 .04 .04	444	5.1 3.7 7.7	0.32 4.2 .26	0.03 .02	<pre>60.1 </pre>	000	0.14 .18 .18	 40.06 4.06 4.06 	30 30	11 12	44.
0930 65 3.98 .2 .2 0915 31 4.01 .2 .07	3.98 .2 .2 4.01 .2 .07	.2 .2	.07			<.01 <.01	. 2 S . 2 S	.05	₽₽	5.6 2.3	<.26 <.2	.04 03	*.1 .1		.12	<.06 <.06	20 <10	16 9	41
0935 26 4.16 .3 .09	4.16 .3	. 16 3 .	•	60'		.04	<.2	. 12	₽	2.0	.16	<.01	<.01	0	ł	<.01	10	9	ч
Ma	Ha	백	Ma	A	Ma	Water Ou	Quality Data	- 4	PL YOOL (Water Yeer October 1984	1984 to St	to September	1985						
0930 36 4.08 <0.1 <0.08 0	4.08 <0.1 <0.08	<0.1 <0.08	<0.08		o	0.05	<0.2	0.04	4	2.9	0.2	0	0	٥	ł	0	30	٢	₽
0930 13 4.41 .4 .09	4. IP.A	4. 14.		60.		.03	<.02	.01	4	1.2	. 19,	.01	<.01	0	ł	<,01	10	12	<1.0
2400 26 4.3 1030 50 4.1 .1 .2	4.3 4.1 .1	14		7		 .05	?		1.0	3.8		.02 	 .18	¦ ?	.51	- 10 .	104	¦ თ	
1000 35 4.27 .1 .2	4.27 .1	ſ.		લં		.03	.15	.05	5.	3.0	.27	.03	.01	0	.40	ł	20	ŝ	S
1200 85 4.1 .1 .1	4.1.1	۲.		۲.		. 05	4	.05	1.0	4.5	.26	.04	.02	0	.74	. 02	30	12	4
1300 47 4.01 .1 .34 1200 42 4.06 .1 .65 2400 41 3.89 .1 .3	4.01 .1 4.06 .1 3.89 .1			.34 .65 .3		.04 .14	991	.08 .03 .06	1.0 4.5	845. 849.	.2 .19	• • • • • • • • • • • • • • • • • • •	.03 .02 .02	000	84 	400 400 400	50 50 50	888 4	20 P
31	ΞI	31	31	31	3	<u>Water Qu</u>	islity De	ts. Wate	r Year (Quality Data. Water Year October 1985 to September 1985	1985 to Se	eptember	1986						
1400 11 4.6002	4.60	ł		.02		<.01	.03	.04	;	8.	.12	.01	<.01	0	.11	.07	ł	ł	ł
1115	4.4	1 5		.07 <.01		.03	.12 .24	.02	::	3.1 1.5	.37	.04	.01 .01	::	.20	.16	11	::	11

Table 7.--Chemical data for precipitation samples from South Fork Bens Creek near Thomasdale, 1983-86--Continued

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¹Sample contamination probable

Table 8.--Volume-weighted mean pH and concentrations of major ions in precipitation at four monitoring stations in the northeastern part of the study area

[mg/L, milligrams per liter; $\mu eq/L$, microequivalents per liter; --, no data available]

	<u>1984 wa</u>	South Fork ater year		eek iter year	Shenandoa 198	h Park, VA 0-81 ¹		Hill Park, PA 1984 ²		Brook, NY 84 ³
	mg/L	µeq/L	mg/L	µeq∕L	mg/L	µeq∕L	mg/L	µeq/L	mg/L	µeq/l
Calcium	0.23	11.3	0.19	9,5	0.25	12.6	0.21	10.5		
Magnesium	.04	3.3	.05	4.1	.054	4.4	.07	5.8		
Sodium	. 26	11.3	.25	10.9	.014	6	. 04	1.7		
Potassium	.06	1.5	.08	2.1	.081	2.1	.06	1.5		
pH	4.06	87.1	4.05	88.5	4.27	58.7	4.14	72.4	4.25	55
Nitrate	2.43	39.3	1.95	31.4	1.50	24.3	2.17	35	1.48	23.9
Sulfate	4.13	86	3.3	68.7	2.79	58.1	2.41	50.2	1.93	40.1
Chloride	.31	8.75	. 22	6.17	.35	9.8	.30	8.5	. 22	6.3

¹Shaffer and Galloway, 1982.

²J. Lynch, Pennsylvania State University, written commun. 1985. ³P. Murdock, U.S. Geological Survey, written commun., 1986.

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	Season ¹	Loads at South Fork, 1984	Loads at North Fork, 1985
Amount of			
precipitation	growing	751	444
	dormant	731	572
	annual	1,482	1,016
Calcium	growing	1.18	.74
	dormant	2.72	1.98
	annual	3.89	2.72
Magnesium	growing	. 25	.18
	dormant	. 39	.29
	annual	. 64	.47
Sodium	growing	1.39	.92
	dormant	2.28	1.98
	annual	3.67	2.90
Potassium	growing	. 39	.23
	dormant	.82	.47
	annual	1.21	.70
Nitrate	growing	3.48	2.07
	dormant	4.85	4.10
	annual	8.33	6.17
Sulfate	growing	34.11	20
	dormant	25.32	20.30
	annual	59.43	40.30
Hydrogen	growing	.727	. 393
	dormant	.634	.471
	annual	1.361	. 864
Chloride	growing	1.79	1.20
	dormant	2.54	2.13
	annual	4.33	3.33

Table 9.--Seasonal and annual input loads of major ions in precipitation at South Fork and North Fork Bens Creek watersheds [Units are kilograms per hectare except for amount of

precipitation, which is given in millimeters]

¹growing - May to October

dormant - November to April

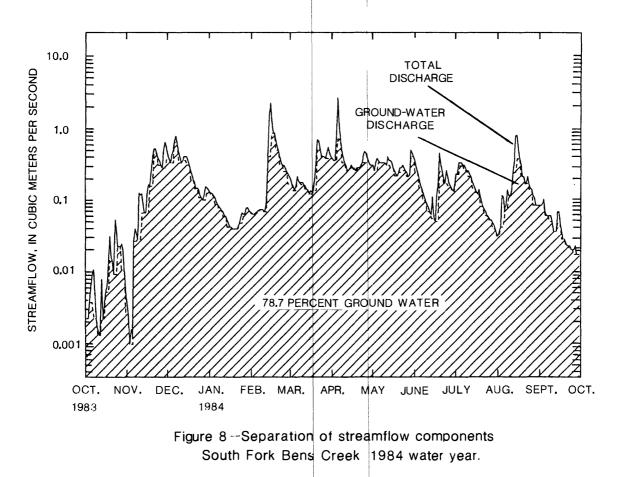
Streamflow

Quantity

Streamflow was recorded continuously at South Fork Bens Creek during the 1984-85 water year and at North Fork Bens Creek during the 1985 water year. Daily discharge in 1984 at South Fork ranged from 0.0008 m³/s to 3.2 m³/s; the maximum discharge of 5.21 m³/s was on April 5. Daily discharge in 1985 ranged from 0.01 m³/s to 1.9 m³/s; the maximum discharge of 2.78 m³/s was on March 31. The annual flow in 1984 was 0.26 m³/s compared to 0.19 m³/s in 1985.

Daily mean discharge at North Fork Bens Creek in 1985 ranged from 0.02 m^3/s to 1.87 m^3/s ; the maximum instantaneous discharge of 2.61 m^3/s was on March 31 during rain and snowmelt runoff. Annual flow was 0.17 m^3/s .

Hydrograph separation plots of daily mean discharge (figs. 8-10) by the mid-interval method of Pettyjohn and Henning (1979) show that ground-water discharge was 78.7 percent of the total discharge of South Fork Bens Creek in 1984 and 81.6 percent in 1985. The ground-water component of North Fork Bens Creek in 1985 was 81.5 percent. Despite about 30 percent less precipitation in the 1985 water year compared to the 1984 water year, the ground-water component of streamflow increased by omly about 3 percent.



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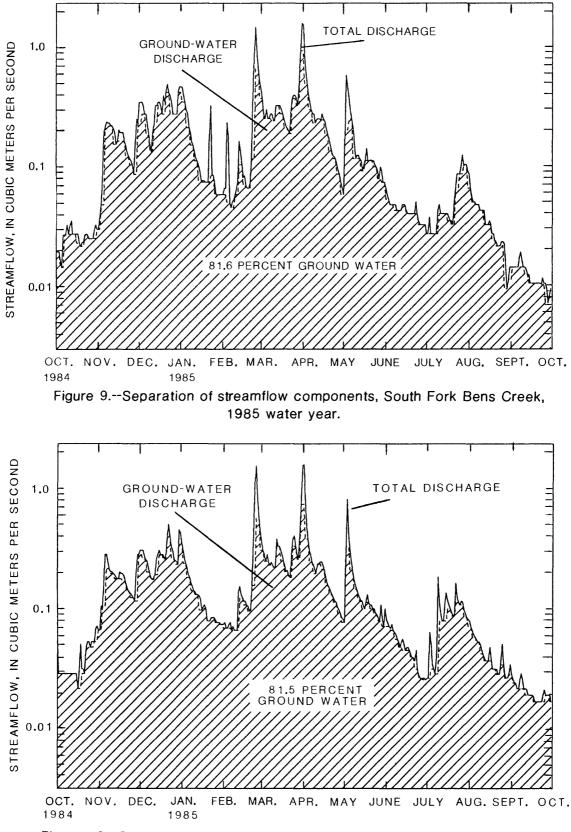


Figure 10.--Separation of streamflow components, North Fork Bens Creek, 1985 water year.

Chemistry

Monthly streamflow chemistry of the South Fork Bens Creek, North Fork Bens Creek, Garys Run, Cole Run, and North Branch Quemahoning Creek was measured over a range of flow conditions typical of the high and low base-flow periods. Temporal variability in constituent concentration of major ions is illustrated in figure 11. Concentrations of pH, acid-neutralizing capacity, (ANC), and chloride were greater during low base-flow periods when streamflow was composed predominantly of water from the saturated zone. Dissolved aluminum concentrations were greater during winter and during spring snowmelt than at other times of the year. Sulfate concentrations have no obvious seasonal or flow-related trends. Nitrate concentrations, on the other hand, increase during the dormant season in both the North Fork Bens Creek and Garys Run.

The ANC of streams on Laurel Hill, as described by DeWalle and others (1987), is a function of carbonate-rock burial depth, extent of carbonate-rock recharge areas, and length of stream channel flowing in reaches underlain by carbonate rock. The illustrations in figure 12 depict the dependence of ANC on streamflow and the variability of ANC for three streams in the study area of Laurel Hill. At low flow, when discharge is primarily from ground water, ANC values are about 4 to 5 times greater than during periods of stormflow runoff. ANC at South Fork Bens Creek averaged about 90 μ eq/L (microequivalents per liter), North Fork Bens Creek averaged about 19 μ eq/L, and Garys Run averaged about 7 μ eq/L. The other two satellite streams had no available source of buffering and, thus, no neutralizing capacity.

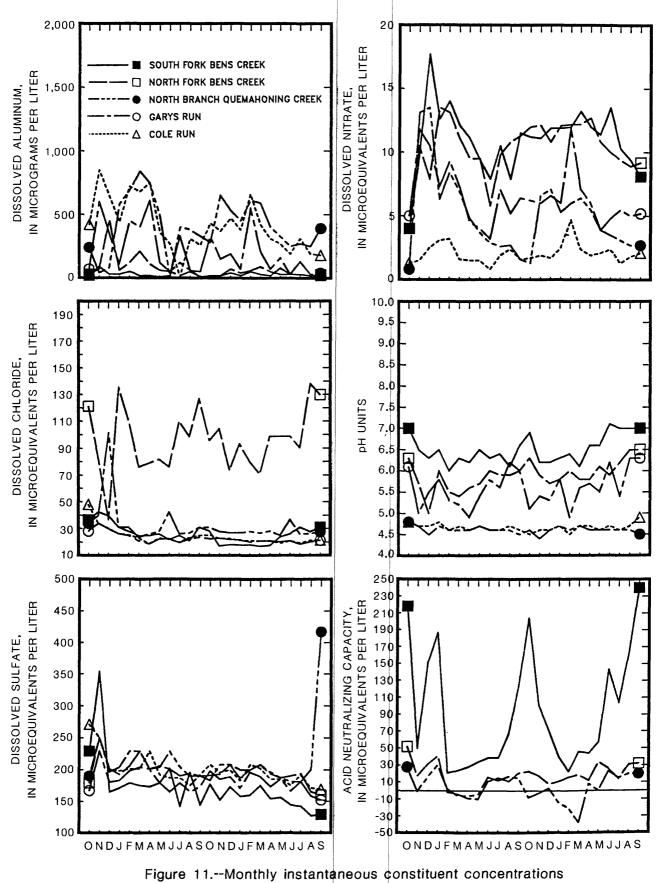
Analysis of the chemistry of the five study streams indicates there is considerable variability in the composition and degree of acidification of streams in the Laurel Hills. Cole Run and North Branch Quemahoning Creek are strongly acidic and concentrations of most constituents change little over time, whereas Garys Run, North Fork Bens Creek, and South Fork Bens Creek are less acidified. Because all the watersheds receive about the same atmospheric inputs, bedrock geology determines the rate of the acidification process. The importance of bedrock geology to the acidification process is described in detail by DeWalle and others (1987), Sharpe and others (1987), and Katz and others (1985).

The volume-weighted mean concentration of the major constituents in the South Fork, North Fork, and in precipitation (table 10) indicates there may be considerable exchange of minerals and gases between the atmospheric inputs and the watershed. Hydrogen, which was the major cation in precipitation, becomes insignificant with respect to the ionic balance of the stream chemistry. Because of the alkaline earths in the watershed soils, calcium replaces hydrogen as the dominant cation, accounting for about 40 percent of the total cationic concentration. Dissolved aluminum, which is discussed more fully in a later section, is a significant cation during periods of runoff and increased acidity.

2B

Sulfate was the dominant anion in the streams; it comprised 63 to 68 percent of the total anions on the basis of equivalents compared to about 38 percent of the total loss in precipitation, whereas nitrate accounted for only 3 or 4 percent of the total anions. Chloride accounted for 9 and 27 percent of the anions in the South Fork Bens Creek and North Fork Bens Creek, respectively. The high percentage of chloride in the North Fork may be attributed to possible contamination of the ground water by an abandoned gas well or road salt applied at the crest of the basin or both, but this was not confirmed.

