SENSITIVITY OF STREAM BASINS IN

SHENANDOAH NATIONAL PARK TO ACID DEPOSITION

By Dennis D. Lynch and Nancy B. Dise

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CONVERSION TABLE

The following factors may be used to convert inch-pound units to metric (International System) units.

Multiply inch-pound unit	By	To obtain metric unit
	Length	
inch (in)	25.40	millimeter (mm)
foot (ft)	.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
square mile (mi^2)	259.0	hectare (ha)
	Volume	
gallon (gal)	3.785	liter (L)
cubic foot (ft^3)	.02832	cubic meter (m^3)
	Flow	
cubic foot per second (ft^3/s)	.02832	cubic meter per second (m^3/s)

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) as follows:

$$°F = (1.8 \times °C) + 32$$

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ABSTRACT

Six synoptic surveys of 56 streams that drain the Shenandoah National Park, Virginia, were conducted in cooperation with the University of Virginia to evaluate sensitivity of dilute headwater streams to acid deposition and to determine the degree of acidification of drainage basins. Stream samples were collected from August 1981 through June 1982; each sample was analyzed for alkalinity, major anions and cations, silica, and pH.

Flow-weighted alkalinity concentration of most streams is below 200 microequivalents per liter, which is commonly considered the threshold of sensitivity. Stream-water sensitivity is strongly affected by drainage basin bedrock type. Streams draining the resistant siliceous bedrocks show extreme sensitivity (alkalinity below 20 microequivalents per liter); streams draining granite and granodiorite show a high degree of sensitivity (20 to 100 microequivalents per liter); and streams draining the metamorphosed volcanics show moderate to marginal sensitivity (101 to 200 microequivalents per liter).

The strong relation between bedrock type and stream-water chemistry in the Park is evaluated statistically by multiple-regression analysis. This technique indicates that concentrations of alkalinity, silica, and base cations are strongly related to bedrock type, and that sulfate concentration is strongly related to geographic location. The regression equation for alkalinity is shown to be a useful tool for predicting sensitivity of unsampled streams within the Park and for streams in areas with similar geology outside the Park. Predicted values are generally within 30 microequivalents per liter of the measured value.

A comparison of current stream-water chemistry to that predicted by a model based on carbonic-acid weathering reactions suggests that all basins in the Park show signs of acidification by atmospheric deposition. Acidification is defined as a neutralization of stream-water alkalinity and/or an increase in the base cation weathering rate. These processes cannot be distinguished with the available data, but both are detrimental to stream basins in the Park. Acidification averages 50 microequivalents per liter, which is fairly evenly distributed in the Park. However, the effects of acidification are most strongly felt in extremely sensitive basins, such as those underlain by the Antietam Formation, which have stream-water pH values averaging 4.99 and a mineral acidity of 7 microequivalents per liter. Acidification of basins in the other geologic formations also may be significant, but higher "pre-acidification" concentrations of stream-water alkalinity and base cations make it less apparent.

INTRODUCTION

Background

The degradation of surface-water quality by anthropogenic ("man-caused") acid deposition has been well documented in Scandinavia (Gjessing and others, 1976), in the Canadian shield areas of Ontario and Quebec (Beamish and Harvey, 1972; Thompson and others, 1980), in the Adirondack Mountains of New York State (Schofield, 1976), and in various other parts of the world (Wright and others, 1980). These regions commonly contain noncalcareous, acidic soils overlying siliceous or granitic bedrock and receive highly acidic precipitation with an average pH value less than 4.6 (Henriksen, 1980). Anthropogenic acid deposition is not easily defined because conditions prior to the combustion of fossil fuels are not known with certainty. However, after measuring precipitation chemistry in locations remote from local anthropogenic acidification sources, Galloway and others (1982b) state that the lower limit for the natural mean pH is probably greater than or equal to 5. Thus, in this report, acid deposition is defined as precipitation with a mean pH less than 5.0, as suggested by Turk (1983).

Depending on a combination of parameters including soil type, bedrock mineralogy, hydrologic flowpath, vegetative cover, climate, and elevation of land surface, basins may be more or less "sensitive" to acid deposition. Sensitivity describes the capability of a basin to neutralize incoming strong acids, and it is commonly expressed as alkalinity (Hendrey and others, 1980), the acid-neutralizing capacity of water, although mathematical relations among alkalinity, pH, calcium, and/or specific conductance have also been used as sensitivity indices (Conroy and others, 1974; Zimmerman and Harvey, 1980; Altshuller and McBean, 1979). Acidification, as defined in this report, is a measure of the degree to which a basin has been chemically altered by acid deposition, and is distinct from sensitivity. A basin is considered acidified if atmospheric deposition has decreased the alkalinity (or increased mineral acidity) of its surface runoff or increased the rate of base cation leaching from its soils and rocks. Prolonged acidification of a basin may cause loss of valuable species, increases in the concentration of aluminum and other potentially toxic metals in surface runoff, declines in organic matter decomposition rates, and other possible consequences (Linthurst, 1983).

Defining and identifying regions sensitive to acid deposition is necessary not only for making informed policy decisions, but also for gaining increased understanding of the processes that control acidification. However, many regions of the world do not have adequate chemical data to accurately estimate stream-water sensitivity for these purposes. Therefore, the major determinants of sensitivity (bedrock type, soil type, vegetation, land surface, altitude, and climate), which typically are better documented, are commonly used to identify these areas. Bedrock-geology maps have been used to identify sensitive areas nationally (Gjessing and others, 1976; Omernik and Powers, 1982) and regionally (Hendrey and others, 1980; Shewchuk, 1982). Based on the assumption that buffering capacity of water that drains from calcareous rocks is high, whereas that of siliceous and granitic rocks is low, maps of bedrock geology provide a useful first step towards identifying potentially sensitive areas. Detailed analysis of stream-water quality data from these identified areas is necessary to document actual sensitivity and assess the extent, if any, of acidification.

Purpose and Scope

The Appalachian Mountains are identified on national maps as potentially sensitive to acid deposition (Galloway and Cowling, 1978; Omernik and Powers, 1982). The purpose of this report is to describe the stream-water quality of a region of the Appalachian Mountains, Shenandoah National Park, Virginia, to determine more precisely the sensitivity of this area and to estimate how this area is responding to the current input of acid deposition. Specifically, the objectives are to:

1) Determine the sensitivity of basins in Shenandoah National Park to acid deposition.

2) Assess the extent and degree of acidification of basins in the Park.

3) Identify relations between sensitivity and basin characteristics to allow extrapolation beyond Park boundaries.

4) Hypothesize the major geochemical controls on surface runoff quality.

To meet these objectives, 56 streams draining Shenandoah National Park, Virginia, were sampled during six synoptic surveys made from August 1981 through June 1982. Samples were analyzed for major anions and cations, silica, and pH. These water-quality constituents were flow weighted for individual streams to give an estimate of mean annual volume-weighted concentrations.

Flow-weighted alkalinity concentration was used to indicate basins in the Park that are sensitive to acid deposition. Base cation and alkalinity concentrations, together with mineralogic and geologic data from the Park, are used to determine the weathering reactions that most strongly influence water quality. The extent of drainage-basin acidification by atmospheric deposition is estimated with an acidification model that uses flow-weighted concentrations of base cations, hydrogen ion, alkalinity, and chloride as input data.

Acknowledgments

This study was greatly assisted by the cooperation of researchers in the Department of Environmental Sciences, University of Virginia. James Galloway, Paul Shaffer, and George Hornberger deserve special recognition. Tom Gathright of the Virginia Division of Mineral Resources shared his wealth of knowledge on the geology of the Park. The support and cooperation of the National Park Service and the Shenandoah National Park Staff is also gratefully acknowledged.

LOCATION AND DESCRIPTION OF STUDY AREA

Shenandoah National Park straddles a 70-mile segment of the Blue Ridge mountains in north central Virginia (fig. 1) and covers more than 300 mi^2 in parts of eight counties. The Park is located in the Blue Ridge physiographic province--an ancient anticlinorium that extends from southeastern Pennsylvania into southwestern Virginia and forms part of the larger Appalachian Mountain

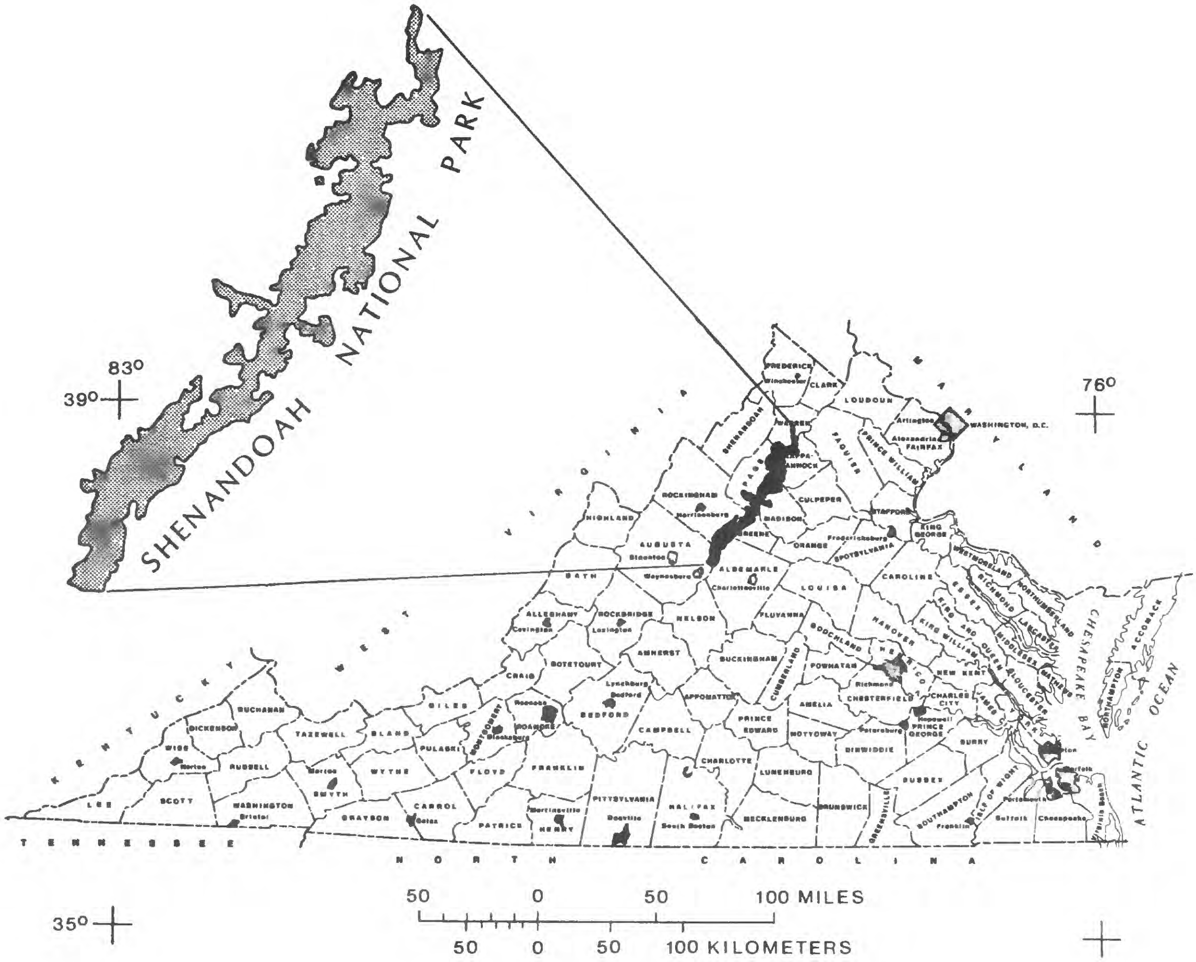

Figure 1.--Location of Shenandoah National Park in Virginia.

chain. Topographically, the area is characterized by rounded hills and gently sloping valleys with nearly complete vegetational cover. The mountains grade into the foothills of the Piedmont Province to the east and the Valley and Ridge Province to the west. Land surface within the Park ranges from 600 to 4,050 feet above sea level.

Topography and geology strongly influenced the location of early settlements in the Park. Most homesites were located in the northern half of the Park and the eastern part of the southern half because only in these areas were conditions suitable for small farms (Gathright, 1976). In the southwestern quarter, which is underlain by metamorphosed sandstone and shale, farming was rare because soils are thin and rocky, springs are intermittent, and slopes are very steep.

Logging in Shenandoah National Park began in the mid to late 19th century. This and the outbreak of chestnut blight in the region left the Park all but devoid of virgin timber by the early 20th century. Concurrent with the logging, the mountains and southwestern foothills of the region were mined for iron, manganese, and copper. More than 40 abandoned mine pits are located in or just west of the Park boundary. Logging, mining, and farming ceased after the establishment of the Park in 1935, which permitted second growth timber to reclaim cleared areas.

Geology

The Blue Ridge is an area of extensive folding and faulting characterized by great uplift that has exposed billion-year-old plutonic rocks along the axis of this anticlinorium (Gathright, 1976). Thick sequences of metamorphosed volcanic and clastic sedimentary rocks of the late Precambrian and early Cambrian age delineate the flanks of this anticlinorium. The geologic history of the Park has been compiled by Gathright (1976) from personal mapping and published reports; Schwab (1970, 1971) and Reed (1969) have also reported extensively on the Cambrian clastics and the volcanic rocks, respectively.

The Park is underlain by five major bedrock types. In order of decreasing age these are the Old Rag Granite (as used by Gathright, 1976) (8 percent of the Park's area), Pedlar Formation (as used by Gathright, 1976) (25 percent), Catoctin Formation (38 percent), Hampton Formation (17 percent), and Antietam Formation (8 percent). Additionally, there are two minor bedrock types in the Park: the Swift Run (1 percent) and Weverton (3 percent) Formations. The distribution of the major bedrock types is shown in figure 2. The geologic history of the Park based primarily on the work of Gathright (1976) is summarized in the following paragraphs.

The plutonic rocks of the Old Rag Granite and Pedlar Formations, which have been dated at 1.1 billion years, are among the oldest exposed rock units in the Appalachian Mountains. These rocks formed at great depth and crystallized under high temperature and pressure. The Old Rag Granite, well exposed on the crest of Old Rag Mountain in the east-central part of the Park, is a light gray, coarsely crystalline, resistant granite. This formation is unconformably overlain by the Catoctin Formation to the west and south of Old Rag Mountain and grades into, or is in fault contact with, the Pedlar Formation to the north and northwest (fig. 2).

The Pedlar Formation is a medium-grained, highly feldspathic granodiorite that commonly exhibits gneissic foliation, especially in the northern part of the Park. The crystals of this rock have been extensively metamorphosed to a uniform size and texture and later altered by extensive folding and shearing. The Pedlar Formation is unconformably overlain by the Swift Run, Catoctin, and Weverton Formations, and grades laterally or is in fault contact with the Old Rag Granite.

During the late Precambrian, the exposed plutonic rocks were eroded by rivers. The granitic debris, along with volcanic ash and breccia produced during early volcanism, was metamorphosed and cemented by hot mineralizing gases, forming the Swift Run Formation. The Swift Run Formation unconformably overlies the plutonic rocks and grades upward into the Catoctin Formation. Because of its limited distribution in the Park, the Swift Run Formation is combined with the Catoctin Formation in figure 2.

The Catoctin Formation is a thick (2000 feet) bed of multilayered metamorphosed basalt that originated as ancient lava flows (Reed, 1969). Dense, tough greenstone, formed from the basaltic lava, accounts for more than 80 percent of the Catoctin Formation and underlies most of the higher ridges in the Park. Thin bands of slate or phyllite are interlayered with the greenstone; these originated as ash and tuff deposited after violent volcanic

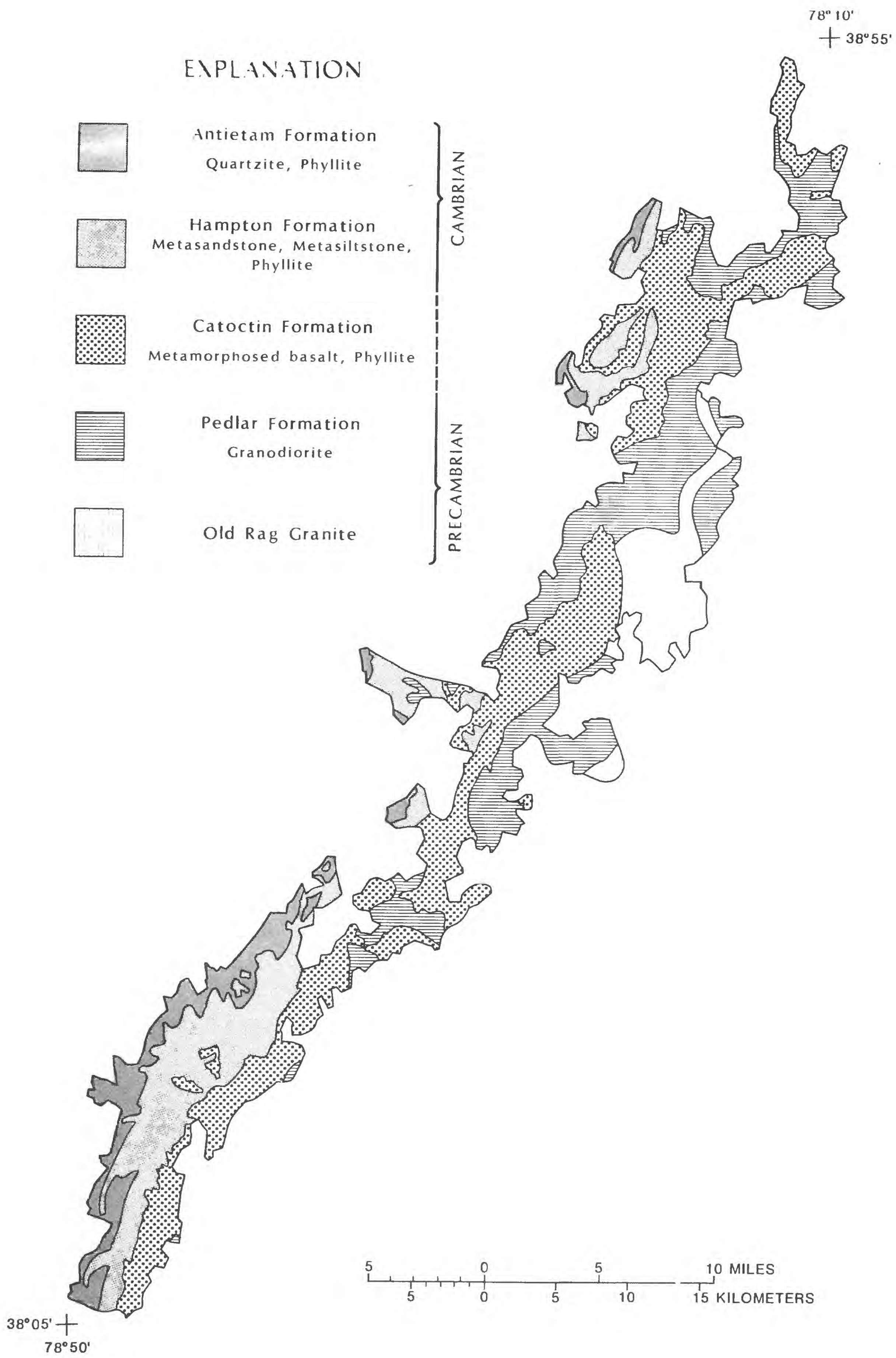

Figure 2.--Geology of Shenandoah National Park.

explosions. Sedimentary material from paleostream deposits is preserved as metamorphosed sandstone and phyllite within many of the Catoctin beds, especially in the south. The Catoctin Formation overlies the Swift Run Formation except where the latter is absent; there it unconformably overlies the plutonic rocks. The formation lies unconformably below the Weverton Formation.

The Cambrian deposits within the Park compose the Chilhowee Group, and are represented by three units: the Weverton, the Hampton, and the Antietam Formations. These clastic sedimentary rocks originated from fluvial action of streams eroding the Catoctin lava plains (Weverton Formation), by the formation and subsequent burial of fine-grained, sandy muds and clays deposited by the Cambrian sea (Hampton Formation), and by burial and metamorphosis of beach and bar sands deposited by the same sea as it migrated westward (Antietam Formation).

The Weverton Formation is a thin (100 to 500 feet thick) series of light gray, pebbly conglomerate quartzite beds cemented locally with iron oxide and interlayered with phyllite and metasandstone. Characteristic rounded quartz pebbles may be scattered throughout the rock or concentrated in discrete beds within the formation. The Weverton Formation is usually present as several feldspathic quartzite ledges, each from 5 to 25 feet thick. It unconformably overlies the older igneous formations and grades upward into the Hampton Formation. Because of its limited distribution, this formation is combined with the Hampton Formation in figure 2.

The lower third of the Hampton Formation is a thick series of grayish green phyllite and shale. The upper two-thirds is dominated by interbedded metasandstone and phyllite with intermittent appearance of quartzite beds. These quartzite beds commonly are thick deposits, 10 to 50 feet thick, and form extensive talus deposits downslope of outcrops. Total formation thickness is 1,800 to 2,200 feet. The Hampton Formation conformably grades downward into the Weverton and upward into the Antietam Formation.

The uppermost member of the Chilhowee Group, the Antietam Formation, is an extremely resistant, 700 to 1,000-foot thick bed of light gray quartzite and quartz-rich clastics, which may be sparsely interbedded with less resistant metasandstone and phyllite. The formation is readily visible as quartzite ledges and sharp peaks along the southwestern segment of the Park and forms thick boulder fields and talus deposits downslope. The Antietam Formation grades conformably downward into the Hampton Formation. Cambrian and Ordovician carbonate rocks, which form the floor of the Shenandoah Valley to the west and the upper contact of the Antietam Formation, are not present in the Park.

Soils

Soils in the Park are derived either from in situ weathering of parent bedrock or transport of weathered material from upslope (Elder and Pettry, 1975; Carter, 1961; Hockman and others, 1979). As such, the soils generally reflect the characteristics of the underlying bedrock.

Major soil associations include the Myersville-Catoctin (derived from greenstone schist), the Porters-Halewood (derived from granite and granodiorite), the Lew-Cataska-Harleton (derived from shale-sandstone and phyllite), and the Hazleton-Drall (derived from quartzite/sandstone). Colluvial fans in valleys and on mountain footslopes, talus deposits, and exposed rock are common throughout the Park. All of these soils are classified as well drained and medium to very strongly acidic. Organic-matter content of the Porters-Halewood is described as medium to fairly high, whereas the Lew-Cataska-Harleton and Hazleton-Drall are generally medium low to low in organic matter. Organic content of Myersville-Catoctin soils has been classified as both high (Carter, 1961) and low (Elder and Pettry, 1975). Local conditions such as slope and elevation of the land surface may substantially affect soil organic matter content.

Soil chemistry in the southwestern segment of the Park has been extensively studied (Shaffer, 1982b). Generally, these soils are thin, highly acidic, sandy loams to clay loams that formed from underlying or upslope bedrock and are probably characteristic of other soils derived from Hampton and Antietam bedrock. Elsewhere in the Park, soils are probably thicker and better developed due to gentler slopes (Gathright, 1976) and more weatherable parent material.

Soils are a major modifier of precipitation chemistry. Base cations such as calcium and magnesium and acid anions such as sulfate may be released, retained, or immobilized by the soil, depending upon the chemical, biological, and physical characteristics of the soil. The behavior of sulfur in soil is of particular interest in acid deposition research because its mobility may directly influence the acidity of runoff (Johnson and Cole, 1980). Sulfur mobility is controlled by a number of processes, including sulfate adsorption, sulfate reduction, and precipitation/dissolution of aluminium sulfate or related complexes. Current research in a basin underlain by the Hampton Formation (Shaffer, 1984) suggests that adsorption is the primary means of sulfate retention in soils derived from the Hampton Formation. Field observation reveals no evidence of reducing conditions in the soils (necessary for sulfate reduction), and chemical analyses indicate that aluminum sulfate minerals are undersaturated in these soils. Sulfate adsorption kinetics, however, indicate mobility is indeed controlled by adsorption. Rapid equilibration (2 to 5 minutes) between sorbed and dissolved phases is observed. Shaffer estimates, using phosphate extraction techniques, that currently about 65 percent of the sulfate adsorption capacity of Hampton Formation derived soils has been filled; however, this can vary widely between sites and at different soil depths.

Little is known about the behavior of sulfur in other soil types in the Park. As in soils derived from the Hampton Formation, casual observation indicates no obvious reducing conditions in other soils in the Park. Limited experimentation (P. W. Shaffer, University of Virginia, Department of Environmental Sciences, oral commun., 1984) with soils derived from the Catoctin Formation suggests sulfate mobility is also largely controlled by soil adsorption processes and not by dissolution/precipitation reactions.

Soils derived from the Hampton and Antietam Formation have a very low cation exchange capacity, about 10 microequivalents per 100 grams in the A and B horizons, due to a low percentage of organic matter and the low exchange capacity of the clays (primarily kaolinite). Very low soil base saturation, about 4-5 percent, reflects the poor base cation source of the underlying parent material and its resistance to weathering. Primary weathering in these basins is estimated to be very slow, and the soil cation denudation rate is about one percent removal per year (Shaffer, 1982b). This rate is comparable to a number of similar sites in North America (Johnson and others, 1983).

