AREAL AND TEMPORAL VARIABILITY OF SELECTED WATER-QUALITY CHARACTERISTICS IN TWO HYDROLOGIC-BENCHMARK BASINS IN THE NORTHEASTERN UNITED STATES

Robert A. Hainly and John R. Ritter

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 85-4025

Harrisburg, Pennsylvania

1986

UNITED STATES DEPARTMENT OF THE INTERIOR

DONALD PAUL HODEL, Secretary

GEOLOGICAL SURVEY

Dallas L. Peck, Director

For additional information
write to:

District Chief
U.S. Geological Survey
4th Floor, Federal Building
P.O. Box 1107
Harrisburg, Pennsylvania 17108-1107

Copies of this report
can be purchased from:

Open-File Services Section
Western Distribution Branch
U.S. Geological Survey
Box 25425, Federal Center
Denver, Colorado 80225
(Telephone: (303) 234-5888)

CONTENTS

	Page
Abstract	1
Introduction	1
Purpose and scope	2
Methods	7
Water-quality	9
Young Womans Creek basin	9
Esopus Creek basin	12
Areal and temporal variations in water quality	15
Young Womans Creek basin	15
Areal variations	15
Temporal variations	15
Esopus Creek basin	17
Areal variations	17
Temporal variations	19
Suggestions for further studies	20
Summary	21
References cited	22

ILLUSTRATIONS

Figure 1.--Map of the Young Womans Creek basin	3
2.--Map of the Esopus Creek basin	4
3.--Graph showing the range of streamflows sampled in the Young Womans Creek basin and the range and mean for 1965-82 at the Benchmark station	10
4.--Graph showing the range of streamflows sampled in the Esopus Creek basin and the range and mean for 1964-82 at the Benchmark station	13
5.--Graphs of the value for Site 1 and the range and median for measurements of six water-quality characteristics elsewhere in the Young Womans Creek basin, 1983	16
6.--Graphs of the value for Site 1 and the range and median for measurements of six water-quality characteristics elsewhere in the Esopus Creek basin, 1983	18

TABLES

Page

Table 1.--Descriptions of two Hydrologic benchmark stations, Young Womans Creek near Renovo, PA and Esopus Creek at Shandaken, NY ---------- 5
2.--Sampling sites in the Young Womans Creek basin---------- 8
3.--Sampling sites in the Esopus Creek basin---------- 8
4.--Summary of the measurements made in the Young Womans Creek basin---------- 9
5.--Minimum, median, mean, and maximum of six water-quality characteristics measured at Young Womans Creek near Renovo (Site 1), PA 1965-83---------- 11
6.--Summary of the measurements made in the Esopus Creek basin--- 12
7.--Minimum, median, mean, and maximum of six water-quality characteristics measured at Esopus Creek at Shandaken (Site 1), NY 1963-83---------- 14
8.--Comparisons of the measurements of seven water-quality characteristics made at Site 1 and the average for the three smallest sub-basins in the Young Womans Creek basin, 1983---------- 17
9.--Comparisons of the measurements of seven water-quality characteristics made at Site 1 and the average for the three smallest sub-basins in the Esopus Creek basin, 1983-- 19

FACTORS FOR CONVERTING INCH-POUND UNITS
TO METRIC (INTERNATIONAL SYSTEM) UNITS

Multiply Inch-Pound Units	By	To Obtain Metric Units
inch (in.)	25.40	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
acre	0.4047	hectometer (hm^2)
ton, short	907.2	kilogram (kg)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
cubic foot per second-day (ft^3/s-d)	0.02832	cubic meter per second-day (m^3/s-d)
cubic foot per second per square mile ($ft^3/s)/mi^2$	0.01093	cubic meter per second per square kilometer ($m^3/s)/km^2$
square foot (ft^2)	0.0929	square meter (m^2)
square mile (mi^2)	2.590	square kilometer (km^2)
ton per square mile (ton/mi^2)	350.3	kilogram per square kilometer (kg/km^2)
ton per day (ton/d)	907.2	kilogram per day (kg/d)
degree Fahrenheit (°F)	-32 x 5/9	degree Celsius (°C)

AREAL AND TEMPORAL VARIABILITY OF SELECTED WATER-QUALITY CHARACTERISTICS IN TWO HYDROLOGIC-BENCHMARK BASINS IN THE NORTHEASTERN UNITED STATES

By Robert A. Hainly and John R. Ritter

ABSTRACT

Two U.S. Geological Survey National Hydrologic Benchmark stations--Young Womans Creek near Renovo, Pennsylvania and Esopus Creek at Shandaken, New York--were studied to (1) define, both areally and temporally, variations of stream acidity and other water-quality characteristics within the basins; (2) evaluate how well the data collected at the Benchmark station represent the water-quality conditions upstream; (3) define relations between streamflow and acidity or pH; and (4) provide a data base to detect trends in quality of headwater streams.

Samples were collected at nine sites, including the Benchmark station, in each basin for three series of measurements over a range of streamflows. Along with streamflow, samples were analyzed for water temperature, specific conductance, pH, dissolved oxygen, acidity, alkalinity, dissolved sulfate, and dissolved nitrite plus nitrate.

The results of the measurements indicated little water-quality variation in the Young Womans Creek basin. Therefore, the data collected at the Benchmark station can be used to reflect upstream changes in water quality. The data collected at the Esopus Creek station did not reflect upstream conditions as well as the Young Womans Creek data because the water quality varied throughout the basin. Few strong relations were found between streamflow and the water-quality characteristics examined in this study. The Esopus Creek data indicated the possibility of relationships between streamflow and alkalinity, dissolved nitrite plus nitrate, and specific conductance. No relations were found between streamflow and the Young Womans Creek water-quality data.

INTRODUCTION

"Acid rain" is a term commonly used to describe rain having a pH of less than 5.6, but in a broader sense, the term is used to describe atmospheric deposition that contains pollutants. Atmospheric deposition occurs not only as rain but also as snow, dew, frost, fog, and dry material (U.S. Environmental Protection Agency, 1980). In the northeastern United States, the pH of rain is generally less than 4.5. The low pH is usually attributed to oxides of sulfur and nitrogen in the air that react with water vapor to form sulfuric and nitric acid (U.S. Environmental Protection Agency, 1979).

Acid rain is a cause for concern because of its possible effect on the environment, particularly the aquatic environment. Studies of the effect of acid rain on streams are generally hampered because of the lack of long-term data. Some of the best sites for studies may be U.S. Geological Survey National Hydrologic Benchmark stations, because water-quality data have been collected at many of them since the mid-1960's. Generally, Hydrologic Benchmark stations are selected because of the undisturbed, natural conditions in the areas drained by the streams. They are usually relatively free from the direct influences of man. Because many of these stations have drainage areas of more than 40 mi^2, water quality at the stations may not reflect variations in water quality in the headwaters. The effects of acid rain on the small upstream tributaries may be sufficiently masked by relatively small amounts of moderately buffered waters, so that by the time the water reaches the station, an analysis of water-quality trends with respect to acid rain would be meaningless.

Two Hydrologic Benchmark stations--Young Womans Creek near Renovo, PA (fig. 1) and Esopus Creek at Shandaken, NY (fig. 2)--were selected for study. Descriptions of the stations, adapted from Cobb and Biesecker (1971), are given in table 1. Data collected at the stations were previously used in reports on trends in water quality; the Young Womans Creek station in an evaluation of the effects of acid rain on headwater streams in Pennsylvania (Ritter and Brown, 1981) and in an analysis of water-quality variability in the West Branch Susquehanna River basin (R. A. Hainly and others, U.S. Geological Survey, written commun., 1984). Data from the Esopus Creek station were analyzed for temporal trends in the acidity of surface waters of New York (Peters and others, 1982). Data from both stations were analyzed for (1) acid-precipitation-induced trends in stream chemistry (Smith and Alexander, 1983a) and (2) trends in comprehensive stream chemistry (Smith and Alexander, 1983b).