The volume-weighted pH for the 1984 water year at South Fork Bens Creek ranged from 5.60 to 7.00 and averaged 6.29, and the North Fork ranged from 5.30 to 6.51 and averaged 5.68 in the 1984 water year and 5.88 in the 1985 water year. As illustrated in figures 13 and 14, the lowest pH values were associated with periods of peak runoff from precipitation and snowmelt.



during base flow, 1984-85 water years.

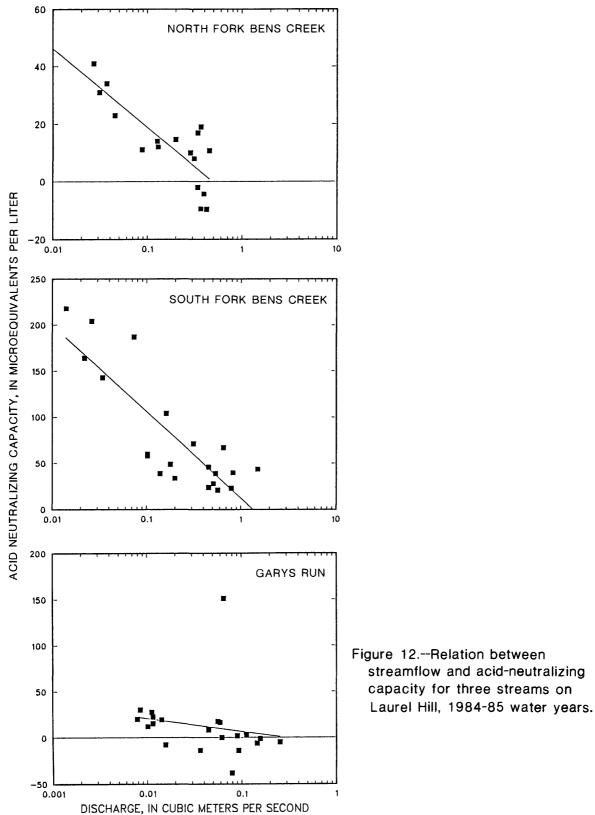


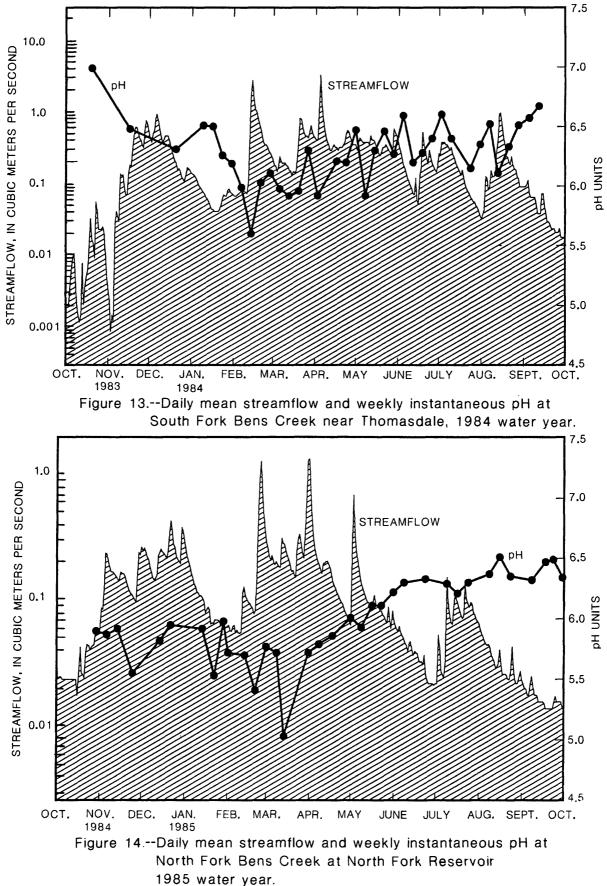


Table 10.--Volume-weighted mean concentrations of major ions and silica in precipitation and stream water, 1984-84 water years

[mg/L, milligrams per liter; µeq/L, microequivalent per liter; wy, water year; --, no data available]

		<u>Precip</u>	<u>itation</u>		rk Bens Creek <u>Thomasdale</u>		rk Bens Creek Fork Reservoir
		mg/L	µeq/L	mg/L	µeq/L	mg/L	µeq/L
Ca ⁺	1984 wy	0.23	11.3	3.5	172.16		
	1985 wy	.19	9.5			3.4	170.28
Mg ⁺	1984 wy	.04	3.3	1.1	86.38		
U	1985 wy	.05	4.1			.96	78.97
Na ⁺	1984 wy	. 26	11.3	.6	23.93		
	1985 wy	.25	10.9			1.4	60.9
к+	1984 wy	.06	1.5	.73	18.67		
	1985	.08	2.1			.61	15.6
NН ₄ +	1984 wy			.05			
4	1985 wy						
н ⁺	1984 wy		87.1		.513		2.09
	5		(pH 4.06)		(pH 6.29)		(pH 5.68)
	1985 wy		88.5 (pH 4.05)				1.32
			-				
^{NO} 3-	1984 wy	2.43		3.01	48.5		
-	1985 wy	1.95	31.4			3.05	49.3
so _{4 -}	1984 wy	4.13	86	9.1	189.55		
4 -	1985 wy	3.3	68.7			9.6	200
C1 ⁻	1984 wy	.31	8.75	.99	27.93		
	1985 wy	. 22	6.17			3	84.63
HCO3-	1984 wy				73		12
3-	1985 wy				96		24
Si0 ₂	1984 wy			3.48			
SBC ¹	1984 wy		27.4		301		
000	1984 wy 1985 wy		27.4				326

¹SBC = Sum of base cations (Ca + Mg + Na + K)



Water Budgets

Table 11 summarizes the monthly water-budget estimates for the study period. Runoff at South Fork Bens Creek was about 67 percent of precipitation during 1984 and 1985 and about 59 percent at North Fork in 1985. Evapotranspiration plus change in storage for the study area averaged about 420 mm per year, or 36 percent of precipitation (Kohler and others, 1959).

Chemical Budgets

Results of chemical loading, outflow, and net flux, summarized in figures 15 and 16 and tables 12 and 13, indicate a net loss of base cations, sulfate, and chloride, and a net accumulation of nitrate in both basins. Some of the apparent net losses may be because of the unmeasured dry deposition component in the precipitation load calculation.

Sulfate output from both the South Fork and North Fork basins greatly exceeded wet-deposition loads. Wet deposition loads can account only for about 77 percent of the output in the South Fork basin in 1984 and 1985, respectively. The net outputs not accounted for are from natural sources within the watershed and from dry deposition of unknown quantities.

The Running Net Flux (RNF) for sulfate is depicted in figures 15 and 16, which illustrate seasonal change in slope for net flux in 1984 and 1985. Sulfate was nearly steady state (RNF=0) during the period of snow cover; large releases of sulfate occurred during snowmelt periods and net accumulations occurred during the growing season. This pattern is nearly identical to the one observed in the Catskill Mountains of New York (Murdoch, P.S., U.S. Geological Survey, written commun., 1986).

The net flux for nitrate shows that about 46 percent was retained in the South Fork and about 50 percent was retained in the North Fork ecosystems. Some evidence of a seasonal pattern in nitrate flux can be observed in the RNF plots for South Fork Bens Creek and North Fork Bens Creek (figs. 15 and 16). Negative slopes of the NO₃ RNF in February and March indicate release of NO₃ from the melting snow pack or from leaf litter. Positive slopes in late spring and summer indicate periods of rapid assimilation when biological productivity is high.

Chloride, as pointed out by Galloway and others (1983), commonly is used as an atmospheric tracer in watershed studies because of its naturally low concentration in rock and soil and its low reactivity. The negative accumulation running net flux and retention indices indicate a net loss of chloride from South Fork and North Fork watersheds. The high chloride yields from North Fork watershed, as pointed out earlier, may derive from an abandoned gas well or from road-deicing salt.

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The net losses of cations and sulfate from both watersheds are typical of those observed elsewhere in the northeastern U.S. (Murdoch, P.S., U.S. Geological Survey, written commun., 1986; Galloway and others, 1983). The periodic large negative flux of constituents illustrated in figures 14 and 15 is associated with episodic runoff from snowmelt and storms. Calcium and magnesium, principally from the chemical disassociation and replacement of minerals in the soils account for 99 percent of the total base-cation flux in the South Fork and 74 percent in the North Fork basin. The net-flux data presented in tables 11 and 12 indicate that nearly all the hydrogen ions available from precipitation are retained by the watershed.

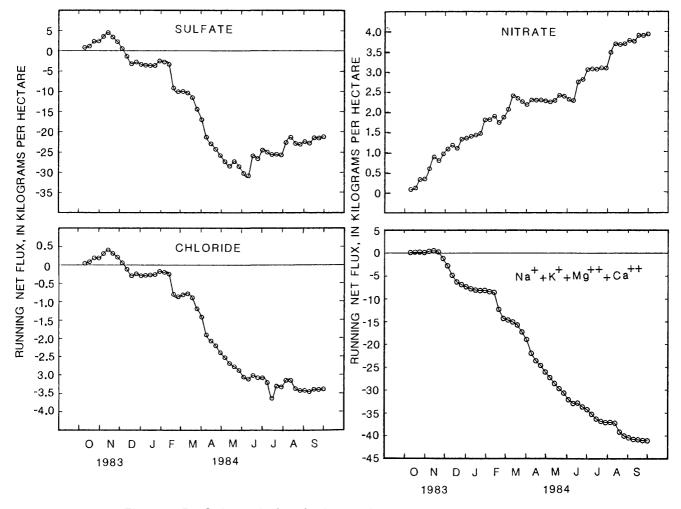


Figure 15.--Selected chemical-constituent net flux for 1984 water year, South Fork Bens Creek near Thomasdale.

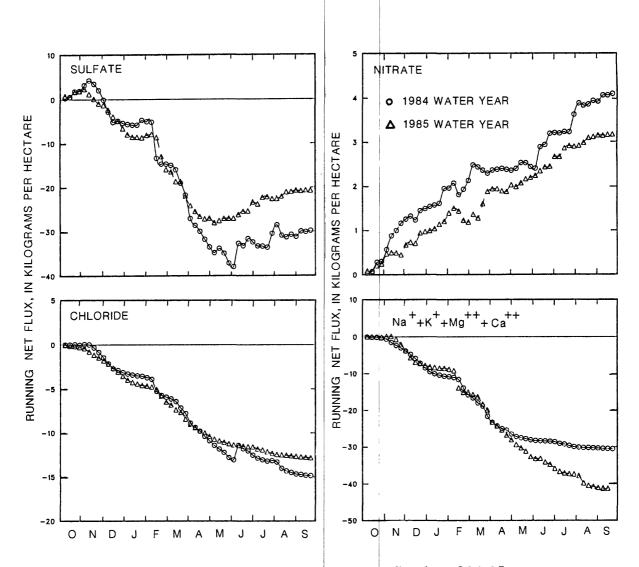


Figure 16.--Selected chemical-constituent net flux for 1984-85 water years, North Fork Bens Creek at North Fork Reservoir.

	Month	Precipitation (mm)	Runoff (mm)	Evapotranspiration + Δ storage (mm)
<u></u>	······································	South Fork Bens Creek	near Thomasdale	
1984 wy	October	104.9	07.9	97.0
	November	159.5	76.2	83.3
	December	134.4	115.1	19.3
	January	61.2	27.2	34.0
	February	107.2	146.3	-39.1
	March	110.2	103.6	6.6
	April	158.5	166.6	-8.1
	May	157.0	114.3	42.7
	June	163.1	61.7	101.4
	July	83.3	60.2	23.1
	August	174.0	76.2	97.8
	September	68.8	18.8	5.0
	Total	1,482.1	974.1	508.0
Growing season		751.1		
Nongrowing season		731.0		
1985 wy	October	62.7	13.5	49.2
	November	87.6	59.2	28.4
	December	120.7	117.9	2.8
	January	70.1	62.2	7,9
	February	53.6	84.6	-31.0
	March	201.4	136.7	64.7
	April	51.8	106.2	-54.4
	May	132.6	60.2	72.4
	June	54.9	18.5	36.4
	July	144.3	22.9	121.4
	August	57.4	16.0	41.4
	September	17.0	<u>6.6</u>	10.4
	Total	1,054.1	704.5	349.6
Growing season Nongrowing season		468.9 585.2		
	No	rth Fork Bens Creek at N	orth Fork Reserv	<i>v</i> oir
1985 wy	October	62.7	11.9	50.8
-	November	87.6	56.6	31.0
	December	120.7	95.3	25.4
	January	73.2	43.7	29.5
	February	54.4	77.0	-22.6
	March	180.8	113.0	67.8
	April	54.9	85.6	-30.7
	May	143.3	53.3	90.0
	June	41.9	14.2	27.7
	July	131.8	28.2	103.6
	August	53.1	13.0	40.1
	September	<u>11.4</u>	05.8	05.6
	Total	1,015.8	597.6	418.2
Growing season		444.2 571.6		
Nongrowing season				

Table 11.--Monthly water-budget estimates for the 1984-85 water years at the Bens Creek sites

[mm, millimeter; Δ , change]

Table 12.--Summary of annual input and output flux for precipitation and streamflow at South Fork Bens Creek in 1984 water year

	PPT input	Output	Net flux	Retention index (RI) ¹
H ₂	1,482	974	+	
Calcium	3.89	30.57	-26.77	-6.88
Magnesium	.64	8.81	-8.17	-12.77
Sodium	3.67	4.49	-0.82	22
Potassium	1.21	6.11	-4.90	-4.05
Nitrate	8.33	5.61	3.85	.46
Sulfate	59.43	76.81	-22.5	38
Chloride	4.33	8.13	-3.50	81
Hydrogen	1.361	.013	1.348	.99
SBC ²	9.41	49.99	-40,58	-4.31

[Units are kilograms per hectare except for water, which is in millimeters. Positive net flux values represent accumulation in the watershed.]