Precipitation

Precipitation in the Park averages about 45 inches (115 centimeters) per year, which is fairly evenly distributed seasonally. Altitudinal transects in the southwestern part of the Park indicate that annual precipitation increases about 2.5 inches per 1000 feet increase in altitude (P. W. Shaffer, University of Virginia, Department of Environmental Sciences, written commun., 1983). However, short term variations in the amount of precipitation, both laterally and vertically, may be considerable due to localized storm events.

Figure 3 shows how precipitation at Big Meadows, located in the central region of the Park at an altitude of 3535 feet (fig. 4), deviated from mean monthly conditions during the study period. Following an unusually wet July was a dry period in the late summer of 1981, a variably wet and dry autumn and early winter, and average or higher than average precipitation from January to June, 1982. The study period of July 1981 through June 1982 is considered an average to slightly wetter-than-average period (National Oceanic and Atmospheric Administration, 1981 and 82).

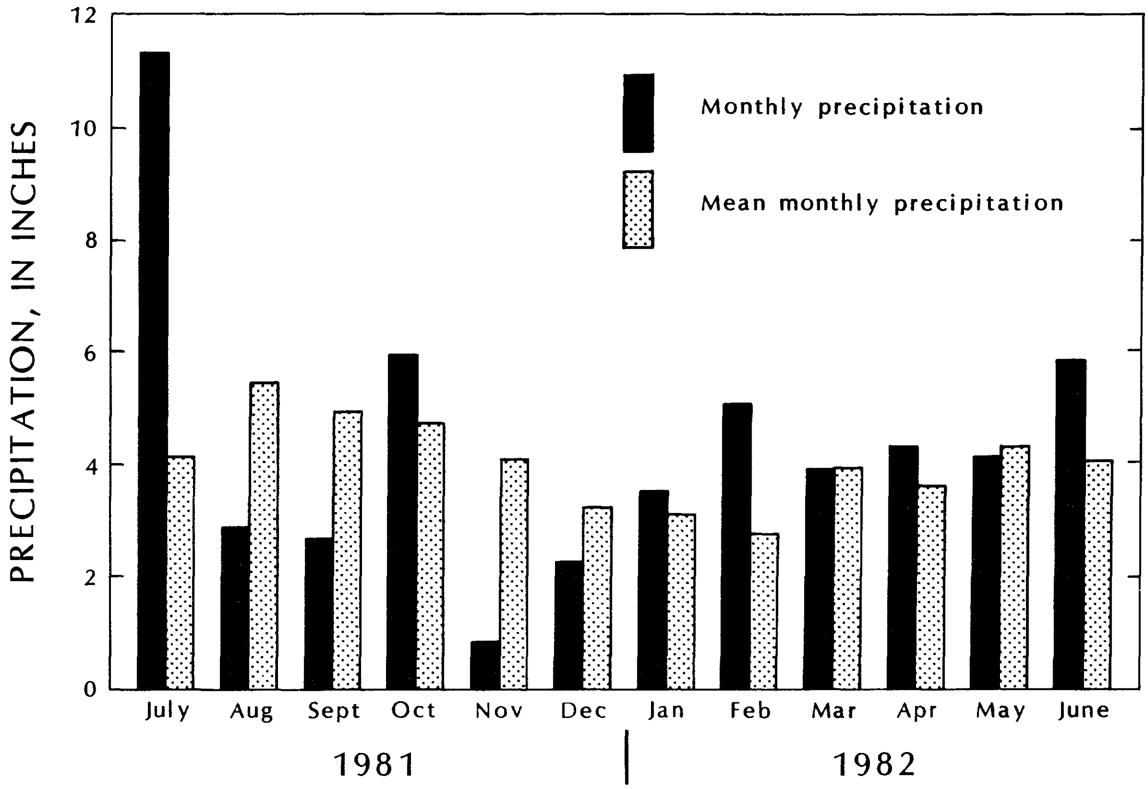

Figure 3.--Monthly and mean monthly (1941-70) precipitation at Big Meadows.

During calendar years 1981 and 1982 the bulk precipitation at Grottoes, located on the western border of the Park (fig. 4), had a volume-weighted pH of 4.22 (Shaffer, 1984). Sulfate is the dominant anion (65 percent of total anions by charge), and hydrogen the dominant cation (67 percent of total cations by charge). Approximately 90 percent of this atmospheric sulfate is thought to be of anthropogenic origin (Shaffer, 1982a; Galloway and Whelpdale, 1980). Table 1 gives the volume-weighted concentrations of major chemical constituents of bulk precipitation for these years.

Table 1.--Volume-weighted mean concentration of major ions in bulk precipitation in the southwestern area of the Park, 1981-82.

Ion	Bulk-precipitation concentration, in microequivalents per liter
Calcium	8.7
Magnesium	2.9
Sodium	4.7
Potassium	1.5
Ammonium	12.1
Hydrogen	59.6 (pH 4.22)
Sulfate	54.2
Nitrate	22.5
Chloride	6.8

METHODS OF STUDY

Selection of Sampling Sites

Approximately 65 stream-water sites within or near the Park were selected for reconnaissance using the following criteria:

1) Predominance of one of the major geological formations in the basin.

2) Accessibility of site from roads within or near the Park.

3) Negligible direct human impact upstream from sampling site.

4) Fishing or other recreational value of the stream.

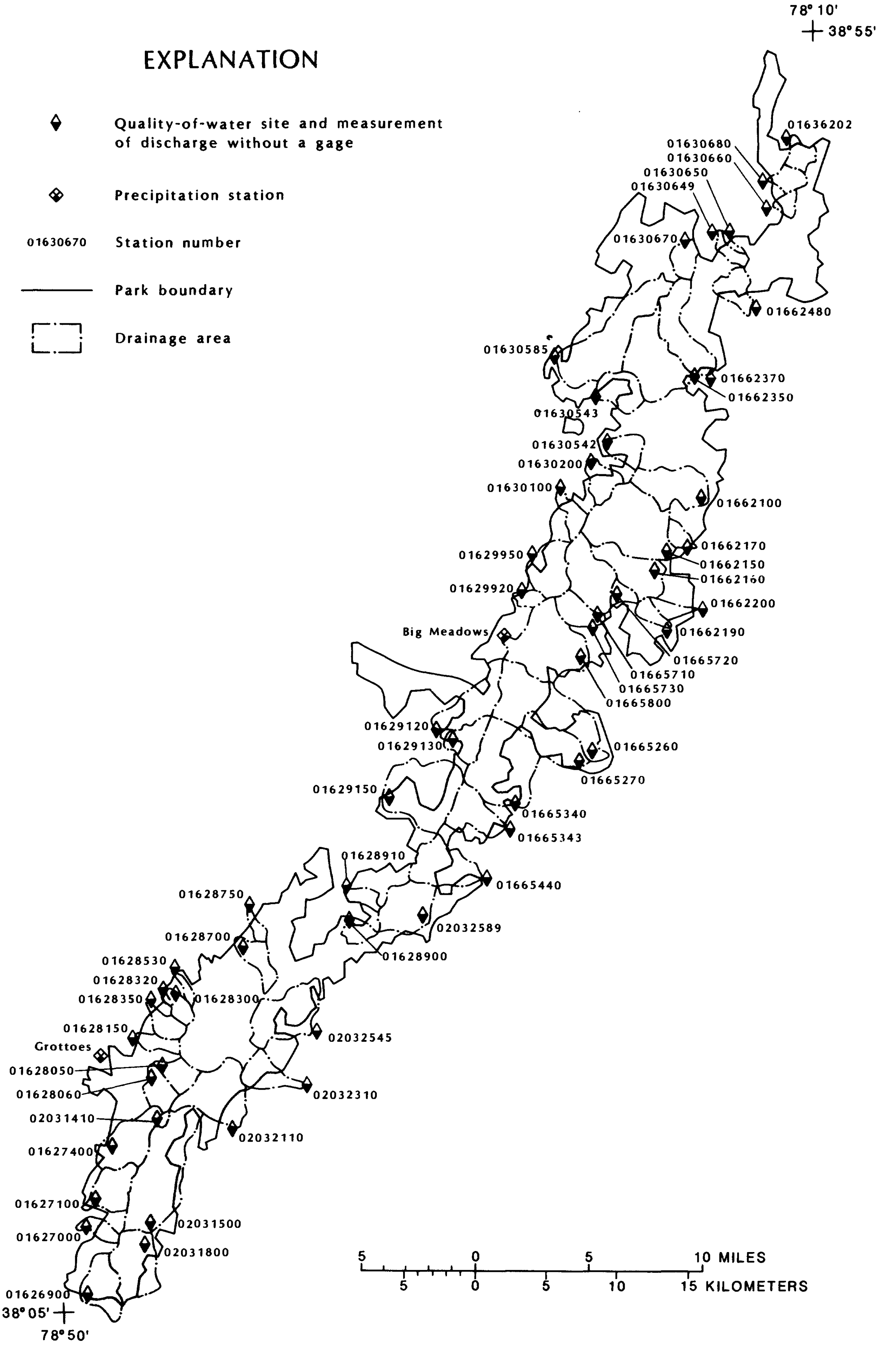

Figure 4.-- Surface-water sampling stations with contributing drainage basins and precipitation stations.

These initial sites were surveyed from August 10-21, 1981. A number of the original sites were deleted during or after the survey due to access problems, obvious drainage basin disturbance, or chemical/geological redundancy. In addition, three sites (Walls Run, U.S. Geological Survey site number 01628750; Hangman Run, 01628530; and a tributary to Upper Lewis Run, 01628320) were later established to better characterize conditions in the Antietam Formation. In all, 56 sites make up the final sampling network (figure 4) including Deep Run (01628150) and White Oak Run (01628060), which were sampled and analyzed by personnel of the University of Virginia (Shaffer, 1984). Six synoptic surveys of these sites were completed between August 1981 and June 1982.

Description of Basin Characteristics

Basin characteristics for each site in the network are listed in table 2. Drainage area (AREA), drainage density (DD), east/west orientation (EW), and development (DEV) are obtained from 7 1/2 minute topographic maps. Drainage density is defined as total stream length divided by drainage area (Trainer, 1969). EW describes the location of each site in reference to the Blue Ridge mountains. Sites on the west and east slopes are coded "1" and "0", respectively. This geographic code is used as binary dummy variable in the regression models. DEV in table 2 flags sites with a "1" if more than five percent of the drainage basin is developed. Development is defined as areas cleared for pastures, farms, and homes, as shown on the most recent 7 1/2 minute topographic maps. In addition, Pass Run (01630542), West Swift Run (01628910), and Swift Run (02032589) are also considered developed because they are strongly influenced by road salting along State Highways 33 and 211 which cross the Park.

Geologic characteristics and percentage of drainage basin above 2,400 feet (AB2400) are obtained from geologic/topographic maps (Gathright, 1976). Table 2 provides the percentages of each of the following rock formations in a drainage basin: Antietam (ANTI), Hampton (HAMP), Weverton (WEV), Catoctin (CAT), Swift Run (SR), Pedlar (PEDL), and Old Rag Granite (OR). AB2400 is used as a surrogate for altitude in the regression analyses.

Sample Collection and Analytical Techniques

Stream-water samples were prepared for analysis by filtering through a prerinsed 0.45 micron membrane filter into two rinsed polyethylene bottles. One bottle was kept chilled until analysis and the other was preserved with chloroform (2 mL per 250 mL sample) for analysis later if needed (Galloway and others, 1982b). Field measurements of pH, specific conductance, temperature, and streamflow accompanied sample collection. Measurement of pH follows procedures outlined by Galloway and others (1979) using a Leeds and Northrop pH meter (model 7417)[1] and a Corning model 476182 calomel combination electrode.

[1]Reference to trade names or use of any materials containing a registered trademark, patent, or logo do not constitute endorsement by the U.S. Government or the Geological Survey.

Table 2.—Basin characteristics.

Station number	Station name	Latitude	Longitude	Area (mi²)	Basin characteristics[1]										
					%Anti	%Hamp	%Wev	%Cat	%SR	%Pedl	%OR	%Ab2400	DD	EW	Dev
01626900	Sawmill Run nr Dooms	380546	0784838	3.62	8	57	16	19	0	0	0	15	2.3	1	0
01627000	Mine Branch nr Crimora	380836	0784854	1.26	54	46	0	0	0	0	0	6	2.4	1	0
01627100	Meadow Run nr Crimora	380929	0784838	3.45	51	49	0	0	0	0	0	48	1.9	1	0
01627400	Paine Run nr Harriston	381155	0784738	4.92	10	90	0	0	0	0	0	20	1.8	1	0
01628050	Madison Run above WOR nr Grottoes	381505	0784450	2.00	0	34	39	27	0	0	0	28	2.5	1	0
01628060	White Oak Run nr Grottoes	381501	0784457	1.94	0	89	11	0	0	0	0	31	2.1	1	0
01628150	Deep Run nr Grottoes	381623	0784536	1.17	20	80	0	0	0	0	0	10	2.1	1	0
01628300	Lower Lewis Run nr Lynwood	381806	0784402	1.12	28	72	0	0	0	0	0	18	2.0	1	0
01628320	Lower Lewis Run trib nr Lynwood	381803	0784420	0.18	100	0	0	0	0	0	0	0	0.0	1	0
01628350	Upper Lewis Run nr Lynwood	381735	0784455	1.58	21	79	0	0	0	0	0	15	1.8	1	0
01628530	Hangman Run nr Rocky Bar	381842	0784302	0.44	100	0	0	0	0	0	0	10	3.2	1	0
01628700	Twomile Run nr McGaheysville	382004	0784020	2.17	23	77	0	0	0	0	0	2	1.8	1	0
01628750	Walls Run nr Rocky Bar	382123	0783947	0.60	100	0	0	0	0	0	0	10	3.5	1	0
01628900	Hawksbill Creek trib nr Swift Run	382047	0783435	1.32	0	0	0	27	5	68	0	50	2.4	1	1
01628910	West Swift Run at Swift Run	382155	0783447	0.96	0	0	0	62	0	38	0	16	2.8	1	1
01629120	East Branch Naked Creek nr Jollett	382807	0782950	4.58	0	3	16	81	0	0	0	66	1.3	1	0
01629130	Big Creek nr Jollett	382737	0782935	2.43	0	0	24	73	1	2	0	70	1.2	1	0
01629150	S Branch Naked Creek nr Furance	382534	0783251	8.72	7	32	8	51	1	1	0	29	1.5	1	1
01629920	Little Hawksbill Ck trib near Ida	383323	0782555	0.78	0	0	0	5	0	95	0	66	2.2	1	0
01629950	East Hawksbill Creek nr Ida	383453	0782452	4.03	0	0	0	5	3	92	0	58	2.0	1	0
01630100	South Fork Dry Run nr Fairview	383737	0782323	1.53	0	0	0	5	3	92	0	45	2.0	1	0
01630200	North Fork Dry Run nr Thornton Gap	383841	0782209	2.15	0	0	0	1	0	99	0	44	2.0	1	0
01630542	Pass Run nr Thornton Gap	383905	0782114	2.00	0	0	0	22	0	78	0	36	3.2	1	1
01630543	Rocky Branch nr Thornton Gap	384106	0782110	2.76	0	5	4	91	0	0	0	34	1.4	1	1
01630585	Jeremys Run nr Oak Hill	384318	0782315	9.72	0	31	8	61	0	0	0	26	2.1	1	0
01630649	Phils Arm Run nr Browntown	384734	0781429	0.98	0	0	0	16	0	84	0	35	1.6	1	0
01630650	Phils Arm Run trib nr Browntown	384733	0781426	0.38	0	0	0	0	0	100	0	18	3.7	1	0
01630660	Smith Creek nr Browntown	384823	0781155	0.78	0	0	0	2	0	98	0	32	1.7	1	0
01630670	Greasy Run nr Browntown	384717	0781603	1.70	0	0	0	12	3	85	0	31	3.7	1	1
01630680	Lands Run nr Browntown	384920	0781222	1.38	0	0	0	20	0	80	0	32	2.0	1	0
01636202	Happy Creek trib nr Glen Echo	385117	0781049	1.51	0	0	0	40	1	59	0	31	2.0	0	0
01662100	Hazel River nr Nethers	383654	0781544	5.15	0	0	0	0	0	78	22	51	1.9	0	0
01662150	Hughes River nr Nethers	383427	0781749	9.92	0	0	0	7	0	55	38	51	1.1	0	0
01662160	Brokenback Run nr Nethers	383416	0781801	4.30	0	0	0	9	0	0	91	41	1.0	0	0
01662170	Rocky Run nr Nethers	383439	0781657	1.09	0	0	0	0	0	3	97	3	1.4	0	0
01662190	Ragged Run nr Etlan	383156	0781744	1.14	0	0	0	0	0	0	100	34	1.1	0	0
01662200	Rosson Hollow Run trib nr Etlan	383233	0781624	1.05	0	0	0	0	0	0	100	11	2.1	0	0
01662350	N F Thornton River nr Sperryville	384136	0781633	7.21	0	2	4	68	0	24	2	18	1.3	0	0
01662370	Piney River nr Sperryville	384146	0781530	5.58	0	0	0	59	0	41	0	35	1.7	0	0
01662480	Rush River at Rt 622 nr Washington	384429	0781308	2.34	0	0	0	53	3	44	0	24	1.5	0	1
01665260	Rapidan River nr Graves Mill	382638	0782211	9.74	0	0	0	30	0	66	4	65	1.4	0	0
01665270	Staunton River nr Graves Mill	382638	0782212	4.21	0	0	0	0	0	94	6	54	1.6	0	0
01665340	Conway River nr Kinderhook	382459	0782617	9.66	0	0	0	8	1	91	0	58	2.1	0	0
01665343	Conway River trib nr Kinderhook	382416	0782622	3.62	0	0	0	13	2	85	0	60	1.3	0	0
01665440	South River nr McMullen	382201	0782738	4.94	0	0	0	71	0	29	0	61	1.3	0	0
01665710	White Oak Canyon trib nr Syria	383223	0782053	5.41	0	0	0	83	2	4	11	75	1.4	0	0
01665720	Berry Hollow trib nr Nethers	383245	0782037	1.01	0	0	0	0	0	0	100	18	2.3	0	0
01665730	Cedar Run nr Syria	383222	0782101	2.32	0	0	0	97	1	2	0	75	1.0	0	0
01665800	Rose River nr Syria	383055	0782159	9.15	0	0	0	87	0	13	0	72	1.0	0	0
02031410	N Fk Moormans R trib nr Harriston	381233	0784452	0.21	0	100	0	0	0	0	0	100	1.9	0	0
02031500	N Fk Moormans River nr Whitehall	380825	0784505	11.40	0	21	10	69	0	0	0	49	1.8	0	0
02031800	S Fk Moormans River nr Whitehall	380813	0784459	5.56	0	12	8	80	0	0	0	31	1.7	0	0
02032110	Doyles River nr Browns Cove	381228	0784030	6.44	0	1	7	75	3	14	0	43	1.8	0	0
02032310	Muddy Run trib nr Boonesville	381402	0783708	2.59	0	0	0	75	4	21	0	43	1.9	0	0
02032545	Ivy Creek nr Boonesville	381607	0783645	6.11	0	11	6	71	3	9	0	45	1.8	0	1
02032589	Swift Run at Lydia	382031	0783040	4.80	0	0	0	53	12	35	0	46	2.0	0	1

[1]Basin charactersitics: %Anti, %Hamp, %Wev, %Cat, %SR, %Pedl, %OR correspond to percent Antietam, Hampton, Weverton, Catoctin, Swift Run, and Pedlar Formations and Old Rag Granite, respectively; %Ab2400, percent of basin above 2400 feet; DD, drainage density in mi^{-1}; EW, basins on east side of Blue Ridge are coded "0" and basins on west side are coded "1"; Dev, basins with more than five percent development or affected by road salting are flagged with a "1".

Alkalinity was measured by double-endpoint titration of a 50 ml aliquot with 0.005 Normal HCl to pH 4.5 and 4.2 (American Public Health Association, 1980; Henriksen, 1982). This pH change of 0.3 units between the two endpoints corresponds to a doubling of the hydrogen ion concentration in solution, and the equivalence point of the titration is determined by extrapolation. This procedure is a simplification of the Gran's method (Gran, 1952), which involves stepwise addition of mineral acid followed by extrapolation to the equivalence point. Henriksen (1982), in comparing double endpoint, fixed endpoint, and Gran's methods, states that while the Gran's method is the most precise for low alkalinity samples, it is also time-consuming. He notes that double endpoint titration is recommended as a standard method for alkalinities less than 400 µeq/L.

Sulfate, nitrate, chloride, ammonia, and silica concentrations were determined colorimetrically using a Technicon II autoanalyzer. The major cations calcium, magnesium, sodium, and potassium were analyzed by atomic absorption spectroscopy using an Instrumentation Laboratory AA/AE Spectrophotometer Model 751 (EMSL, 1978). Table 3 summarizes the field and laboratory methods used.

Data Reduction and Statistical Techniques

In order to evaluate water-quality trends, flow-weighted concentrations of constituents are calculated for each stream using concentration and streamflow data from the six synoptic surveys (table 4). These values are presented in table 5. The calculations are made as follows:

$$C_w = \Sigma (C_i * Q_i) / \Sigma Q_i$$

where C_w = Calculated flow-weighted concentration
C_i = Measured concentration on the i^{th} trip
Q_i = Measured streamflow on the i^{th} trip.

To obtain flow-weighted pH, pH values are converted to hydrogen ion concentration, flow weighted using the above equation, and then converted back to pH units.

Flow-weighted concentrations calculated using the six synoptic surveys reasonably approximate annual flow-weighted concentrations, as shown in table 6 for White Oak Run (01628060). At White Oak Run very similar results were obtained whether flow weighting was based on the six synoptic surveys or on weekly samples (Shaffer, 1984) collected during the study period.

Multiple linear regression is used in this study to quantify the relationship between stream-water chemistry and basin characteristics within the Park and to provide a predictive model for estimating alkalinity (sensitivity) of streams draining similar rocks and soils outside the Park, primarily in the Blue Ridge Province. Multiple regression analysis evaluates the extent, direction, and strength of the relationship between several independent variables X_1, X_2, . . . X_i and a single continuous dependent variable Y. The general form of the regression equation is:

$$Y' = B_0+B_1X_1+B_2X_2....B_iX_i$$

in which Y' is the predicted value of the dependent variable Y. The intercept

Table 3.--Analytical techniques.

Constituent or Property	Instrumentation	Techniques
Mg^{++}	Instrumentation Laboratory Atomic Absorption sprectrophotometer, model 751	lanthanum added, aspirated in oxidizing flame, read at 285.2 nm using deuterium background correction [EMSL, 1978]* [APHA, 1980]**
Ca^{++}	Instrumentation Laboratory Atomic Absorption spectrophotometer, model 751	lanthanum added, aspirated in oxidizing flame, read at 422.7 nm [EMSL, 1978]* [APHA, 1980]**
Na^{++}	Instrumentation Laboratory Atomic Absortpion spectrophotometer, model 751	lithium added, aspirated in reducing flame, read at 589.0 nm [APHA, 1980]**
K^{+}	Instrumentation Laboratory Atomic Absorption spectrophotometer, model 751	lithium added, aspirated in reducing flame, read at 766.5 nm [APHA, 1980]**
$SO_4^{=}$	Technicon Auto-Analyzer II with custom-designed manifold	modification of thorin technique developed by Norwegian Institute for Air Research (NILU)
NO_3^{-}	Technicon Auto-Analyzer II with custom-designed manifold	standard cadmium reduction technique [TIS, 1972]†
NH_4^{+}	Technicon Auto-Analyzer II with custom-designed manifold	standard indophenol blue technique [TIS, 1973]†
Cl^{-}	Technicon Auto-Analyzer II with custom-designed manifold	standard ferricyanide method modified for low levels [TIS, 1976a]†
$SiO_4^{=}$	Technicon Auto-Analyzer II with custom-designed manifold	standard molybdenum blue technique [TIS, 1976b]†
pH	Orion Ionanalyzer Research pH meter (model 801) with Corning model 476182 probe	standard two-point calibration with pH 7.00 and pH 4.00 buffers [Galloway and others, 1979, 1981]
Alk	Sargent Welch pH meter with Corning model 476182 probe	double endpoint titration to pH 4.5 and 4.2 [APHA, 1980]

*Environmental Monitoring and Support Laboratory
**American Public Health Association
†Technicon Industrial Systems

Table 4.—Water-quality and discharge data from synoptic surveys.