Purpose and Scope

This report presents the results of a study to (1) determine the areal and temporal variability of selected water-quality characteristics within two Hydrologic Benchmark basins; (2) evaluate how well chemical data collected at the Hydrologic Benchmark stations represent upstream conditions in the basins; (3) define relations between streamflow and acidity and other chemical characteristics; and (4) provide a data base to detect trends in headwater streams.

The study was limited to the two stations--Young Womans Creek near Renovo, PA and Esopus Creek at Shandaken, NY. Originally, the Hydrologic Benchmark station, McDonalds Branch in Lebanon State Forest, NJ, was also selected but its basin was too small (2.31 mi^2) and its chemistry was too strongly affected by acidic water from upstream swamps to be used for the analysis done in this report.

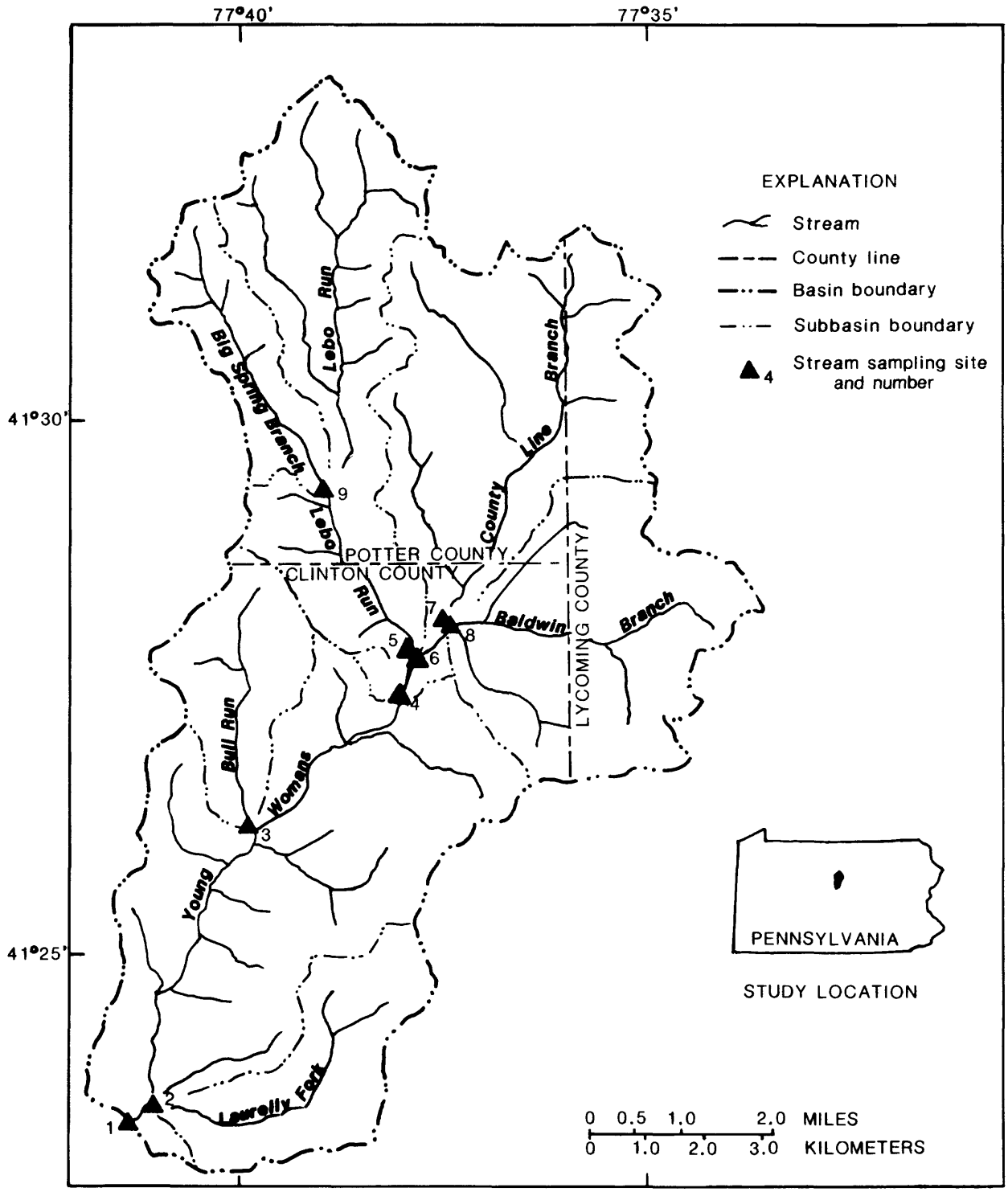

Figure 1.--Young Womans Creek basin. For site names see table 2.

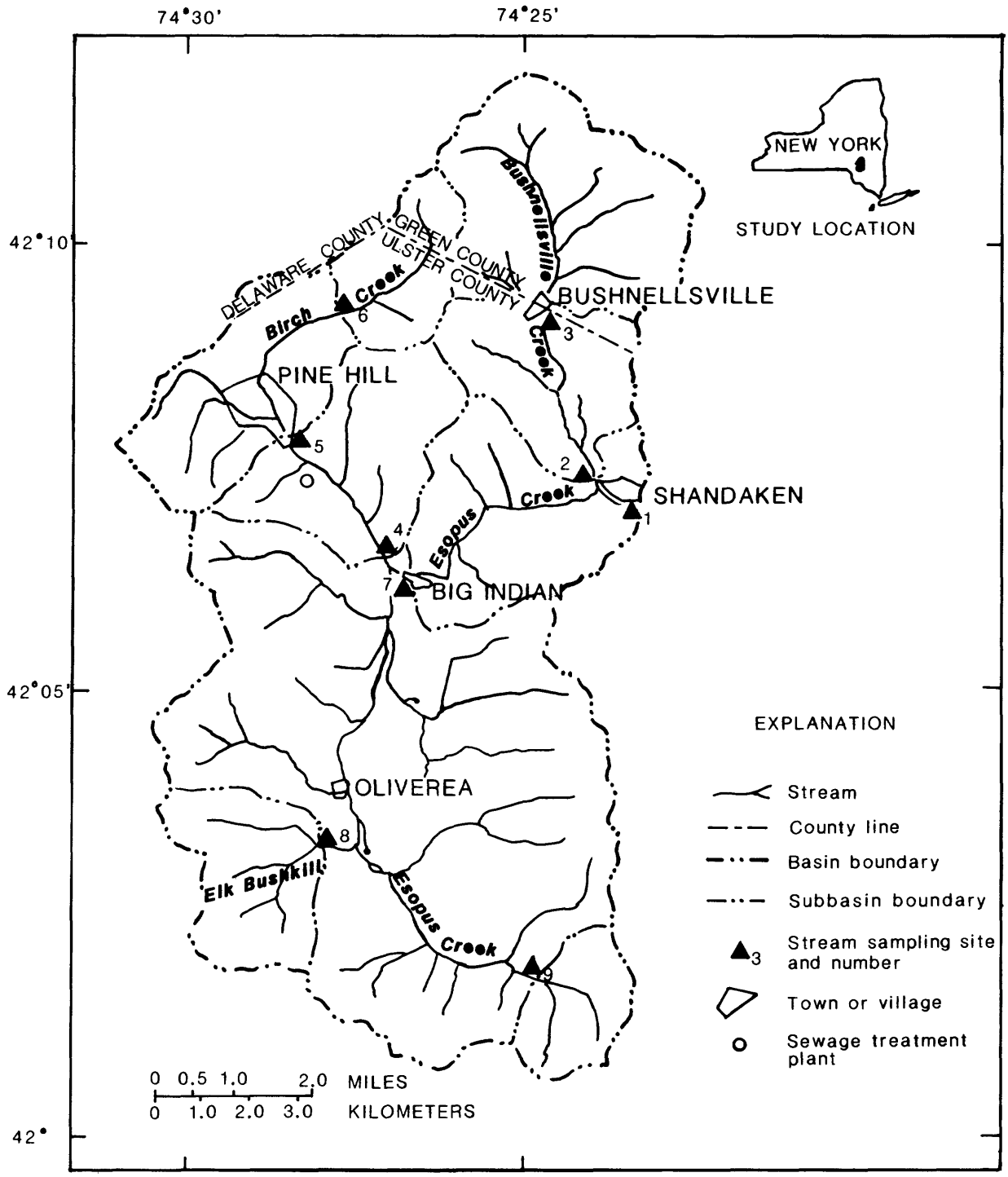

Figure 2.--Esopus Creek basin. For site names see table 3.