¹ RI = $\frac{\text{Net Flux}}{n}$ $\Sigma \text{ (inputs)}_{i=1}$

² SBC = Sum of base cations (Ca + Mg + Na + K)

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Table 13.--Summary of annual input and output flux for precipitation and streamflow at North Fork Bens Creek in 1984-85 water years¹

[Units are kilograms per hectare except for water, which is in millimeters. Positive net-flux values represent accumulation in the watershed, negative net-flux values represent loss in the watershed; --, no data available]

	1	PPT						ntion
	i	nput	Out	put	Net	flux	inde:	$(RI)^2$
	1984	1985	1984	1985	1984	1985	1984	1985
H ₂ O	1,482.1	1,015.7	974.1	598				
Calcium	3.89	2.72		21.24		-18.52		-6.8
Magnesium	.64	.47		5.77		-5.30		-11.3
Sodium	3.67	2.90		8.19		-5.29		-1.8
Potassium	1.21	.70		3.84		-3.14		-4.5
Nitrate	8.33	6.17	4.34	3.02	4.09	3.13	.5	.5
Sulfate	59.43	40.30	88.84	62.26	-29.84	-20.74	5	5
Chloride	4.33	3.33	20.89	16.21	-14.86	-12.87	-3.8	-3.9
Hydrogen	1.36	.86	. 13	.16	1.35	. 85	. 99	.98
SBC ³	9.41	6.79	50,62	39.04	-41.36	-30.57		-4.5

¹1984 water year values calculated by correlation-analysis procedures.

$$2_{RI} = \frac{Net flux}{n}$$
$$\sum_{i=1}^{n} (inputs)_{i}$$

³SBC = Sum of base cations (Ca + Mg + Na + K).

EFFECTS OF ACIDIC PRECIPITATION ON THE WATER QUALITY OF STREAMS IN THE LAUREL HILL AREA

Part of this study was devoted to observing the response of chemistry to stormflow. To do this, both primary sites, South Fork Bens Creek and North Fork Bens Creek, were instrumented for sampling water quality during selected precipitation events. South Fork Bens Creek was stormflow sampled from September 1983 through October 1984; North Fork Bens Creek was sampled from October 1984 through February 1986. Funding was not available for a two-site stormflow sampling program during the first year of study. During the second year of study both sites were to be sampled concurrently so variations in chemical response between the sites could be compared. However, the installation of a production well within the South Fork Bens Creek basin, as previously discussed, compromised the water-quality data for that site. None of the other first order streams in the area could be substituted to do concurrent sampling. The stormflow sampling aspect of this study was done to provide evidence of stream chemistry change using only physical and chemical data collected from each stream. An in-depth interpretation with conclusions based on geochemical stability, solubility, and dissolution kinetic relationships cannot be made because no soilwater, ground water, or solid-phase data were collected. Consequently, much uncertainty exists about the nature of acid precipitation in relation to the weathering of soils and bedrock. In addition, it must be realized that although the theme of the following discussion is directed towards exogenous sources of chemical constituents to the basins, there are a number of endogenous sources that were not investigated.

Relations Among pH, Chemical Concentration, and Discharge

The analyses of 14 rainfall and snowmelt runoff events in the South Fork and North Fork Bens Creek basins show that their response to such events with respect to discharge is similar despite and other characteristics in the basins. measured by the change in concentration sulfate, chloride, iron, and manganese, saturation of the unconsolidated zone in addition to other factors, such as season, magnitude and duration of rainfall, and weather pattern.

Throughout the study, pH was related inversely to runoff (figs. 17 and The decreases in pH during periods of rapid, short-duration thunderstorm 18). runoff were smaller than the decreases during prolonged snowmelt runoff. Recovery of pH to prerunoff values from peak discharge values depended on the magnitude and type of precipitation event. Generally, pH recovery for storms of short duration was related directly to discharge recovery, whereas pH recovery for rainfall and snowmelt of long duration took as long as one week after discharge receded to base flow. During the initial stages of major runoff events, pH increased slightly before decreasing. Repeated recurrence of this phenomenon suggest that water "pooled" within the unconsolidated zone during gradual ice and snow melt lost much of its hydrogen ion content as a result of extended residence in the deeper soil horizons and then was displaced by the initial volumes of storm water. Examples of streamflow response during runoff events at South Fork and North Fork Bens Creek are illustrated in figure 19.

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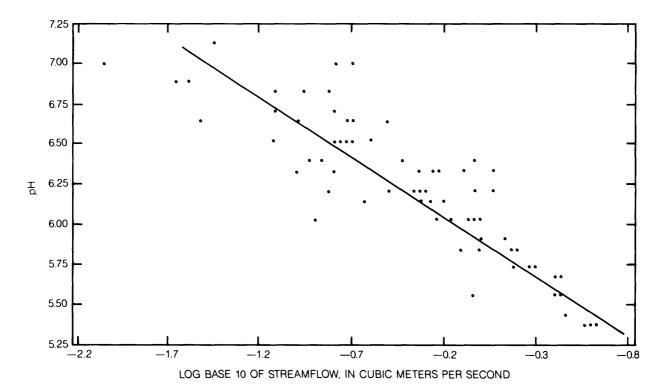


Figure 17.--Relation between streamflow and pH for the South Fork Bens Creek near Thomasdale.

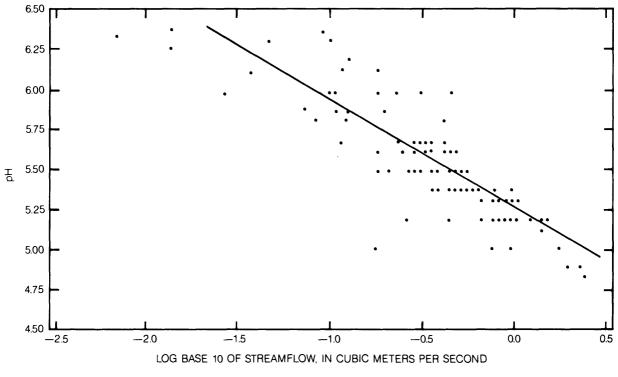


Figure 18.--Relation between streamflow and pH for the North Fork Bens Creek at North Fork Reservoir.

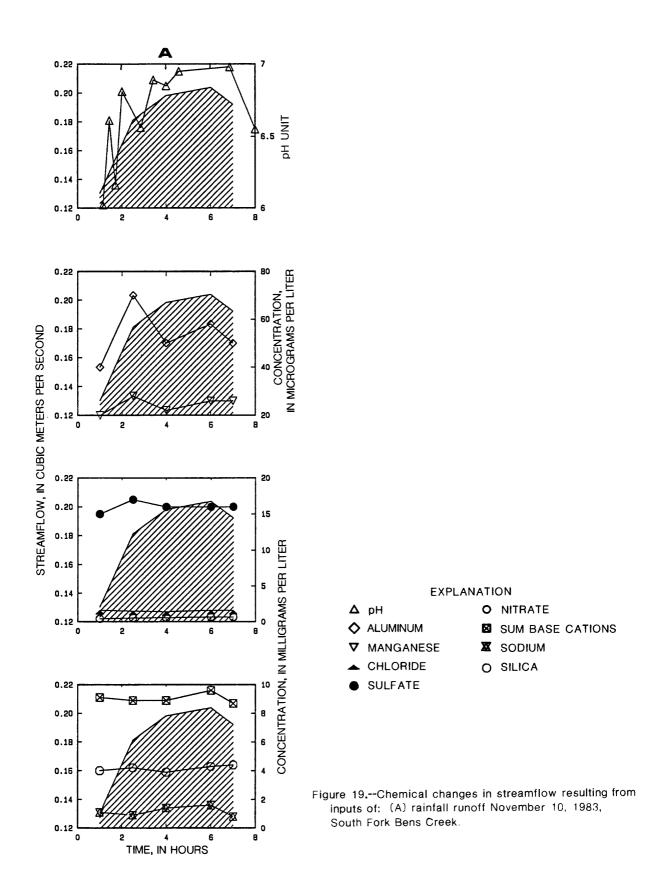
Concentrations of aluminum, iron, and manganese were related directly to discharge, whereas chloride concentrations and pH were related inversely to discharge. Aluminum concentrations increased the most during long-duration rainfall episodes that came from the west. Dissolved aluminum reached concentration potentially toxic to fish in four of the five streams at least once during the 2 1/2-year study period.

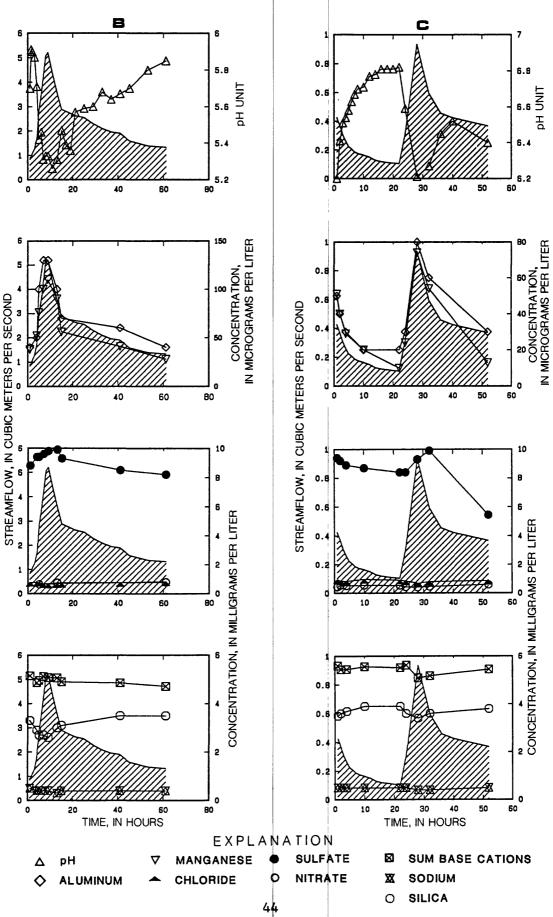
The sum of base cations decreased during peak runoff periods for four of the six storms on the South Fork Bens Creek. The sum of base cations slightly increased during the peak of snowmelt and rainfall runoff of April 4-7, 1984 (fig. 19-B). The results from the May 2-3, 1985 event (fig. 19-E) deviated from the response trends.

Base cations for the North Fork Bens Creek responded similarly (figs. 19-G thru M). Concentrations of the base cations and silica decreased during the peak runoff in seven of eight events. The March 12-13, 1985 (fig. 19-I) event was a short-duration, low-magnitude storm; therefore, increased concentrations of base cations and silica during peak flow could result from "flushing" of the unconsolidated zone. This "flushing" or displacement is similar to that described by Edwards (1973) and Walling and Foster (1975). The "flushing effect" is not uncommon, particularly during autumn, when the decrease in concentrations may be preceded by a rise or an initial drop may be followed by an increase before giving way to a subsequent decrease (Walling and Foster, 1975). The "flushing effect" observed in this study is discussed later in the report.

Sulfate concentration generally was related directly to discharge during all rainfall events, but no such relation was observed during snowmelt runoff. The response of sulfate concentrations to discharge was similar to that of other constituents studied in that the magnitude of discharge did not dictate the magnitude of change in concentration. Concentrations of sulfate increased during runoff events preceded by a prolonged period of dry weather (figs. 19-C and G), probably because of the washout of dry deposition that built up on the soils and vegetation during the extended dry periods. The elevated densities of sulfur dioxide emitted to the atmosphere west of the study area (fig. 2) correlates well with the elevated percentages of sulfate found in the wet deposition samples. Statistical analysis of sulfate and pH on an event basis has shown significant correlation for all runoff episodes. Therefore, sulfuric acid was determined to be the largest contributor of hydrogen ion to stream acidity during rainfall runoff.

Nitrate concentrations generally did not increase during any of the rainfall/runoff episodes. In some instances nitrate decreased during episodic discharge. However, nitrate concentrations did increase during one period of snowmelt runoff (fig. 19-M) and was significantly correlated with pH. Nitrate concentrations have been shown to be greater than sulfate concentrations in snowpacks near the study area (DeWalle and others, 1983). Therefore, nitric acid contributes to stream acidity during snowmelt runoff. Sources of nitrate within the snowpack were not examined; however, they are believed to be a combination of atmospheric inputs, leaf litter leachate, and microbial action within the detrital layer beneath the snowpack. Graphic presentations and data tables of all runoff events sampled are shown in figure 19 and tables 14 and 15.





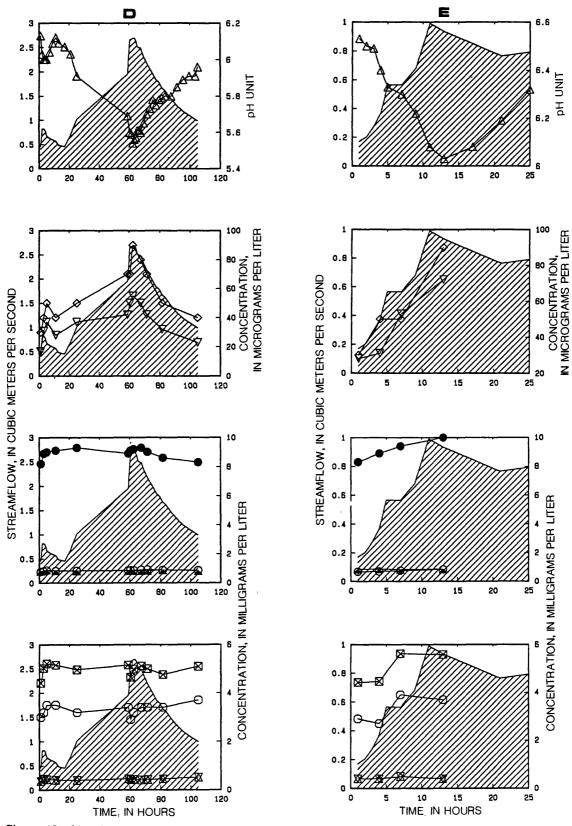
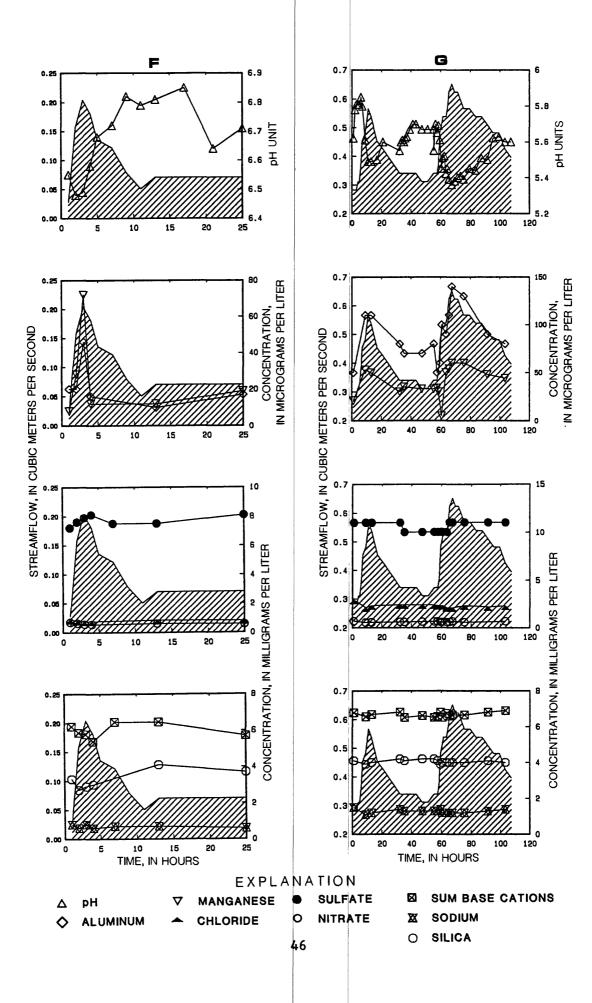


Figure 19 .-- Chemical changes in streamflow resulting from inputs of:

- (B) snowmelt and rainfall runoff April 4-7, 1984 South Fork Bens Creek:
- (C) rainfall runoff June 17-20, 1984, South Fork Bens Creek;
- (D) rainfall runoff March 29 to April 2, 1985, South Fork Bens Creek;
- (E) rainfall runoff May 2-3, 1985, South Fork Bens Creek -- Continued.