Station number	Station name	Date	Time	Discharge (ft^3/sec)	Conductivity (microsiemen/cm)	pH units	Temp (°C)	Dissolved concentration in microequivalents per liter except Si which is in micromoles per liter: Ca	Mg	Na	K	Alk	SO4	Cl	Si	NO3	NH4
01626900	Sawmill Run nr Dooms	081981	1130	0.21	33	6.29	16.5	73	79	46	31	156	71	23	126	2	<1
01627100	Meadow Run nr Crimora	081981	1015	0.29	18	5.78	15.5	15	33	24	25	10	73	23	96	3	<1
01628050	Madison Run above WOR nr Grottoes	081881	1600	0.05	31	6.33	17.5	51	90	59	28	144	72	24	145	2	<1
01628060	White Oak Run nr Grottoes	081281	1100	0.01	—	6.08	—	33	58	26	47	60	85	23	89	2	<1
01628150	Deep Run nr Grottoes	081281	1200	0.04	—	5.95	—	20	38	36	48	17	90	36	103	7	2
01628900	Hawksbill Creek trib nr Swift Run	081881	1130	0.13	52	7.48	16.0	300	158	129	6	508	81	23	259	5	<1
01628910	West Swift Run at Swift Run	081881	1045	0.12	48	7.28	14.5	168	148	115	9	387	47	35	288	15	<1
01629120	East Branch Naked Creek nr Jollett	081181	1300	4.22	32	7.11	19.0	99	94	66	8	185	67	21	168	25	<1
01629130	Big Creek nr Jollett	081181	1430	1.10	47	7.38	19.0	190	138	66	8	325	81	24	175	14	<1
01629150	S Branch Nsked Creek nr Furance	081181	1100	1.31	47	7.29	20.0	165	139	72	21	314	91	30	152	1	<1
01629920	Little Hawksbill Ck trib near Ida	082181	1330	0.07	28	6.82	15.5	93	53	81	5	138	78	24	207	14	<1
01629950	East Hawksbill Creek nr Ida	082181	1230	0.24	35	6.54	15.0	123	66	76	7	164	95	28	195	11	<1
01630100	South Fork Dry Run nr Fairview	081081	1810	0.18	53	7.01	19.5	196	111	94	35	278	126	36	202	17	1
01630200	North Fork Dry Run nr Thornton Gap	081081	1600	0.42	35	6.99	24.0	112	73	85	12	155	98	35	150	14	1
01630542	Pass Run nr Thornton Gap	081081	1500	0.47	88	7.37	19.5	305	227	261	10	395	64	375	288	8	<1
01630543	Rocky Branch nr Thornton Gap	081181	1830	0.20	64	7.30	22.0	246	203	109	15	518	71	38	281	11	<1
01630585	Jeremys Run nr Oak Hill	081281	1000	0.56	52	6.53	19.0	167	172	90	20	328	108	32	194	4	<1
01630649	Phils Arm Run nr Browntown	081281	1630	0.58	36	6.93	20.0	106	79	93	9	166	109	26	270	3	<1
01630650	Phils Arm Run trib nr Browntown	081281	1600	0.08	49	6.94	22.0	148	108	146	27	329	82	39	373	6	<1
01630660	Smith Creek nr Browntown	082081	1830	0.14	31	6.85	16.5	86	58	100	7	153	81	28	245	16	<1
01630670	Greasy Run nr Browntown	081281	1900	0.64	52	7.23	21.0	183	130	102	12	329	94	32	262	16	<1
01630680	Lands Run nr Browntown	082081	1700	0.18	39	6.93	18.0	117	86	111	9	215	101	32	252	5	<1
01636202	Happy Creek trib nr Glen Echo	081981	1330	0.43	40	7.19	16.0	125	100	100	8	255	72	32	282	15	<1
01662100	Hazel River nr Nethers	081881	1200	1.56	22	6.92	16.0	75	45	71	11	119	49	23	191	6	<1
01662150	Hughes River nr Nethers	081381	1200	4.80	25	6.94	18.0	65	49	65	8	114	65	28	173	7	<1
01662160	Brokenback Run nr Nethers	081381	1100	1.95	22	6.85	18.0	55	39	62	9	98	64	20	166	7	<1
01662170	Rocky Run nr Nethers	081881	1100	0.03	31	6.49	16.5	68	55	111	17	176	66	25	231	5	<1
01662190	Ragged Run nr Etlan	081381	1830	0.25	26	6.71	20.0	77	45	93	14	123	65	25	200	14	<1
01662200	Rosson Hollow Run trib nr Etlan	081381	1300	0.10	27	6.68	23.0	79	41	117	14	146	67	28	236	4	<1
01662350	N F Thornton River nr Sperryville	081881	1500	0.29	48	7.41	16.5	157	154	118	9	384	73	28	297	5	<1
01662370	Piney River nr Sperryville	081881	1630	0.41	36	7.23	17.0	130	123	92	6	225	63	27	262	4	<1
01662480	Rush River at Rt 622 nr Washington	081881	1900	0.15	60	7.38	18.0	238	170	127	12	469	99	37	263	9	<1
01665260	Rapidan River nr Graves Mill	081781	1700	6.90	21	7.05	18.0	65	46	58	6	128	42	22	146	4	<1
01665270	Staunton River nr Graves Mill	081781	1630	2.30	18	6.79	17.0	46	23	62	8	75	45	22	146	7	<1
01665340	Conway River nr Kinderhook	081781	1420	3.47	23	6.89	17.0	80	42	67	8	124	64	23	161	3	<1
01665343	Conway River trib nr Kinderhook	081781	1300	0.97	28	7.13	17.0	91	54	79	7	167	67	22	188	9	<1
01665440	South River nr McMullen	081781	1130	0.89	37	7.09	17.5	138	104	70	5	258	69	23	188	16	<1
01665710	White Oak Canyon trib nr Syria	082081	1230	1.14	30	6.97	17.0	99	91	50	3	187	57	27	151	5	<1
01665720	Berry Hollow trib nr Nethers	081481	1300	0.10	29	6.85	19.0	72	44	94	16	155	69	23	222	7	<1
01665730	Cedar Run nr Syria	082081	1100	0.19	33	6.54	17.0	136	103	56	3	213	66	30	169	6	<1
01665800	Rose River nr Syria	081381	1630	10.51	30	7.10	18.0	97	85	53	4	176	67	23	164	5	<1
02031500	N Fk Moormans River nr Whitehall	081781	1130	0.92	35	7.19	19.0	89	106	80	17	215	72	22	173	6	<1
02031800	S Fk Moormans River nr Whitehall	081781	1300	0.44	44	7.29	17.8	127	147	99	17	313	74	26	229	6	<1
02032110	Doyles River nr Browns Cove	081781	1530	0.31	47	7.02	19.5	135	135	114	9	317	83	27	253	6	<1
02032310	Muddy Run trib nr Boonesville	081781	1615	0.25	44	7.43	21.5	143	136	113	5	321	85	27	246	3	<1
02032545	Ivy Creek nr Boonesville	081781	1700	0.18	50	6.58	20.0	137	139	103	12	302	95	25	199	7	<1
02032589	Swift Run at Lydia	081881	0900	0.96	65	7.34	14.5	226	149	162	7	338	64	194	203	8	<1

Table 4.—Water-quality and discharge data from synoptic surveys--Continued.

Station number	Station name	Date	Time	Discharge (ft³/sec)	Conductivity (microsiemen/cm)	pH units	Temp (°C)	Ca	Mg	Na	K	Alk	SO4	Cl	Si	NO3	NH4
								Dissolved concentration in microequivalents per liter except Si which is in micromoles per liter									
01626900	Sawmill Run nr Dooms	092281	1330	1.36	28	6.58	17.0	64	73	46	20	109	95	29	137	1	<1
01627100	Meadow Run nr Crimora	092281	1430	0.09	16	5.77	17.0	19	30	20	28	9	70	21	100	2	<1
01627400	Paine Run nr Harriston	092381	1005	0.34	22	6.22	14.0	20	46	24	53	21	109	24	92	1	<1
01628050	Madison Run above WOR nr Grottoes	092381	1115	0.08	29	6.44	14.0	57	94	48	24	157	76	24	133	2	<1
01628060	White Oak Run nr Grottoes	092581	1100	0.01	—	6.40	—	33	61	25	47	61	81	22	89	2	<1
01628150	Deep Run nr Grottoes	092581	1200	0.03	—	5.50	- —	29	44	30	44	30	88	29	98	1	<1
01628700	Twomile Run nr McGaheysville	092381	0825	0.17	20	6.10	13.5	20	41	31	26	26	88	20	103	3	<1
01628900	Hawksbill Creek trib nr Swift Run	092381	1420	0.17	58	7.45	14.0	304	157	134	6	516	78	28	237	7	<1
01628910	West Swift Run at Swift Run	092381	1345	0.06	51	7.28	14.0	192	161	130	13	427	37	45	276	12	<1
01629120	East Branch Naked Creek nr Jollett	092381	1615	0.56	32	7.10	14.5	104	95	67	7	223	38	22	171	20	<1
01629130	Big Creek nr Jollett	092381	1550	0.20	68	7.75	14.5	393	229	78	9	634	49	25	165	15	1
01629150	S Branch Naked Creek nr Furance	092381	1510	0.36	37	7.43	15.5	148	124	63	19	282	75	34	150	2	<1
01629920	Little Hawksbill Ck trib near Ida	092181	1200	0.09	29	6.86	14.5	104	54	81	6	165	61	22	229	15	<1
01629950	East Hawksbill Creek nr Ida	092181	1330	0.10	36	6.51	14.5	132	65	75	9	195	78	31	186	12	<1
01630100	South Fork Dry Run nr Fairview	092181	1500	0.02	40	6.34	16.0	157	87	92	10	228	104	35	216	11	<1
01630200	North Fork Dry Run nr Thornton Gap	092181	1600	0.11	36	7.26	18.0	120	78	98	11	213	75	36	169	7	<1
01630542	Pass Run nr Thornton Gap	092181	1700	0.29	93	7.39	15.5	337	248	222	11	454	34	376	300	6	<1
01630543	Rocky Branch nr Thornton Gap	092181	1750	0.13	65	7.41	16.5	305	223	133	13	578	51	52	271	10	<1
01630585	Jeremys Run nr Oak Hill	092181	1830	0.08	49	6.48	18.0	144	154	81	15	295	97	38	193	2	<1
01630649	Phils Arm Run nr Browntown	092281	1300	0.17	33	6.96	16.5	104	73	95	7	142	119	29	232	4	<1
01630650	Phils Arm Run trib nr Browntown	092281	1300	0.03	50	7.20	20.5	151	106	161	20	372	52	37	395	6	<1
01630660	Smith Creek nr Browntown	092281	1500	0.09	31	6.95	16.0	92	56	94	7	152	76	30	240	18	<1
01630670	Greasy Run nr Browntown	092281	1130	0.23	49	7.47	18.5	183	129	116	10	340	83	42	265	7	<1
01630680	Lands Run nr Browntown	092281	1600	0.14	40	7.11	17.0	127	85	118	9	216	103	36	243	8	<1
01636202	Happy Creek trib nr Glen Echo	092281	1830	0.36	41	7.26	16.5	141	100	103	9	265	71	41	276	19	<1
01662100	Hazel River nr Nethers	092481	1330	1.48	22	6.97	13.0	57	46	68	9	120	42	24	173	3	<1
01662150	Hughes River nr Nethers	092381	1600	1.31	23	6.95	14.0	68	51	71	8	133	33	30	177	6	<1
01662160	Brokenback Run nr Nethers	092381	1700	0.35	21	6.92	13.5	64	43	66	9	127	37	24	163	6	<1
01662170	Rocky Run nr Nethers	092381	1800	0.01	32	6.47	16.5	77	60	108	15	194	59	30	222	6	<1
01662190	Ragged Run nr Etlan	092481	1530	0.05	26	6.70	14.5	64	47	80	14	136	50	29	207	14	<1
01662200	Rosson Hollow Run trib nr Etlan	092481	1430	0.01	30	6.29	22.0	71	41	100	17	160	46	35	230	7	<1
01662350	N F Thornton River nr Sperryville	092381	1500	0.63	50	7.44	13.5	163	164	122	9	381	76	33	284	2	<1
01662370	Piney River nr Sperryville	092381	1400	0.80	40	7.25	14.5	139	125	96	7	280	64	32	250	2	<1
01662480	Rush River at Rt 622 nr Washington	092381	1200	0.41	57	7.42	14.0	221	155	112	8	375	115	42	220	4	<1
01665260	Rapidan River nr Graves Mill	092481	0925	3.51	22	7.00	12.0	68	46	61	6	136	30	23	143	3	<1
01665270	Staunton River nr Graves Mill	092481	0850	1.37	19	6.86	12.5	52	24	58	8	91	34	24	148	5	<1
01665340	Conway River nr Kinderhook	092481	1035	1.66	25	6.99	12.5	73	48	71	8	136	56	25	159	3	<1
01665343	Conway River trib nr Kinderhook	092481	1130	1.15	27	7.09	12.5	94	54	83	6	168	60	26	168	6	<1
01665440	South River nr McMullen	092481	1205	0.58	39	6.99	14.0	146	104	78	6	246	69	28	168	17	<1
01665710	White Oak Canyon trib nr Syria	092481	1800	0.22	30	7.02	14.5	104	89	54	4	200	47	28	147	5	<1
01665720	Berry Hollow trib nr Nethers	092481	1900	0.02	28	6.70	14.0	71	43	98	13	170	56	27	227	8	<1
01665730	Cedar Run nr Syria	092481	1730	0.06	35	6.45	16.0	110	97	63	3	215	50	33	167	7	<1
01665800	Rose River nr Syria	092481	1630	2.10	28	7.10	14.0	96	81	57	4	199	39	26	161	4	<1
02031410	N Fk Moormans R trib nr Harriston	092181	1510	0.02	17	6.39	15.0	42	28	22	24	58	46	16	85	6	<1
02031500	N Fk Moormans River nr Whitehall	092281	1145	1.51	33	7.07	16.5	89	99	66	13	188	86	28	167	3	<1
02031800	S Fk Moormans River nr Whitehall	092281	1120	2.25	43	7.31	16.5	143	134	94	10	298	98	38	197	3	1
02032110	Doyles River nr Browns Cove	092281	0950	0.82	44	7.17	16.5	137	136	104	8	295	94	32	229	3	<1
02032310	Muddy Run trib nr Boonesville	092281	0915	0.64	43	7.25	16.0	136	129	99	4	278	91	32	234	3	<1
02032545	Ivy Creek nr Boonesville	092281	0825	0.49	45	6.38	17.0	131	122	93	9	259	103	29	200	4	<1
02032589	Swift Run at Lydia	092481	1330	1.07	61	7.29	15.0	218	141	155	8	325	56	194	202	5	<1

Table 4.—Water-quality and discharge data from synoptic surveys--Continued.

Station number	Station name	Date	Time	Dis- charge (ft^3/ sec)	Conduc- tivity (micro- siemen/ cm)	pH units	Temp (°C)	Dissolved concentration in microequivalents per liter except Si which is in micromoles per liter									
								Ca	Mg	Na	K	Alk	SO4	Cl	Si	NO3	NH4
01626900	Sawmill Run nr Dooms	012882	0820	2.42	21	6.43	1.0	51	59	37	22	46	81	27	79	2	<1
01627000	Mine Branch nr Crimora	012782	1440	0.30	15	5.79	1.5	21	37	23	20	10	64	26	75	<1	<1
01627100	Meadow Run nr Crimora	012782	1520	1.56	16	5.72	1.0	25	39	23	25	7	72	24	80	1	<1
01627400	Paine Run nr Harriston	012782	1330	2.56	23	5.72	2.0	31	59	24	39	7	114	24	82	3	<1
01628050	Madison Run above WOR nr Grottoes	012782	1210	1.83	22	6.50	1.0	49	69	40	18	66	75	27	102	1	<1
01628060	White Oak Run nr Grottoes	012882	1100	0.56	—	6.02	—	25	45	25	39	21	77	19	70	2	1
01628150	Deep Run nr Grottoes	012882	1200	0.34	—	5.65	—	22	46	30	30	7	101	21	83	<1	1
01628350	Upper Lewis Run nr Lynwood	012982	1730	0.30	22	5.62	1.0	27	54	28	43	5	121	25	93	<1	<1
01628700	Twomile Run nr McGaheysville	012782	0930	0.36	22	5.82	2.0	33	53	28	34	12	103	24	87	5	<1
01628900	Hawksbill Creek trib nr Swift Run	012582	1527	0.60	40	7.16	2.5	199	108	92	7	239	86	34	200	28	<1
01628910	West Swift Run at Swift Run	012582	1605	0.31	66	7.12	1.5	233	168	218	10	328	56	220	237	20	<1
01629120	East Branch Naked Creek nr Jollett	012982	1700	4.90	28	6.85	1.0	106	86	63	9	120	64	28	138	63	<1
01629130	Big Creek nr Jollett	012582	1222	2.66	29	7.07	1.5	132	93	59	7	156	84	27	139	30	<1
01629150	S Branch Naked Creek nr Furance	012582	1430	4.04	35	7.13	1.0	152	105	105	14	187	103	37	127	12	<1
01629920	Little Hawksbill Ck trib near Ida	012682	1040	0.32	25	6.54	1.0	94	46	61	5	62	83	30	151	23	<1
01629950	East Hawksbill Creek nr Ida	012682	1230	1.54	30	6.54	3.0	119	55	62	6	74	100	36	143	21	<1
01630100	South Fork Dry Run nr Fairview	012682	1300	0.39	32	6.40	2.0	127	67	65	7	65	137	38	142	39	<1
01630200	North Fork Dry Run nr Thornton Gap	012682	1400	0.78	30	6.74	1.0	110	64	81	9	87	103	36	176	33	1
01630542	Pass Run nr Thornton Gap	012682	1500	0.82	76	7.03	1.0	293	221	241	9	229	66	430	215	23	1
01630543	Rocky Branch nr Thornton Gap	012682	1600	0.63	43	7.14	1.0	183	136	87	11	249	98	55	194	25	<1
01630585	Jeremys Run nr Oak Hill	012682	1700	2.80	35	6.89	0.5	118	112	61	13	132	135	36	131	10	<1
01630649	Phils Arm Run nr Browntown	012782	1110	0.72	29	6.59	0.5	99	65	86	7	89	104	28	204	27	1
01630650	Phils Arm Run trib nr Browntown	012782	1100	0.18	28	6.70	0.5	90	60	103	10	123	104	31	250	4	<1
01630660	Smith Creek nr Browntown	012782	1200	0.30	29	6.60	1.0	90	51	90	8	70	101	32	202	32	<1
01630670	Greasy Run nr Browntown	012782	1000	0.56	42	6.95	0.0	173	111	86	8	189	122	42	200	35	<1
01630680	Lands Run nr Browntown	012782	1300	0.48	39	6.84	0.5	133	81	104	11	130	131	39	215	33	<1
01636202	Happy Creek trib nr Glen Echo	012782	1600	0.70	34	6.90	0.0	135	85	95	13	172	77	40	244	42	<1
01662100	Hazel River nr Nethers	012882	1700	3.10	20	6.73	1.5	63	42	61	11	88	44	29	159	12	1
01662150	Hughes River nr Nethers	012882	1300	6.97	20	6.70	1.5	69	45	62	7	82	51	32	146	16	<1
01662160	Brokenback Run nr Nethers	012882	1230	2.40	18	6.62	1.0	55	33	56	8	65	52	25	140	11	1
01662170	Rocky Run nr Nethers	012882	1400	0.24	23	6.55	1.0	54	39	84	12	75	73	30	171	7	<1
01662190	Ragged Run nr Etlan	012582	1700	0.65	19	6.62	3.0	54	32	66	12	79	53	27	158	1	<1
01662200	Rosson Hollow Run trib nr Etlan	012882	1030	0.27	22	6.56	1.0	55	34	85	12	82	65	33	192	3	<1
01662350	N F Thornton River nr Sperryville	012982	1400	2.10	36	7.10	1.0	136	119	89	8	198	92	37	210	23	<1
01662370	Piney River nr Sperryville	012982	1300	2.10	30	7.05	2.0	113	91	66	5	152	71	33	180	23	<1
01662480	Rush River at Rt 622 nr Washington	012882	1630	1.52	41	7.04	1.0	176	114	83	9	193	118	43	187	31	<1
01665260	Rapidan River nr Graves Mill	012682	1000	10.10	20	6.74	0.5	72	44	53	6	97	35	24	134	16	<1
01665270	Staunton River nr Graves Mill	012682	0900	3.11	17	6.58	1.5	55	22	55	7	60	39	23	131	8	<1
01665340	Conway River nr Kinderhook	012682	1200	6.72	21	6.72	1.0	74	41	62	7	76	67	25	143	9	<1
01665343	Conway River trib nr Kinderhook	012682	1110	5.35	24	6.82	3.0	89	46	70	6	101	68	25	158	13	<1
01665440	South River nr McMullen	012682	1320	4.44	29	6.88	2.5	116	77	59	5	127	74	27	146	33	<1
01665710	White Oak Canyon trib nr Syria	012582	1400	3.30	24	6.81	2.0	88	68	44	5	94	59	31	120	16	1
01665720	Berry Hollow trib nr Nethers	012582	1530	0.27	23	6.72	2.0	68	36	90	15	90	74	29	185	4	<1
01665730	Cedar Run nr Syria	012582	1330	2.20	25	6.72	2.0	89	71	47	4	93	63	33	129	18	<1
01665800	Rose River nr Syria	012582	1130	8.09	24	6.83	0.0	92	68	51	5	108	59	32	135	19	<1
02031500	N Fk Moormans River nr Whitehall	012882	1230	7.21	26	6.83	4.5	80	84	49	12	96	91	27	124	6	<1
02031800	S Fk Moormans River nr Whitehall	012882	1110	2.85	31	6.99	5.5	100	102	62	10	147	83	33	157	4	<1
02032110	Doyles River nr Browns Cove	012682	1615	4.17	34	6.99	2.0	117	109	80	7	150	97	34	161	27	<1
02032310	Muddy Run trib nr Boonesville	012682	1530	2.19	35	6.90	3.0	121	103	86	5	127	97	46	161	39	<1
02032545	Ivy Creek nr Boonesville	012682	1450	3.89	35	6.83	2.5	118	110	71	9	117	113	34	149	32	<1
02032589	Swift Run at Lydia	012582	1700	4.10	57	6.96	2.5	204	123	174	7	162	69	225	167	23	<1

Table 4.--Water-quality and discharge data from synoptic surveys--Continued.