Table 1.--Descriptions of Hydrologic-Benchmark Stations--Young Womans Creek near Renovo, PA and Esopus Creek at Shandaken, NY (adapted from Cobb and Biesecker, 1971, p. 24, 29)

	Young Womans Creek near Renovo, PA (01545600)	Esopus Creek at Shandaken, NY (01362198)
Location	Northcentral Pennsylvania.	Catskill Mountains, southeastern New York.
Drainage Area	46.2 mi^2	59.5 mi^2
Physiographic	Allegheny Mountain section of the Appalachian Plateaus province of the Appalachian Highlands.	Catskill section of the Appalachian Plateaus province of Appalachian Highlands.
Climate	Average annual precipitation: 38 inches of which about 10 percent occurs as snow.	Average annual precipitation: about 40-45 inches, about 25 percent occurs as snow.
	Monthly mean temperature extremes: 27° and 71°F.	Monthly mean temperature extremes: 20° and 70°F.
Topography	Broad flat mountains and narrow, steep-sided valleys. The general elevation of the divide is about 1,800 ft. Basin elevations range from 780 to 2,160 ft. The slope of the main stream is about 60 ft per mile.	Mountainous. Basin elevations range from 1,017 to 3,760 ft. Stream slopes vary from 73 to 350 ft per mile.
Rock type	Predominantly sandstone and shale. Some unconsolidated glacial outwash lines the creek bottom.	The basin rocks are reddish, non-marine sandstones. Except in the narrow stream valleys, glacial till, 10 to several tens of feet in thickness, covers the sandstone. The valleys contain a variety of glacial and alluvial deposits of Holocene age as much as 200 ft or more in thickness.

Table 1.--Descriptions of Hydrologic-Benchmark Stations--Young Womans Creek near Renovo, PA and Esopus Creek at Shandaken, NY (adapted from Cobb and Biesecker, 1971, p. 24, 29)--Continued

	Young Womans Creek near Renovo, PA (01545600)	Esopus Creek at Shandaken, NY (01362198)
Vegetation	The area is covered with northern hardwoods, namely ash, beech, birch, cherry, and maple.	Except for a quarter-mile cleared strip in the valley of the main stream and the two principal tributaries, the basin is densely forested with conifers and hardwoods.
Man-made influences	Two secondary roads and some fire trails traverse the basin. The area is very sparsely populated except during hunting season when lodges are occupied. Some logging is done privately but under State supervision. About 95 percent of the basin is publicly owned.	Some small communities and several scattered homes are along the streams in the basin. One community maintains a sewage-treatment plant. There is considerable recreational use of water in the basin including the development of off-stream pools and ponds for recreation. One small reservoir exists on Birch Creek.
Gage location	Lat 41°23'22", long 77°41'28", 5 miles northeast of Renovo.	Lat 42°06'59", long 74°23'20" at Shandaken.
Flow characteristics	Stream is perennial. Average annual runoff: about 17 in.	Stream is perennial. Average annual runoff: about 25 in.
Water quality	Principal constituents: calcium; bicarbonate and sulfate; and silica. Low-flow dissolved-solids concentration: about 35 mg/L. Average annual sediment load: 50 tons per sq mi.	Principal constituents: calcium and magnesium; bicarbonate and sulfate. Lowflow dissolved-solids concentrations: about 35 mg/L.

Table 1.--Descriptions of Hydrologic-Benchmark Stations--Young Womans Creek near Renovo, PA and Esopus Creek at Shandaken, NY (adapted from Cobb and Biesecker, 1971, p. 24, 29)--Continued

	Young Womans Creek near Renovo, PA (01545600)	Esopus Creek at Shandaken, NY (01362198)
Ground water	The shallow deposit of unconsolidated sand and gravel in the stream valley yields suitable water for domestic supplies. The bedrock is capable of supplying large yields of water of good quality to wells at moderate depth. Locally, some deep wells may yield salty water.	Numerous springs supply water for domestic use and small resout communities. The plain is underlain by water-bearing coarse and sand gravel. Glacial clays fill the remainder of the bedrock valleys. Wells tapping the underlying bedrock are usually artesian.
Data collected	Continuous streamflow-12/64 to present. Continuous precipitation-12/64 to present.	Continuous streamflow-10/63 to present. Daily precipitation (two gages by U.S. Weather Bureau)-2/43 to present, 7/40 to present. Continuous precipitation (from U.S. Weather Bureau) 1/53 to present. Continuous surface-water temperature-10/63 to present.
	Water quality-9/67 to present.	Water quality-9/67 to present.

Methods

This study was designed to measure water-quality characteristics over a range of streamflows. In each of the two Hydrologic Benchmark basins, measurements were made at nine stations, including the Hydrologic Benchmark station. The station locations are shown in figures 1 and 2. The station names and the area drained by each are shown in tables 2 and 3. Three measurements were made at each station from April to July 1983. Sample intervals were designed to include measurements of high, medium, and low base flow and snowmelt if possible. Measurements made in the field immediately following sample collection included streamflow, water temperature, pH, specific conductance at 25°C, dissolved oxygen, acidity, and alkalinity.

Table 2.--Sampling sites in the Young Womans Creek basin

Station Number	Site Number (fig. 1)	Site Name	Drainage Area (mi^2)
01545600	1	Young Womans Creek near Renovo	46.2
01545597	2	Laurelly ?ork at mouth	3.73
01545552	3	Bull Run at mouth	3.07
01545542	4	Young Womans Creek below Lebo Run	26.8
01545540	5	Lebo Run at mouth	11.1
01545530	6	Young Womans Creek above Lebo Run	15.7
01545510	7	County Line Branch at mouth	8.51
01545520	8	Baldwin Branch at mouth	6.86
01545535	9	Big Spring Branch at mouth	2.68

Table 3.--Sampling sites in the Esopus Creek basin

Station Number	Site Number (fig. 2)	Site Name	Drainage Area (mi^2)
01362198	1	Esopus Creek at Shandaken	59.7
01362197.05	2	Bushnellsville Creek at mouth at Shandaken	11.2
01362196.50	3	Bushnellsville Creek at Bushnellsville	7.25
01362195.60	4	Birch Creek at mouth at Big Indian	12.8
01362195.40	5	Birch Creek at Pine Hill	7.66
01362195.20	6	Birch Creek near Pine Hill	2.58
01362195.10	7	Esopus Creek at Big Indian	33.0
01362192.05	8	Elkbushkill at mouth at Oliverea	3.75
01362189	9	Esopus Creek near Oliverea	1.96

Acidity and alkalinity titrations were performed with a burette to endpoints of pH 8.3 and 4.5, respectively. Samples were collected, filtered immediately through a 0.45 µm filter, and kept chilled and in the dark until dissolved sulfate and dissolved nitrite plus nitrate were analyzed in the U.S. Geological Survey Atlanta Central Laboratory. Methods for field measurements and sample preservation techniques used are according to techniques described by Brown and others, 1970. The methods used for the chemical analyses are documented in Skougstad and others, 1979.