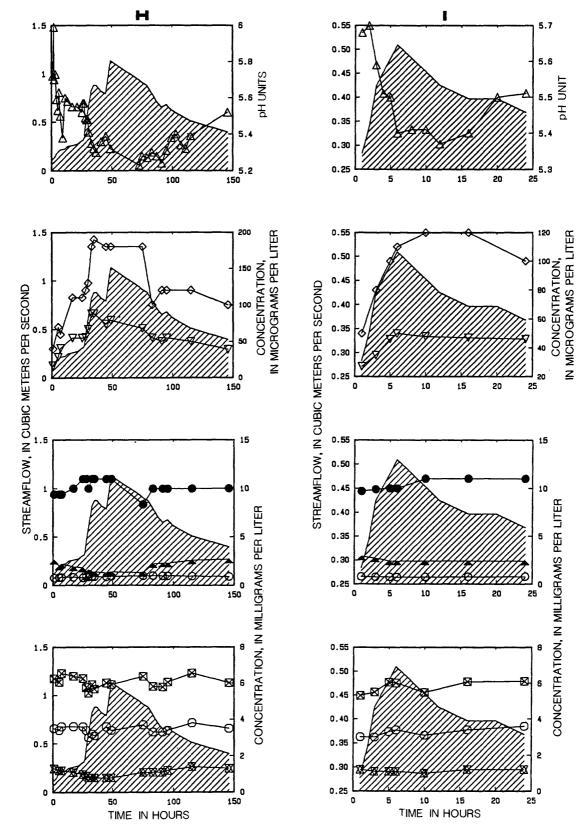
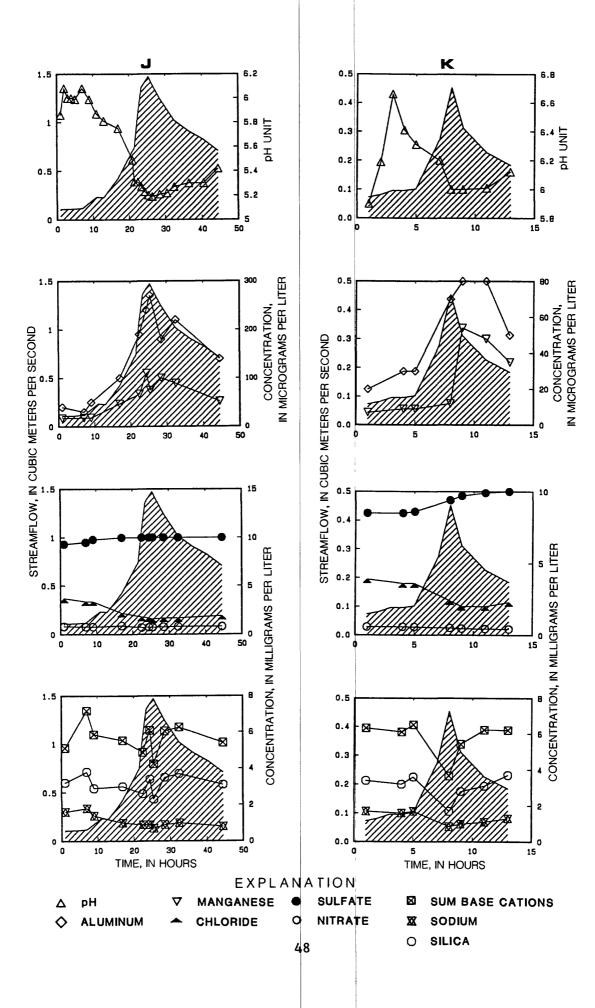


Figure 19.--Chemical changes in streamflow resulting from inputs ot:

- (F) rainfall runoff July 21-22, 1985, South Fork Bens Creek;
- (G) rainfall runoff December 19-21 and 21-23, 1984, North Fork Bens Creek;
- (H) snowmelt runoff February 22 to March 1, 1985, North Fork Bens Creek;
- (I) rainfall runoff March 12-13, 1985, North Fork Bens Creek-- Continued.



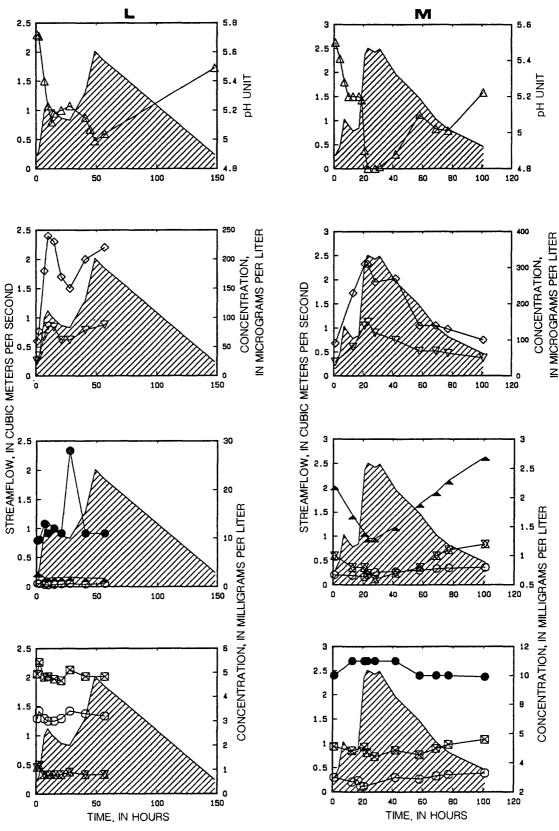


Figure 19.--Chemical changes in streamflow resulting from inputs of: (J) rainfall runoff May 2-4, 1985, North Fork Bens Creek; (K) rainfall runoff July 8-9, 1985, North Fork Bens Creek; (L) rainfall runoff November 26-28, 1985, North Fork Bens Creek: (M) snowmelt runoff February 4-8, 1986, North Fork Bens Creek --Continued.

 $[m^3/s,$ cubic meters per second; μ^3/cm , microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; μ_g/L , micrograms per liter; <, less than; --, indicates no data]

Date	Time	Stream- flow, instan- taneous (m ³ /s)	Spe- cific con- duct- ance (µS/cm)	pH (stand- ard units)	Acidity (mg/L as H ⁺)	Calcium, dis- solved (mg/L)	Magne- sium, dis- solved (mg/L)	Sodium, dis- solved (mg/L)	Potas- sium, dis- solved (mg/L)	Alka- linity, lab (mg/L as CaCO ₃)	Sulfate dis- solved (mg/L)
NOV						1983					
	1500	0.13	54	6.02	<0.1	6.5	1.5	1.1		10.0	15
10 10	1515	0.13	53	6.61	~0.1	0.5	1.5	1.1		10.0	15
10	1530	. 15	53 56	6.16	<.1						
10	1545		58	6.81			·				
10 10 10 10	1600										
10	1630	. 18	54	6.56	.1	6.5	1.5	.90	1.1	9.0	17
10	1700		57	6.89							
10	1730		59	6.85							
10 10	1800	. 20	57	6.95	.1	6.1	1.4	1.4		10.0	16
10	1900										
10 10	2000	.20	59	6.98	<.1	6.4 6.3	1.6	1.6		9.0	16
10	2100	. 19	60	6.55	<.1	6.3	1.6	. 80		8.0	16

Nitro-

Date	Chlo- ride, dis- solved (mg/L)	Fluo- ride, dis- solved (mg/L)	Bromide, dis- solved (mg/L)	Silica, dis- solved (mg/L)	gen ammonia, dis- solved (mg/L as N)	Phos- phorus, ortho, dis- solved (mg/L)	Alum- inum, dis- solved (µg/L)	Iron, dis- solved (μg/L)	Manga- nese, dis- solved (µg/L)	Carbon, organic, dis- solved (mg/L)	Nitrogen nitrate, dissolved (mg/L as N)
NOV											
10	1.6	0.01	<0.1	4.0	0.018	<0.06	40	36	20	4.0	0.41
10							-+				
10					.019	<.001	-+			3.6	
10							-+				
10	·						-+				
10	1.5	.09	<.1	42	.042	<.06	70	33	28	3.4	. 54
10							-+				
10							-+				
10	1.4	<.01	<.1	3.9	. 198	<.06	50	40	22	4.3	. 55
10							-+				
10 10 10 10 10 10 10 10	1.6	.09	<.1	4.3	.065	<.06	58 50	27	26	3.6	.66
10	1.6	.07	<.1	4.4	.029	<.06	50	25	26	4.2	.67

50

 $[m^3/s]$, cubic meters per second; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; μ g/L, micrograms per liter; <, less than; --, indicates no data]

		Stream- flow, instan- taneous	Spe- cific con- duct- ance	pH (stand- ard	Acidity (mg/L	Calcium, dis- sclved	Magne- sium, dis- solved	Sodium, dis- solved	Potas- sium, dis- solved	Alka- linity, lab (mg/L as	Sulfate, dis- solved
Date	Time	(m ³ /s)	$(\mu S/cm)$	units)	as H ⁺)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	CaCO ₃)	(mg/L)
	<u>-</u> -					1984					·····
APR 04	1715	0.91	34	5.70	<0.1	3.0	0.93	0.50	0.72	3.0	8.8
04 04	1745 1815	.93 1.08	35 33	5.91 5.90							
04	1915	1.27	33	5.87							
04 04	2015 2115	1.70 2.86	34 34	5.71 5.42	<.1 <.1	2.9 3.0	.90 .86	. 40 . 40	.66 .69	3.0 3.0	9.4 9.4
04	2215	3.48	36	5.46							
04	2315	4.25	36	5.31	<.1 	3.1	.88	.40	.74	2.0	9.6
05 05	0015 0115	5.07 5.21	36 36	5.33	<.1	3.1	.82	.40	.75	2.0	9.8
05 05	0315 0515	4.36 3.57	38 37	5.26 5.31	<.1	3.1	.92	.30	.74	2.0	9.9
05	0715	2.89	37	5.47	<.1	2.9	.88	.40	.72	2.0	9.3
05 05	0915 1115	2.80 2.72	35 34	5.39 5.36							
05 05	1315 1715	2.63 2.55	34 35	5.57 5.59							
05	2115	2.29	34	5.60							
06	0115 0515	2.09 1.95	35 34	5.68							
06 06	0915	1.90	34	5.64 5.67	<.1	2.8	.95	.40	.71	2.0	8.5
06 06	1315 2115	1.59 1.39	34 32	5.70 5.80							
07	0515	1.33	32	5.85	<.1	2.7	. 90	. 40	.71	3.0	8.2
				- Tulutt C	Nitro-	į					
					gen	Phos-					
	Chlo-	Fluo-			ammonia,		Alum-		Manga-	Carbon,	Nitrogen
	ride,	ride,	Bromide,	Silica,	dis-	ortho,	inum,	Iron,	nese,	organic,	nitrate,
	dis-	dis-	dis-	dis-	solved	dis-	dis-	dis-	dis-	dis-	dissolved
	solved	solved	solved	solved	(mg/L	solved	solved	solved	solved	solved	(mg/L
Date	(mg/L)	(mg/L)	(mg/L)	(mg/L)	as N)	(mg/L)	(µg/L)	(µg/L)	(µg/L)	(mg/L)	as N)
APR	- <u></u>			<u> </u>							
04	0.78	<0.01	<0.1	3.3	0.062	<0.06	40	27	38	1.5	
04											
04 04											
04	. 77	.04	<.1	2.9	. 157	<.06	50	14	52	3.7	
04 04	.78	.05	.1	2.7		<.06	100	18	76 		0.64
04	. 67	.06	<.1	2.7	.180	<.06	130	35	100	2.6	
05 05	 .66	.04	<.1	2.6	 .161	 <.06	 130	 18	 110	2.2	
05											
	.68 .72	.06 .05	<.1 <.1	3.0 3.1	.047	<.06 <.06	100 70	17 6	90 56	2.0	.75
05											
05 05 05											
05 05 05 05											
05 05 05 05 05 05											
05 05 05 05 05 05 05	 	 									
05 05 05 05 05 05 05 05											
05 05 05 05 05 05 05 05 06 06	 .77	 	 <.1	 3.5	 	 <.06	 60	 10	 41	 	
05 05 05 05 05 05 05 05 05 06	 	 	 		 	 	 			 	

 $[m^3/s, cubic meters per second; \mu^5/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; <math>\mu$ g/L, micrograms per liter; <, less than; --, indicates no data]