Station number	Station name	Date	Time	Discharge (ft^3/sec)	Conductivity (microsiemen/cm)	pH units	Temp (°C)	Dissolved concentration in microequivalents per liter except Si which is in micromoles per liter									
								Ca	Mg	Na	K	Alk	SO4	Cl	Si	NO3	NH4
01626900	Sawmill Run nr Dooms	031882	1700	6.90	20	6.46	9.5	50	58	39	22	46	86	28	93	1	<1
01627000	Mine Branch nr Crimora	031682	1615	1.18	16	5.63	7.0	22	41	25	25	5	71	27	67	1	<1
01627100	Meadow Run nr Crimora	031682	1530	8.33	19	5.46	7.0	29	46	24	26	0	90	26	68	2	<1
01627400	Paine Run nr Harriston	031682	1410	11.10	23	5.48	7.0	29	52	26	41	3	110	26	78	6	<1
01628050	Madison Run above WOR nr Grottoes	031682	1140	5.09	19	6.45	7.0	44	63	38	20	62	70	25	98	3	<1
01628060	White Oak Run nr Grottoes	031882	1100	8.00	—	6.02	—	23	41	21	32	15	78	21	71	5	1
01628150	Deep Run nr Grottoes	031882	1200	2.80	—	5.48	—	21	44	26	40	0	104	25	80	<1	<1
01628300	Lower Lewis Run nr Lynwood	031682	0940	0.66	22	5.54	7.0	34	50	27	42	3	105	23	78	10	<1
01628320	Lower Lewis Run trib nr Lynwood	031682	1000	0.24	16	4.98	7.0	12	37	25	14	-5	60	27	63	1	<1
01628700	Twomile Run nr McGaheysville	031682	0820	4.67	20	5.79	6.0	31	50	27	37	9	96	23	79	8	<1
01628900	Hawksbill Creek trib nr Swift Run	031582	1540	1.74	36	6.96-	6.0	163	97	74	7	174	97	34	180	28	<1
01628910	West Swift Run at Swift Run	031582	1625	1.40	63	7.01	6.0	218	145	221	9	255	90	252	224	12	<1
01629120	East Branch Naked Creek nr Jollett	031582	1310	16.50	23	6.81	1.5	107	89	62	10	108	75	24	132	55	<1
01629130	Big Creek nr Jollett	031582	1220	9.21	27	6.96	5.0	114	87	59	8	123	89	26	130	26	<1
01629150	S Branch Naked Creek nr Furance	031582	1420	20.60	31	6.96	1.0	132	99	60	16	138	110	35	131	15	<1
01629920	Little Hawksbill Ck trib near Ida	031982	1400	2.92	26	6.63	8.0	99	48	62	5	53	95	28	141	22	<1
01629950	East Hawksbill Creek nr Ida	031882	1300	15.80	28	6.58	8.0	126	57	58	6	55	122	35	106	28	<1
01630100	South Fork Dry Run nr Fairview	031682	1615	4.43	32	6.47	4.5	133	66	69	9	59	138	31	139	40	<1
01630200	North Fork Dry Run nr Thornton Gap	031682	1520	7.11	26	6.60	6.0	102	59	74	9	66	108	30	152	30	<1
01630542	Pass Run nr Thornton Gap	031682	1430	7.25	70	6.91	5.0	226	156	214	10	158	72	343	167	27	<1
01630543	Rocky Branch nr Thornton Gap	031682	1710	10.50	39	7.03	5.5	142	119	78	13	170	109	51	170	22	<1
01630585	Jeremys Run nr Oak Hill	031982	1130	40.40	30	6.89	8.5	117	114	61	17	106	150	33	139	15	<1
01630649	Phils Arm Run nr Browntown	031882	1510	4.59	29	6.65	9.0	99	67	79	9	64	122	27	163	37	<1
01630650	Phils Arm Run trib nr Browntown	031882	1500	2.02	26	6.74	9.5	81	54	94	13	91	112	34	198	4	1
01630660	Smith Creek nr Browntown	031882	1620	5.31	31	6.55	8.0	106	60	88	10	53	136	32	167	44	<1
01630670	Greasy Run nr Browntown	031882	1345	7.78	35	6.90	8.0	158	101	75	8	119	146	34	161	38	<1
01630680	Lands Run nr Browntown	031882	1720	7.97	41	6.86	8.5	147	95	106	12	105	166	35	191	36	<1
01636202	Happy Creek trib nr Glen Echo	031882	1230	6.02	40	7.01	7.0	159	105	93	12	147	131	38	206	53	<1
01662100	Hazel River nr Nethers	031782	1500	18.00	18	6.57	8.5	58	39	59	11	58	56	26	134	9	<1
01662150	Hughes River nr Nethers	031782	1300	40.90	21	6.72	9.0	67	46	62	8	70	64	34	136	12	<1
01662160	Brokenback Run nr Nethers	031782	1212	16.90	17	6.63	7.5	50	32	55	8	54	62	25	130	6	<1
01662170	Rocky Run nr Nethers	031782	1400	2.77	21	6.60	9.5	54	37	79	13	61	79	29	155	3	<1
01662190	Ragged Run nr Etlan	031582	1640	2.66	18	6.56	5.0	46	33	63	11	59	57	27	140	3	<1
01662200	Rosson Hollow Run trib nr Etlan	031782	1110	2.46	20	6.62	8.5	50	33	78	13	60	76	30	160	<1	<1
01662350	N F Thornton River nr Sperryville	031782	1620	37.60	37	7.09	9.0	145	129	89	9	171	121	35	199	31	<1
01662370	Piney River nr Sperryville	031782	1710	28.10	31	6.95	8.0	121	100	69	6	136	95	30	176	33	<1
01662480	Rush River at Rt 622 nr Washington	031782	1815	14.50	43	6.99	8.0	187	125	82	9	164	148	37	172	42	<1
01665260	Rapidan River nr Graves Mill	031882	1000	20.60	18	6.80	7.5	76	45	54	6	89	44	23	124	13	<1
01665270	Staunton River nr Graves Mill	031882	1035	13.20	16	6.63	7.5	54	22	57	8	57	43	24	123	8	<1
01665340	Conway River nr Kinderhook	031882	1240	26.80	21	6.73	9.0	81	46	64	7	73	85	25	136	8	<1
01665343	Conway River trib nr Kinderhook	031882	1330	8.91	23	6.87	8.0	97	50	72	6	100	77	26	151	13	<1
01665440	South River nr McMullen	031882	1435	13.50	29	6.94	9.0	125	85	64	5	115	92	27	143	38	<1
01665710	White Oak Canyon trib nr Syria	031582	1530	11.00	22	6.78	4.5	90	71	50	4	104	61	30	125	13	<1
01665720	Berry Hollow trib nr Nethers	031582	1400	1.55	21	6.62	6.0	63	35	81	14	83	72	27	160	5	<1
01665730	Cedar Run nr Syria	031582	1450	18.40	24	6.79	5.0	94	76	51	3	99	71	32	131	15	<1
01665800	Rose River nr Syria	031582	1140	34.90	23	6.88	5.0	92	73	52	4	108	62	29	132	17	<1
02031410	N Fk Moormans R trib nr Harriston	031782	1700	0.48	14	5.97	10.0	22	22	20	32	14	53	18	67	4	<1
02031500	N Fk Moormans River nr Whitehall	031782	1000	41.20	24	6.83	8.0	83	84	54	14	91	96	28	139	10	<1
02031800	S Fk Moormans River nr Whitehall	031782	0945	18.20	30	7.00	10.0	102	101	62	11	140	92	33	171	6	<1
02032110	Doyles River nr Browns Cove	031982	0820	23.10	35	7.05	8.0	122	112	80	8	150	102	32	193	34	<1
02032310	Muddy Run trib nr Boonesville	031982	0920	8.50	34	6.95	8.5	131	104	77	6	127	110	32	170	42	<1
02032545	Ivy Creek nr Boonesville	031982	1015	18.50	32	6.91	9.5	121	106	72	10	121	119	31	161	30	<1
02032589	Swift Run at Lydia	031882	1530	14.80	47	6.99	9.0	165	99	152	6	142	84	164	162	25	<1

Table 4.--Water-quality and discharge data from synoptic surveys--Continued.

Station number	Station name	Date	Time	Dis-charge (ft^3/sec)	Conduc-tivity (micro-siemen/cm)	pH units	Temp (°C)	Ca	Mg	Na	K	Alk	SO4	Cl	Si	NO3	NH4
								Dissolved concentration in microequivalents per liter except Si which is in micromoles per liter									
01626900	Sawmill Run nr Dooms	052082	0815	1.42	22	6.52	14.0	60	69	38	28	81	77	28	101	<1	1
01627000	Mine Branch nr Crimora	052082	0915	0.17	17	6.12	14.0	20	38	22	24	11	60	28	71	<1	1
01627100	Meadow Run nr Crimora	052082	1000	1.71	17	5.75	14.0	24	41	22	25	0	79	28	70	<1	1
01627400	Paine Run nr Harriston	052082	1125	2.09	22	6.01	15.0	24	47	22	41	9	102	27	62	<1	1
01628050	Madison Run above WOR nr Grottoes	052082	1245	0.70	22	6.58	15.0	55	82	45	27	111	64	28	119	1	1
01628060	White Oak Run nr Grottoes	052082	1100	0.30	—	6.10	—	26	47	22	39	31	73	21	77	<1	<1
01628150	Deep Run nr Grottoes	052082	1200	0.44	—	5.60	—	22	42	25	40	2	96	27	89	<1	<1
01628300	Lower Lewis Run nr Lynwood	052082	1515	0.22	23	5.50	15.0	30	47	27	42	19	97	25	75	6	1
01628320	Lower Lewis Run trib nr Lynwood	052082	1445	0.04	17	5.22	15.0	11	33	23	14	5	43	28	59	<1	1
01628350	Upper Lewis Run nr Lynwood	052082	1410	0.35	22	5.53	16.0	23	47	26	53	12	111	27	74	<1	1
01628530	Hangman Run nr Rocky Bar	061082	1230	0.19	19	4.97	16.0	21	45	20	12	-10	88	23	63	<1	<1
01628700	Twomile Run nr McGaheysville	052182	0845	0.92	20	6.01	14.5	25	52	29	38	18	84	24	78	6	2
01628750	Walls Run nr Rocky Bar	061082	1320	0.15	19	4.95	17.0	28	43	19	14	-10	91	23	61	1	1
01628900	Hawksbill Creek trib nr Swift Run	051782	1420	0.64	40	7.20	15.0	204	115	94	7	288	78	38	210	<1	1
01628910	West Swift Run at Swift Run	052182	1015	0.44	45	7.15	14.0	195	139	123	8	326	44	78	246	10	1
01629120	East Branch Naked Creek nr Jollett	051782	1200	3.26	28	7.10	15.0	116	93	66	10	157	56	28	151	38	1
01629130	Big Creek nr Jollett	051782	1245	1.71	33	7.36	14.0	165	115	66	9	233	70	31	151	19	1
01629150	S Branch Naked Creek nr Furance	051782	1100	4.93	42	7.40	15.5	165	116	65	19	244	86	35	122	5	1
01629920	Little Hawksbill Ck trib near Ida	052082	1240	0.44	27	6.79	14.0	103	49	70	5	110	73	27	176	<1	1
01629950	East Hawksbill Creek nr Ida	052082	1330	2.07	30	6.73	14.0	127	55	65	6	114	95	32	149	13	1
01630100	South Fork Dry Run nr Fairview	052082	1430	0.32	30	6.63	13.5	135	69	75	9	118	123	37	164	14	<1
01630200	North Fork Dry Run nr Thornton Gap	052082	1615	1.05	32	6.93	20.5	105	61	79	10	107	99	32	166	19	1
01630542	Pass Run nr Thornton Gap	052082	1700	1.15	75	7.22	16.0	264	191	168	10	244	53	396	237	3	1
01630543	Rocky Branch nr Thornton Gap	051982	1620	1.11	46	7.42	18.5	176	141	91	12	306	67	37	235	<1	1
01630585	Jeremys Run nr Oak Hill	051982	1700	2.10	40	6.99	17.5	148	139	73	20	220	119	39	167	<1	1
01630649	Phils Arm Run nr Browntown	051982	1300	0.52	29	6.95	16.5	115	74	90	10	162	94	33	227	1	1
01630650	Phils Arm Run trib nr Browntown	051982	1245	0.28	28	7.01	17.5	105	66	108	11	175	80	34	279	4	1
01630660	Smith Creek nr Browntown	051982	1200	0.79	31	6.81	14.5	105	56	91	9	107	95	33	204	1	1
01630670	Greasy Run nr Browntown	051982	1400	0.79	40	7.31	18.5	188	114	92	12	258	105	39	218	1	1
01630680	Lands Run nr Browntown	051982	1115	0.80	38	7.07	16.5	134	91	112	12	154	122	38	230	1	1
01636202	Happy Creek trib nr Glen Echo	051882	1730	1.17	37	7.25	16.0	147	92	97	10	221	71	39	255	1	1
01662100	Hazel River nr Nethers	051882	1220	6.39	19	6.94	15.0	59	41	60	10	97	37	27	162	6	1
01662150	Hughes River nr Nethers	051782	1750	8.82	22	6.91	16.0	71	46	64	8	101	47	33	151	12	1
01662160	Brokenback Run nr Nethers	051782	1700	3.89	18	6.85	15.0	60	36	59	10	88	44	27	143	1	1
01662170	Rocky Run nr Nethers	051882	1115	0.50	24	6.78	15.5	63	45	102	14	105	63	30	190	4	1
01662190	Ragged Run nr Etlan	051782	1500	0.98	21	6.80	17.5	58	39	72	14	97	47	30	169	1	1
01662200	Rosson Hollow Run trib nr Etlan	051782	1600	0.40	24	6.82	19.5	64	38	90	16	114	59	34	193	1	1
01662350	N F Thornton River nr Sperryville	051882	1445	4.00	39	7.35	16.5	157	138	101	10	239	78	37	251	1	1
01662370	Piney River nr Sperryville	051882	1350	3.24	33	7.22	16.5	136	107	81	6	219	62	36	223	9	1
01662480	Rush River at Rt 622 nr Washington	051882	1615	1.48	48	7.28	19.5	217	132	99	19	270	106	44	223	1	2
01665260	Rapidan River nr Graves Mill	051882	0815	11.60	20	6.98	14.0	80	45	58	7	106	35	26	130	11	1
01665270	Staunton River nr Graves Mill	051882	0900	7.31	18	6.79	13.0	59	25	57	9	72	38	26	129	10	1
01665340	Conway River nr Kinderhook	051882	1015	9.28	20	6.90	13.5	80	44	69	9	97	62	28	143	9	1
01665343	Conway River trib nr Kinderhook	051882	1110	4.34	25	7.07	14.0	101	49	77	7	129	58	29	163	<1	1
01665440	South River nr McMullen	051882	1200	2.70	24	7.09	14.0	131	84	68	6	179	57	31	163	16	1
01665710	White Oak Canyon trib nr Syria	051782	1230	3.16	27	7.06	16.0	106	79	53	4	151	48	34	135	9	1
01665720	Berry Hollow trib nr Nethers	051782	1320	0.66	23	6.83	14.0	65	37	88	15	113	56	42	189	4	1
01665730	Cedar Run nr Syria	051782	1200	1.43	31	6.74	14.0	116	91	73	4	162	58	37	146	10	1
01665800	Rose River nr Syria	051782	1030	7.90	26	7.22	14.5	104	75	58	5	154	51	32	147	9	1
02031410	N Fk Moormans R trib nr Harriston	051982	1110	0.17	13	6.19	12.0	29	23	18	31	26	44	18	63	3	1
02031500	N Fk Moormans River nr Whitehall	051982	1410	6.39	35	7.27	16.0	124	122	74	11	229	55	34	203	5	1
02031800	S Fk Moormans River nr Whitehall	051982	1320	2.66	31	7.16	16.0	95	96	64	16	161	66	29	144	5	1
02032110	Doyles River nr Browns Cove	051882	1405	2.92	38	7.20	17.0	131	117	95	9	229	76	37	209	10	1
02032310	Muddy Run trib nr Boonesville	051882	1320	1.36	38	7.34	18.0	144	114	88	6	221	91	35	194	6	1
02032545	Ivy Creek nr Boonesville	051882	1500	1.80	37	7.16	18.0	136	118	86	10	196	97	32	174	13	1
02032589	Swift Run at Lydia	052182	1100	4.21	55	7.23	13.5	201	118	168	7	202	64	152	182	<1	1

Table 4.--Water-quality and discharge data from synoptic surveys--Continued.

Station number	Station name	Date	Time	Discharge (ft^3/sec)	Conductivity (microsiemen/cm)	pH units	Temp (°C)	Dissolved concentration in microequivalents per liter except Si which is in micromoles per liter									
								Ca	Mg	Na	K	Alk	SO4	Cl	Si	NO3	NH4
01626900	Sawmill Run nr Dooms	062482	0750	1.34	24	6.74	13.5	59	70	43	26	81	87	30	111	<1	<1
01627000	Mine Branch nr Crimora	062482	0850	0.34	17	6.18	13.0	22	41	25	28	17	69	26	74	1	<1
01627100	Meadow Run nr Crimora	062482	0940	2.33	18	5.63	13.5	25	42	24	28	3	87	26	73	1	<1
01627400	Paine Run nr Harriston	062482	1100	3.00	22	5.99	14.5	29	50	27	45	9	104	25	78	<1	<1
01628050	Madison Run above WOR nr Grottoes	062482	1215	0.74	20	6.62	15.0	54	79	44	28	130	66	25	123	1	<1
01628060	White Oak Run nr Grottoes	062482	1100	0.38	—	5.93	—	26	46	21	38	29	69	21	84	<1	<1
01628150	Deep Run nr Grottoes	062482	1200	0.64	—	5.60	—	24	46	25	37	3	104	27	94	<1	<1
01628300	Lower Lewis Run nr Lynwood	062182	1445	0.30	21	5.55	14.0	29	47	27	41	14	102	25	80	3	<1
01628320	Lower Lewis Run trib nr Lynwood	062482	1425	0.32	15	5.10	14.0	7	36	23	14	-3	53	27	64	<1	<1
01628350	Upper Lewis Run nr Lynwood	062482	1345	0.52	21	5.61	15.5	23	49	27	52	8	111	26	85	1	<1
01628530	Hangman Run nr Rocky Bar	062582	0755	0.07	22	4.96	14.0	22	45	22	14	-7	87	25	68	<1	<1
01628700	Twomile Run nr McGaheysville	062282	1415	1.59	20	6.01	15.0	27	46	27	37	14	90	24	80	3	<1
01628750	Walls Run nr Rocky Bar	062282	1525	0.01	23	4.96	15.0	31	46	22	17	-4	92	24	66	<1	<1
01628900	Hawksbill Creek trib nr Swift Run	062282	1305	0.75	37	7.18	15.0	192	109	90	6	271	82	30	201	6	1
01628910	West Swift Run at Swift Run	062182	1430	1.06	69	7.23	15.0	260	166	240	9	348	59	270	242	9	<1
01629120	East Branch Naked Creek nr Jollett	062182	1320	7.66	25	7.06	15.0	111	87	66	8	163	49	23	150	32	<1
01629130	Big Creek nr Jollett	062182	1240	4.84	27	7.22	14.5	129	95	66	7	184	65	25	149	13	<1
01629150	S Branch Naked Creek nr Furance	062182	1120	9.06	32	7.38	14.5	156	110	65	16	223	87	29	149	4	<1
01629920	Little Hawksbill Ck trib near Ida	062482	1215	0.59	25	6.76	14.5	97	47	71	6	100	87	25	165	7	<1
01629950	East Hawksbill Creek nr Ida	062482	1320	3.08	27	6.73	14.0	125	56	66	6	104	106	28	143	9	<1
01630100	South Fork Dry Run nr Fairview	062482	1415	0.68	28	6.68	14.5	140	69	76	9	120	118	36	157	12	<1
01630200	North Fork Dry Run nr Thornton Gap	062482	1500	2.04	22	6.89	20.0	107	62	78	10	107	93	30	168	13	<1
01630542	Pass Run nr Thornton Gap	062482	1530	2.83	81	7.25	15.5	280	194	251	9	281	44	368	223	8	1
01630543	Rocky Branch nr Thornton Gap	062482	1630	2.75	41	7.30	17.5	163	128	85	11	276	50	33	220	7	<1
01630585	Jeremys Run nr Oak Hill	062382	1145	7.15	37	7.10	17.0	141	126	70	18	188	122	34	164	4	<1
01630649	Phils Arm Run nr Browntown	062382	1520	0.66	28	6.93	17.0	107	67	87	7	123	98	27	207	6	<1
01630650	Phils Arm Run trib nr Browntown	062382	1515	0.35	30	7.07	18.0	101	64	113	13	170	76	32	277	2	<1
01630660	Smith Creek nr Browntown	062382	1630	1.11	29	6.84	15.0	104	57	92	8	96	103	30	195	24	<1
01630670	Greasy Run nr Browntown	062382	1430	1.63	38	7.20	18.0	173	104	90	9	215	105	34	203	8	1
01630680	Lands Run nr Browntown	062382	1720	1.27	38	7.08	16.5	136	82	110	11	155	125	33	222	15	<1
01636202	Hsppy Creek trib nr Glen Echo	062282	1930	1.81	38	7.14	16.0	150	93	100	12	226	79	38	249	22	1
01662100	Hazel River nr Nethers	062282	1200	14.60	17	6.86	16.0	54	38	60	10	89	34	26	153	4	<1
01662150	Hughes River nr Nethers	062182	1700	24.50	20	6.82	16.5	68	44	64	9	97	42	30	146	8	<1
01662160	Brokenback Run nr Nethers	062182	1615	10.40	16	6.73	16.5	55	33	58	9	75	38	25	135	2	<1
01662170	Rocky Run nr Nethers	062182	1800	1.43	23	6.77	15.5	61	43	88	15	104	64	28	188	1	<1
01662190	Ragged Run nr Etlan	062182	1430	2.32	20	6.79	17.5	54	38	72	12	86	55	27	166	2	<1
01662200	Rosson Hollow Run trib nr Etlan	062182	1530	1.41	21	6.77	19.5	62	38	86	15	107	56	31	200	1	<1
01662350	N F Thornton River nr Sperryville	062282	1520	10.70	38	7.26	15.5	152	139	95	10	267	77	32	247	15	<1
01662370	Piney River nr Sperryville	062282	1430	8.28	32	7.25	16.0	134	106	79	7	219	63	28	218	10	<1
01662480	Rush River at Rt 622 nr Washington	062182	1815	4.05	46	7.22	17.5	211	136	95	10	278	119	36	212	12	<1
01665260	Rapidan River nr Graves Mill	062282	0800	29.50	20	6.91	13.0	73	44	57	6	108	33	24	132	8	<1
01665270	Staunton River nr Graves Mill	062382	0840	21.60	17	6.74	13.0	56	24	59	9	72	34	24	125	6	<1
01665340	Conway River nr Kinderhook	062282	1005	28.40	21	6.87	13.0	78	45	67	9	97	63	24	140	5	<1
01665343	Conway River trib nr Kinderhook	062282	1100	8.24	26	7.01	13.5	101	51	76	7	134	64	26	156	7	<1
01665440	South River nr McMullen	062282	1150	9.56	28	7.10	14.0	113	81	52	3	168	61	22	158	17	1
01665710	White Oak Canyon trib nr Syria	062182	1200	8.16	24	7.00	16.0	95	71	52	5	138	45	29	130	6	<1
01665720	Berry Hollow trib nr Nethers	062182	1300	1.77	23	6.86	15.5	66	37	86	15	104	62	27	179	3	<1
01665730	Cedar Run nr Syria	062182	1130	8.27	27	6.84	15.5	101	76	54	5	140	58	31	138	7	1
01665800	Rose River nr Syria	062182	1020	22.50	23	7.08	14.5	101	74	57	5	147	47	27	147	7	<1
02031410	N Fk Moormans R trib nr Harriston	062382	1145	0.24	15	6.14	12.0	22	20	19	31	27	34	17	62	2	<1
02031500	N Fk Moormans River nr Whitehall	062382	1420	10.60	28	7.16	16.0	92	89	65	15	158	68	26	165	3	<1
02031800	S Fk Moormans River nr Whitehall	062382	1345	5.85	34	7.27	15.0	119	110	76	10	220	60	31	212	4	<1
02032110	Doyles River nr Browns Cove	062582	1230	5.39	36	7.34	16.0	138	119	91	9	236	77	29	217	10	<1
02032310	Muddy Run trib nr Boonesville	062582	1120	2.21	39	7.18	17.0	153	119	90	7	220	88	34	197	15	<1
02032545	Ivy Creek nr Boonesville	062582	1035	3.42	37	7.02	16.5	137	114	87	11	211	97	31	181	9	<1
02032589	Swift Run at Lydia	062582	0910	6.13	49	7.20	13.5	185	104	143	7	235	58	133	178	9	<1

Table 5.--Flow-weighted concentration of water-quality constituents.

Station number	Station name	pH (units)	Dissolved concentration in microequivalents per liter except Si which is in micromoles per liter									
			Ca	Mg	Na	K	Cb[1]	Alk[2]	SO_4	Cl	Si	NO_3
01626900	Sawmill Run nr Dooms	6.49	54	62	40	23	179	61	85	28	98	1
01627000	Mine Branch nr Crimora	5.74	22	40	24	24	110	8	69	27	70	1
01627100	Meadow Run nr Crimora	5.54	27	43	23	26	120	1	86	26	71	1
01627400	Paine Run nr Harriston	5.61	29	52	25	42	148	5	109	26	77	4
01628050	Madison Run above WOR nr Grottoes	6.48	47	68	40	21	176	74	70	26	103	2
01628060	White Oak Run nr Grottoes	6.02	24	42	22	33	120	16	78	21	71	4
01628150	Deep Run nr Grottoes	5.52	22	44	26	39	131	2	103	26	84	<1
01628300	Lower Lewis Run nr Lynwood	5.53	32	49	27	42	149	9	103	24	78	7
01628320	Lower Lewis Run trib nr Lynwood	5.05	9	36	24	14	83	-3	55	22	63	1
01628350	Upper Lewis Run nr Lynwood	5.59	24	50	27	50	150	8	113	26	84	<1
01628530	Hangman Run nr Rocky Bar	4.97	21	45	20	13	99	-9	88	24	65	<1
01628700	Twomile Run nr McGaheysville	5.86	29	50	28	36	143	12	93	23	80	6
01628750	Walls Run nr Rocky Bar	4.95	28	43	19	14	103	-10	91	23	61	1
01628900	Hawksbill Creek trib nr Swift Run	7.08	190	108	87	7	393	245	88	34	197	18
01628910	West Swift Run at Swift Run	7.11	227	153	209	9	598	308	69	221	237	12
01629120	East Branch Naked Creek nr Jollett	6.91	108	89	64	9	270	136	65	24	143	46
01629130	Big Creek nr Jollett	7.08	132	97	62	8	298	168	80	26	141	22
01629150	S Branch Naked Creek nr Furance	7.10	145	106	67	17	334	182	100	34	134	11
01629920	Little Hawksbill Ck trib near Ida	6.66	99	48	65	5	217	69	90	28	151	17
01629950	East Hawksbill Creek nr Ida	6.61	125	56	60	6	248	70	116	34	119	23
01630100	South Fork Dry Run nr Fairview	6.50	135	68	71	9	283	76	134	33	145	34
01630200	North Fork Dry Run nr Thornton Gap	6.69	104	61	76	10	250	83	103	31	158	26
01630542	Pass Run nr Thornton Gap	7.02	251	177	222	10	659	213	62	361	196	19
01630543	Rocky Branch nr Thornton Gap	7.10	153	125	82	12	372	210	94	47	187	17
01630585	Jeremys Run nr Oak Hill	6.91	122	117	63	17	319	126	144	33	143	13
01630649	Phils Arm Run nr Browntown	6.70	102	68	83	9	262	89	115	28	186	27
01630650	Phils Arm Run trib nr Browntown	6.79	89	59	100	13	261	120	103	34	225	4
01630660	Smith Creek nr Browntown	6.61	105	59	89	10	263	68	124	32	179	35
01630670	Greasy Run nr Browntown	6.98	164	105	81	9	360	161	132	35	180	29
01630680	Lands Run nr Browntown	6.90	143	92	107	12	354	119	154	35	200	30
01636202	Happy Creek trib nr Glen Echo	7.06	153	100	96	11	359	179	107	38	227	38
01662100	Hazel River nr Nethers	6.72	58	40	60	10	168	80	45	26	149	7
01662150	Hughes River nr Nethers	6.77	68	45	63	8	184	85	54	32	144	11
01662160	Brokenback Run nr Nethers	6.69	53	33	57	9	152	68	52	25	136	5
01662170	Rocky Run nr Nethers	6.65	57	40	84	13	195	79	73	29	169	3
01662190	Ragged Run nr Etlan	6.67	52	36	69	12	169	78	55	27	157	3
01662200	Rosson Hollow Run trib nr Etlan	6.67	56	35	83	14	188	82	68	31	179	1
01662350	N F Thornton River nr Sperryville	7.14	147	131	91	9	380	199	108	34	214	25
01662370	Piney River nr Sperryville	7.02	125	102	72	6	305	163	85	31	190	25
01662480	Rush River at Rt 622 nr Washington	7.05	193	128	86	10	417	200	137	38	185	32
01665260	Rapidan River nr Graves Mill	6.88	74	45	56	6	181	104	37	24	131	10
01665270	Staunton River nr Graves Mill	6.71	55	24	58	8	145	68	38	24	127	7
01665340	Conway River nr Kinderhook	6.81	79	45	66	8	198	89	71	25	141	7
01665343	Conway River trib nr Kinderhook	6.94	97	50	74	7	227	119	68	26	157	9
01665440	South River nr McMullen	6.99	121	84	60	5	270	145	76	26	151	28
01665710	White Oak Canyon trib nr Syria	6.88	94	73	50	5	221	123	54	30	128	10
01665720	Berry Hollow trib nr Nethers	6.75	65	36	85	15	201	99	66	29	175	4
01665730	Cedar Run nr Syria	6.79	97	76	53	4	229	114	66	32	134	13
01665800	Rose River nr Syria	6.97	96	75	54	4	229	133	57	28	142	12
02031410	N Fk Moormans R trib nr Harriston	6.05	24	21	19	32	96	21	46	18	66	3
02031500	N Fk Moormans River nr Whitehall	6.91	88	89	58	14	249	119	87	28	149	8
02031800	S Fk Moormans River nr Whitehall	7.07	107	105	68	11	291	170	83	33	178	5
02032110	Doyles River nr Browns Cove	7.09	125	113	84	8	330	174	96	32	195	27
02032310	Muddy Run trib nr Boonesville	7.01	134	109	83	6	331	159	102	35	179	32
02032545	Ivy Creek nr Boonesville	6.90	124	109	75	10	317	140	114	31	163	26
02032589	Swift Run at Lydia	7.06	183	108	156	7	453	183	73	167	171	17

[1]Sum of base cations (calcium, magnesium, sodium, and potassium).
[2]Mineral acidity is shown as negative alkalinity.