WATER QUALITY

Young Womans Creek Basin

The streamflow and water quality at nine sites in the basin were measured on April 13, May 25, and July 13, 1983. A summary of the data collected is shown in table 4. The streamflows measured would be considered a medium-high flow, a medium flow, and a medium-low flow. The flows measured at the Benchmark station (Site 1) are equaled or exceeded 6.2, 20, and 73 percent of the time. The average flow at Site 1 from 1964 to 1983 was 77 ft^3/s.

Table 4.--Summary of measurements made in the Young Womans Creek basin

Site Number	Time	Streamflow (ft^3/s)	Water Temperature (°C)	Specific Conductance (µS/cm)	pH (units)	Dissolved Oxygen (mg/L)	Dissolved Oxygen (percent saturation)	Acidity (mg/L as $CaCO_3$)	Alkalinity (mg/L as $CaCO_3$)	Dissolved Sulfate (mg/L)	Dissolved Nitrite + Nitrate (mg/L as N)
					April 13, 1983						
1	0930	231	5.5	42	6.4	12.6	100	2	4	-	-
2	1815	20	8.0	36	7.0	11.9	100	2	2	-	-
3	1745	13	7.5	42	7.2	11.8	100	2	4	-	-
4	1700	114	8.0	36	7.2	11.6	100	2	4	-	-
5	1530	44	8.5	42	7.4	11.6	100	2	6	-	-
6	1615	71	8.0	33	7.0	11.6	100	2	3	-	-
7	1415	36	8.5	33	7.1	11.1	97	2	3	-	-
8	1330	32	8.0	33	6.9	11.6	100	2	3	-	-
9	1140	9.4	8.5	42	7.4	11.2	98	1	7	-	-
					May 25, 1983						
1	0915	116	8.5	40	7.0	11.2	99	2	7	9	0.24
2	1800	8.2	10.5	37	6.5	10.6	98	2	3	7	.45
3	1700	7.8	10.5	43	6.6	10.6	99	2	4	9	.55
4	1610	75	11.0	38	6.8	10.5	100	2	5	8	< .10
5	1510	32	11.0	43	6.9	10.3	98	2	7	8	.12
6	1430	43	11.0	35	6.6	10.3	98	2	4	7	< .10
7	1330	22	10.5	34	6.6	10.5	99	2	3	7	.11
8	1250	17	10.0	35	6.6	10.4	97	2	3	8	< .10
9	1115	7.8	9.0	43	6.9	10.9	99	2	7	9	.17
					July 13, 1983						
1	0915	18	16.5	44	7.1	9.2	97	2	7	7	.28
2	1800	2.4	16.0	37	6.6	9.1	95	2	4	5	.46
3	1715	.68	15.5	46	6.8	9.4	97	2	6	7	.52
4	1630	8.2	17.5	43	6.9	8.6	94	2	8	8	.19
5	1540	3.2	17.5	51	7.2	8.8	96	2	11	9	.24
6	1500	5.0	17.0	39	6.9	8.8	95	2	6	6	.16
7	1400	2.6	17.0	38	6.8	8.8	95	2	6	8	.20
8	1320	2.1	15.0	39	6.8	9.3	96	2	5	6	.12
9	1145	.62	15.0	50	7.2	9.2	96	2	11	6	.31

Figure 3 shows the range of streamflows measured at each site in the Young Womans Creek basin and and the maximum, minimum, and mean for the period of surface water record at Site 1, the Benchmark station.

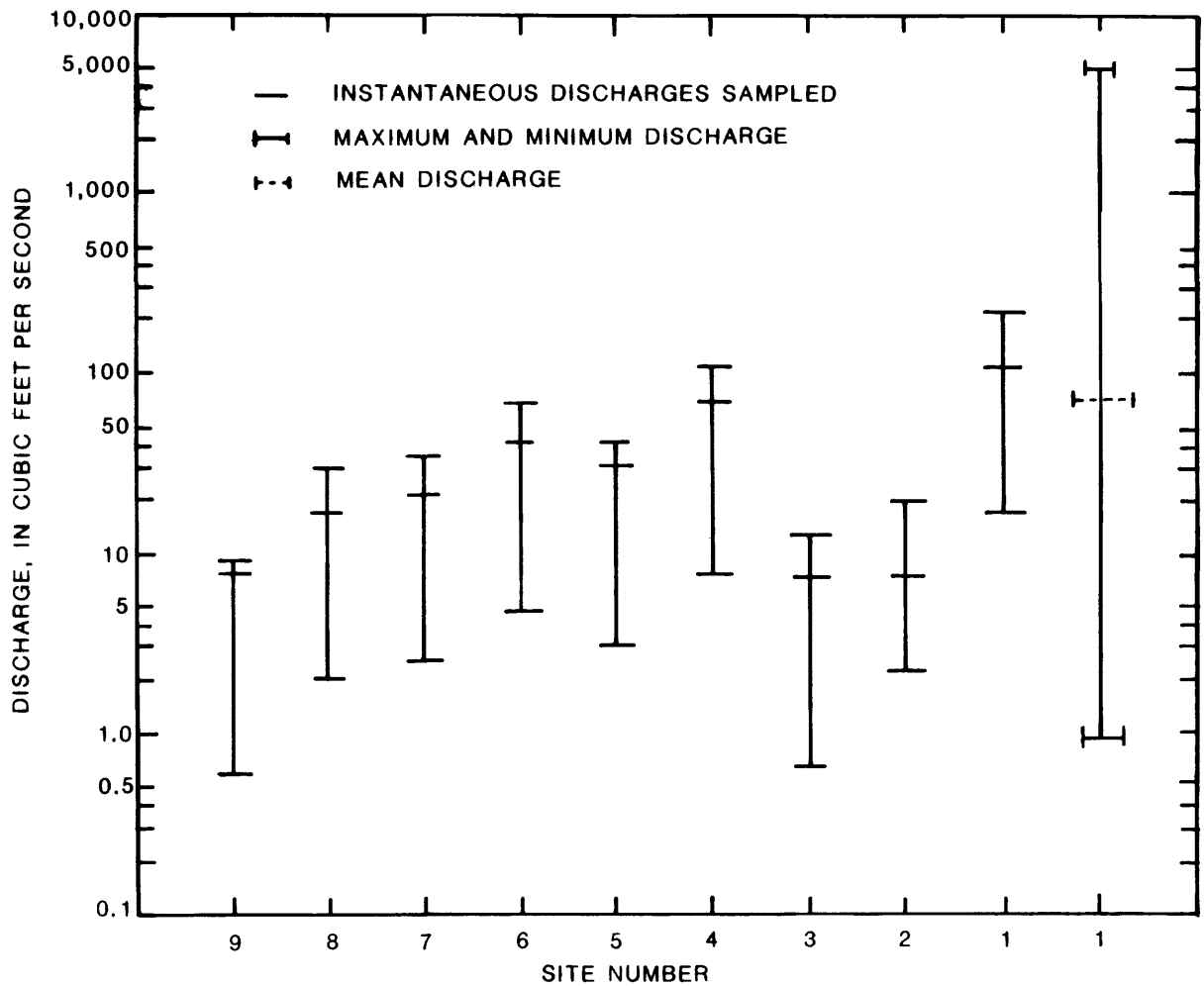

Figure 3.--Range of the streamflows sampled in the Young Womans Creek basin and the range and mean for 1965-82 at the Benchmark station.

The specific conductances measured at Site 1 were within 4 µS/cm (microsiemens per centimeter) of the median for the period of record (table 5). The range of the conductances for the April, May, and July samplings were 33-42, 34-43, and 37-51 µS/cm, respectively. At all sites but Site 1, the specific conductances increased slightly with a decrease in streamflow.

The pH values measured at Site 1 were within one-half unit of the median for the period of record (table 5). The ranges of pH in the basin were within one unit for each series of measurements. The pH at Site 1 was the lowest in the basin on April 13 and the highest on May 25. For the April 13 and July 13 samples, the highest pH's were found at Sites 5 and 9. These two stations are in the same sub-basin.