Date	Time	Stream- flow, instan- taneous (m ³ /s)	Spe- cific con- duct- ance (µS/cm)	pH (stand- ard units)	Acidity (mg/L as H ⁺)	Calcium, dis- solved (mg/L)	Magne- sium, dis- solved (mg/L)	Sodium, dis- solved (mg/L)	Potas- sium, dis- solved (mg/L)	Alka- linity, lab (mg/L as CaCO ₃)	Sulfate, dis- solved (mg/L)
						1984					
JUNE 17 17	2300 2400	0.42 .37	37 35	6.20 6.41	<0.1 <0.1	3.2 3.3	0.94	0.50 .50	0.96 .69	3.0 4.0	9.4 9.2
18 18 18 18 18 18 18 18 18 18 18 18 18 1	0100 0200 0300 0500 0600 0800 1000 1200 1400 1600 1800 2200 2200 0200 0600	.31 .26 .22 .19 .18 .16 .15 .13 .12 .11 .10 .31 .93 .59	34 34 35 35 34 34 34 34 34 34 34 34 34 34 32 33	6.51 6.54 6.58 6.63 6.67 6.70 6.71 6.78 6.81 6.81 6.81 6.82 6.59 6.21 6.27	<0.1 <0.1 <0.1 <0.1 <0.1 <0.1 <0.1 <0.1	3.3 	.96 .96 1.0 .95 .92 .94	.50 .50 .50 .50 .50 .40	.69 .70 .72 .87 .67 .64	4.0 5.0 4.0 4.0 3.0 4.0	8.9 8.7 8.4 8.4 9.3 9.9
19 19	1000 1400	.46	34 33	6.45 6.52							
20	0200	. 37	34	6.40	<0.1	3.3	.97	. 50	.68	3.0	8.7
Date	Chlo- ride, dis- solved (mg/L)	Fluo- ride, dis- solved (mg/L)	Bromide, dis- solved (mg/L)	Silica, dis- solved (mg/L)	Nitro- gen ammonia, dis- solved (mg/L as N)	Phos- phorus, ortho, dis- solved (mg/L)	Alum- inum, dis- solved (µg/L)	Iron, dis- solved (μg/L)	Manga- nese, dis- solved (µg/L)	Carbon, organic, dis- solved (mg/L)	Nitrogen nitrate, dissolved (mg/L as N)
JUNE											
17 17	0.96 .84	0.04 .03	<0.1 <0.1	3.5 3.6		<.06 <.06	50 40	12 13	51 40		0.43 .54
18 18 18 18 18 18 18 18 18 18 18 18 18 1	.83 .97 .97 .90 .84 .69 .79 	.03 .05 .03 .04 .05 .05	<0.1 	3.7 3.9 3.9 3.6 3.4 3.7 			30 	8 8 8 20 21 10 	29 20 10 24 74 54 		.51 .55
20	. 86	.05	<0.1	3.8		<.06	30	8	13		. 59

 $[m^3/s,$ cubic meters per second; $\mu S/cm,$ microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; $\mu g/L$, micrograms per liter; <, less than; --, indicates no data]

Date	Time	Stream- flow, instan- taneous (m ³ /s)	Spe- cific con- duct- ance (µS/cm)	pH (stand- ard units)	Acidity (mg/L as H ⁺)	Calcium, dis- solved (mg/L)	Magne- sium, dis- solved (mg/L)	Sodium, dis- solved (mg/L)	Potas- sium, dis- solved (mg/L)	Alka- linity, lab (mg/L as CaCO ₃)	Sulfate dis- solved (mg/L)
MAR						1985					
29	0530	0.45	34	6.13	0.016	2.6	0.85	0.37	0.59	1.1	8.2
29	0630	. 82	34	6.03							
29 29	0730 0830	.82 .79	35 34	6.00 6.00	.018	2.9	.94	.47	.71	.60	8.9
29	0930	.68	35	6.00	.016	3.1	1.0	.43	.68	.70	9.0
29	1130	. 62	35	6.04							
29	1330	. 59	36	6.09							
29 29	1530 1730	. 57	36 36	6.12 6.09	.015	3.1	1.0	.41	.64	.80	9.1
29	2130	.45	36	6.07							
30	0130	.71	37	6.03							
30	0530	1.02	36	5.91	.017	3.0	.94	. 40	. 62	. 50	9.3
31	1530	1,95	36	5.69	.026	3.0	. 96	.46	.73	. 50	8.9
31	1700	2.66	36	5.60	.026	2.7	.85	. 42	.67	. 50	9.1
31	1800	2.66	38	5.59							
31 31	1900 2000	2.69 2.69	37 37	5.54 5.56	.024	2.9	.93	.43	.72	. 50	9.2
31	2100	2.63	39	5.57							
31	2200	2.52	37	5.61							
31	2300	2.49	36	5.61							
31	2400	2.49	38	5.60	.024	3.0	. 98	.41	.72	. 50	9.3
APR											
01	0200	2.32 2.18	37	5.65							
01	0400	2.18	37	5.70							
01 01	0600 0800	2.07 1.95	36 36	5.73 5.78	.020	2.9	.95	.42	.72	. 50	9.0
01	1000	1.84	35	5.75							
01	1200	1.78	36	5.78							
01	1400	1.67	35	5.79							
01 01	1600 2000	1.61 1.44	35 35	5.80 5.0	.016	2.7	.90	.45	.70	. 50	8.6
01	2400	1.30	35	5.85							
02	0400	1.19	34	5.89							
02	0800	1.10	34	5.91							
02 02	1200	1.02 .99	34 33	5.91	.017	2.8	 .98		70		8.3
02	1430	.99	33	5.96	.017	2.8	.98	. 52	.79	. 50	8.

 $[m^3/s,$ cubic meters per second; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; μ g/L, micrograms per liter; <, less than; --, indicates no date]

Date	Chlo- ride, dis- solved (mg/L)	Fluo- ride, dis- solved (mg/L)	Bromide, dis- solved (mg/L)	Silica, dis- solved (mg/L)	Nitro- gen ammonia, dis- solved (mg/L as N)	Phos- phorus, ortho, dis- solved (mg/L)	Alum- inum, dis- solved (μg/L)	Iron, dis- solved (μg/L)	Manga- nese, dis- solved (μg/L)	Carbon, organic, dis- solved (mg/L)	Nitrogen nitrate, dissolved (mg/L as N)
						1985	1			· · · · · · · · · · · · · · · · · · ·	
MAR											
29	0.8	0.07	0.02	3.0	0.011	0.001	30	5	17	0.70	0.78
29 29	 .86	.06	.03	3.2	.006	.001	 40	 6	31	1.2	.82
29											
29 29	.90	.06	.03	3.5	.005	.001	50	5	37	1.0	.88
29											
29 29	.86	.07	.03	3.5	.005	.001	40	4	28	.90	.83
29											
30											
30	. 84	.05	.03	3.2	.01 0	.002	50	5	37	.80	.85
31	. 84	.05	.02	3.4	.014	.001	70	5	42		.86
31 31	.83	.05	.02	2.9	.029	.001	70	5	50		.88
31	.83	.05	.02	3.2	.034	.001	90	5	55		.88
31											
31 31											
31											
31	. 84	.05	.02	3.4	.008	.001	80	4	50		.91
APR											
01											
01	. 84	.06	.03	3.4	.010	.001	70	4	42		.91
01 01											
01											
01											
01	.89	.05	.03	3.4	.009	.001	50	3	32		.89
01 01											
01											
02											
02 02											
02	. 84	.05	.03	3.7	.008	.001	40	4	23		. 87

 $[m^3/s,$ cubic meters per second; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; μ g/L, micrograms per liter; <, less than; --, indicates no data]

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Date	Time	Stream- flow, instan- taneous (m ³ /s)	Spe- cific con- duct- ance (µS/cm)	pH (stand- ard units)	Acidity (mg/L as H ⁺)	Calcium, dis- solved (mg/L)	Magne- sium, dis- solved (mg/L)	Sodium, dis- solved (mg/L)	Potas- sium, dis- solved (mg/L)	Alka- linity, lab (mg/L as CaCO ₃)	Sulfate dis- solved (mg/L)
MAY						1985				<u></u>	
02	1445	0.17	38	6.53	0.037	2.6	0.80	0.40	0.62	2.5	8.3
02	1545	.20	36	6.50							
02	1645	.27	37	6.49							
02 02	1745 1845	.37 .57	36 37	6.40 6.33	.044	2.5	.80	.40	.76	. 50	8.9
02	2045	. 57	38	6.30	.043	3.5	1.1	. 50	. 52	. 50	9.4
02	2245	.68	38	6.22							
02	0045	. 99	38	6.08							
03	0245	.93	38	6.03	.047	3.6	1.1	. 40	. 48	. 50	10
03	0645	.85	39	6.08							
03 03	1045 1445	.76 .79	38 38	6.19 6.32							
Date	Chlo- ride, dis- solved (mg/L)	Fluo- ride, dis- solved (mg/L)	Bromide, dis solved (mg/L)	Silica, dis- solved (mg/L)	Nitro- gen ammonia, dis- solved (mg/L as N)	Phos- phorus, ortho, dis- solved (mg/L)	Alum- inum, dis- solved (µg/L)	Iron, dis- solved (μg/L)	Manga- nese, dis- solved (µg/L)	Carbon, organic, dis- solved (mg/L)	Nitrogen nitrate, dissolve (mg/L as N)
MAY											
02 02	0.86	0.05	0.02	2.9	0.015	0.002	30 	5	28	3.0	0.68
02 02	 .86	.05	.02	2.7	 .014	.010	50	 6	31	2.6	.70
02	.00	.05	.02	<i>2.1</i>	.014	.010	50		31	2.0	.70
02	.85	.06	.02	3.9	.026	.006	50	6	53	2.6	. 76
02 02											
	07	0.5	00		0.15	000		c	70		•
03 03	.87	.06	.02	3.7	.015	.003	90	6	72		.84
03											
03											

 $[m^3/s$, cubic meters per second; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; μ g/L, micrograms per liter; <, less than; --, indicates no data]

Date	Time	Stream- flow, instan- taneous (m ³ /s)	Spe- cific con- duct- ance (µS/cm)	pH (stand- ard units)	Acidity (mg/L as H ⁺)	Calcium, dis- solved (mg/L)	Magne- sium, dis- solved (mg/L)	Sodium, dis- solved (mg/L)	Potas- sium, dis- solved (mg/L)	Alka- linity, lab (mg/L as CaCO ₃)	Sulfate, dis- solved (mg/L)
				· · · · · · · · · · · · · · · · · · ·		985		<u></u>			
JULY											
21 21 21	2145 2245 2345	0.03 .16 .20	40 38 37	6.55 6.48 6.49	0.067 .058	3.9 3.7 3.5	0.90 .90 .80	0.80 .60 .80	0.61 .66 .68	5.6 3.6 2.9	7.2 7.6 7.9
22 22 22	0045 0145 0345 0545	.18 .14 .12 .08	38 38 39 40	6.58 6.68 6.72	.050 	3.4 4.1	.80 1.0	.60 .70	.58 .66	3.3 4.8	8.1 7.5
22 22 22 22 22 22 22 22	0745 0945 1345 1745 2145	.05 .07 .07 .07 .07 .07	40 39 39 38 38 40	6.82 6.79 6.81 6.85 6.64 6.71	.033 .035	4.1 	1.0 .90	 .70 .60	.66 .50	4.8 4.0	7.5 8.1
Date	Chlo- ride, dis- solved (mg/L)	Fluo- ride, dis- solved (mg/L)	Bromide, dis- solved (mg/L)	Silica, dis- solved (mg/L)	Nitro- gen ammonia, dis- solved (mg/L as N)	Phos- phorus, ortho, dis- solved (mg/L)	Alum- inum, dis- solved (μg/L)	Iron, dis- solved (µg/L)	Manga- nese, dis- solved (μg/L)	Carbon, organic, dis- solved (mg/L)	Nitrogen nitrate, dissolved (mg/L as N)
JULY							ſ				
21 21 21	0.89 .80 .76	0.06 .06 .08	0.03 .02 .02	3.3 2.7 2.9	0.036 .024 .014	<0.001 <.001 <.001	20 20 46	9 16 31	8 28 72	2.2 3.6 3.6	0.70 .64 .57
22 22 22 22 22	.78 	.08 	.02 	3.0	.013 	<.001 	16 	9 	12	3.1	.56
22 22 22 22 22	 .84 	.06	.03	4.1	.014	<.001	10	9.4 	12	2.4	.62
22	. 82	.07	.02	3.7	.022	<.001	17	9.4	19	3.5	. 58

Table 15.--Water-quality data for rainfall and snowmelt runoff at North Fork Bens Creek at North Fork Reservoir, 1984-86

 $[m^3/s,$ cubic meters per second; $\mu S/cm,$ microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; $\mu g/L$, micrograms per liter; <, less than; --, indicates no data]

Date	Time	Stream- flow, instan- taneous (m ³ /s)	Spe- cific con- duct- ance (µS/cm)	pH (stand- ard units)	Acidity (mg/L as H ⁺)	Calcium, dis- solved (mg/L)	Magne- sium, dis- solved (mg/L)	Sodium, dis- solved (mg/L)	Potas- sium, dis- solved (mg/L)	Alka- linity, lab (mg/L as CaCO ₃)	Sulfate, dis- solved (mg/L)
			·····			1984			· · · · · ·		
DEC 19 19 19 19 19 19 19 19 19 19	0300 0400 0500 0600 0700 0800 1000 1200 1400 1600 2000 2400	0.28 .28 .31 .31 .36 .45 .48 .56 .54 .45 .42	444 444 445 443 443 443 443 442 444	5.62 5.78 5.81 5.81 5.85 5.80 5.61 5.49 5.49 5.49 5.50 5.60	0.10	3.6 3.6 3.7 	1.0 1.0 1.1	1.5 1.1 1.2 	0.68 .86 .68 	1.0 1.0 1.0	11 11 11
20 20 20 20 20 20 20 20 20 20	1115 1215 1315 1415 1515 1615 1815 2015 2215	. 34 . 34 . 34 . 34 . 34 . 34 . 34 . 34	42 42 43 42 42 40 41 41	5.55 5.60 5.61 5.62 5.63 5.63 5.67 5.70 5.70	.10 .10 	3.7 3.6 	1.1	1.4	.62 .62 	1.0	11
21 21 21	0215 0615 1015	.31 .31 .34	40 39 39	5.67 5.67 5.67	<u>.10</u> .10	3.6 	1.1	1.3	.62 .62	1.0 1.0	10 10
Date	Chlo- ride, dis- solved (mg/L)	Fluo- ride, dis- solved (mg/L)	Bromide, dis- solved (mg/L)	Silica, dis- solved (mg/L)	Nitro- gen ammonia, dis- solved (mg/L as N)	Phos- phorus, ortho, dis- solved (mg/L)	Alum- inum, dis- solved (μg/L)	Iron, dis- solved (μg/L)	Manga- nese, dis- solved (µg/L)	Carbon, organic, dis- solved (mg/L)	Nitrogen nitrate, dissolved (mg/L . as N)
DEC		<u></u>									
19 19 19 19 19 19 19 19 19	2.9 2.1 2.3	0.07	0.02	4.1 3.9 4.0	0.005	0.01 .01 .002 	50 110 110	5 8 	21 53 50	2.2 2.2	0.68
20 20 20 20 20 20 20	2.4 2.4 	.07 .07 	.02 .02 	4.2 4.1 	.005 .005 	.01 .01 	80 70 	5 	30 35 	1.4 1.0 	.62 .60
20 21 21 21	2.4 2.4	 .07 .07	.02 .02 .02	 4.2 4.2	 .005 .006	.01 .01	 70 80	 4 8	33 33 33	.80 .90	.63 .64