Table 6.--Water-quality flow-weighted mean concentrations at White Oak Run (01628060) using weekly data (1981-82) and synoptic survey data.

	Flow-weighted mean concentrations in microequivalents per liter unless otherwise noted	
	weekly data (1981-82)	six synoptic surveys
Calcium	25	24
Magnesium	44	42
Sodium	22	22
Potassium	35	33
Ammonium	<1	<1
pH (units)	6.05	6.02
Nitrate	3	4
Chloride	22	21
Sulfate	79	78
Alkalinity	20	16
Silica (μmoles/L)	75	71

(B_0) and the regression coefficients (B_1, $B_2 ... B_i$) are selected such that the sum of squared residuals is minimized. The overall accuracy of the prediction equation is reflected by the coefficient of determination (r^2), which is the proportion of variation in Y explained by the independent variables in the equation.

Although regression analysis is extremely useful as a predictive tool, a strong association between variables does not imply causality. Controlled experimentation is necessary to formulate inferences about causality. Regression analysis merely indicates if variables are strongly related in a statistical sense.

Some of the independent variables in the regression analysis are represented as proportions--namely, the percentage of bedrock types (Antietam, Hampton, Old Rag, Pedlar, and Catoctin) in each basin. The sum of these five percentages equals, or nearly equals, 100 percent, which produces a problem of data multicollinearity in that the final bedrock independent variable is almost perfectly predicted by the first four (Goldberger, 1968). This problem is prevented by excluding one of the bedrock independent variables from the regression analyses which effectively incorporates it into the intercept term (Watson, 1969). To minimize multicollinearity, percent Catoctin was eliminated from the regression equations because it is the most common formation in the Park. However, excluding formations other than Catoctin did not appreciably affect the results.

Residual analysis was undertaken to determine if any basic assumptions of multiple linear regression were violated. Scatter plots of residuals versus predicted values of the dependent variable (Y) indicated a problem of data heteroscedacisity. That is, the variance of Y was not constant for any fixed combination of independent variables. To remedy this problem, the dependent variable was log transformed (base e) prior to analysis to stabilize the variance. For alkalinity data, 25 μeq/L was added onto each value prior to log transformation to eliminate zero and negative (mineral acidity) values (Walpole and Myers, 1978). An examination of residuals after log transformation showed that data heteroscedacisity had been largely reduced. In addition, plots of residuals versus independent variables showed no discernable patterns.

A wide range of hydrologic variability was covered by the six sampling trips from August 1981 to June 1982; however, relatively constant streamflow conditions prevailed throughout the span of each survey. Figure 5 shows mean unit discharge for the streams during each survey as well as flow duration values. Concurrent record from long-term gaging stations near the Park are used to calculate flow duration values which provide an indication of hydrologic conditions at the time of sampling. These stations are: Hazel River at Rixeyville, Va. (U.S. Geological Survey number 01663500), Rappahannock River near Warrenton, Va. (01662000), Robinson River near Locust Dale, Va. (01666500), and Rapidan River near Ruckersville, Va. (01665500). For example, mean flow

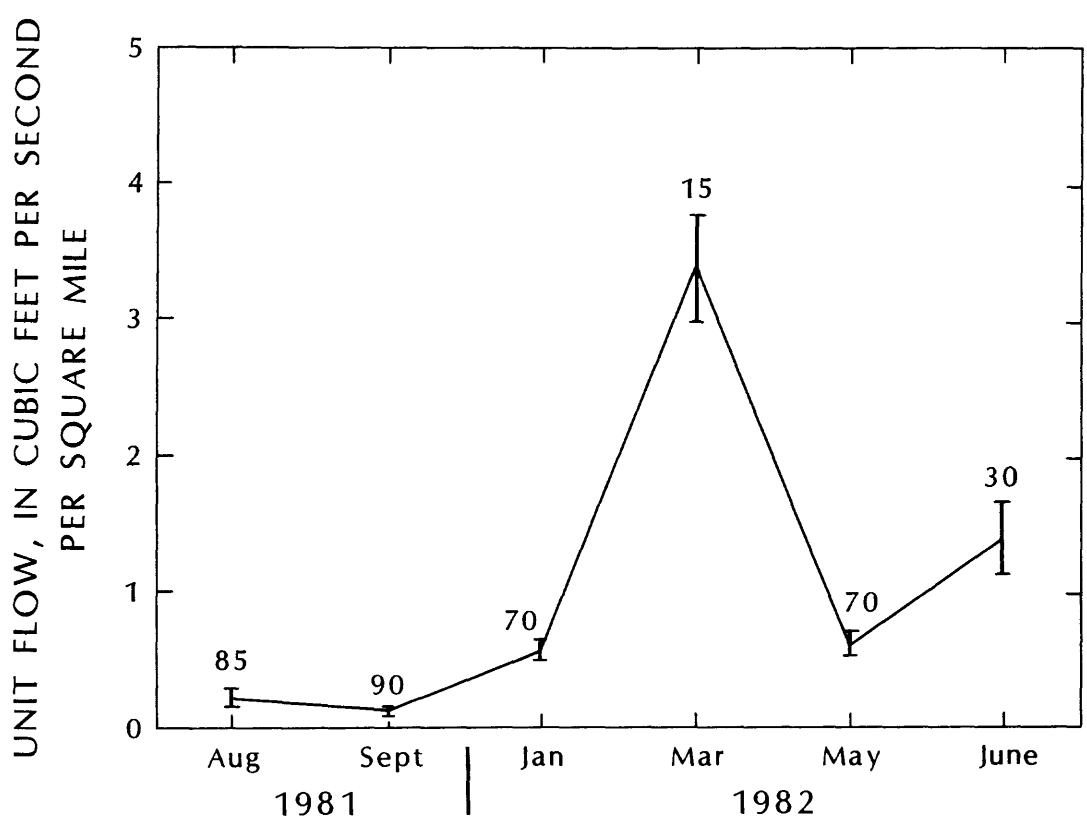

Figure 5.--Mean unit runoff, with 95 percent confidence intervals, and approximate values for percent of flow duration for each synoptic survey.

duration in the Park during the August 1981 synoptic survey was about 85 percent. In other words, streamflows exceed those measured during that survey 85 percent of the time. Thus, fairly low flows were encountered during this survey. Low flows were also sampled during the September survey with streams near 90 percent of flow duration. During these surveys, streamflows were sustained primarily by ground-water discharge. Streams at higher flow were sampled in January (70 percent of flow duration), March (15 percent), May (70 percent), and June (30 percent) of 1982. The contribution from surface runoff during these surveys was greater and ground-water discharge made up a smaller percentage of total streamflow.

To determine streamflow and seasonal effects on stream-water chemistry for each major rock formation, comparisons are made between selected synoptic surveys. Only basins dominated by single rock types (greater than or equal to 75 percent) are included so differences between surveys as well as drainage basin geology can be discerned. Similar streamflows during the January and May 1982 surveys (fig. 5) permit an assessment of the seasonal component without the complication of dissimilar flow conditions. Measurements in September 1981 and June 1982 are compared to determine effects of dissimilar flow conditions on water quality within the same season; flows in June 1982 were about ten times greater than in September 1981. Comparisons of constituents between trips are made using a paired-difference test which eliminates the effect of stream-to-stream variability within a particular bedrock type. The difference between surveys is calculated for each stream, and the mean for each rock type is compared to zero (a null hypothesis of no significant difference) using a two-tailed t-test.

INDICES OF SENSITIVITY TO ACID DEPOSITION

Factors Affecting Sensitivity

The extent to which a system can resist change due to acid deposition is determined by the geochemistry, geomorphology, and hydrodynamics of that system (Haines, 1981). Resistance to acidification includes resisting changes in pH and alkalinity, resisting increased release of base cations, and conserving the capacity to retain heavy metals, acid anions, and organic compounds. Sensitivity evaluations such as lake/stream alkalinity or calcite saturation (Conroy and others, 1974) do not necessarily reflect the long-term capacity of a basin to neutralize acid deposition. Ideally, as many terrestrial and aquatic factors as possible should be considered together to evaluate sensitivity to acid deposition (Cowell and others, 1981; U.S.-Canada Impact Assessment, 1983).

The present data base for much of North America, however, is not sufficient to evaluate all or even most of these factors affecting sensitivity. Consequently, most researchers assume the resultant lake or stream chemistry adequately reflects the combined interaction of soil-bedrock-hydrologic characteristics to provide a satisfactory assessment of sensitivity (United States-Canada Impact Assessment, 1983). Total alkalinity, as an expression of sensitivity, is the most generally accepted and applied criterion for water quality evaluations (Omernik and Powers, 1982). Other sensitivity indices have been utilized by researchers employing alkalinity in conjunction with other ions to determine response to acid deposition. A brief summary of the major indices follows.

The calcite saturation index (CSI), proposed by Conroy and others (1974), is the logarithm of the degree of saturation of a water body with respect to calcium carbonate. Waters saturated with calcium carbonate typically show CSI values near zero. Undersaturated waters with CSI values of 4 to 6 are considered sensitive, with minimal capacity to assimilate hydrogen ions. However, in reviewing several different studies, Haines and others (1983) concluded that CSI does not predict sensitivity any better than pH or alkalinity measurements alone. CSI is highly correlated to alkalinity, and may serve as a predictor of sensitivity, although it is more complex, requires more data, and has no clear advantage other than to link pH and calcium to alkalinity.

Zimmerman and Harvey (1980) suggest a triad of parameters to define sensitivity of surface waters: pH $<$ 6.3 to 6.7, conductivity $<$ 30 to 40 microsiemen per centimeter (μS/cm, formerly termed micromho per centimeter) and alkalinity $<$ 300 μeq/L. Altshuller and McBean (1979) propose a similar categorical classification using alkalinity $<$ 200 μeq/L, calcium $<$ 200 μeq/L, and conductivity $<$ 30 μS/cm as critical values. In a study of New England surface waters, Haines and others (1983) noted good agreement between distribution of sensitive waters based on alkalinity and calcium, but poor agreement between these distributions and that based on conductivity. The presence in many waters of elements such as chloride and sodium that may contribute little to buffering capacity but considerably to conductivity may explain this discrepancy. In view of the marginal advantage of these other methods, alkalinity is chosen as the simplest and most reliable sensitivity index for the purposes of this study.

The classification schemes for separating sensitive from nonsensitive basins based on alkalinity concentration tend to vary with the study area and the purpose of the study (Omernik and Powers, 1982). A surface runoff concentration of 200 μeq/L is generally accepted as the upper limit for a basin to be considered sensitive to acid deposition (Hendrey and others, 1980; Linthurst, 1983). This criterion reflects both a physical and a biological component. Titration of a bicarbonate solution with dilute acid produces a curve in which the pH of the solution decreases gradually until about 200 to 150 μeq/L alkalinity. Further acid addition leads to a steeper slope, that is a greater reduction of pH per increment of added acid (fig. 6). Effects of acid deposition on major species of fish and invertebrates during any time of year are usually unnoticeable in stream and lake waters with alkalinity values near or above 200 μeq/L. However, the adverse effects on fish and invertebrates associated with low pH and alkalinity concentrations have been extensively documented (Schofield, 1976; Hendrey and Wright, 1975; Beamish and others, 1975).

Distribution of Alkalinity and pH

A strong association between geology and mean flow-weighted alkalinity concentration for the 56 surveyed streams is apparent in figure 7. Streams associated with the Antietam and Hampton Formations (fig. 2) in the southwestern segment of the Park show the lowest alkalinity concentrations and are considered extremely sensitive to acid deposition. Nine of the 12 streams draining these formations have flow-weighted mean alkalinity concentrations of less than 10 μeq/L; the remaining three have a concentration of 10 to 20 μeq/L. A bedrock trend is also evident in the remainder of the Park; alkalinity concentration is generally low (20 to 100 μeq/L) throughout areas

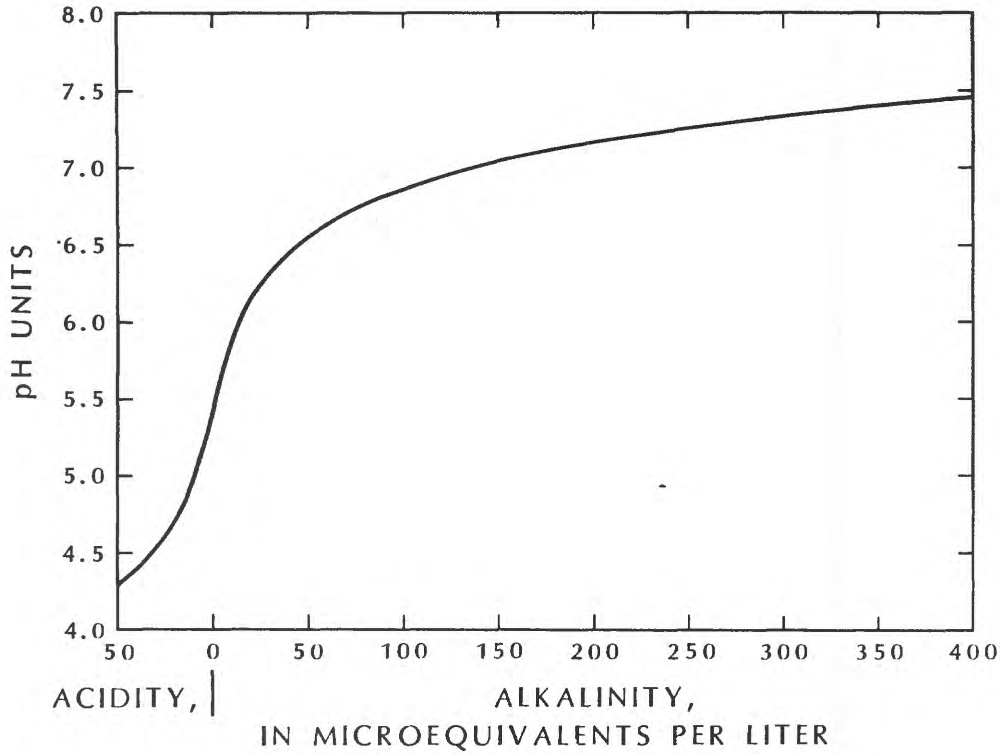

Figure 6.--Titration curve of a bicarbonate solution at 25°C and a CO_2 partial pressure of $10^{-3.0}$ atmospheres.

underlain by Old Rag Granite and Pedlar granodiorite and indicates a high sensitivity. The highest alkalinity concentrations are found in regions underlain by significant quantities of the Catoctin Formation. This is evident as a sinuous trend of alkalinities between 101 and 200 µeq/L from the northeasternmost basins in the Park to the central west region, and to the southeasternmost basins, and generally reflects a geology of pure Catoctin or Pedlar-Catoctin mix (fig. 7). These basins are considered moderately to marginally sensitive to acid deposition.

Although the Park has a low overall alkalinity, the Piedmont Province to the east and the Shenandoah Valley to the west are both considered well buffered against the effects of acid deposition (Omernik and Powers, 1982). The Piedmont Province is dominated by metamorphic rocks and igneous intrusives overlain by thick, well developed soils, and the Shenandoah Valley is underlain by calcareous deposits.

Figure 8 shows the map of volume-weighted values of pH for the surveyed streams. Overall, pH follows the same trend as alkalinity — it is lowest in the southwest in streams draining Antietam and Hampton bedrocks, and highest in streams draining Catoctin and Catoctin-Pedlar mixed bedrocks. Values of pH for streams draining Catoctin Formation are about neutral (6.9 to 7.2) while those associated with Old Rag Granite and Pedlar Formations are slightly below neutral (6.3 to 6.8). The pH of streams draining the Hampton and Antietam Formations are below 6.2, with most below pH 5.7. Surface-water runoff from three basins underlain by pure Antietam bedrock, Lower Lewis Run tributary (01628320), Hangman Run (01628530), and Walls Run (01628750), have a mean pH of 5.0.

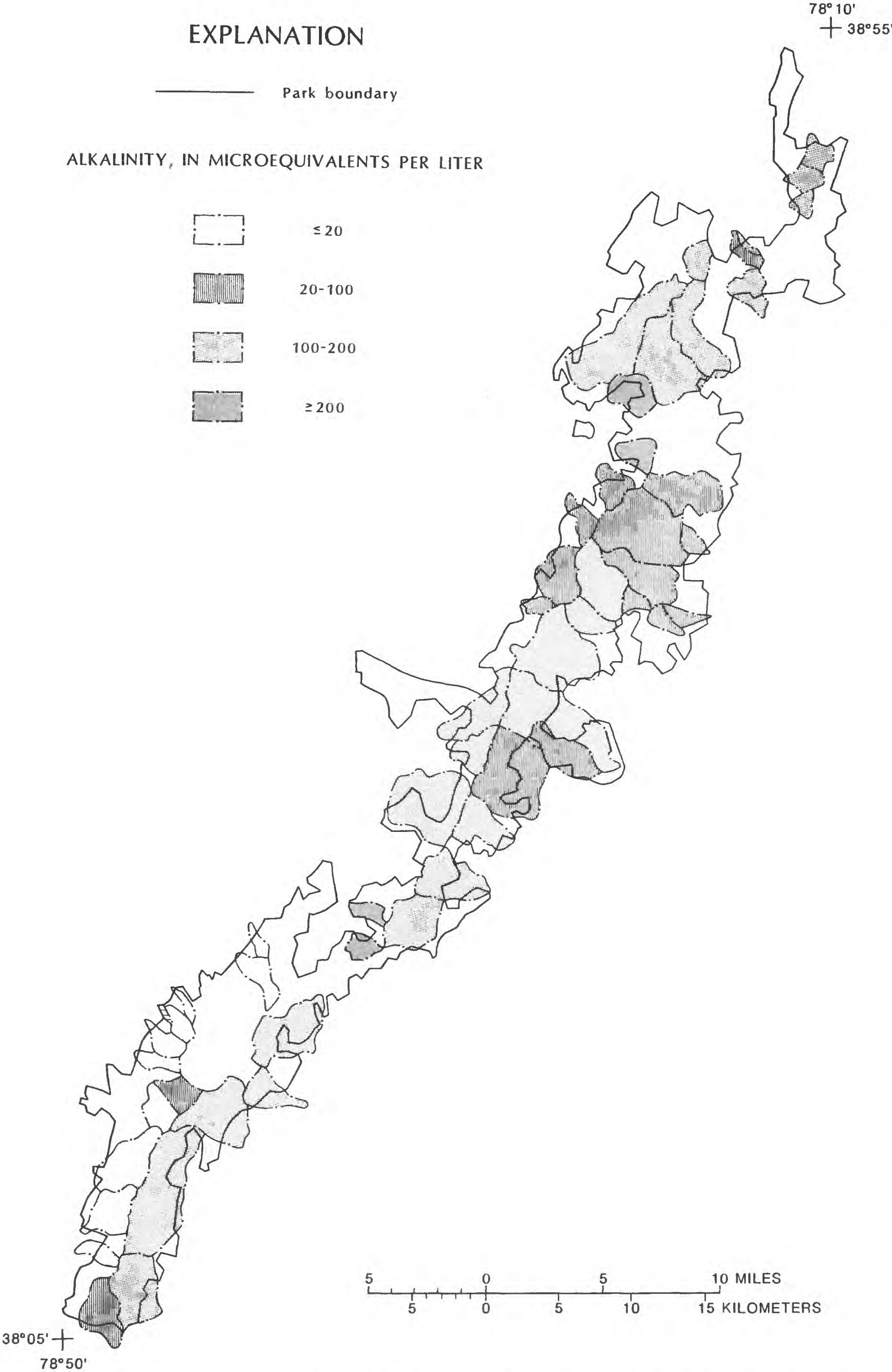

Figure 7.--Flow-weighted alkalinity concentration of stream water, August 1981 through June 1982.

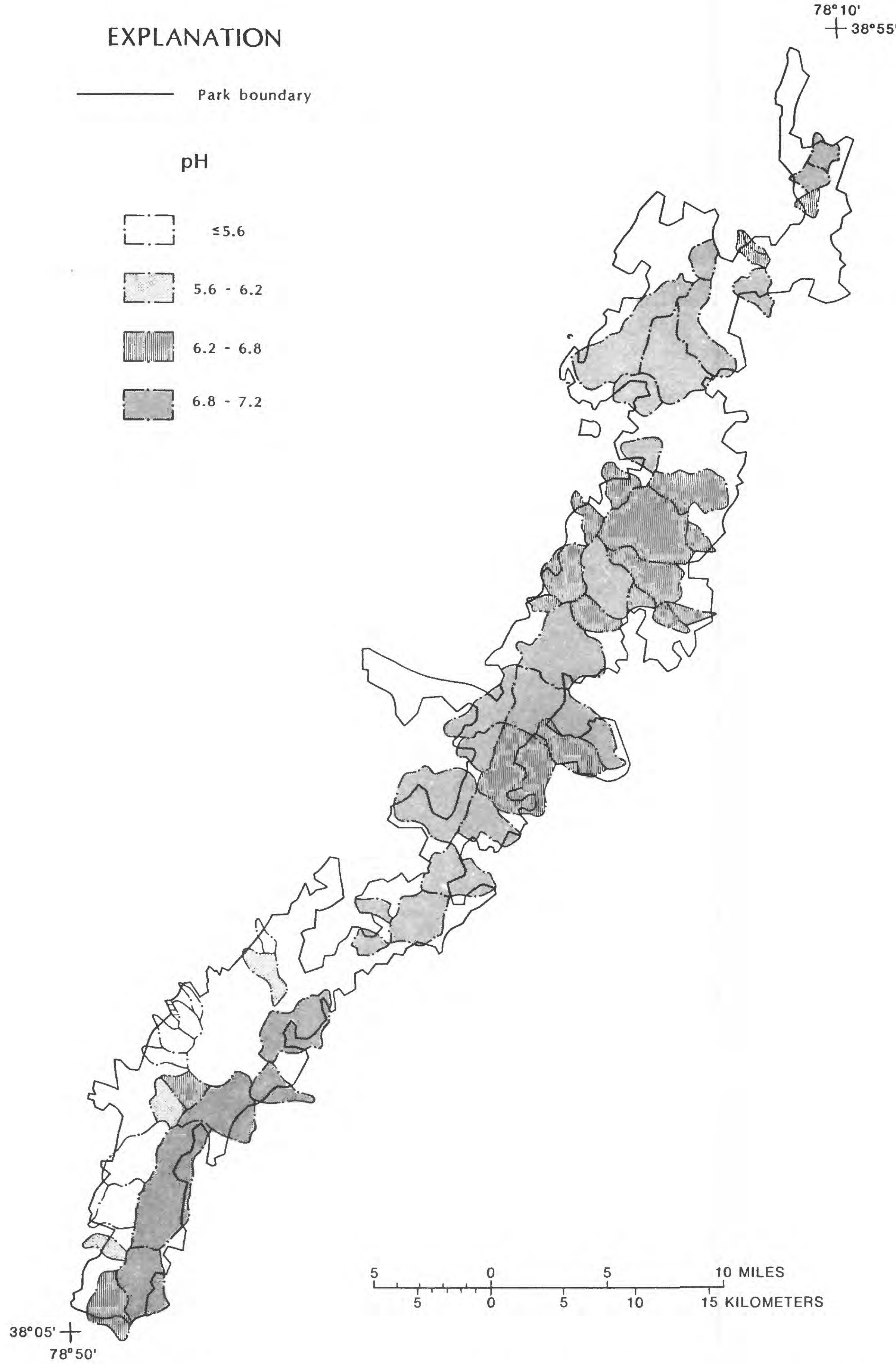

Figure 8.--Flow-weighted pH of stream water, August 1981 through June 1982.