Table 5.--Minimum, median, mean, and maximum of six water-quality characteristics measured at Young Womans Creek near Renovo (Site 1), PA., 1965-83

	Specific Conductance (µS/cm	pH (units)	Acidity (mg/L as $CaCO_3$)	Alkalinity (mg/L as $CaCO_3$)	Dissolved Sulfate (mg/L)	Dissolved Nitrite + Nitrate (mg/L as N)
Minimum	20	5.7	0	2	3	0.10
Median	40	6.8	5	8	8	.26
Mean	41	6.8	5	8	8	.27
Maximum	261	7.8	20	33	95	.51
No. Samples	224	224	13	167	170	38

The dissolved oxygen in basin streams was at more than 94 percent of saturation for each of the measurements at all nine sites. The values given in table 4 for Site 1 on April 13 and May 25 are probably higher than the others only because the water temperature was lower. The saturation level at Site 1 was within 5 percent of the other sites for each series of measurements.

The acidity of the water in the basin was almost constant areally and temporally. Only one measurement deviated from the level of 2 mg/L found for all the other measurements.

The three alkalinity measurements made at Site 1 are close to the median measured for the period of record (table 5). The largest difference in alkalinity values throughout the basin was 7 mg/L. This occurred during the medium-low flow measurements. The smallest difference of 4 mg/L occurred during the medium flow sample on May 25. Alkalinity increased slightly at each sampling site as flow decreased. Generally, Sites 2 and 8 had the lowest alkalinity and Site 9, the smallest subbasin, had the highest alkalinity. In all cases, alkalinity was greater than acidity.

Samples of dissolved sulfate and nitrite plus nitrate were not collected on April 13 in this basin. The other two samplings showed that concentrations of dissolved sulfate did not vary much. The range of values, including both sample sets, was 4 mg/L. The concentrations at Site 1 were nearly equal to the median of the concentrations for the period of record (table 5).

The concentrations of dissolved nitrite plus nitrate at Site 1 are nearly equal to the median for the period of record (table 5). The concentrations of nitrite plus nitrate varied more than any of the other constituents. The two small streams in the southern half of the basin (Sites 2 and 3) had the highest concentrations for both samplings. The concentrations at these two sites did not appear to change as flow decreased. This indicates that

ground-water may have a significant influence on the water quality of these small streams. The concentrations at Site 1 were close to the mean for both samplings.

Esopus Creek Basin

Streamflow and water-quality measurements were made at nine sites in the Esopus Creek basin on April 27, June 1, and July 21, 1983. The measurements at the nine sites are summarized in table 6. The flows at the time of the measurements were medium-high, medium, and medium-low. The flows measured are equaled or exceeded about 2.5, 25, and 82 percent of the time, respectively at Esopus Creek at Shandaken (Site 1). The samples taken on April 27 and June 1 include some snowmelt. The average flow at Site 1 was 140 ft^3/s during 1963-81. Figure 4 shows the range of streamflows measured at each site and the maximum, minimum, and mean for the period of surface water record at Site 1, the Benchmark station.

Table 6.—Summary of the measurements made in the Esopus Creek basin

Site Number	Time	Streamflow (ft^3/s)	Water Temperature (°C)	Specific Conductance (µS/cm)	pH (units)	Dissolved Oxygen (mg/L)	Dissolved Oxygen (percent saturation)	Acidity (mg/L as $CaCO_3$)	Alkalinity (mg/L as $CaCO_3$)	Dissolved Sulfate (mg/L)	Dissolved Nitrite + Nitrate (mg/L as N)
					April 27, 1983						
1	0900	690	5.0	43	6.5	12.4	100	2	6	6	0.27
2	1645	156	7.5	47	6.6	11.2	96	2	6	7	.33
3	1610	92	6.5	48	6.5	—	—	2	4	7	.42
4	1500	127	8.5	51	6.8	10.9	97	2	6	6	.27
5	1410	83	7.5	52	6.7	—	—	2	6	6	.35
6	1330	25	7.0	36	6.4	—	—	2	4	5	.41
7	1215	372e	8.0	36	6.4	11.4	100	2	4	6	.24
8	1120	37	6.5	36	6.4	11.3	96	2	4	6	.55
9	1030	26	4.0	38	6.4	12.6	100	2	3	5	.28
					June 1, 1983						
1	0800	166	9.0	47	7.1	11.4	100	2	8	7	.17
2	1600	23	11.0	54	7.2	10.5	99	1	10	8	.22
3	1510	15	8.5	50	6.8	11.4	100	2	7	9	.31
4	1410	24	12.0	72	7.3	10.6	100	2	12	8	.20
5	1310	14	10.5	75	7.0	10.4	98	2	11	8	.32
6	1210	4.2	10.5	40	6.8	10.3	99	2	6	7	.24
7	1115	96	11.0	38	6.8	10.6	100	2	5	7	.12
8	1015	16	8.0	36	6.6	11.2	100	2	4	8	.35
9	0915	8.4	8.0	39	6.6	10.9	99	2	4	7	.17
					July 21, 1983						
1	0800	21	17.0	62	7.3	8.6	92	2	14	7	.14
2	1600	3.8	18.5	68	7.0	8.6	95	2	16	7	.28
3	1530	1.1	13.5	52	6.8	9.4	95	3	9	7	.39
4	1420	4.0	23.0	107	7.6	8.2	99	2	18	7	.20
5	1330	1.9	17.5	105	7.0	8.4	92	4	17	6	.35
6	1230	.41	15.5	45	6.9	9.3	99	2	8	5	.39
7	1130	12	18.5	45	6.8	8.4	93	3	9	5	.06
8	1030	1.0	14.0	48	6.8	9.3	94	2	6	7	.80
9	0920	.65	12.0	50	6.8	9.4	93	2	7	6	.44