Table 15.--Water-quality data for rainfall and snowmelt runoff at North Fork Bens Creek at North Fork Reservoir, 1984-86--Continued

	µS/cm, mi¢rosiemens per centimeter at
25 degrees Celsius; mg/L, millig liter: <. less than;, indicat	rams per liter; µg/L, micrograms per es no data]

Date	Time	Stream- flow, instan- taneous (m ³ /s)	Spe- cific con- duct- ance (µS/cm)	pH (stand- ard units)	Acidity (mg/L as H ⁺)	Calcium, dis- solved (mg/L)	Magne- sium, dis- solved (mg/L)	Sodium, dis- solved (mg/L)	Potas- sium, dis- solved (mg/L)	Alka- linity, lab (mg/L as CaCO ₃)	Sulfate, dis- solved (mg/L)
						1984		<u> </u>			
DEC 21 21 21 21 21 21 21 21 21 21 21 21 21	1030 1130 1230 1330 1430 1530 1530 1530 1530 1530 1530 1530 2030 2030 2230	.34 .34 .36 .48 .51 .54 .54 .54 .54 .56 .62 .65	41 42 39 39 39 40 40 40 40 40	5.55 5.70 5.65 5.69 5.61 5.51 5.51 5.52 5.42 5.42 5.39 5.36	0.1 .1 .1 .1 .1 .1	 3.6 3.6 3.6 3.6 3.6 3.7	1.0 1.1 1.0 	1.3 1.4 1.2 1.2 1.2 1.2 1.2	 0.66 .70 .72 .84 .79 .76	1.0 1.0 1.0 1.0 1.0 1.0	10 10 10 10 10 11 11
22 22 22 22 22 22 22 22 22	2430 0230 0630 1030 1430 1830 2230	.62 .59 .56 .56 .56 .54 .54 .54	41 40 41 38 43 40 39	5.38 5.40 5.41 5.39 5.45 5.44 5.51 5.50	.1 .1	3.7 	1.0 1.1	1.2 1.3	.76	1.0 1.0	 11 11
23 23 23 23 23	0230 0630 1030 1430	. 48 . 48 . 42 . 40	38 38 40 40	5.62 5.63 5.60 5.60	.1	3.7	1.1	1.4	.70	1.0	 11
Date	Chlo- ride, dis- solved (mg/L)	Fluo- ride, dis- solved (mg/L)	Bromide, dis- solved (mg/L)	Silica, dis- solved (mg/L)	Nitro- gen ammonia, dis- solved (mg/L as N)	Phos- phorus, ortho, dis- solved (mg/L)	Alum- inum, dis- solved (µg/L)	Iron, dis- solved (μg/L)	Manga- nese, dis- solved (μg/L)	Carbon, organic, dis- solved (mg/L)	Nitrogen nitrate, dissolved (mg/L as N)
DEC											
21 21 21 21 21 21 21 21 21 21 21 21	2.3 2.3 2.3 2.1 2.1 2.1 2.1	.09 .07 .09 .07 .09 .09	 0.02 .02 .02 .02 .02 .02 .02	4.1 3.9 4.0 4.0 4.0 4.0	0.005 .005 .138 	0.01 .01 .004 	 50 100 90 110 140	 5 15 22 5 -5 14	34 30 5 50 54 60		 0.65 .58 .60 .66
22 22 22 22 22 22 22 22 22 22 22	 2.3 2.2	.08	.02 .02	4.0	.022 .005	.01 .01	 130 90	 15 4	 60 48		 .57
23 23 23 23	2.3	 .07	 .02	4.0	.017	 . 10	 80	 27 	 44 		 .69

Table 15.--Water-quality data for rainfall and snowmelt runoff at North Fork Bens Creek at North Fork Reservoir, 1984-86--Continued

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. 3	· · · · · · · · · · · · · · · · · · ·
im /s. cubic meters	per second; μ S/cm, microsiemens per centimeter at
ZO degrees Celsius;	mg/L, milligrams per liter; μ g/L, micrograms per
liton < loss than	indicates no data]
titet; <, tess unan;	, indicates no dataj

Date	Time	Stream- flow, instan- taneous (m ³ /s)	Spe- cific con- duct- ance (µS/cm)	pH (stand- ard units)	Acidity (mg/L as H ⁺)	Calcium, dis- solved (mg/L)	Magne- sium, dis- solved (mg/L)	Sodium, dis- solved (mg/L)	Potas- sium, dis- solved (mg/L)	Alka- linity, lab (mg/L as CaCO ₃)	Sulfate, dis- solved (mg/L)
FEB		···· <u>·</u> ······	····	<u></u>	198	35		······			
22 22 22 22	1030 1200 1215 1315	0.12 .13 .13 .15	43 44 43 44	5.72 5.99 5.70 5.73	<0.1	3.4	1.0	1.3	0.55	1.0	9.4
22 22 22 22 22 22	1415 1515 1615 1715 1915	.18 .19 .20 .21 .22	43 43 41 43 43	5.59 5.53 5.63 5.50 5.38	<.1 <.1	3.3 3.6	1.0	1.2 1.2	.57 .65	1.0	9.4 9.4
22 22	2115 2315	.23 .25	4 4 4 4	5.60 5.58							
23 23 23 23 23 23 23 23 23 23	0315 0715 1115 1200 1300 1400 1500 1600 1700	.26 .27 .31 .34 .45 .54 .59 .68	44 43 42 43 43 44 44 44	5.55 5.55 5.52 5.57 5.57 5.49 5.48 5.48 5.48	<.1 <.1 <.1 <.1	3.6 3.5 3.3 3.1	1.1 1.1 1.0 1.0	1.1 1.0 90 80	.59 .68 .57 .56	1.0 1.0 1.0 1.0	10 11 11 10
23 23 23	1900 2100 2300	.82 .88 .88	45 44 44	5.35 5.32 5.30	<.1 <.1	3.5 3.3	1.0	.80 .80	.63 .59 	1.0	11 11
24 24 24	0300 0700 1100	.82 .79 1.13	43 44 44	5.36 5.39 5.32	<.1 <.1	3.6 3.5	1.0 1.0	.80 .80	.63 .64	1.0 1.0	11 11
26 26 26 26	1045 1415 1815 2215	.93 .91 .88 .79	44 42 42 41	5.23 5.28 5.27 5.30	<.1 <.1	3.6	1.0 .90	1.1 1.1	.68 .61	1.0	8.4 10
27 27 27 27 27 27 27	0215 0615 1015 1415 1815 2215	.71 .65 .68 .62 .59 .57	41 42 42 41 41	5.28 5.24 5.31 5.38 5.40 5.34	<.1 <.1 	3.2 3.3 	.90 .90 	1.1 1.2 	.59 .66 	1.0 1.0	10 10
28 28	0215 0615	. 54 . 51	41 41	5.32 5.39	<.1	3.5	1.0	1.4	.65	1.0	10
MAR 01	1245	. 40	41	5.52	<.1	3.2	.90	1.3	.61	1.0	10

Table 15.--Water-quality data for rainfall and snownelt runoff at North Fork Bens Creek at North Fork Reservoir, 1984-86--Continued

 $[m^3/s, cubic meters per second; \mu S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; <math>\mu$ g/L, micrograms per liter; <, less than; --, indicates no data]

Date	Chlo- ride, dis- solved (mg/L)	Fluo- ride, dis- solved (mg/L)	Bromide, dis- solved (mg/L)	Silica, dis- solved (mg/L)	Nitro- gen ammonia, dis- solved (mg/L as N)	Phos- phorus, ortho, dls- solved (mg/L)	Alum- inum, dis- solved (μg/L)	Iron, dis- solved (μg/L)	Manga- nese, dis- solved (μg/L)	Carbon, organic, dis- solved (mg/L)	Nitrogen nitrate, dissolved (mg/L as N)
FEB						1985					
22	2.6	0.06	0.03	3.5	0.008	0.010	40	5	17	0.40	0.76
22 22											
22											
22 22	2.0	.06	.03	3.4	.015	.010	 70	 3	 29	.80	.80
22											
22 22	2.2	.22	.03	3.6	.014	.010	60	3	41		.83
22											
22										`	
23 23	1.9	.08	.03	3.6	.012	.010	110	5	55	1.2	.83
23 23	1.8			3.6		.010	110				
23	1.8	.10	.03		.008			5	55 		.78
23											
23 23	1.0	.07	.03	3.4	.013	.010	120	4	56	.90	.88
23 23	1.6	.07	. 03	3.0	.014	.010	130	6	67		. 84
23 23	1.4	 .07	.03	3.2	.014	.010	180	 8	88		. 88
23	1.4	.07	.03	3.1	.012	.010	190	8	88		.88
23											
24											
24	1.3	. 07	.03	3.6	.010	.010	180	4	74		. 88
24	1.4	.07	. 03	3.4	.010	.010	180	7	79	1.1	.91
26											
26 26	1.3	.13	.03	3.7	.038	.010	180	5	68 		.98
26	2.2	.09	.10	3.3	.031	.010	100	6	55		. 98
27											
27	2.3	. 08	.03	3.3	.013	.010	120	4	50		.98
27 27	2.3	.05	.03	3.4	.022	.010	120	4	55		.99
27											
27							'				
28											
28	2.6	. 07	.03	3.8	.027	.010	120	5	50		.95
MAR											
01	2.7	.06	.03	3.5	.006	.010	100	4	39		.91

Table 15.--Water-quality data for rainfall and snowmelt runoff at North Fork Bens Creek at North Fork Reservoir, 1984-86--Continued

Date	Time	Stream- flow, instan- taneous (m ³ /s)	Spe- cific con- duct- ance (µS/cm)	pH . (stand- ard units)	Acidity (mg/L as H ⁺)	Calcium, dis- solved (mg/L)	Magne- sium, dis- solved (mg/L)	Sodium, dis- solved (mg/L)	Potas- sium, dis- solved (mg/L)	Alka- linity, lab (mg/L as CaCO ₃)	Sulfate dis- solved (mg/L)
MAR						1985					
12	0230	0.28	43	5.68	0.040	2.8	0.70	1.2	0.60	1.9	9.7
12 12	0330 0430	.34 .42	43 43	5.70 5.59	.037	2.9	.90	1.1	.61	. 50	9.9
12 12	0530 0630	. 45 . 48	42 42	5.51 5.50	.014	3.3	.99	1.1	.66	. 50	10
12	0730	. 51	45	5.40	.013	3.3	.95	1.1	.66	. 50	10
12 12	0930 1130	.48 .45	44 44	5.41 5.41	.024	3.0	.90	1.0	. 58	. 50	11
12	1330	. 42	44	5.37							
12 12	1730 2130	. 40 . 40	45 44	5.40 5.50	.044	3.3	.99	1.2	. 59	. 50	11
13	0130	.37	44	5.51	.042	3.3	1.0	1.2	.60	. 50	11
	Chlo- ride,	Fluo- ride,	Bromide,	Silica,	Nitro- gen ammonia, dis-	Phos- phorus, ortho,	Alum- inum,	Iron,	Manga- nese,	Carbon, organic,	Nitrogen nitrate,
	dis-	dis-	dis-	dis-	solved	dis-	dis-	dis-	dis-	dis-	dissolved
	solved	solved	solved	solved	(mg/L	solved	solved	solved	solved	solved	(mg/L
Date	(mg/L)	(mg/L)	(mg/L)	(mg/L)	as N)	(mg/L)	(µg/L)	(µg/L)	(µg/L)	(mg/L)	as N)
MAR		-									
12	2.9	0.05	0.02	3.0	0.009	0.001	50	2	27	1.2	0.77
12 12	2.7	.06	.02	3.0	.008	.001	80 	3	35	1.6	.75
12	2.4	.06	.02	3.3	.011	.001	100	2	46	1.3	.75
12 12	2.4	.06	.02	3.4	.005	.001	110	2	50	2.0	.74
12	2.4	.06	.02	3.1	.012	.001	120	2	48	1.5	. 74
12 12	2.4	.06	.02	3.4	.013	.001	120	 2	 47	1.1	 .76
12											
	2.4	.06	. 02	3.6	.009	.001	100	2	46	1.1	. 78

 $[m^3/s,$ cubic meters per second; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; μ g/L, micrograms per liter; <, less than; --, indicates no data]

Table 15.--Water-quality data for rainfall and snowmelt runoff at North Fork Bens Creek at North Fork Reservoir, 1984-86-Continued

 $[m^3/s, cubic meters per second; \mu S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; <math>\mu$ g/L, micrograms per liter; <, less than; --, indicates no data]