RELATION OF SURFACE-WATER QUALITY TO BASIN CHARACTERISTICS

Statistical Relations

Alkalinity

Sampled Streams

Nine of the 56 surveyed streams are not included in the remaining data analysis. Three of these streams, Swift Run (02032589), West Swift Run (01628910), and Pass Run (01630542), parallel the two highways which pass through gaps in the Park. Sodium and chloride concentrations in these streams range up to ten times higher than in other streams in the Park and undoubtedly reflect the effect of road salting. The other six streams were not included because five or more percent of the contributing drainage area is "developed", as indicated by clearings shown on 7½ minute topographic maps. These streams are: Hawksbill Creek tributary (01628900), South Branch Naked Creek (01629150), Rocky Branch (01630543), Greasy Run (01630670), Rush River (01662480), and Ivy Creek (02032545).

Results of the stepwise multiple regression for the log of flow-weighted alkalinity versus all independent variables (full model) and versus geology alone (reduced model) are shown in table 7. The r^2 (coefficient of determination) value of 0.95 for the reduced model indicates that a very high proportion of the variability in log of alkalinity is accounted for by drainage basin geology. When the other four independent variables (AB2400, EW, AREA and DD) are added to the model, only AB2400 (percent above 2400 feet) and EW (east or west of the Blue Ridge) are significant, in addition to bedrock geology.

These results suggest that bedrock and associated soils largely determine the sensitivity of streams in the Park to acid deposition. Bedrock mineralogy dictates the rates and products of primary mineral weathering as well as the composition and development of the overlying soils, including cation exchange capacity, percent base saturation, and sulfate adsorption capacity. The ability of a basin to generate stream-water alkalinity is closely tied to these soil characteristics. The regression coefficients in the reduced model (table 7) indicate that flow-weighted alkalinity concentrations of surface runoff from bedrock and associated soils decrease in the following order:

Catoctin > Pedlar > Old Rag > Hampton > Antietam

Based on this model the respective alkalinities in runoff from basins underlain by each of these bedrocks is: 175, 85, 79, 15, and -7 µeq/L.

Stream-water alkalinities on the west side of the Park, after geologic effects are factored out with the regression equation, are significantly lower than on the east side. The negative EW regression coefficient in the full alkalinity model (table 7) decreases the predicted concentration of stream water alkalinity on the west side of the Park. This effect may be related to upwind sources of acid deposition being in closer proximity to the Park's western boundary, which results in greater deposition, both wet and dry, on western facing slopes. However, additional studies on air quality in the area would be required to substantiate these findings.

Table 7.--Regression models relating flow-weighted water-quality constituents to basin characteristics. [Concentrations in microequivalents per liter except for silica which is in micromoles per liter.]

Dependent variable[a] (flow weighted)	Basin characteristics: Intercept	Percent Pedlar	Percent Old Rag	Percent Hampton	Percent Antietam	Percent of basin above 2400 feet	E/W[b]	Drainage area (mi^2)	Drainage Density (mi^{-1})	r^2	Mean Square Error (S^2)
Log_e [Alk+25]:											
All Variables	5.5814	-0.00574	-0.00843	-0.01605	-0.02499	-0.00475	-0.1563	(NS)[c]	(NS)	0.962	0.0234
Rock type only	5.3000	-0.00603	-0.00656	-0.01609	-0.02400	----	----	----	----	0.947	0.0310
Log_e [SO_4]:											
All Variables	4.6421	(NS)	-0.00399	(NS)	-0.00574	-0.00749	0.2634	(NS)	(NS)	0.535	0.0580
Rock type only	4.4266	(NS)	-0.00375	(NS)	(NS)	----	----	----	----	0.115	0.1029
Log_e [NO_3+.01]:											
All Variables	3.7085	(NS)	-0.02051	-0.01834	-0.04177	(NS)	(NS)	(NS)	-0.4948	0.695	0.9310
Rock type only	2.8459	(NS)	-0.01950	-0.01957	-0.04411	----	----	----	----	0.662	1.0077
Log_e [Cl]											
All Variables	3.5941	(NS)	-0.00172	-0.00326	-0.00332	-0.00394	(NS)	(NS)	(NS)	0.600	0.0101
Rock type only	3.3883	(NS)	(NS)	-0.00243	-0.00145	----	----	----	----	0.344	0.0158
Log_e [Ca]:											
All Variables	4.5744	-0.00371	-0.00866	-0.01629	-0.02044	(NS)	(NS)	(NS)	0.1760	0.898	0.0547
Rock type only	4.8260	-0.00267	-0.00849	-0.01520	-0.01909	----	----	----	----	0.876	0.0651
Log_e [Mg]:											
All Variables	5.1919	-0.00812	-0.01435	-0.01173	-0.01374	-0.00937	(NS)	(NS)	(NS)	0.855	0.0298
Rock type only	4.6931	-0.00742	-0.01149	-0.00964	-0.00922	----	----	----	----	0.687	0.0628
Log_e [Na]:											
All Variables	4.6246	(NS)	-0.00170	-0.01188	-0.01495	-0.00734	(NS)	(NS)	(NS)	0.944	0.0162
Rock type only	4.2678	(NS)	(NS)	-0.01064	-0.01173	----	----	----	----	0.871	0.0355
Log_e [K]:											
All Variables	2.4098	(NS)	0.00326	0.01639	(NS)	-0.00919	0.1760	(NS)	(NS)	0.910	0.0434
Rock type only	2.0197	(NS)	0.00499	0.01873	0.00620	----	----	----	----	0.828	0.0809
Log_e [Ca+Mg+Na+K]:											
All Variables	6.0511	-0.00299	-0.00750	-0.00937	-0.01421	-0.00664	(NS)	(NS)	(NS)	0.867	0.0226
Rock type only	5.6977	-0.00249	-0.00548	-0.00788	-0.01101	----	----	----	----	0.765	0.0389
Log_e [Si]:											
All Variables	5.4304	(NS)	-0.00220	-0.00809	-0.01138	-0.00629	-0.885	(NS)	(NS)	0.924	0.0126
Rock type only	5.0817	(NS)	(NS)	-0.00735	-0.00912	----	----	----	----	0.840	0.0247

The alkalinity regression equation in table 7 also suggests that altitude of land surface (AB2400) significantly affects runoff concentrations. After factoring out the geologic effect, it appears that basins with a larger proportion of their area above 2,400 feet have lower runoff alkalinities, as evidenced by a negative AB2400 regression coefficient. This suggests that an altitudinal gradient of alkalinity should be discernable in streams. To investigate this relationship, altitudinal transects were made along the Staunton River (100 percent Pedlar granodiorite) and Brokenback Run (90 percent Old Rag Granite) during base flow conditions. These streams were considered suitable for the study because their basins are strongly dominated by single bedrock types (therefore, geologic composition is relatively constant upslope) and both have altitudinal gradients and soil development typical of other streams in the Park.

Alkalinity gradients were apparent in both streams increasing from 78 μeq/L (at 2,440 feet elevation) to 89 μeq/L (at 1,000 feet) in the Staunton River (fig. 9a), and from 118 μeq/L (at 1,980 feet) to 140 μeq/L (at 1,010 feet) in Brokenback Run. Altitudinal differences in soil type and development may partially explain these observed gradients. At higher altitudes in the Staunton River basin, well developed soils are less common (fig. 9b) and, because of steeper slopes (fig. 9c), areas dominated by outcrops and very thin overburden are more prevalent (Elder and Pettry, 1975). In contrast, a larger percentage of the drainage basin is covered by relatively thick, dark-brown stony loams of the Porters and Tusquitee Series at lower altitudes. Slower runoff and more soil/water contact in these areas favor alkalinity-producing reactions, contributing to the alkalinity gradient. A similar relation between soil structure and altitude is observed in the Brokenback Run basin.

Low temperatures, typically associated with higher altitudes may also contribute to the observed alkalinity gradients. The intensity of carbonic acid weathering, and thus the rate of alkalinity production, may be significantly less at higher altitudes because respiration within soil is less at cooler temperatures resulting in lower soil CO_2 concentrations. The concentration of carbonic acid available for weathering, which is derived from hydration of CO_2, is proportional to the concentration of dissolved CO_2 (Stumm and Morgan, 1970). Consequently, stream water alkalinity may increase downstream as the mean soil partial pressure of CO_2 of the contributing drainage basin increases.

Greater amounts of precipitation at higher altitudes, and consequently greater deposition of associated acids, may also contribute to the observed alkalinity gradient. This could occur by dilution or neutralization of alkalinity in runoff. A determination of which processes mentioned above most strongly influence the alkalinity gradients cannot be made with the available data.

Chemical gradients associated with stream altitude have been observed elsewhere. Johnson and others (1981) completed a detailed study of the geochemical changes that occur in a dilute acid headwater stream as it moves downstream in a forested basin. Significant increases in base cations and silica and a significant decrease in hydrogen ion concentrations occurred at progressive downstream stations. Silsbee and Larson (1982) observed a significant negative correlation between mean basin altitude and stream-water alkalinity in basins underlain by a uniform geology in Great Smoky Mountains National Park, Tennessee. Shorter water/soil contact time in basins at higher altitudes is hypothesized as the primary cause of the observed gradients.

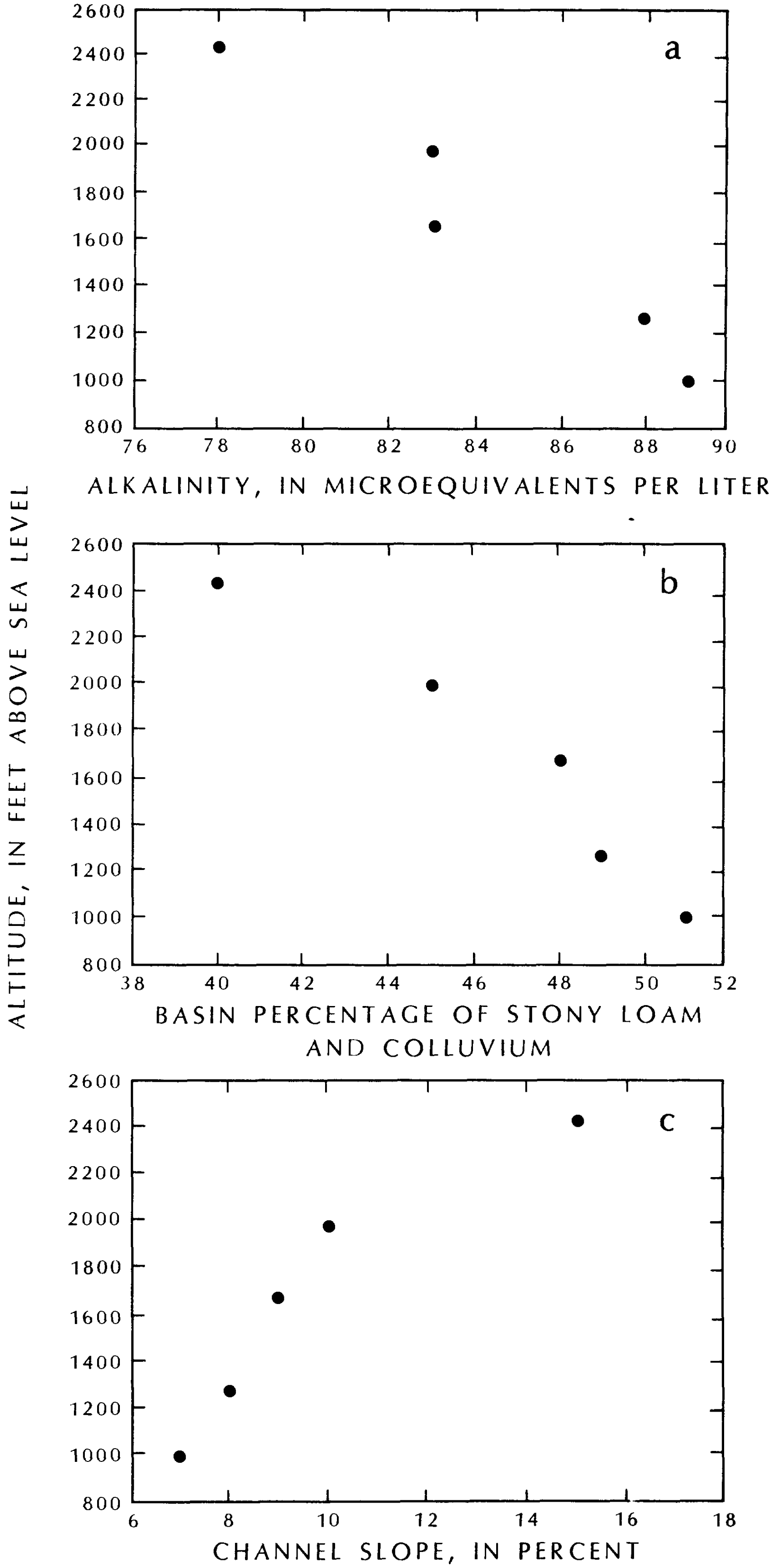

Figure 9.--Relation between altitude and (a) alkalinity concentration, (b) basin percentage of stony loam and colluvium, and (c) channel slope, for Staunton River.

Prediction in Unsampled Streams

The flow-weighted alkalinity model (rock type only, see table 7) developed for the Park can also be used as a tool for predicting alkalinity (sensitivity) of unsampled streams within the Park or streams draining these same formations outside the Park. The Antietam and Hampton Formations (or their lithologic equivalents) extend from southern Pennsylvania through Maryland and Virginia along the Blue Ridge mountains and into the Great Smoky Mountains of eastern Tennessee. The Pedlar Formation extends discontinuously from northern Virginia south to about 37° north latitude, and the Catoctin Formation is mapped from Pennsylvania south to about 38° north latitude, just south of Shenandoah National Park. Old Rag Granite is primarily associated with Old Rag Mountain and does not extend appreciably outside the Park (T. M. Gathright, Virginia Division of Mineral Resources, oral commun., 1984). It should be noted, however, that these formations and their associated soils may show considerable variation in composition from place to place which could affect the applicability of the model. For example, the Antietam Formation changes in composition from quartzite with a siliceous cement in the northern Virginia Blue Ridge to quartzite with a calcareous cement in the Blue Ridge of southern Virginia (Schwab, 1970). Local variations such as this could make the difference between runoff with significant mineral acidity and runoff with appreciable acid-neutralizing capacity.

The applicability of the regression model for predicting the alkalinity of unsampled streams in the Park was tested with a model developed using data from 31 streams from the original network to predict the alkalinity concentrations in the remaining 16 streams. Selection of 31 streams for the model entailed grouping streams according to drainage basin rock type and then randomly selecting about two-thirds of the streams from each group. This process ensured representation of each rock type in the model without biasing the results.

The model developed from the subset of stream data is very similar to the model developed using all 47 streams. As expected, the intercept and regression coefficients vary slightly and the r^2 for the model using only 31 streams is smaller. This model, however, accurately predicts the observed flow-weighted alkalinities for the 16 test streams over a wide concentration range from -10 to 170 μeq/L (fig. 10). The mean difference between observed and predicted alkalinity is 8 μeq/L, or about 9 percent. Thus, the bedrock model developed using data from all 47 streams (table 7) is very robust and capable of accurately predicting stream water flow-weighted alkalinity in the Park. Caution should be exercised, however, in applying this model to streams which have significant drainage basin disturbances or point source inputs of wastewater from developed areas in the Park.

To test the applicability of the flow-weighted alkalinity model (bedrock only) to areas outside the Park, alkalinity data from 13 streams with drainage basins underlain by similar geology are compared to concentrations predicted by the model given in table 7. Alkalinity was measured in 11 streams draining Hampton, Catoctin, Antietam, and Pedlar Formations in the Blue Ridge mountains 10 to 30 miles south of the Park. Additional data were obtained from Hunting Creek near Foxville, Maryland (01640970), which drains the Catoctin Formation of the Catoctin Mountains (Katz, 1984, unpublished data), and South Fork

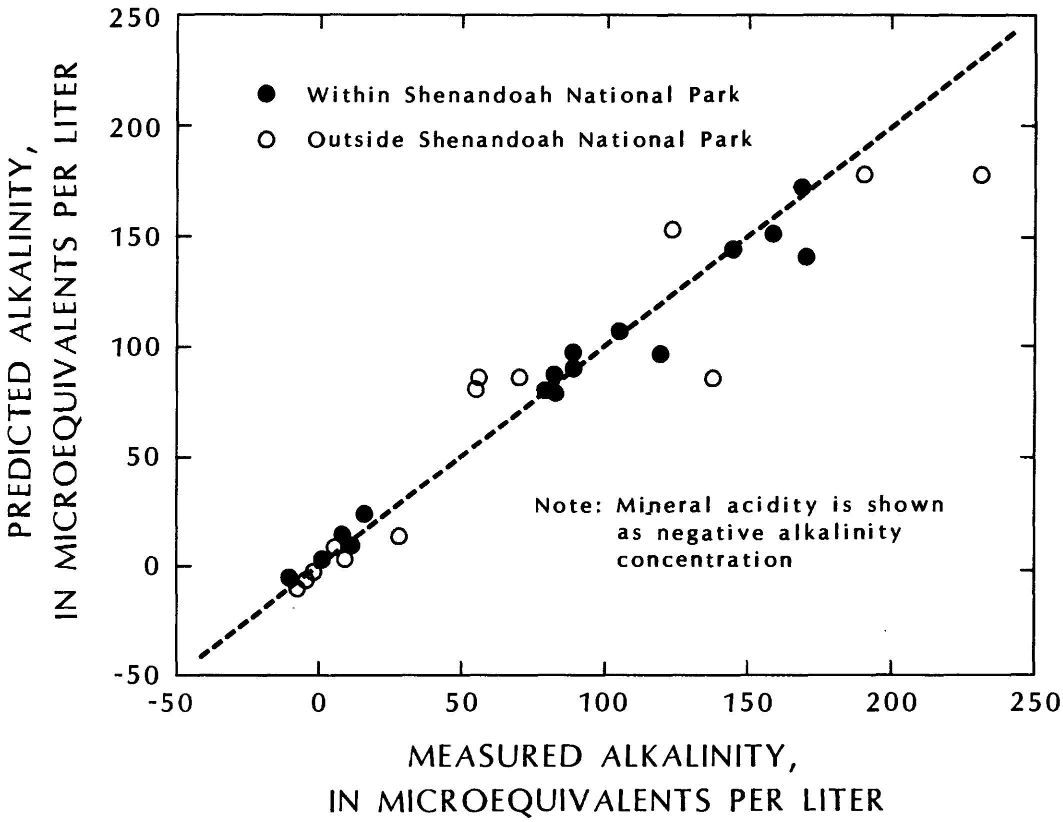

Figure 10.--Relation of predicted to measured flow-weighted alkalinity of 16 test streams in Shenandoah National Park and 13 streams outside the Park.

Brokenback Run near Nethers, Va (01662156), which drains Old Rag Granite (Bricker, 1984, unpublished data). This latter site is actually within the Park but is included here because this formation rarely exists outside the Park.

The model results of predicting alkalinity of similar streams outside the Park are presented in table 8 and plotted in figure 10. Although runoff alkalinity concentration is not perfectly predicted by the model, it is well categorized by this approach. Extremely sensitive streams draining the Hampton and Antietam Formations are segregated from highly sensitive streams draining the Old Rag Granite and Pedlar Formations, which are segregated from moderately to marginally sensitive streams draining the Catoctin Formation. Predicted values are generally within 30 µeq/L of measured values. If the observed alkalinities in table 7 better represented mean flow-weighted alkalinities, a closer comparison might be obtained. One measurement or a few measurements do not necessarily provide a good estimate of the flow-weighted mean concentration. However, it is apparent that models of this type are extremely useful for identifying potentially sensitive streams in a region and estimating their alkalinity class from detailed bedrock maps.

Table 8.—Results of regression model (bedrock only) for predicting mean flow-weighted alkalinity of stream water from basins outside Shenandoah National Park with similar rock types.

Station number	Station name	Latitude	Longitude	Area (mi^2)	Drainage basin geology: % Catoctin	% Pedlar	% Old Rag	% Hampton	% Antietam	Observed alkalinity (μeq/L)	Predicted alkalinity (μeq/l)
[a]01625830	Stoney Run near Stuarts Draft, Va	385858	0790428	1.01	0	0	0	52	48	9	3
[a]01625840	Johns Run near Stuarts Draft, Va	385847	0790205	1.25	0	0	0	29	71	-2	-2
[a]01625860	Kennedy Creek near Sherando, Va	385818	0790035	2.92	0	0	0	3	97	-4	-6
[b]01640970	Hunting Creek trib near Foxville, Md	393742	0772744	4.01	100	0	0	0	0	231	178
[c]01662156	S.F. Brokenback Run near Nethers, Va	383400	0781902	0.98	0	0	100	0	0	55	81
[d]02023100	Chimney Branch near Vesuvius, Va	375607	0790441	0.78	0	0	0	79	21	5	9
[d]02023150	Saint Marys River trib in Cellar Hollow near Vesuvius, Va	375548	0790845	0.84	0	0	0	0	100	-5	-6
[d]02023400	South River trib in Taylor Hollow near Marlbrook, Va	375136	0791335	1.30	0	0	0	83	13	28	14
[e]02026400	S.F. Tye River at Nash, Va	375724	0790247	14.2	0	100	0	0	0	138	86
[d]02027100	Greasy Spring Branch near Alhambra, Va	374715	0790915	1.04	0	100	0	0	0	56	86
[d]02027200	Shoe Creek at Alhambra, Va	374723	0790612	4.88	0	100	0	0	0	70	86
[d]02028460	Mill Creek near Avon, Va	375838	0785208	1.89	95	0	0	0	0	190	178
[d]02028465	Meriwether Creek near Greenfield, Va	375723	0785207	0.99	76	22	0	0	0	123	153

[a]Mean of two samples collected in November 1982 and February 1984.
[b]Observed alkalinity represents flow-weighted mean of samples collected at times of the last four synoptic surveys (Katz, B.G., U.S. Geological Survey, Water Resources Division, Towson, Maryland, oral commun., 1984).
[c]Stream within Shenandoah National Park but not part of sampling network. Observed alkalinity is flow-weighted mean of 6 samples from January to June 1983 (Bricker, O.P., U.S. Geological Survey, Water Resources Division, Reston, Virginia, oral commun., 1984).
[d]Sampled between February and April 1984 (Webb, R., University of Virginia, Department of Environmental Sciences, written commun., 1984).
[e]Sampled in November 1982.

Several other studies that have attempted to use basin characteristics as predictors of alkalinity have met with varying success, depending upon the level of "noise" associated with variables which affect alkalinity but are not included in the model. Turk and Adams (1983), working in Colorado, used multiple regression analysis to predict alkalinity from a variety of basin characteristics. Only altitude was found to be a significant predictor of alkalinity for the model. Basins in their study, however, were far more uniform geologically than those found in Shenandoah National Park, which may explain why geology was not a significant predictor of alkalinity.

Other Chemical Constituents

Results of regression analysis for silica and major anions and cations are presented in table 7 for both the reduced model (bedrock independent variables only) and the full model (all independent variables). The r^2 value for the bedrock-only model indicates the strength of association between concentration of a constituent and drainage basin rock type; the degree of improvement in r^2 between the reduced and full models indicate the importance of the non-bedrock explanatory variables in the regression equation.

Constituents most strongly associated with drainage basin rock type include: calcium, magnesium, sodium, potassium, sum of base cations, silica, nitrate, and as discussed previously, alkalinity. In contrast, sulfate and (less strongly) chloride are associated with the non-bedrock independent variables (table 7). For example, inclusion of only bedrock type in the sulfate regression analysis results in an r^2 of 0.12. By adding the non-bedrock independent variables to the analysis--namely, east/west basin location (EW) and altitude (AB2400)--the r^2 value increases to 0.54 which suggests the importance of these basin characteristics. East/west basin location alone explains 30 percent of the variability in sulfate concentration in runoff; higher concentrations are observed in western draining streams. And, as hypothesized for alkalinity, this may also reflect a greater amount of wet and dry deposition on western facing slopes because the major upwind sources of anthropogenic sulfur come from west of the Park.

Variability in runoff concentrations of chloride from undeveloped basins is quite small (table 5) suggesting a fairly even distribution source such as atmospheric deposition of entrained sea salt. However, 34 percent of the observed variability is ascribable to bedrock type (table 7). Higher concentrations associated with streams draining the Catoctin and Pedlar Formations and the Old Rag Granite suggest they may be minor sources of chloride ions.

The reduced and full regression models for logarithm of sum of base cations (Cb) are 0.77 and 0.87, respectively, indicating a strong association between bedrock type (including the overlying soils) and base cation concentrations. The relatively small r^2 increase between the two models indicates a weaker association between non-bedrock independent variables and base cation concentrations. However, this difference between the reduced and full log Cb models is significant and due entirely to the AB2400 independent variable (table 7). As shown for alkalinity, this association may be attributed to lower carbonic acid weathering rates (thus lower Cb concentrations) at higher altitudes due to thinner soils, lower temperatures, and/or shorter hydraulic retention times (Johnson and others, 1981).

Both the full and reduced models indicate that basins underlain by the Catoctin Formation have the highest runoff Cb concentrations in the Park. Cb follows a trend similar to alkalinity with concentrations in runoff associated with bedrock type decreasing in the following order:

Catoctin > Pedlar > Old Rag > Hampton > Antietam

Based on the bedrock-only model the respective Cb concentration of runoff from each of these formations are 304, 237, 176, 138, and 101 microequivalents per liter.