e = estimated

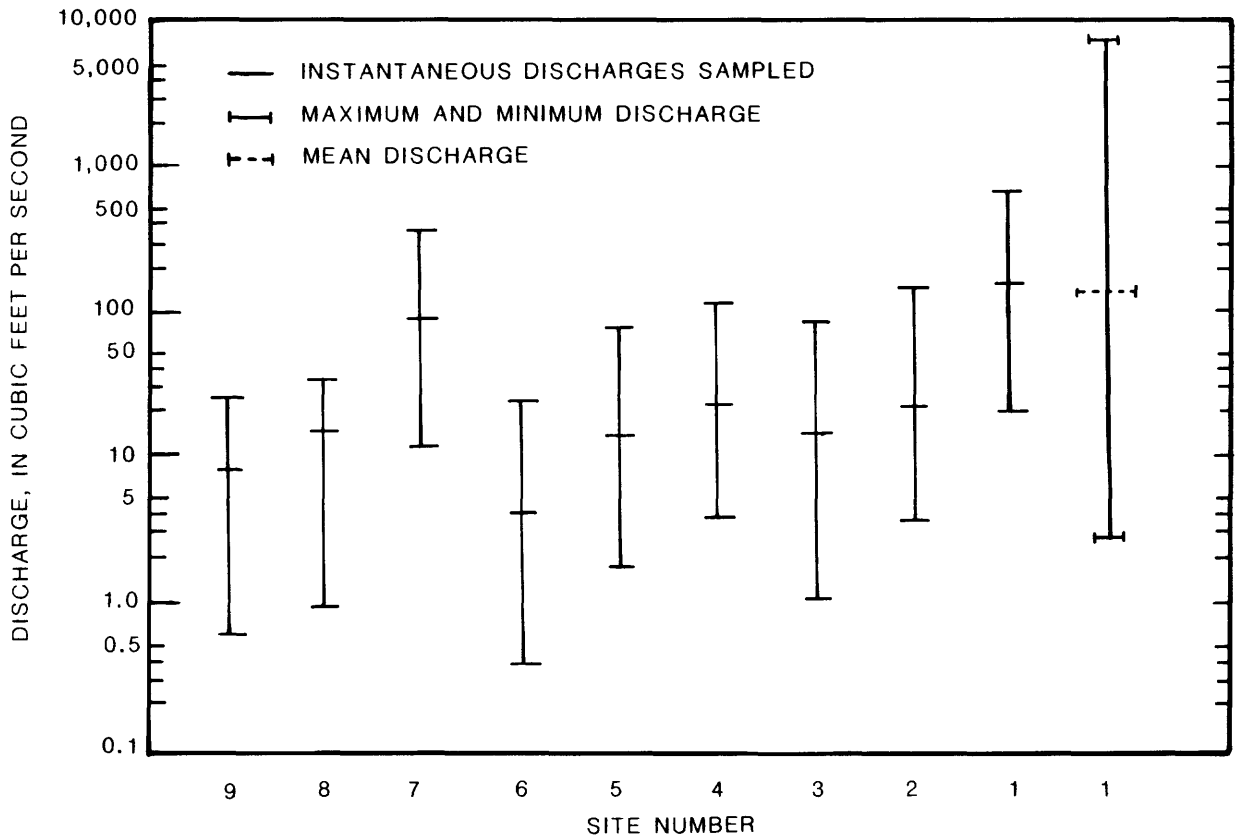

Figure 4.--Range of streamflows sampled in the Esopus Creek basin and the range and mean for 1964-82 at the Benchmark station.

The specific conductances measured at Site 1 bracketed the median and mean for the period of record, 1963-83 (table 7). The mean of the three measurements is nearly equal to the mean for the period of record. On April 27 the difference between the maximum and the minimum in the basin was only 16 µS/cm; on June 1, it was 39 µS/cm; and on July 21, 62 µS/cm. Generally, the specific conductances at each station increased as flow decreased. The highest specific conductances consistently occurred at Sites 4 and 5; both are on Birch Creek below the village of Pine Hill (fig. 2). Because the specific conductances at Site 6 above the village were among the lowest measured each time, the village appears to have a significant effect on the water quality of the lower reaches of Birch Creek. The values at Site 1 were either the median or close to the median for each set of measurements, but for the last two measurements its specific conductance was well below the highest conductances measured in the basin.

The pH values measured at Site 1 were close to the median for the period of record (table 7). Once again, the mean of the three measurements is nearly equal to the mean for the period of record. The smallest range of pH values measured in the basin was 0.4 units and the range increased as flow decreased. The largest range of pH values in the basin was 0.8 units. Because of the narrow ranges, the pH measured at Site 1 was always close to the median.

Table 7.--Minimum, median, mean, and maximum of six water-quality characteristics measured at Esopus Creek at Shandaken, NY (Site 1), 1963-83

	Specific Conductance (µS/cm)	pH (units)	Alkalinity (mg/L as $CaCO_3$)	Dissolved Sulfate (mg/L)	Dissolved Nitrite + Nitrate (mg/L as N)
Minimum	33	5.5	2	1	0.03
Median	51	6.9	11	8	.25
Mean	54	6.9	11	8	.29
Maximum	100	8.7	21	15	.81
No. Samples	211	209	171	199	45

The dissolved oxygen at every site was at least 92 percent of saturation for every measurement. The water at Site 1 had the highest saturation percentage in the basin for the April and June measurements. This is most likely due to the time of the measurement and the water temperature. For the July measurement, the saturation percentage was one of the lowest of the nine measurements. There appears to be no oxygen deficiency in the basin.

Acidity as $CaCO_3$ in the basin was fairly constant areally and temporally. The range for each series of measurements never exceeded 2 mg/L. The concentrations ranged from 1 to 4 mg/L.

Alkalinity measured at Site 1 was well within the range measured over the period of record (table 7). The ranges of alkalinity in the basin increased as flow decreased. The values at each site similarly increased. The alkalinity at Site 1 was close to the median for the first two series of measurements, but was much higher than the median for the third measurement at medium-low flow. In all cases, alkalinity was higher than acidity. Like specific conductance, alkalinity was highest at Sites 4 and 5, whereas Site 6 was typical of other headwater sites. The alkalinity at Sites 4 and 5 was undoubtedly influenced by the village of Pine Hill.

The concentrations of dissolved sulfate at Site 1 for the three measurements are close to the median for the period of record (table 7). The range of values for dissolved sulfate was narrow for each measurement. The range and concentrations of dissolved sulfate only changed slightly as the flow conditions changed. It appears that this characteristic is unrelated to streamflow.

The concentrations of nitrite plus nitrate at Site 1 were well within the range of concentrations measured over the period of record (table 7) and within 0.11 mg/L of the median. The values measured at Site 1 were all less than the mean for the period of record. The concentrations at Site 8 were consistently the highest; the ones at Site 7 on Esopus Creek, the lowest.

AREAL AND TEMPORAL VARIATIONS IN WATER QUALITY

Young Womans Creek Basin

Areal Variations

Results show that, in Young Womans Creek, there was little areal variation in the water-quality characteristics studied. For the three series of measurements at the nine stations, specific conductance ranged from 33 to 51 µS/cm; pH from 6.4 to 7.4; acidity from 1 to 2 mg/L as $CaCO_3$; alkalinity from 2 to 11 mg/L; dissolved sulfate from 5 to 9 mg/L; and dissolved nitrite plus nitrate as N from <0.10 to 0.55 mg/L. Dissolved oxygen was at least 94 percent of saturation for all measurements. Figure 5 shows the range and median value of the measurements at all nine stations and the value of Site 1 for the six chemical characteristics for each series of measurements.

Because of the small ranges found, the values at the Hydrologic Benchmark station, Young Womans Creek near Renovo, PA seem to represent upstream conditions fairly well with the possible exception of nitrite plus nitrate concentrations. As a check to see if measurements at Site 1 are representative of the headwater streams, values at Site 1 were compared to the average values of the sites at the three smallest subbasins for each sampling (Sites 2, 3, and 9). The drainage areas of these subbasins range from 2.68 to 3.73 mi^2. Table 8 shows the values for Site 1 are close to the average; as noted above, however, the nitrite plus nitrate concentrations compare the least favorably. The values at Site 1 appear to represent upstream conditions best at low flows. This fact is illustrated by the smaller difference between the value at Site 1 and the median of all the values at the later, medium-low flow measurements as shown in figure 5.

No relation was evident between flow and acidity or between flow and pH. Sulfate values appear to increase with flow while a slight increase in specific conductance, alkalinity, and nitrite plus nitrate with a decrease in flow appears to also occur. However, regressions of the characteristics against streamflow for the long-term record from Young Womans Creek show that no such relations exit.

Temporal Variations

Analyses of trends of chemical characteristics from the long-term data available from Young Womans Creek were performed by Hainly and others (U.S. Geological Survey, written commun., 1984), and Smith and Alexander (1983a). Both groups used the Seasonal Kendall test, a distribution-free test that adjusts the data for seasonality. Both groups found small increases in alkalinity at the Benchmark station. From 1972 to 1982, Hainly and others found small increases in pH and sulfate. Using the entire period of record, Smith and Alexander found a very small decrease in sulfate concentration and no significant trend in pH.