Date	Time	Stream- flow, instan- taneous (m ³ /s)	Spe- cific con- duct- ance (µS/cm)	pH (stand- ard units)	Acidity (mg/L as H ⁺)	Calcium, dis- solved (mg/L)	Magne- sium, dis- solved (mg/L)	Sodium, dis- solved (mg/L)	Potas- sium, dis- solved (mg/L)	Alka- linity, lab (mg/L as CaCO ₃)	Sulfate, dis- solved (mg/L)
						1985					
MAY 02 02 02 02 02 02 02 02 02 02 02 02	0800 0900 11000 1200 1400 1600 1800 2000 2400	0.11 .11 .11 .11 .12 .18 .24 .23 .42	45 45 45 45 45 45 45 44 42	5.86 6.08 6.00 5.99 6.08 5.99 5.81 5.81 5.75	<0.05 <0.05 <0.05 <0.05	3.0 3.7 2.8 2.8	0.8	1.6 1.8 1.4 1.0	0.71 .67 .85 .83	0.50 .50 .50 .50	9.3 9.5 9.8 10
03 03 03 03 03 03 03 03 03 03 03	0400 0430 0530 0730 0830 0930 1130 1330 1530 1930 2330	.71 .74 1.08 1.36 1.42 1.47 1.39 1.25 1.25 1.02 .91 .82	41 41 42 42 43 44 44 44 44	5.49 5.31 5.27 5.23 5.20 5.19 5.21 5.21 5.22 5.27 5.30 5.30	<0.05 <0.05 <0.05 <0.05 <0.05	2.6 3.4 2.3 3.4 3.5		.90 .90 .70 .90 .90	.78 .54 .74 .75	.50 .50 .50 .50 .50	10 10 10 10 10 10
_04 Date	Chlo- ride, dis- solved (mg/L)	.71 Fluo- ride, dis- solved (mg/L)	44 Bromide, dis- solved (mg/L)	5.42 Silica, dis- solved (mg/L)	<0.05 Nitro- gen ammonia, dis- solved (mg/L as N)	2.9 Phos- phorus, ortho, dis- solved (mg/L)	.90 Alum- inum, dis- solved (µg/L)	.80 Iron, dis- solved (µg/L)	.81 Manga- nese, dis- solved (µg/L)	.50 Carbon, organic, dis- solved (mg/L)	10 Nitrogen nitrate, dissolved (mg/L as N)
MAY 02 02 02 02 02 02 02 02 02 02 02 02 02	3.7 3.4 3.4 2.2	0.07 .07 .06 .07	0.02	3.2 3.8 2.9 3.0	0.03 .041 .040 .021	0.004 .001 .003 .002	40 30 50 100	4 0 3 4	17 18 18 47	2.8 2.0 2.4 2.2	0.81 .78 .77 .88
03 03 03 03 03 03 03 03 03 03 03	1.8 1.7 1.6 1.7 1.7	.08 .08 .07 .07 .07 .07	.02 .02 .02 .02 .02 .02	2.6 3.4 2.3 3.5 3.7	.015 .012 .15 .012 .012	 .004 .003 .003 	190 240 270 180 220	6 7 7 7 3	67 110 75 100 	3.3 3.8 3.4 	.71 .74 .74 .77 .80

Table 15.--Water-quality data for rainfall and snowmelt runoff at North Fork Bens Creek at North Fork Reservoir, 1984-86--Continued

Date	Time	Stream- flow, instan- taneous (m ³ /s)	Spe- cific con- duct- ance (μS/cm)	pH (stand- ard units)	Acidity (mg/L as H ⁺)	Calcium, dis- solved (mg/L)	Magne- sium, dis- solved (mg/L)	Sodium, dis- solved (mg/L)	Potas- sium, dis- solved (mg/L)	Alka- linity, lab (mg/L as CaCO ₃)	Sulfate, dis- solved (mg/L)
JULY			<u> </u>			1985		<u></u>			
08 08 08	2145 2245 2345	0.07 .08 .10	47 48 48	5.90 6.19 6.66	0.041	3.3	0.84	1.7	0.48	0.5	8.5
09	0045	.10	45	6.41	.038	3.2	.80	1.6	. 50	1.0	8.5
09 09 09 09 09 09	0145 0345 0445 0545 0745 0945	.10 .27 .45 .31 .23 .18	46 43 43 42 43 43	6.31 6.20 6.00 6.00 6.01 6.12	.037 .048 .050 .046 .038	3.4 1.8 3.1 3.2 3.5	.89 .45 .78 .82 .91	1.7 .84 .98 1.1 1.3	.52 .57 .51 1.1 .50	1.0 .5 .5 .5	8.6 9.4 9.7 9.9 10
Date	Chlo- ride, dis- solved (mg/L)	Fluo- ride, dis- solved (mg/L)	Bromide, dis- solved (mg/L)	Silica, dis- solved (mg/L)	Nitro- gen ammonia, dis- solved (mg/L as N)	Phos- phorus, ortho, dis- solved (mg/L)	Alum- inum, dis- solved (µg/L)	Iron, dis- solved (μg/L)	Manga- nese, dis- solved (μg/L)	Carbon, organic, dis- solved (mg/L)	Nitrogen nitrate, dissolved (mg/L as N)
JULY											
08 08 08	3.9 	0.07	0.0	3.4	0.022	0.003	20 	2 	7 	1.4 	0.58
09 09 09	3.6 3.6	.05 .06	.02	3.2 3.6	.055 .029	.003 .003	30 30	6 4 	9 9	1.6 1.5	. 58 . 57
09 09 09 09	2.4 2.0 2.0 2.3	.06 .05 .05 .06	.02 .02 .02 .02	1.7 2.8 3.1 3.7	.027 .024 .027 .026	.003 .003 .003 .003	70 80 80 50	5 10 7 4	12 54 48 35	3.6 3.7 3.1 2.2	. 50 . 46 . 44 . 42

 $[m^3/s,$ cubic meters per second; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; μ g/L, micrograms per liter; <, less than; --, indicates no data]

Table 15.--Water-quality data for rainfall and snowmelt runoff at North Fork Bens Creek at North Fork Reservoir, 1984-86--Continued

 $[m^3/s,$ cubic meters per second; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; μ g/L, micrograms per liter; <, less than; --, indicates no data]

Date	Time	Stream- flow, instan- taneous (m ³ /s)	Spe- cific con- duct- ance (µS/cm)	pH (stand- ard units)	Acidity (mg/L as H ⁺)	Calcium, dis- solved (mg/L)	Magne- sium, dis- solved (mg/L)	Sodium, dis- solved (mg/L)	Potas- sium, dis- solved (mg/L)	Alka- linity, lab (mg/L as CaCO ₃)	Sulfate, dis- solved (mg/L)
NOV						1985					
26 26 26 26 26	1200 1330 1800 2100 2400	0.24 .31 .99 1.12 1.03	43 47 42 44 44	5.72 5.71 5.40 5.23 5.12	0.038 .043 .067 .076	2.5 2.8 2.7 2.7	0.80 .90 .80 .80	1.1 1.2 .800 .80	0.54 .53 .51 .54	<0.5 <.5 <.5 <.5	9.5 9.7 13 11
27 27 27	0200 0800 1500	.98 .87 .83	45 42 41	5.18 5.20 5.23	.072 .055 .058	2.6 2.5 2.8	.80 .80 .90	.80 .80 .90	. 53 . 56 . 51	<.5 <.5 <.5	12 11 11
28 28 28 28	0400 0800 1200 2000	1.30 1.67 2.02 1.85	41 49 4.3 4.3	5.15 5.07 4.99 5.04	<.060 .067	2.7 2.7	.80 .80	.80 .80	.54 .53	<.5 <.5	11 11
DEC											
04	1015	.25	45	5.49							
Date	Chlo- ride, dis- solved (mg/L)	Fluo- ride, dis- solved (mg/L)	Bromide dis- solved (mg/L)	Silica, dis- solved (mg/L)	Nitro- gen ammonia, dis- solved (mg/L as N)	Phos- phorus, ortho, dis- solved (mg/L)	Alum- inum, dis- solved (µg/L)	Iron, dis- solved (µg/L)	Manga- nese, dis- solved (µg/L)	Carbon, organic, dis- solved (mg/L)	Nitrogen nitrate, dissolved (mg/L as N)
NOV											
26 26 26 26 26	2.9 2.8 1.9 1.8	0.06 .06 .07 .08	0.02 .02 .02 .02	3.1 3.4 3.1 3.0	0.034 .020 .81 .045	0.001 <.001 .001 <.001	60 77 180 240	2.7 3.7 9.8 13	26 35 68 86	1.4 1.5 3.3 3.5	0.69 .62 .40 .35
27 27 27	1.9 1.9 2.0	.08 .08 .08	.02 .02 .02	3.0 3.1 3.4	.015 .013 .019	<.001 <.001 <.001	230 17 150	10 5.7 2.1	84 62 62	2.8 3.2	. 42 . 53 . 61
28 28 28 28	1.8 1.7	.08 .08	.02 .02	3.3 3.2	.019 .035	<.001 <.001	200	4.4 3.2	79 88	 	. 49 , 59

Table 15.--Water-quality data for rainfall and snowmelt runoff at North Fork Bens Creek at North Fork Reservoir, 1984-86--Continued

$[m^3/s, cubic meters per second; \mu S/cm, microsiemens per centimet$	er at
25 degrees Celsius; mg/L, milligrams per liter; μ g/L, micrograms	
liter: <, less than;, indicates no data]	F

Date	Time	Stream- flow, instan- taneous (m ³ /s)	Spe- cific con- duct- ance (µS/cm)	pH (stand- ard units)	Acidity (mg/L as H ⁺)	Calcium, dis- solved (mg/L)	Magne- sium, dis- solved (mg/L)	Sodium, dis- solved (mg/L)	Potas- sium, dis- solved (mg/L)	Alka- linity, lab (mg/L as CaCO ₃)	Sulfate dis- solved (mg/L)
FEB						1986					·
04 04 04 04	1130 1430 1730 2030 2330	0.28 .46 1.04 .90 .78	40 41 40 40	5.5 5.41 5.28 5.20 5.2	0.019 039	2.7 2.7	0.90 .80	1.0 .80	0.52 .53	<0.5 <.5	10 11
05 05 05 05 05 05	0330 0530 0730 0930 1430 1730	.84 1.61 2.37 2.51 2.42 2.49	42 41 42 44 45 44	5.20 5.18 4.9 4.8 4.8 4.8	.055 .056 .055	2.9 2.7 2.5	.80 .70 .70	.80 .70 .60	.59 .61 .63	<.5 <.5 <.5	11 11 11
06 06	0430 2030	1.96 1.47	44 42	4.88 5.10	.046 .055	2.7 2.5	. 80 . 70	.70 .80	.67 .55	<.5 <.5	11 10
07 07	0730 1930	1.03 .82	44 44	5.02 5.01	.032 .028	2.6 2.7	. 80 . 80	1.0 1.1	.58 .66	<.5 <.5	10 10
08	1930	. 46	42	5.22	.045	2.8	. 80	1.2	. 8	<.5	10
Date	Chlo- ride, dis- solved (mg/L)	Fluo- ride, dis- solved (mg/L)	Bromide, dis- solved (mg/L)	Silica, dis- solved (mg/L)	Nitro- gen ammonia, dis- solved (mg/L as N)	Phos- phorus, ortho, dis- solved (mg/L)	Alum- inum, dis- solved (μg/L)	Iron, dis- solved (μg/L)	Manga- nese, dis- solved (µg/L)	Carbon, organic, dis- solved (mg/L)	Nitrogen nitrate, dissolved (mg/L as N)
FEB											
04 04 04 04 04	2.2 1.7	0.07 .07	0.02	3.0 2.7	0.019 .014	<0.001 <.001	91 230	<2 <2	39 81	2.4 2.7	0.67 .66
05 05 05 05	1.4 1.3 1.3	.09 .08 .08	.02 .02 .02	2.8 2.4 2.4	.007 .014 .013	.002 .003 .001	310 310 260	2.3 4.2 <2 	140 150 120	4.6 3.3 2.5	.64 .67 .72
06 06	1.5 1.9	.08 .07	.03 .03	3.0 2.9	.016 .011	.002 .002	270 140	<2 10	100 69	2.6 1.6	.73 .75
07 07	2.1 2.3	.06 .06	.03 .03	3.1 3.2	.034 .025	.002	140 130	<2 <2	69 63	1.2 1.2	.78 .79
08	2.7	.06	.03	3.3	.050	.001	100	<2	50	1.3	. 80

Interactions of Acid Precipitation on Watershed Soils

The potential for acidic runoff to alter stream chemistry is influenced by such factors as season, magnitude and duration of rainfall, weather pattern, and the degree of saturation of the unconsolidated zone. Most interactions between runoff and the watershed can be attributed to various cation-exchange processes within the soil horizons. Consequently, passage of the runoff through the layers of the unconsolidated zone will affect the quality of the stream.

The sensitivity of watershed soils to leaching by sulfuric and nitric acid has been shown to be site specific. For example, Johnson and others (1982) stated that soils sensitive to leaching by sulfuric acid generally are those low in iron, aluminum oxides, and clay but high in organic matter and pH, whereas soils sensitive to nitric acid leaching generally are those with an abundance of nitrogen. This generalization contradicts the finding in the North Fork and South Fork Bens Creek watersheds where the unconsolidated zones characteristically have low pH, large cation exchange capacities, and a mix of highly weathered sandstone and organic matter within the upper horizon of the mineral soil layer. Both watersheds are sensitive to leaching by sulfuric acid, especially during large storms of long duration. Excess nitrate leaves the watershed during snowmelt runoff, indicating possible nitric acid leaching during the nongrowing season.

Chemical recovery of stormflow and snowmelt events is highly variable. Stream chemistry for stormflow events generally recovers to pre-event conditions in conjunction with the hydrograph. Stream-chemistry recovery following snowmelt-runoff events may require as much as a week after discharge recovery. The pre- and post-event mechanisms for the passage of acid precipitation through the North Fork Bens Creek and South Fork Bens Creek watersheds are described in a general way, by attempting to follow the input water through the canopy, detrital layer, and soil layers.

The layers of the unconsolidated soil zone having the greatest influence on stream chemistry during runoff events are the detrital and mineral soil layer. The detrital layer is a potential source of both acids and bases through decomposition and root-respiration. Contribution to and growth within the detrital layer will control whether the pre-precipitation conditions will be either acidic or basic. Also, byproducts of microbial action can be significant factors in cation exchange as they become available to the mineral soil layer by percolation from the detrital layer. Generally, the reactions that occur within the detrital layer at the beginning of runoff events are short lived and only alter stream chemistry when there have been several days between events. Most water that percolates through the detrital layer will pass through the mineral soil layer before entering the stream; water initially buffered by the detrital layer would quickly be reacidified after the buffering components of the mineral soil layer are neutralized.