Table 7 shows the results of the full and reduced multiple regressions for the four major base cations and silica. Concentrations of these constituents in Park streams are primarily explained by the underlying bedrock; however, altitude (AB2400) explains additional variation in all but the calcium model. While calcium and magnesium appear to be represented (like alkalinity) in a more or less uniformly declining concentration from Catoctin to Pedlar to Old Rag to Hampton to Antietam, potassium is distinctly divided into a high group (Hampton) and a low group (Catoctin, Pedlar, Old Rag and Antietam). Sodium concentrations in Park streams are lowest for basins dominated by the Hampton and Antietam Formations and higher for basins underlain by Old Rag Granite, Pedlar and Catoctin Formations. The variation of these constituents and the variation of alkalinity are discussed in terms of bedrock mineralogy in the following section.

Relations Between Geology and Surface Runoff

Analysis of the synoptic survey data by multiple linear regression indicates that stream-water alkalinity, base cation, and silica concentrations vary in a predictable way depending on the underlying bedrock. Bedrock mineralogy affects the rate and end products of primary mineral weathering which in turn affects the composition of the overlying soil, including saturation and relative mix of base cations on exchange sites and the concentration of soil primary and secondary minerals. Soil and bedrock both influence the capacity of a basin to resist acidification by acid deposition (Johnson and others, 1981) and for this reason possible pathways of weathering are examined to gain insight into observed differences in the chemistry of surface runoff from each formation. Because soils are not well characterized in the Park, emphasis is placed on bedrock minerals, but it should be remembered that the associated soils are extremely important in controlling stream-water chemistry.

The predominant rock formations in Shenandoah National Park are the metabasaltic Catoctin Formation, the granitic Pedlar Formation and Old Rag Granite and the metamorphosed sediments of the Hampton and Antietam Formations. Each of these rock types, and their associated soils, are characterized by a particular set of minerals that control the chemical composition of water in contact with them through various weathering reactions (table 9). Among the most important weathering reactions are the incongruent dissolution of aluminum-silicates in which a primary mineral is transformed into a secondary mineral. Essentially, the exchange of hydrogen ion for cations results in a partial breakdown of the primary mineral, releasing silicic acid and cations. In these reactions, the dissolved phase increases in alkalinity whereas the

Table 9.--Mineralogy and carbonic-acid weathering products for major rock formations in Shenandoah National Park.

Formation	Mineralogy: Major Minor	Weathering Products
CATOCTIN (From Dekay, 1972; Reed, 1969; Gathright and others, 1977)	Albite	Na, SiO_2, HCO_3
	Chlorite	Mg, SiO_2, HCO_3
	Epidote	Ca, SiO_2, HCO_3
	Plagioclase	Ca, Na, SiO_2, HCO_3
	Calcite	Ca, HCO_3
	Pyroxenes	Ca, Mg, SiO_2, HCO_3
	Actinolite	Ca, Mg, SiO_2, HCO_3
	Sphene	Ca, SiO_2, HCO_3
PEDLAR (From Dekay, 1972; Gathright, 1976; Gathright and others, 1977)	Plagioclase	Ca, Na, SiO_2, HCO_3
	Microperthite	Na, K, SiO_2, HCO_3
	Quartz	SiO_2
	Calcite	Ca, HCO_3
	Biotite	Mg, K, SiO_2, HCO_3
	Chlorite	Mg, SiO_2, HCO_3
	Epidote	Ca, SiO_2, HCO_3
	Pyroxenes	Ca, Mg, SiO_2, HCO_3
	Amphibole	Ca, Mg, SiO_2, HCO_3
OLD RAG GRANITE (From Gathright, 1976; Furcron, 1934)	Albite	Na, SiO_2, HCO_3
	K-Feldspars	K, SiO_2, HCO_3
	Microperthite	Na, K, SiO_2, HCO_3
	Quartz	SiO_2
	Biotite	Mg, K, SiO_2, HCO_3
	Chlorite	Mg, SiO_2, HCO_3
	Epidote	Ca, SiO_2, HCO_3
	Sphene	Ca, SiO_2, HCO_3
HAMPTON (From Schwab, 1971; Gathright and others, 1977)	Sericite	K, SiO_2, HCO_3
	K-Feldspars	K, SiO_2, HCO_3
	Quartz	SiO_2
	Chlorite	Mg, SiO_2, HCO_3
	Plagioclase	Ca, Na, SiO_2, HCO_3
	Biotite	Mg, K, SiO_2, HCO_3
ANTIETAM (From Schwab, 1970; Gathright and others, 1977)	K-Feldspars	K, SiO_2, HCO_3
	Quartz	SiO_2
	Plagioclase	Ca, Na, SiO_2, HCO_3
	Sericite	K, SiO_2 HCO_3
	Chlorite	Mg, SiO_2, HCO_3

solid residue increases in acidity. Carbonic acid is the usual proton donor in the hydrolysis of primary silicates, thus bicarbonate is the predominant anion in fresh waters. This can be represented as follows (Stumm and Morgan, 1970):

$$\text{Cation-Al-Silicate(s)} + H_2CO_3 + H_2O \rightarrow HCO_3^- + H_4SiO_4 + \text{cation} + \text{H-Al-Silicate(s)}$$

Some of the common minerals in the Park which may undergo incongruent dissolution include: chlorite, epidote, plagioclase, biotite, sericite, albite, K-feldspars, and microperthite.

Congruent dissolution may also be an important weathering reaction in the Park. Although found only in small quantities in the Catoctin and Pedlar Formations, highly reactive calcite deposits may significantly increase calcium and alkalinity concentrations in runoff through the following reaction:

$$CaCO_3(s) + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$

Congruent dissolution of quartz, along with incongruent dissolution of aluminum-silicates, contribute to the dissolved silica in runoff.

Weathering via oxidation/reduction reactions are throught to be relatively insignificant in the Park. Oxidation of pyrite traces in the Catoctin Formation (Dekay, 1972) may contribute a limited quantity of hydrogen ion and sulfate to runoff from this formation.

Adsorption/desorption reactions are very important in the soil and saprolite of the Park and may largely control the chemistry of surface runoff (Galloway and others, 1982a). About 65 percent of the atmospherically-derived sulfate deposited on two small basins (White Oak Run 01628060 and Deep Run 01628150) within the Hampton Formation of the Park is retained in the overlying soils (Shaffer, 1982a). Adsorption onto oxyhydroxide coatings is thought to be the controlling mechanism. Sulfate adsorption produces a negatively charged surface which adsorbs available cations from solution, thus preserving electroneutrality. Hydrogen ion in acid deposition is probably the primary adsorbed cation, which partially explains its net accumulation in drainage basins (Shaffer, 1982a) and its low concentration in stream water relative to precipitation.

Cation-exchange reactions in soil solution also may strongly influence stream-water chemistry. Cation exchange with hydrogen ions associated with carbonic acid leads to a loss of base cations in soil (divalent or monovalent) and a stoichiometric production of alkalinity:

$$M{+}X + H_2CO_3 \rightarrow H{+}X + M^+ + HCO_3^-$$

where X = a cation exchange surface, and
M^+ = a base cation

Hydrogen ions associated with strong acids in atmospheric deposition, such as sulfuric acid, may also exchange for base cations in soil:

$$M^+X + \tfrac{1}{2}H_2SO_4 \rightarrow H{+}X + M^+ + \tfrac{1}{2}\,SO_4^{2-}$$

However, this reaction removes soil base cations without a production of alkalinity. The extent to which any of these processes occur depends upon composition of the soil and atmospheric input and the partial pressure of carbon dioxide in soil.

In order to hypothesize which minerals most strongly influence the chemistry of surface runoff from each formation, it is necessary to factor out atmospheric contributions of base cations in stream water in order to characterize terrestrial contributions. It is estimated that conservative ions from atmospheric deposition (table 1) are concentrated in a drainage basin by a factor of 2.7 due to evapotranspiration. This is calculated for White Oak Run (01628060) for the period July 1981 to June 1982, which corresponds to the time of sampling. During this time 40.7 inches of precipitation fell on the White Oak Run drainage basin (P. W. Shaffer, University of Virginia, Department of Environmental Sciences, oral commun., 1984) and 15.1 inches left the basin as surface runoff (U.S. Geological Survey, 1981, 1982), resulting in a rainfall to runoff ratio of 2.7. It is assumed there is no appreciable change in ground-water storage. Multiplying the concentration of an ion in bulk atmospheric deposition by this ratio provides an estimate of its contribution in runoff, assuming it is conservative. Thus, an ion concentration in excess of this value indicates a net terrestrial source, such as weathering, and a concentration less than or equal to this value suggests no major source or even a net sink. This factor works reasonably well for chloride, which is considered a conservative anion with no major geologic source (Christophersen and others, 1982; Henriksen, 1980). Concentrations in runoff from undisturbed basins average about 20 to 30 μeq/L which is similar to the 18 μeq/L expected from the concentration of atmospheric inputs by evapotranspiration (table 1).

The ion composition of surface runoff from each of the major geologic formations in the Park (figs. 11 and 12) are discussed separately in the following sections in terms of mineralogy and atmospheric contributions. Only basins dominated by single rock types are included in these figures.

Catoctin Formation

The Catoctin Formation is comprised primarily of chlorite, epidote, and plagioclase (albite) with minor contributions of calcite, pyroxenes, and amphiboles (Dekay, 1972; Reed, 1969; Gathright and others, 1977) (table 9). Enrichment of calcium and magnesium in surface runoff from this formation (fig. 11) appears to be related to large deposits of chlorite and epidote which preferentially release these cations upon weathering. However, minor quantities of calcite and other highly reactive minerals may also release significant quantities of these cations through weathering. For example, actinolite, a highly reactive amphibole found in the Catoctin Formation, readily yields calcium, magnesium, silicic acid, and alkalinity upon weathering. The presence of these minerals explain the relatively high Cb and alkalinity concentrations of surface runoff from this formation (and associated soils) and the moderate to marginal sensitivity to acid deposition.

The rare occurrence of potassium bearing minerals in this formation accounts for its low concentration in surface runoff. Atmospheric inputs appear to be the primary source of potassium.

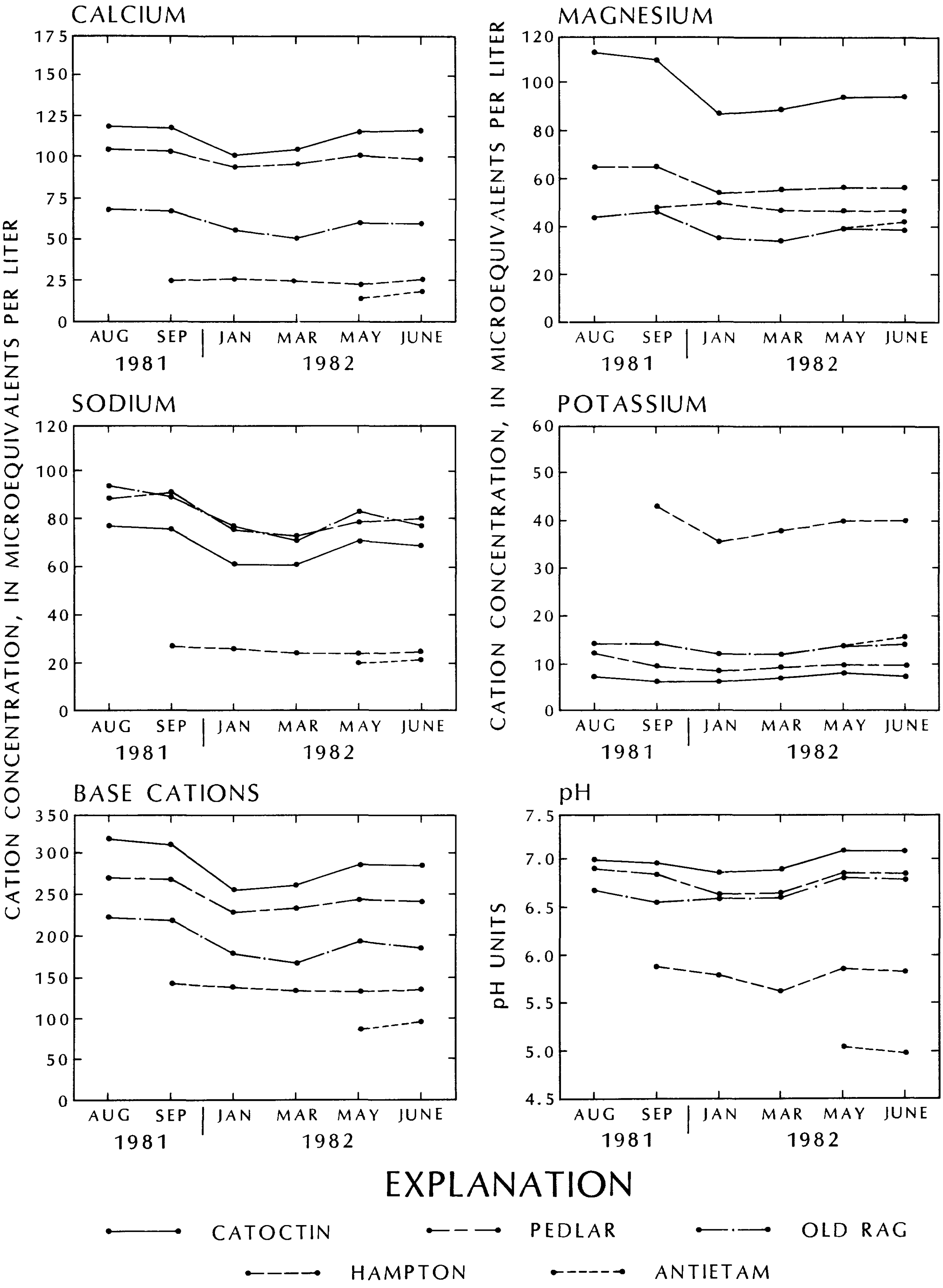

Figure 11.--Mean pH and cation concentration of stream water from major rock formations during synoptic surveys.

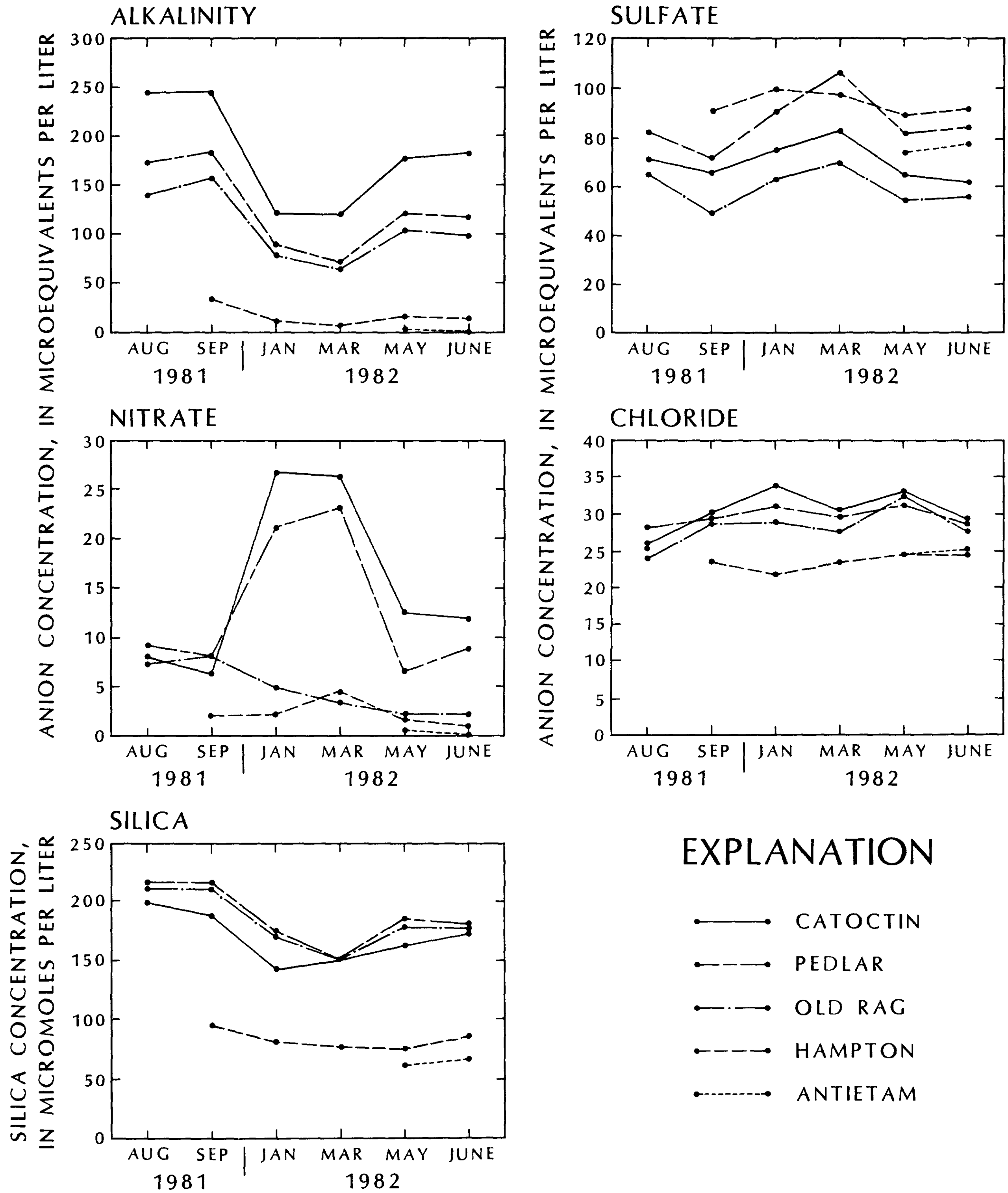

Figure 12.--Mean silica and anion concentration of stream water from major rock formations during synoptic surveys.

Pedlar Formation

The Pedlar Formation is made up of quartz, plagioclase, and microperthite with minor amounts of calcite and dark minerals (table 9). The lack of major chlorite deposits in this formation, as compared to the Catoctin Formation, may account for the lower concentrations of both magnesium and alkalinity in surface runoff and thus the greater sensitivity to acid deposition. Calcium leaching is nearly as high as in the Catoctin Formation, apparently being released from plagioclase and minor amounts of epidote, pyroxenes, amphiboles, and calcite.

The relatively high sodium concentration in runoff from the Pedlar Formation (fig. 11), typical of granites and granodiorites, suggests the importance of plagioclase weathering. Low potassium concentrations in surface runoff imply limited weathering of microperthite, a microcline mineral with albite intergrowths.

Old Rag Granite

Old Rag Granite consists of quartz with K-feldspars, microperthite, and albite (table 9). Just as important, this granite is nearly devoid of the more highly reactive dark minerals and calcite (Gathright, 1976) which accounts for lower concentrations of magnesium and calcium in runoff as compared to the Pedlar and Catoctin Formations (fig. 11). This reduced availability of base cations for carbonic acid weathering of bedrock and the overlying soil also accounts for the greater sensitivity (lower stream-water alkalinity concentration) of this formation to acid deposition.

Calcium and magnesium comprise over half the surface runoff concentration of base cations from Old Rag Granite, and exceed the concentrations expected from atmospheric inputs. However, no major minerals in this formation are a source for these cations, which suggests the importance of trace quantities of highly weatherable minerals such as sphene, biotite, epidote, and chlorite.

As is typical of granites, sodium (the major cation) is enriched compared to calcium and magnesium (fig. 11), probably being released from albite and microperthite. Weathering of these minerals, along with traces of dark minerals, undoubtedly contribute the majority of runoff base cations and alkalinity.

Hampton Formation

The Hampton Formation is a sericitic metasandstone and metasiltstone with interbedded quartz-chlorite-sericite phyllite (Gathright and others, 1977). Considerable weathering of the sediments and subsequent removal of reactive minerals prior to lithification account for the overall low concentration of base cations and alkalinity in surface runoff from this formation (figs. 11 and 12) and the extreme sensitivity to acid deposition. However, the metasandstone and metasiltstone strata contain considerable amounts of sericite, and the phyllite layers are composed of sericite, chlorite, and biotite (Gathright and others, 1977) which yield potassium and magnesium along with silica and alkalinity upon weathering (table 9). These minerals undoubtedly contribute to the high concentration of potassium in runoff, highest of all the formations, and the relatively high concentration of magnesium. In contrast, low concentrations of calcium and sodium in surface runoff reflect the lack of major mineral sources for these cations. Atmospheric contributions account for most of the calcium and about half the sodium in surface runoff.

Antietam Formation

The Antietam Formation in the Park is composed of several resistant quartzite ledges separated by thin strata of less resistant metasandstone or interbedded phyllite. The quartz ledges are metamorphosed quartz sandstone which vary from bluish-gray to nearly white. The interbedded phyllite is a quartz-chlorite-sericite phyllite similar to that found in the Hampton Formation. It should be noted, however, that the phyllite interlayers are much sparser and thinner than in the Hampton Formation which at least partially accounts for the lower surface runoff concentrations of potassium and magnesium (weathering products of sericite and chlorite) (fig. 11). The absence of sericite in the metasediments of the Antietam Formation and its presence in the Hampton Formation may also be partially responsible for the lower runoff concentrations of potassium. However, the surface runoff concentrations of both potassium and magnesium are greater than would be expected from atmospheric inputs, which suggests a significant mineralogical source of these cations. As in the Hampton Formation, calcium- and sodium-bearing minerals are rare in the Antietam Formation (table 9), and thus surface runoff concentrations largely reflect atmospheric inputs.

Overall, the concentration of base cations in surface runoff from this formation is very low, averaging about 100 µeq/L. This is the lowest in the Park and undoubtedly reflects the resistant mineralogy and low base-cation saturation of the overlying soils. The extreme scarcity of weatherable base cations, which are needed for alkalinity formation, accounts for the extreme sensitivity of this Formation to acid deposition.

RELATION OF SURFACE-WATER QUALITY TO SEASONS AND STREAM DISCHARGE

Chemical quality of surface runoff in the Park is largely controlled by drainage basin rocks and soils, that is basins with similar characteristics produce similar type waters. However, stream-water quality within a basin, or between basins with similar characteristics, may also vary with season and stream flow. Generally, alkalinity and base cation concentrations in stream water are higher in the warmer months due to the increased partial pressure of carbon dioxide in soils in response to greater microbial decomposition and root respiration. In addition, alkalinity and base cation concentrations tend to be higher at low flows because of longer residence time in a basin and more extensive soil/water contact (Hall, 1970). Overall, alkalinity concentration is generally highest during summer base-flow periods and lowest at higher flows and during early snowmelt when acid concentrated runoff traverses frozen soils (Scheider and others, 1978; Jeffries and others, 1979). Measurements during different seasons and hydrologic conditions are thus needed to estimate the range and variability of alkalinity concentration.

To discern the effects of seasonal and discharge related variations on stream water chemistry in the Park, comparisons are made between selected synoptic surveys. A comparison of snowmelt conditions during January with the May synoptic survey (table 10) provides an indication of seasonal variability when flow conditions are similar (less than a factor of two difference in

Table 10.--Differences in stream water-quality between surveys in January and May 1982.

Formation	Unit flow, in cubic feet per second per square mile	Concentrations in microequivalents per liter except for silica which is in micromoles per liter										
		H	Ca	Mg	Na	K	Base Cations	Alk	SO4	Cl	NO3	Si
CATOCTIN (n=7)												
January 1982	0.79	0.14	102	87	62	7	258	120	75	34	27	143
May 1982	0.61	0.09	116	95	71	8	290	176	64	33	13	161
Difference	0.18*	0.05**	-14*	-8*	-9*	-1	-32**	-56**	11**	1	14*	-18*
PEDLAR (n=12)												
January 1982	0.57	0.23	95	53	75	8	231	85	90	31	21	173
May 1982	0.80	0.14	102	57	79	9	247	120	81	31	6	183
Difference	-0.23	0.09**	-7**	-4*	-4**	-1**	-16**	-35**	9**	0	15**	-10*
OLD RAG GRANITE (n=5)												
January 1982	0.38	0.24	57	35	76	12	180	78	63	29	5	169
May 1982	0.65	0.15	62	39	82	14	197	103	54	33	2	176
Difference	-0.27**	0.09**	-5	-4*	-6	-2*	-17*	-25**	9**	-4	3	-7
HAMPTON (n=4)												
January 1982	0.32	1.56	28	50	27	35	140	10	100	22	2	81
May 1982	0.34	1.31	24	47	25	39	135	15	89	25	1	75
Difference	-0.02	0.25	4	3	2	-4	5	-5	11*	-3	1	6

* Significant difference ($p \leq 0.05$).
**Significant difference ($p \leq 0.01$).

flow). Low flow conditions in September 1981 (about 0.13 $ft^3/sec/mi^2$) are compared with high flow conditions in June 1982 (about 1.4 $ft^3/sec/mi^2$) to provide an indication of discharge related differences in the summer months (table 11).

Generally, the Catoctin and Pedlar Formations and Old Rag Granite show similar seasonal trends in surface runoff chemistry. Greater carbonic acid weathering in May, as compared to January, is indicated by an average increase of 40 percent for alkalinity and 10 percent for sum of base cations. The stream-water concentration of individual base cations increased 5 to 15 percent (table 10). Concentration of silica shows a similar seasonality, suggesting that an increase in weathering involves, at least to some degree, the incongruent dissolution of aluminum-silicates. As expected with increased carbonic acid weathering and higher stream-water alkalinity concentration, hydrogen ion concentration was lower in May than January.