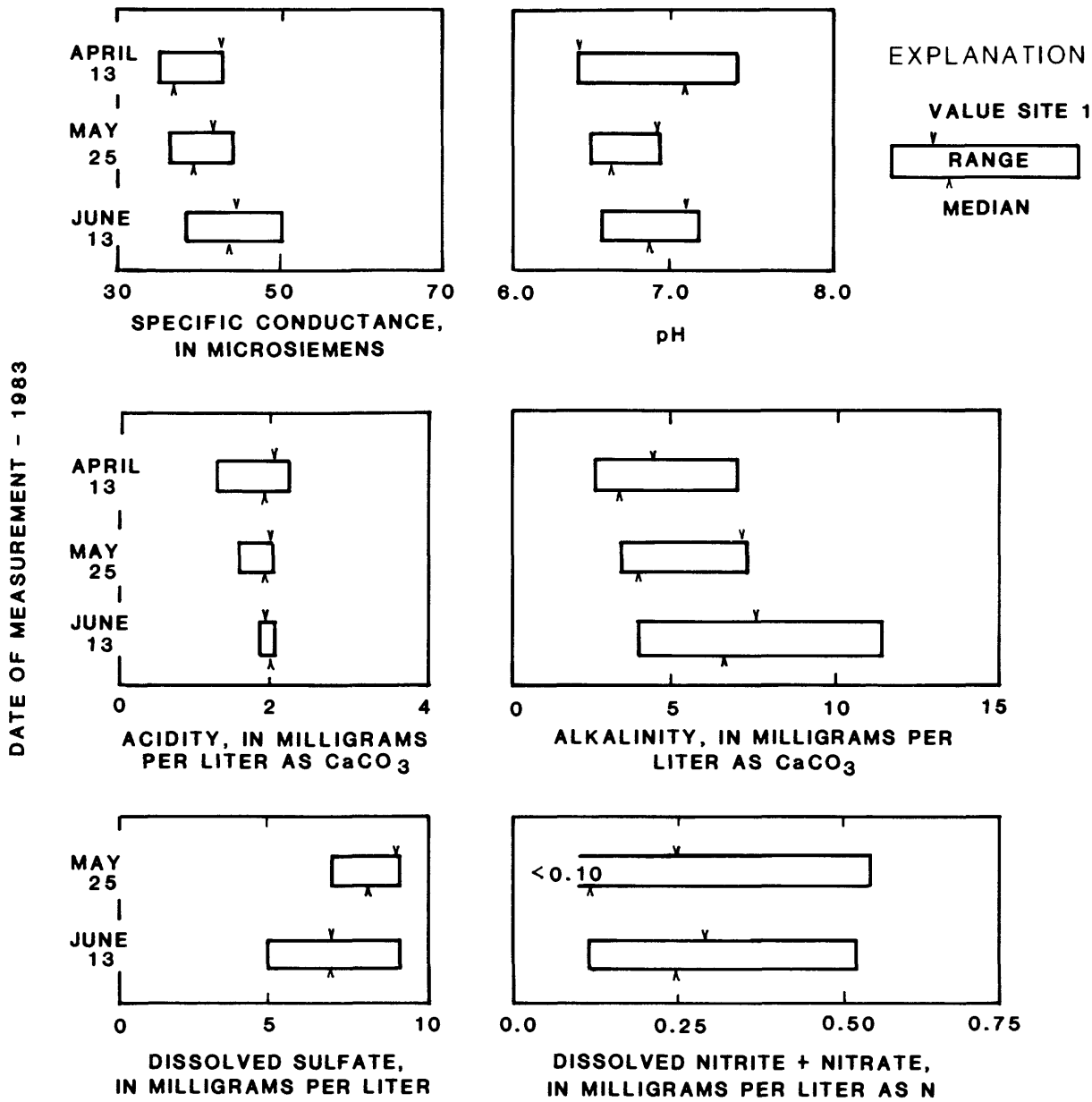

Figure 5.--The value for Site 1 and the range and median for measurements of six water-quality characteristics elsewhere in the Young Womans Creek basin, 1983.

Table 8.--Comparisons of the measurements of seven water-quality characteristics made at Site 1 and the average for the three smallest sub-basins in the Young Womans Creek basin, 1983

	April 13		May 25		July 13	
	Site 1	Average of Small Basins	Site 1	Average of Small Basins	Site 1	Average of Small Basins
Specific Conductance (µS/cm)	42	40	40	41	44	44
pH (units)	6.4	7.2	7	6.7	7.1	6.9
Acidity (mg/L as $CaCO_3$)	2	2	2	2	2	2
Alkalinity (mg/L as $CaCO_3$)	4	4	7	5	7	7
Dissolved Oxygen (percent saturation)	100	99	99	99	97	96
Dissolved Sulfate (mg/L)	-	-	9	8	7	6
Dissolved Nitrate + Nitrite (mg/L as N)	-	-	.24	.39	.28	.43

Esopus Creek Basin

Areal Variations

The data collected in the Esopus Creek basin showed that the chemical characteristics in that basin had more areal variability than those in the Young Womans Creek basin. For the three measurements at the nine stations, specific conductance ranged from 36 to 107 µS/cm; pH from 6.4 to 7.6; acidity from 1 to 4 mg/L as $CaCO_3$; alkalinity from 3 to 17 mg/L as $CaCO_3$; dissolved sulfate from 5 to 9 mg/L; and dissolved nitrite plus nitrate as N from 0.06 to 0.80 mg/L. Dissolved oxygen was at least 92 percent of saturation for all measurements. Figure 6 shows the range and median values of the measurements at all nine stations and the value at Site 1 for the six water-quality characteristics for each series of measurements.

The values of the constituents at the Hydrologic Benchmark station, Esopus Creek at Shandaken, NY, seem to represent basin conditions fairly well for acidity, sulfate, dissolved oxygen, and pH because of the narrow range found for these constituents, but not too well for the others. The values shown in table 9 were developed to determine whether the water quality at Site 1 is representative of the headwater streams' water quality. The data collected at Site 1 were compared to the average values of the sites at the three smallest subbasins for each sampling (Sites 6, 8, and 9). The drainage areas of these subbasins range from 1.96 to 3.75 mi^2. The table shows the poor agreement of the values at Site 1 and the values of the three