The mineral soil layer plays host to most of the cation exchange that occurs within the watershed. Mineral soils in both the North Fork and South Fork Bens Creek basins are very stony silt loams and are characteristically acid, well drained, and moderately deep. As with the detrital layer, the hydrogen-ion concentration within the soils can be increased or decreased by various processes. For example, the mineralization and oxidation of sulfur, nitrogen, and phosphorus from the forest floor (percolation from the detrital layer) results in the formation of acids (sulfuric, nitric, and phosphoric), whereas mineralization of potassium, calcium, magnesium, and manganese leads to the production of bases (Johnson and others, 1982). The combination of carbon dioxide released by decomposition and root respiration with water to form carbonic acid has been shown to be another major natural source of hydrogen ions in many forest soils (McColl and Cole, 1968; Johnson and others, 1977; Andersson and others, 1980). Before precipitation occurs, all of the above processes in the soil are a continuous process. These processes are extremely complex and can vary seasonally and even temporally. As a result, it is unlikely that these processes will ever be quantified. It is known, however, that the watershed soils contain significantly more potassium, calcium, magnesium, and manganese than nitrogen and phosphorus; therefore, an accumulation of buffers would most likely occur. The demineralization of these base complexes, in addition to the formation of aluminum salts during initial runoff, temporarily increases the pH. Mineral soils essentially are acid in the deeper zones; therefore, demineralization of the base complexes formed near the surface of the soil layer would occur rapidly, and, depending on the sampling frequency, increases in pH in streamflow during the first stormflow discharges may not be observed.

During Input of First 20 Percent of Constituents in Acidic Precipitation

The first 20 percent or so of acid precipitation entering the watershed is responsible for the neutralization reactions of all accumulated buffering components from the pre-event period. During the growing season the forest canopy would provide one medium for buffering precipitation pH. For example, Johnson and others (1982) noted a study in Sweden wherein a beech-maple type forest, for which average annual pH values for rainfall and throughfall were 5.2 and 5.7, respectively, indicated that the deciduous canopy can raise pH. The precipitation leaving the canopy would encounter the detrital and mineral soil layers where demineralization of the pre-precipitation base complexes would occur. The resulting flush of this buffered precipitation solution along with the "pooled" buffered solution from previous events, increases the pH. Plots of discharge as a function of pH in figures 19-B, G, H, I, and J, show this phenomenon. Also at this stage in the flow-thru, there is a steady increase of dissolved cations that enter streamflow independent of the decrease in hydrogen ions. This independence is possibly the result of a reserve of dissolved cations in soil solutions from the deeper more acidic part of the unconsolidated zone. The pH range for soils of the Hazleton, Ernest, and Rayne-Gilpin loams is from 4.5 to 5.5 (U.S. Department of Agriculture, 1983). Under these conditions, natural leaching could occur, making dissolved cations available for flushing. Hewlett and Hibbert (1967) contend that the upper horizons of the soils contain readily soluble materials, and any soil water, flushed by the overland runoff and shunted to the stream by throughflow mechanisms, will be highly charged with solutes.

During Input of 50 Percent of Constituents in Acidic Precipitation

As acid deposition continues, half of the total input of constituents in the acid deposition would be interacting with the system. The preprecipitation buffers accumulating in the forest canopy and unconsolidated zone would be completely used by the first 20 percent of the event input. Minor acidification by plant respiration and carbonic acid formation would occur within the canopy. Combined with the acidic rainfall, the system would begin to show stress because of acidification. Dissolved metals mobilized in the detrital layer percolate into the mineral soil layer where they are maintained in solution by the natural acidic conditions. Additional concentrations of hydrogen ions within the mineral soil layer cause further cation exchange and dissolved-metal mobilization. Stream chemistry at this point shows a sharp increase in dissolved metals, a decrease in base cations, and an increase in sulfate as a result of increased drainage from the mineral soil layer.

After Input of 100 Percent of Constituents in Acidic Precipitation

At the conclusion of rainfall or snowmelt input, stream discharge would be near its maximum and the watershed system would be acidic throughout the unconsolidated zone. Runoff at this point generally contains peak concentrations of total dissolved aluminum and dissolved manganese, sulfate, and, during snowmelt runoff, nitrate. Calcium concentration increased and then decreased during runoff events; therefore, no trend was detected. Aluminum had the greatest increase throughout all events. Dissolved aluminum has been shown to be toxic to trout populations at concentration above 200 $\mu g/L$ (Cronan and Schoefield, 1979). Dissolved-aluminum concentrations reached potentially toxic levels for 43 percent of the events sampled on the North Fork Bens Creek; snowmelt runoff events comprise half of the events with toxic levels. The dissolved-aluminum concentrations in South Fork Bens Creek never reached toxic levels during any sampled events; however, large fish kills were reported in the adjoining fish nursery during the snowmelt runoff events of 1984 and 1985.

The mobilization of dissolved aluminum and other constituents is greatest in the mineral soil horizon of the unconsolidated zone. Sharpe and others (1984) have shown that, during four major precipitation events on Laurel Hill, the mineral soil horizon produced leachate with pH greater than the pH of water passing through the detrital layer; the concentration of hydrogen ions decreased 72 percent and concentrations of dissolved calcium, magnesium, sulfate, nitrate, chloride, and aluminum increased. All increases were statistically significant, except for calcium. These results, from samples collected using zero-tension pan lysimeters installed in soil pits, do not reflect what actually entered the stream. Sharpe's lysimeter data, however, do indicate most interaction with hydrogen ions is occurring within the mineral soil layer and that this layer is the primary source of dissolved aluminum. Mineral soils of the North Greek are similar in chemistry to the study; therefore, the interactions should be somewhat similar.

SUMMARY

The amount of precipitation measured at South Fork Bens Creek in the 1984 and 1985 water years was 1,482.1 and 1,051.8 mm, respectively, and 1,015.7 mm at North Fork in the 1985 water year. Average precipitation for this region is about 1,350 mm annually. The minimum and maximum pH measured in precipitation during the 1984-85 water years was 3.59 and 4.85, respectively. The volume-weighted average was 4.06. Precipitation was, on the average, about 35 times more acidic than "pure rain". Precipitation was slightly more acidic during the growing season than during the dormant season. These values are in close agreement with those of other investigators working in southwestern Pennsylvania.

Hydrogen, sulfate, and nitrate are the dominant ions in precipitation. Sulfate is the dominant precursor for acid formation in precipitation and in both watersheds. Nitrate is substantially more abundant than sulfate in snowfall and contributes to streamflow acidification only during snowmelt.

Annual chemical constituent budgets for both watersheds show net losses for base cations, sulfate, and chloride--net accumulation was observed for nitrate and hydrogen ion. The net flux for nitrate shows that about 46 percent was retained in the South Fork and about 50 percent was retained in the North Fork ecosystems. Accumulation of hydrogen ion in both South Fork and North Fork Bens Creek basins was 99 and 74 percent, respectively.

Streamflow chemistry responds to acidic storm runoff with increases in dissolved metals and sulfate concentrations, and decreases in nitrate, base cations, and silica concentrations. Dissolved-aluminum concentrations reached levels potentially toxic to fish in four of the five streams at least once during the 2 1/2-year study period. Pre-precipitation mineralization of manganese, magnesium, potassium, and calcium in the soil horizons appears to be significant in accumulating initial hydrogen influx. Values of pH have been shown to be independent of mobilized solutes during the beginning of stormflow as a result of "flushing" of dissolved metals from the predominantly acidic unconsolidated zone of both watersheds. At peak storm runoff, streamflow reaches its lowest pH and highest dissolved-aluminum concentration.

REFERENCES CITED

- Andersson, Folke, Fagerstrom Torbjorn, and Nilsson S.I., 1980, Forest ecosystem responses to acid deposition-hydrogen ion budget and nitrogen/tree growth model approaches, in Hutchinson, T.C., and Havas, M., eds., Effects of acid precipitation on terrestrial ecosystems: NATO Conference on Effects of Acid Precipitation on Vegetation and Soils, Toronto, Canada, 1978: New York, Plenum Press, p. 319-334.
- Aquatic Effects Task Group, 1985, (revised 3/85). Working protocol for sampling, sample analysis, and QA/QC for the USEPA long-term surface water monitoring program: Draft of document, 20 p.
- Berg, T.M., and Dodge, C.M., 1981, Atlas of preliminary geologic quadrangle maps of Pennsylvania: Pennsylvania Geological Survey, 4th series, 636 p.
- Bigelow, D.S., 1982, Draft NADP instruction manual/site operation, National Atmospheric Deposition Program, NC-141: Colorado State University, 30 p.
- Bowersox, V.C., and DePena, R.G., 1980, Analysis of precipitation chemistry at a central Pennsylvania site: Journal Geophysical Research, v. 85, no. c. 10, p. 5614-5620.
- Cronan, C.S. and Schoefield, C.L., 1979, Aluminum leaching response to acid precipitation: Effects on high elevation watersheds in the northeast: Science, v. 204, 306 p.
- DeWalle, D.R., Dinicola, R.S., and Sharpe, W.E., 1987, Predicting base flow alkalinity as an index to episodic stream acidification and fish presence: Water Resources Bulletin, v. 23, no. 1, p. 29-35.
- DeWalle, D.R., Sharpe, W.E., Dinicola, R.S., Leibfried, R.T., and Kimmel, W.G., 1982, Causes of acidification of four streams on Laurel Hill in southwestern Pennsylvania, Institute for research on land and water resources, the Pennsylvania State University, 62 p.
- DeWalle, D.R., Sharpe, W.E., Izbicki, J.A., and Wirries, D.L., 1983, Acid snowpack chemistry in Pennsylvania, 1979-81: Water Resources Bulletin, v. 19, no. 6, p. 993-1001.
- Edwards, A.M.C., 1973, The variations of dissolved constituents with discharge in some Norfolk rivers: Journal of Hydrology, v. 18, p. 219-242.
- Flint, N.K., 1965, Geology and mineral resources of southern Somerset County, Pennsylvania: Commonwealth of Pennsylvania Department of Environmental Resources, Bureau of Topographic and Geologic Survey, County Report, 56-A, 267 p.
- Galloway, J.N., and Likens, G.E., 1981, Acid precipitation: The importance of nitric acid: Atmospheric Environment, v. 15, no. 6, p. 1081-1085.

- Galloway, J.N., Schofield, C.L., Peters, N.E., Hendrey, G.R., and Altwicker, E.R., 1983, Effects of atmospheric sulfur on the composition of three Adirondack lakes: Canadian Journal of Fisheries and Aquatic Sciences, v. 40, no. 6, p. 799-806.
- Hewlett, J.D. and Hibbert, A.R., 1967, Factors affecting the response of small watersheds to precipitation in humid areas, in W.E. Sopper and H.W. Lull (editors), International Symposium on Forest Hydrology, Pergamon, Oxford, p. 725-736.
- Johnson, D.W., Cole, D.W., Gessel, S.P., Singer, M.J., and Minden, R.V., 1977, Carbonic Acid leaching in a tropical, temperate, subalpine, and northern forest soil: Arctic Alpine Research, v. 9, p. 329-343.
- Johnson, D.W., Turner, J., and Kelly, J.M., 1982, The effects of acid rain on forest nutrient status: Water Resources Research, v. 18, no. 3, p. 449-461.
- Katz, B.G., Bricker, O.P., and Kennedy, M.M., 1985, Geochemical mass-balance relationships for selected ions in precipitation and stream water, Catoctin Mountains, Maryland: American Journal of Science, vol. 285, p. 931-962.
- Kohler, M.A., Norderson, T.J., and Baker, D.R., 1959, Evaporation maps of the U.S.: Tech. Paper no. 37, Weather Bureau, Dept. of Commerce, Washington, D.C., 13 p., 5 plates.
- Likens, G.E., 1976, Acid precipitation: Chemical and Engineering News, v. 54, no. 48, p. 29-37.
- McColl, J.G., and Cole, D.W., 1968, A mechanism of cation transport in a forest soil: Northwest Science, v. 42, p. 134-140.
- National Acid Precipitation Assessment Program, 1985, Annual report, 1985, 113 p.
- National Oceanic and Atmospheric Administration, 1950-1985, Climatologic data annual summary: Asheville, N.C., National Climatic Data Center, v. 62-94 (published annually).
- Pennsylvania Department of Enviromental Resources, 1982, Pennsylvania perspective on acid rain: PaDER, Harrisburg, Pennsylvania, 31 p.
- Pettyjohn, W.A., and Henning, Roger, 1979, Preliminary estimate of groundwater recharge rates, related streamflow and water quality in Ohio: The Ohio State University Department of Geology and Minerology project completion report no. 552, 323 p.
- Porterfield, George., 1972, Computation of fluvial-sediment discharge: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. C3, 66 p.

REFERENCES CITED--Continued

- Rantz, S.E., and others, 1982, Measurement and computation of streamflow, volume 1, Measurement of stage and discharge: U.S. Geological Survey Water-Supply Paper 2175, 284 p.
- Searcy, J.K., 1963, Flow-duration curves, manual of hydrology--Part 2, Low flow techniques: U.S. Geological Survey Water-Supply Paper 1542-A, 33 p.
- Shaffer, P.W., 1982, Precipitation and streamwater chemistry, input and output budgets in the SWAS watersheds: Appendix V, in Shenandoah watershed acidification study, University of Virginia, 25 p.
- Shaffer, P.W. and Galloway, J.N., 1982, Acid precipitation--The impact on two headwater streams in Shenandoah National Park, Virginia: International Symposium on Hydrometeorology, American Water Resources Association, p. 43-53.
- Sharpe, W.E., Leibfried, R.T., and DeWalle, D.R., 1983, Fish Absent from 14 Laurel Hill Streams: Institute for Research on Land and Water Resources Newsletter, v. 14, No. 2, 1 p.
- Sharpe, W.E., DeWalle, D.R., Leibfried, R.T., Dinicola, R.S., Kimmel, W.G., and Sherwin, L.S., 1984, Causes of acidification of four streams on Laurel Hill in southwestern Pennsylvania: Journal of Environmental Quality, v. 13, no. 4, p. 619-631.
- Sharpe, W.E., Leibfried, V.G., Kimmel, W.G., and DeWalle, D.R., 1987, The relationship of water quality and fish occurrence to soils and geology in an area of high hydrogen and sulfate ion deposition; Water Resources Bulletin, v. 23, no. 1, p. 37-46.

Statistical Analysis System Institute, 1979, SAS Users Guide, p. 763-774.

- U.S. Department of Agriculture, 1983, Soils survey of Somerset County, Pennsylvania: Soil Conservation Service, 148 p.
- U.S. Geological Survey, 1985-86, Water resources data for Pennsylvania, water year 1984-85--volume 3: U.S. Geological Survey Water-Data Report PA-84-3 and PA-85-3 (published annually).
- Walling, D.E., and Foster I.P.L., 1975, Variations in the natural chemical concentrations of river water during flood flows, and the log effect: some further comments: Journal of Hydrology, v. 26, no. 3/4, p. 238-243.