May concentrations of sulfate and nitrate in runoff were generally lower than in January (table 10). Utilization of nitrogen species and sulfate by terrestrial plants can strongly decrease summer concentrations of these ions in stream water. Decomposition and leaching from leaf litter may also account for higher sulfate and nitrate concentrations in winter. Base cation leaching from this litter cover at the same time may explain why the winter drop in base cations is not as pronounced as the drop in alkalinity.

With the exception of sulfate, seasonal differences in runoff chemistry for basins in the Hampton Formation are not statistically significant. However, the winter decline in alkalinity and pH similarly suggests there is less carbonic acid weathering during colder months in this formation.

Differences related to discharge within the summer months are shown in table 11. The higher flows in June generally produced lower concentrations of alkalinity and individual concentrations of base cations and silica. Alkalinity concentration averaged about 40 percent lower during the June survey, indicating a dilution and/or a partial neutralization of base flows by runoff from recent precipitation.

Despite these statistically significant seasonal and discharge related differences in stream-water chemistry, large absolute fluctuations have not been observed in runoff from the Hampton, Pedlar, and Catoctin Formations and the Old Rag Granite. These formations, at least at the present, appear to be reasonably stable in that severe pH and alkalinity depressions have not been observed during periods of higher flow or snowmelt. The seasonal and discharge related variation in pH and alkalinity cannot be determined for streams draining the Antietam Formation because of insufficient data.

ESTIMATION OF DEGREE AND EXTENT OF ACIDIFICATION IN SHENANDOAH NATIONAL PARK

The alkalinity map, regression models, and mean plots of streamwater data have been used up to this point to investigate the sensitivity of streams in the Park to acidification and to relate this sensitivity to basin characteristics of geology, soils, hydrology, and altitude. These have identified potentially vulnerable Park streams but do not address the degree of acidification (if any) due to atmospheric deposition. Acidification is defined as a persistent loss of alkalinity in surface runoff (or an increase in mineral acidity), with a concomittant drop in pH, and/or an increased weathering of

Table 11.--Differences in stream water-quality between surveys in September 1981 and June 1982.

Formation	Unit flow, in cubic feet per second per square mile	Concentrations in microequivalents per liter except for silica which is in micromoles per liter										
		H	Ca	Mg	Na	K	Base Cations	Alk	SO4	Cl	NO3	Si
CATOCTIN (n=7)												
September 1981	0.17	0.11	119	109	77	6	311	244	65	30	6	187
June 1982	1.71	0.08	117	94	70	7	288	181	61	30	12	170
Difference	-1.54**	0.03	2	15**	7*	-1*	23*	63**	4	0	-6*	17*
PEDLAR (n=12)												
September 1981	0.15	0.15	105	65	91	9	270	183	72	29	8	221
June 1982	1.67	0.14	100	55	79	9	243	114	84	28	9	176
Difference	-1.52**	0.01	5	10*	12**	0	27	69**	-12*	1	-1	45**
OLD RAG GRANITE (n=5)												
September 1981	0.03	0.27	69	47	90	14	220	157	49	29	8	210
June 1982	1.76	0.17	60	38	78	14	190	95	55	28	2	174
Difference	-1.73**	0.10	9**	9*	12**	0	30	62**	-6*	1	6*	36**
HAMPTON (n=4)												
September 1981	0.04	1.30	26	48	28	43	145	34	91	24	2	96
June 1982	0.52	1.42	27	47	25	40	139	14	92	24	1	84
Difference	-0.48**	-0.12	-1	1	3	3	6	20*	-1	0	1	12

* Significant difference ($p \le 0.05$).
**Significant difference ($p \le 0.01$).

base cations from soils and rocks. Galloway and others (1983) represent acidification and recovery of aquatic ecosystems as a process that occurs in stages. In the early "preacidification stage," there are relatively constant runoff concentrations of sulfate, base cations, and alkalinity. Solution chemistry of these ions is controlled by release of base cations and formation of bicarbonate during primary mineral weathering. Increased sulfur deposition to a basin leads to the second stage, where sulfur is accumulating in the basin by soil adsorption. As the soils become more saturated with respect to the new level of sulfur deposition, runoff concentrations of base cations and sulfate increase. And, although stream-water pH and alkalinity are not greatly depressed during this period, this process may only delay more serious ecological effects. Depending on the percent base saturation of the soils and the weatherability of the underlying rocks, the supply of accessible base cations in the basin may eventually become severely depleted due to this accelerated weathering. This represents the next stage of acidification. Hydrogen and aluminum ion leaching increases to offset the decline in base cation leaching, thereby preserving electroneutrality. A drop in pH and alkalinity concentration results and continues as long as deposition of sulfur and hydrogen remain unchanged. In very "sensitive" basins, with a poor supply of base cations, the formation of alkalinity through carbonic acid weathering reactions may be completely lost, which results in mineral acidity and/or high concentrations of dissolved aluminum in surface runoff.

Most of the basins surveyed in the Shenandoah National Park are in the early stage of acidification (Galloway and others, 1983). They are receiving sustained high concentrations of anthropogenic sulfur, but most of this sulfur is adsorbed by the soil. Shaffer (1984) estimates that given current inputs of acid deposition, the sulfate adsorption capacity and base cation reserves of Hampton-derived soils will be severely depleted in 20 to 40 years and result in a noticeable decrease in runoff alkalinity and pH. Undoubtedly, the capacity of Antietam-derived soils to adsorb sulfate and leach base cations is no higher than for Hampton-derived soils and is probably much lower based on bedrock mineralogy data.

Quantification of acidification (loss of alkalinity or increased leaching of base cations) of an area is ideally achieved by comparing current and historical surface runoff chemistry and determining the chemical changes. This method is rarely applied with confidence, however, because of the scarcity of historic data, undocumented methods of measurements, and differences in climate and season at the time of sampling which make it difficult to distinguish between natural chemical variability and changes due to acidification. Predictive models based on current water chemistry are therefore frequently employed to estimate the degree of acidification of basins. These chemical-acidification models are based on principles of inorganic geochemistry and employ assumptions concerning carbonic acid weathering reactions in the soil-stream system. Most of these models are based on or derived from the Henriksen nomograph (1979, 1980). Henriksen proposed that the acidification of Scandinavian lakes and streams is analogous to titration of a bicarbonate solution with strong acid. In this model, bicarbonate lost in lakes and streams acidified by atmospheric deposition is stoichiometrically replaced by sulfate as strong acids from anthropogenic sources titrate existing alkalinity or replace carbonic acid as a major weathering agent. The acidification nomograph is a product of electroneutrality, carbonic acid weathering reactions, and several assumptions regarding the sources of base cations and sulfate.

From electroneutrality:

$$Ca^{2+} + Mg^{2+} + Na^{+} + K^{+} + NH_4^{+} + H^{+} + Al^{3+} = Cl^{-} + NO_3^{-} + SO_4^{2-} + HCO_3^{-} + \text{organic anions} \quad (1)$$

The seasalt contribution to this equation is subtracted out assuming that all chloride is of marine origin and that other seasalt-derived ions are present in concentrations proportional to the ionic composition of seawater:

$$*Ca^{2+} + *Mg^{2+} + *Na^{+} + *K^{+} + NH_4^{+} + H^{+} + Al^{3+} = NO_3^{-} + *SO_4^{2-} + HCO_3^{-} + \text{organic anions} \quad (2)$$

(* = non-marine fraction)

Then, assuming ammonium, nitrate, organic anions, aluminum ion and hydrogen ion concentrations are negligible, and representing the sum of the four seasalt corrected base cations by *Cb, the electroneutrality condition becomes:

$$*Cb = *SO_4^{2-} + HCO_3^{-} \quad (3)$$

Combining all four base cations into the *Cb term in equation 3 is a modification suggested by Kramer and Tessier (1982) to allow for weathering of minerals containing appreciable quantities of potassium and sodium. In the area studied by Henriksen (1980), sodium and potassium concentrations were low enough to ignore in this equation. However, in Shenandoah National Park these cations make up a significant proportion of the concentration of base cations in stream water.

The validity of equation (3) is based on two inherent assumptions: 1) The sum of base cations is constant with time; that is, freshwater Cb* concentrations do not change with changes in acid loading, and 2) seasalt-corrected sulfate in the lake or stream is derived entirely from atmospheric deposition (negligible terrestrial contribution). From this, Henriksen (1980) represents "preacidification bicarbonate," or bicarbonate concentration before anthropogenic input of hydrogen ion and sulfate, as:

$$[HCO_3^{-}]_o = *Cb \quad (4)$$

Using equation 4, combined with carbonic acid equilibria reactions which define pH in terms of bicarbonate concentrations for a given partial pressure of carbon dioxide, Kramer and Tessier (1982) derived the following:

$$pH = \log *Cb - \log (K_H K_1) - \log PCO_2 \quad (5)$$

where K_H = Henry's law constant for CO_2, 3.16×10^{-2} at 25°C,
K_1 = First equilibrium constant, 5.01×10^{-7} at 25°C, and
PCO_2 = the partial pressure of carbon dioxide in the lake or stream water (in atmospheres)

This equation defines the theoretical linear relation between pH and log *Cb in surface water assuming carbonic acid weathering in a basin. For plotting purposes, the pH values of individual stream waters are corrected (pH_{corr}) to the same fixed partial pressure of CO_2, to eliminate stream to stream variability, using the following equation:

$$pH_{corr} = \log [HCO_3^{-}] - \log PCO_2 - \log (K_H K_1) \quad (6)$$

Bicarbonate concentration is assumed to equal alkalinity plus hydrogen ion concentration. Thus, the chemistry of a number of different stream waters may be compared to a theoretical preacidified condition based on known equilibrium equations. For surface waters plotting below this theoretical preacidification line, it may be inferred that sources of hydrogen ion other than from carbonic acid have contributed to the weathering processes (Kramer and Tessier, 1982).

APPLICATION OF ACIDIFICATION MODEL

The Kramer and Tessier (1982) acidification model is used in this study to provide an estimate of the degree and extent of acidification of Park streams. Since the chemical data available for these streams are based on a limited number of discrete samples taken over the course of a single year, this model can only be viewed as an approximation of acidification.

The seawater correction used by Henriksen (1980) in equation (2) is modified for this study to estimate the concentration of atmospheric-derived cations in surface runoff. The sum of base cations is corrected on the basis of its ratio to chloride in bulk precipitation (table 1), thereby factoring out atmospheric sources, both marine and terrestrial. Chloride is assumed to be a conservative element with no mineralogical source in the Park. Its low and uniform concentration in stream water supports this assumption. The calculation for precipitation correction of base cations in stream water is as follows:

$$[Cb]_{corr} = [Cb_S] - \frac{[Cl_S]\ [Cbp]}{[Clp]} \quad (7)$$

where $[Cb]_{corr}$ = precipitation corrected base cation concentration of stream water
$[Cb_S]$ = sum of base cations concentration in stream water (table 5)
$[Cbp]$ = sum of base cations concentration in precipitation (table 1)
$[Cl_S]$ = chloride concentration in stream water (table 5)
$[Clp]$ = chloride concentration in precipitation (table 1)

This corrected sum of base cations $[Cb]_{corr}$ in stream water better represents cations derived from weathering processes in a basin and is used to replace the seasalt corrected sum of base cations in equation (5):

$$pH = \log [Cb]_{corr} - \log (K_H K_1) - \log PCO_2 \quad (8)$$

The mean calculated partial pressure of CO_2 for the streams is 10^{-3} atmospheres and consequently all stream water pH's are corrected to this value using equation 6. In addition, the theoretical carbonic acid weathering line is calculated given the same partial pressure of CO_2.

The modification of the model proposed by Kramer and Tessier (1982) shows that all stream waters in Shenandoah National Park plot below the line of theoretical carbonic acid weathering (fig. 13). This suggests these waters have been acidified by a source of hydrogen ion other than from carbonic acid. Redox reactions within a drainage basin, such as the oxidation of sulfide deposits, could potentially release strong mineral acids and neutralize streamwater alkalinity and/or weather out additional base cations without the stoichiometric release of alkalinity that is characteristic of carbonic acid weathering reactions. Either process could cause the observed deviation from the theoretical line in figure 13. However, there is little evidence to suggest that the geologic formations in Shenandoah National Park contain appreciable quantities of minerals which can undergo acid forming redox reactions. More likely, atmospheric deposition is the primary source of hydrogen ions responsible for the deviation of stream waters from this theoretical line. Deposition of these strong mineral acids can neutralize the stream water alkalinity released during carbonic acid weathering reactions. This results in a drop in pH without changing the base cation composition of streamwater, which moves points down from the theoretical line in figure 13. Acid deposition can also increase the rate of base cation weathering in a basin but without a concomittant release of alkalinity. This results in an increased concentration of base cations in streamwater without an appreciable change in pH, which moves points to the right of the theoretical carbonic acid weathering line.

These two processes--neutralization of alkalinity or increased weathering of base cations by acid deposition--cannot be distinguished from each other with the available data. Nonetheless, both processes are defined as acidification, and both may adversely affect the stream-water quality in sensitive basins. This is not to imply that the most sensitive basins in the Park have

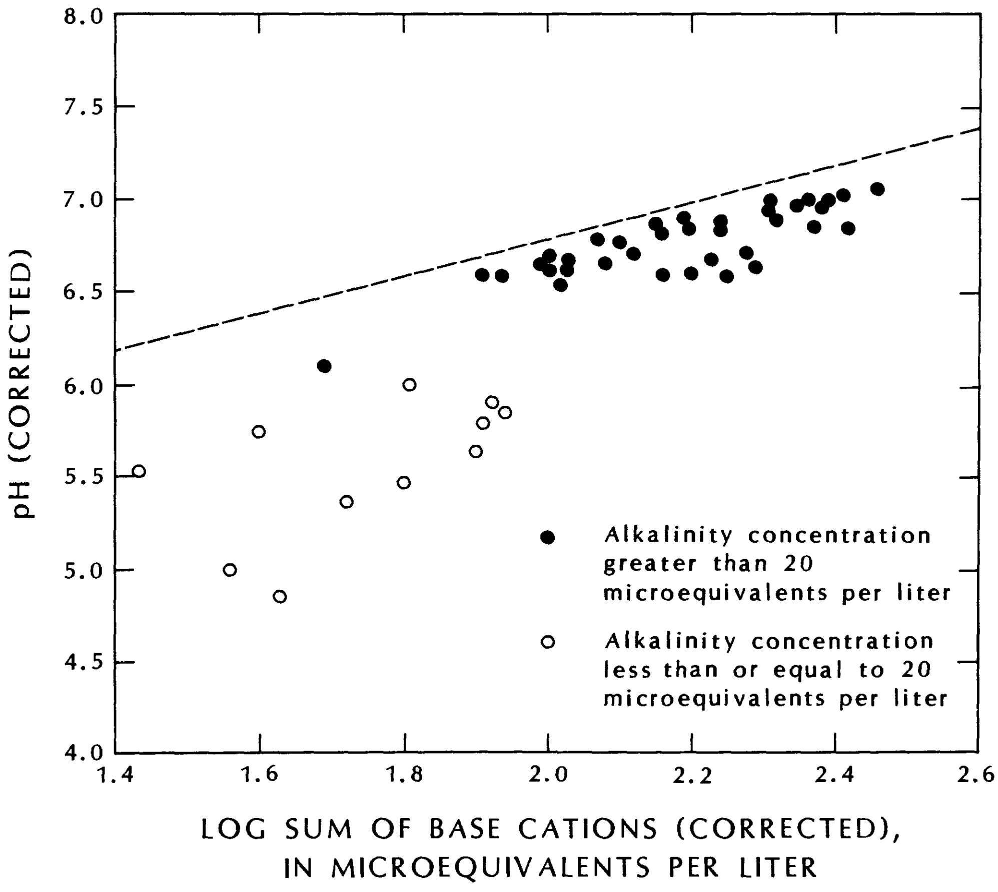

Figure 13.--Relation between precipitation-corrected base cations and pH corrected to a CO_2 partial pressure of 10^{-3} atmospheres for all surveyed streams.

seen the most acidification. In general, most of the basins have been similarly acidified. This is represented as the difference between the total base cation concentration (corrected for atmospheric contributions) and the alkalinity concentration in stream water (fig. 14). Acidification in the Park averages about 50 μeq/L. This acidification, whether it is manifest as a loss of stream-water alkalinity or an increase in the weathering rate of base cations, is similar in the most sensitive basins in the Park, those underlain by the Antietam Formation, and in the least sensitive basins, those underlain by the Catoctin Formation.

Although most basins in the Park have been similarly acidified, the impact on stream-water chemistry is not necessarily the same. The pH depression associated with a modest loss of alkalinity due to acid deposition is negligible in high alkalinity streams, but it becomes much larger in low-alkalinity streams. For example, an alkalinity loss of 20 μeq/L from two streams, one with 20 and the other with 200 μeq/L of alkalinity, results in a pH change of 6.12 to 5.40 and 7.10 to 7.05, respectively, assuming a CO_2 partial pressure of 10^{-3} atmospheres (fig. 6). This nonlinear change in buffering intensity with change in alkalinity concentration may explain why basins with stream-water alkalinity concentrations less than 20 μeq/L, those underlain by the Antietam and Hampton Formations, show the greatest deviation from the theoretical carbonic acid weathering line in figure 13.

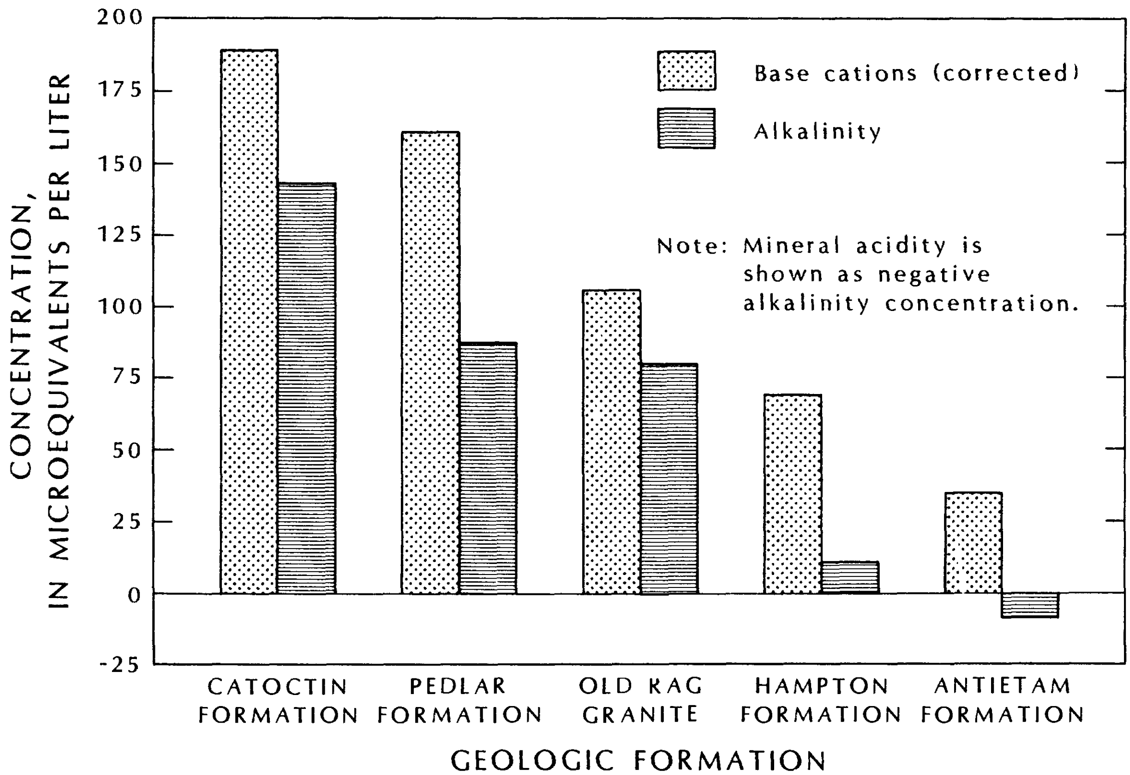

Figure 14.--Mean concentration of precipitation-corrected base cations and alkalinity concentration of stream water from major rock formations.

In addition, basins sensitive to acid deposition, those containing poorly developed soils and resistant bedrock, do not necessarily respond the same as less sensitive basins when subjected to the same increase in the rate of base cation weathering. The reserve of available base cations for carbonic acid weathering reactions is normally small in sensitive basins. Thus, long-term acidification may severely deplete this reserve, thereby decreasing the potential for alkalinity-producing reactions in a basin and decreasing the capacity of soils and rocks to retain hydrogen ions from acid deposition. The result is a drop in stream-water pH and perhaps an increase in the concentration of dissolved aluminum. Because less sensitive basins contain more weatherable minerals and better developed soils, the potential for significantly reducing the reserve of base cations available for carbonic acid weathering is much smaller.

Overall, basins which have been identified as the most sensitive in Shenandoah National Park also appear to be most critically affected by acidification from atmospheric deposition. Stream waters draining the siliceous Antietam Formation have a mean pH of 4.99 and a mineral acidity concentration of 7 μeq/L. In the Hampton Formation, stream-water alkalinity is extremely low, averaging 11 μeq/L, which may eventually be lost altogether as in the Antietam Formation with continued inputs of acid deposition. Drainage basins in the Old Rag Granite and the Pedlar and Catoctin Formations are also acidified. But because these formations contain more weatherable minerals, the current effect of acidification on stream-water pH is smaller. However, further study is needed to determine the long-term impacts of continued acidification in these formations.

SUMMARY

During 1981 and 1982 the Shenandoah National Park, Virginia, received precipitation with a volume-weighted pH value of 4.22 and a sulfate concentration of 54.2 μeq/L. Anthropogenic sources probably account for about 90 percent of the sulfate in this precipitation and at least 80 percent of the hydrogen ion, assuming precipitation pH below 5.0 is anthropogenically induced. Consequently, a large potential exists for acidification of sensitive basins in the Park.

Surface runoff alkalinity concentration, chosen as the index of sensitivity of Park basins to acid deposition, is low throughout the Park, indicating an overall sensitivity. Sensitivity is strongly related to drainage basin geology with the high silica, strongly weathered Antietam and Hampton Formations identified as extremely sensitive (alkalinity less than 20 μeq/L), the granitic Old Rag Granite and Pedlar Formation as highly sensitive (alkalinity of 20 to 100 μeq/L), and the basaltic Catoctin Formation moderately to marginally sensitive (alkalinity of 100 to 200 μeq/L).

A more rigorous relationship between sensitivity and basin characteristics, using multiple regression techniques, reveals that drainage basin geology (and associated soils) explains the majority of variation in alkalinity concentration, and altitude and geographic location of the basin (east or west of the Blue Ridge) explains a lesser, but significant amount of variability. Drainage basin geology and soils control base cation availability for carbonic-acid weathering (CAW) reactions which in turn control runoff alkalinity. Lower temperatures, greater amounts of acid deposition, and more poorly-developed soils at higher altitudes undoubtedly contribute to the lower stream-water alkalinities found there. The lower concentration of alkalinity (and the higher concentration of sulfate) in streams draining the western half of the Park suggests that upwind sources of acid deposition to the west preferentially deposit both wet and dry fallout on western facing slopes.

The regression model of flow-weighted alkalinity versus geology reasonably predicts the sensitivity of streams draining the Blue Ridge with similar geology that are not included in the model. Both inside and outside the Park, this model properly categorizes streams as to sensitivity and generally predicts alkalinity within 30 μeq/L of the observed values.

Similar to alkalinity, variability in base cation and silica concentrations is well explained by drainage basin geology in the regression analyses. To explore this relationship, mineralogical information combined with runoff chemistry is used to identify probable weathering processes in the Park. Carbonic acid weathering of chlorite, epidote, plagioclase, and other dark minerals in the Catoctin and Pedlar Formations and (in lesser amounts) the Old Rag Granite account for relatively high runoff concentrations of alkalinity and base cations. In contrast, the highly weathered, quartz-rich Hampton Formation, with interlayers of phyllite, imparts only a small amount of base cations and alkalinity to streamwater. However, sericite and chlorite in the phyllite interlayers and sericite in the metasediments release significant quantities of potassium and magnesium upon weathering which stabilize streamwater chemistry. Very limited CAW of the extremely quartz-rich Antietam Formation results in streamwater with a low base cation concentration and zero to negative alkalinity (mineral acidity). Thus, both the Hampton and Antietam Formations in the Park are considered extremely sensitive to atmospheric deposition, whereas the other geologic formations are less vulnerable but are nonetheless considered sensitive.

Application of an acidification model based on carbonic-acid-weathering reactions suggests that all basins in the Park have been acidified by atmospheric deposition. Current acidification averages 50 μeq/L, which is fairly evenly distributed in the Park. This acidification is manifest as a neutralization of stream-water alkalinity and/or an increase in the weathering out of base cations from soils and rocks. These two processes are indistinguishable with the model, but both have serious consequences in the Park, especially in the extremely sensitive areas underlain by the Antietam and Hampton Formations. Because of the low "preacidification" concentration of stream-water alkalinity and the small reserve of available base cations in these areas, even modest changes due to acid deposition have large impacts on stream-water chemistry. In the Antietam Formation, the most sensitive formation in the Park, acid deposition has resulted in stream water with an average pH of 4.99 and mineral acidity of 7 μeq/L.

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