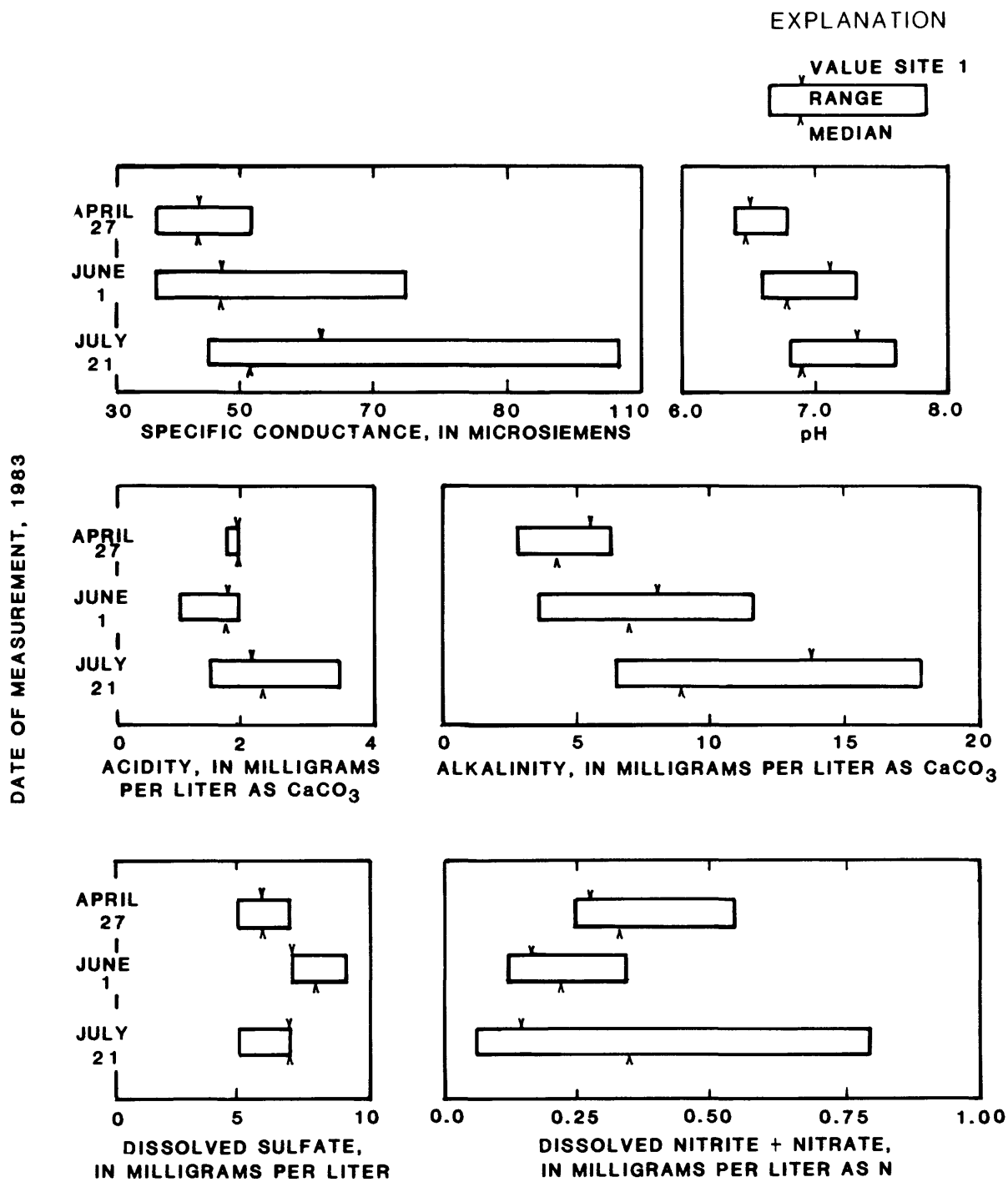

Figure 6.--The value for Site 1 and the range and median for measurments of six water-quality characteristics elsewhere in the Esopus Creek basin, 1983.

Table 9.--Comparisons of the measurements of seven water-quality characteristics made at Site 1 and the average of the three smallest sub-basins in the Esopus Creek basin, 1983.

	April 27		June 1		July 21	
	Site 1	Average of 3 smallest sites	Site 1	Average of 3 smallest sites	Site 1	Average of 3 smallest sites
Specific Conductance (µS/cm)	43	36	47	38	62	48
pH (units)	6.5	6.4	7.1	6.6	7.3	6.8
Acidity (mg/L as $CaCO_3$)	2	2	2	2	2	2
Alkalinity (mg/L as $CaCO_3$)	6	4	8	4	14	7
Dissolved Oxygen (percent saturation)	100	98	100	99	92	95
Dissolved Sulfate (mg/L)	6	5	7	7	7	7
Dissolved Nitrite + Nitrate (mg/L as N)	.27	.41	.17	.25	.14	.54

subbasins for specific conductance, alkalinity, and nitrite plus nitrate. The values for acidity and sulfate agree rather closely and those for dissolved oxygen and pH apparently agree only at higher streamflows. The larger range of values for all the constituents and the differences of the values throughout the basin, relative to the data collected from Young Womans Creek, is probably due to the larger resident population in the Esopus Creek basin but may also be due to differences in slope, residence time, ground-water contribution, soil thickness, or geology.

No relation between flow and acidity or pH was found. A significant inverse relation between flow and alkalinity and specific conductance for the long-term record at the Benchmark station was found by Peters and others (1982). They also noted a significant relation between flow and nitrite plus nitrate concentrations at the Station. The three measurements made for this study at the Benchmark station, indicate a possible decrease in nitrite plus nitrate concentrations with a decrease in streamflow. The relation, however, is not seen at many of the other sites.

Temporal Variations

Analyses for temporal trends in the long-term data at this Hydrologic Benchmark station were performed by Smith and Alexander (1983a) and Peters and others (written commun., 1982). Both groups found small downward trends in sulfate concentration and very small upward trends in alkalinity. Smith and Alexander also found a small downward trend in pH.

SUGGESTIONS FOR FURTHER STUDIES

Although trend tests on the long-term data for precipitation and surface water at the Hydrologic Benchmark stations examined in this study have been fully exhausted, little is known about the changing quality of the headwater streams and the relation of the trends in the headwater streams to the trends at the Benchmark stations. More data collection is required from the small streams draining these areas.

Another area requiring closer scrutiny is the effect of acid rain on the water quality of a stream during a rain storm or during periods of snowmelt. At these times, the effect of acid rain is expected to be the most pronounced; however, few data are available to support this conclusion. The higher sulfate concentrations and lower pH values generally found at the medium to high flows sampled for this study support this conclusion. An investigation with this purpose in mind would require water-quality sampling during storms throughout the year and during periods of runoff from snowmelt.

SUMMARY

Measurements of streamflow, water temperature, specific conductance, pH, dissolved oxygen, acidity, alkalinity, and dissolved sulfate and nitrite plus nitrate were made at nine sites in each of two basins having a Hydrologic Benchmark station. These measurements were made to determine the areal and temporal variability of stream acidity and other acid-rain-related characteristics within the basins and to determine whether measurements at the two Hydrologic Benchmark stations--Young Womans Creek near Renovo, PA and Esopus Creek at Shandaken, NY--are representative of the water-quality conditions upstream. The data were also collected to aid in the definition of relations between streamflow and acid-rain-related constituents and to develop a database for determining trends in headwater streams.

The results showed that little areal variation in water quality occurred in the Young Womans Creek basin. Some variation, probably due to the larger amount of residential land use in the basin, did occur in the Esopus Creek basin. For these reasons, data collected at the Hydrologic Benchmark station on Young Womans Creek were better indicators of upstream conditions than the data collected at the Esopus Creek station.

Several relations were indicated by the three measurements made in this study at each station. However, statistical evidence generated by regressions of the long-term record of streamflow and the chemical characteristics examined in this study indicated very few good relations. An examination of these characteristics for the period of water-quality record at the Esopus Creek station produced relations for flow and alkalinity, specific conductance, and nitrite plus nitrate only. No relations were found in the long-term data collected from Young Womans Creek.

Trends were found in the long-term data at both Benchmark stations. Generally, sulfate concentrations were found to be decreasing and pH and alkalinity were found to be increasing. This is not what would be expected if acid rain was affecting the water quality in the basins and the quality of the precipitation was decreasing. Exceptions to this generalization were a small positive trend in sulfate concentration at the Young Womans Creek station found by Hainly and others (U.S. Geological Survey, written commun., 1984) for the 1972 to 1982 water years and a small negative trend in pH at the Esopus Creek station found by Smith and Alexander (1983a) for the period of record (1964 to 1982 water years).

REFERENCES CITED

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Book 5, Chapter A1: U.S. Geological Survey Techniques of Water-Resources Investigations, 160 p.

Cobb, E. D. and Biesecker, J. E., 1971, The national hydrologic benchmark network: U.S. Geological Survey Circular 460-D, 38 p.

Peters, N. E., Schroeder, R. A., and Troutman, D. E., 1982, Temporal trends in the acidity of precipitation and surface waters of New York: U.S. Geological Survey Water-Supply Paper 2188, 35 p.

Ritter, J. R. and Brown, A. E., 1981, An evaluation of acid rain on low conductivity headwaters streams in Pennsylvania: U.S. Geological Survey Open-File Report 81-1025, 53 p.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. E., 1979, Methods for analysis of inorganic substances in water and fluvial sediments: Book 5, Chapter A1, U.S. Geological Survey Techniques of Water-Resources Investigations, 626 p.

Smith, Richard A. and Alexander, Richard B., 1983a, Evidence for acid-precipitation-induced trends in stream chemistry at hydrologic benchmark stations: U.S. Geological Survey Circular 910, 12 p.

Smith, Richard A. and Alexander, Richard B., 1983b, A statistical summary of data from the U.S. Geological Survey's national water quality networks: U.S. Geological Survey Open-File Report 83-533, 30 p.

U.S. Environmental Protection Agency, 1979, Research summary, acid rain; EPA-600/8-79-028; 23 p.

U.S. Environmental Protection Agency, 1980, Acid rain, v. 1, 4 p.