

GEOCHEMICAL MASS-BALANCE RELATIONSHIPS FOR SELECTED IONS IN PRECIPITATION AND STREAM WATER, CATOCTIN MOUNTAINS, MARYLAND

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ABSTRACT. During 1982 and 1983, precipitation and stream water were sampled weekly for quantity and chemical composition in two small watersheds in the Catoctin Mountains of central Maryland. Both watersheds are underlain by metabasaltic rock consisting of chlorite, albite, epidote, and actinolite and minor amounts of calcite and quartz. Precipitation recorded in 1983 was approx 60 percent greater than in 1982; however, the discharge of streams draining both watersheds, which accounted for 50 percent of precipitation input, remained relatively constant. Hydrogen, sulfate, and nitrate were the major ions in precipitation, whereas calcium, magnesium, and bicarbonate were the major ions in stream water. Seasonally high concentrations were observed for sulfate and hydrogen ions in precipitation during the summer. In stream water, concentrations of bicarbonate were elevated during the summer. Sodium and chloride concentrations in stream water were elevated during the spring because of large quantities of deicing salts applied to main roads during the winter months. Mass balances for major dissolved constituents show that dissolved solids from precipitation input account for 12 to 19 percent of the total dissolved load in stream water. Approx 50 percent more sulfate left each watershed annually than entered in precipitation. Dry deposition of sulfur species apparently accounts for this excess sulfate. Geochemical weathering processes account for the observed changes in the chemistry of streamflow. Dissolution of albite and calcite account for 60 to 90 percent of the neutralization of the total hydrogen-ion input from precipitation and from carbonic-acid weathering. Even though calcite is present in extremely small quantities in the bedrock, its dissolution significantly affects water chemistry because of its relatively high reactivity and location in the hydrologic flow path.

INTRODUCTION

In small forested watersheds, the chemical composition of surface and ground water is generally a result of reactions that take place between atmospheric deposition and the minerals in bedrock and soils. Large areas of the Eastern United States are presently being exposed to influxes of strong acids from anthropogenic, atmospheric sources, commonly referred to as acid rain (Likens and others, 1979). This input of acidity to watershed systems may affect the rates of geochemical processes such as mineral dissolution, alteration, and chemical weathering (Johnson and others, 1981). The chemical character of ground and stream water may be in-

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fluenced by these altered reaction rates, as well as by biological processes and evapotranspiration.

To be able to predict the effect of additions of acidic rain to these watershed systems, it is essential to understand the geochemical reactions occurring in the watershed. Currently, some of these reactions and processes are being investigated in a study area in the Catoctin Mountains located in central Maryland (fig. 1). This area, which consists of two small watersheds, is underlain by metabasalt of the Catoctin Formation. This rock type was selected for two reasons: (1) it is widespread in the Eastern United States, and (2) water associated with silicate bedrock is typically considered to be sensitive to acidification from atmospheric deposition because of the low reactivity of minerals in the bedrock (Hendrey and others, 1980).

Purpose and Scope

The purpose and scope of this report are threefold: (1) to describe input/output mass balances for major ions based on chemical composition of precipitation and stream water, (2) to characterize selected geochemical reactions occurring in the study area with different loading rates of hydrogen ion during 1982 and 1983, and (3) to describe selected watershed processes that influence the chemical character of the stream water.

DESCRIPTION OF STUDY AREA

The Hunting Creek study area, 15.9 km² in size, is located in the Blue Ridge physiographic province in central Maryland (fig. 1). The study area consists of two small watersheds with a mature deciduous forest cover. The areas of Hauver Branch and Hunting Creek watersheds are 550 and 1040 hectares, respectively. The watersheds under investigation are typical of those occurring on metabasalt in the Blue Ridge province of the Appalachians. The maximum relief in the study area is 280 m. Typically, the watersheds have steep-sided valleys at the lower elevations and grade upward into broad, relatively flat upland areas.

Precipitation

The average annual rainfall, based on records from 1891 to 1944 was 112 cm. The lowest annual rainfall during this period was 65.8 cm, and the highest, 166 cm (Bily, 1946). There was an average of 109 days with precipitation of 0.025 cm or more per year. The amount of precipitation was fairly evenly distributed during the year (Bily, 1946). Precipitation in the form of snow was highly variable and ranged from flurries to heavy depths (81 cm in 1942). The average annual relative humidity was 68 percent during this period, and the average annual temperature was 12°C, with a minimum of -31°C in January and a maximum of 40°C in August.

More recent data (1931-1980) from a National Weather Service station located about 32 km to the south confirm the even monthly distribution of precipitation amounts, with a mean annual precipitation amount of 112 cm $\pm$ 18 cm during this period (National Oceanic and Atmospheric Administration, 1981). The mean annual temperature for this period of

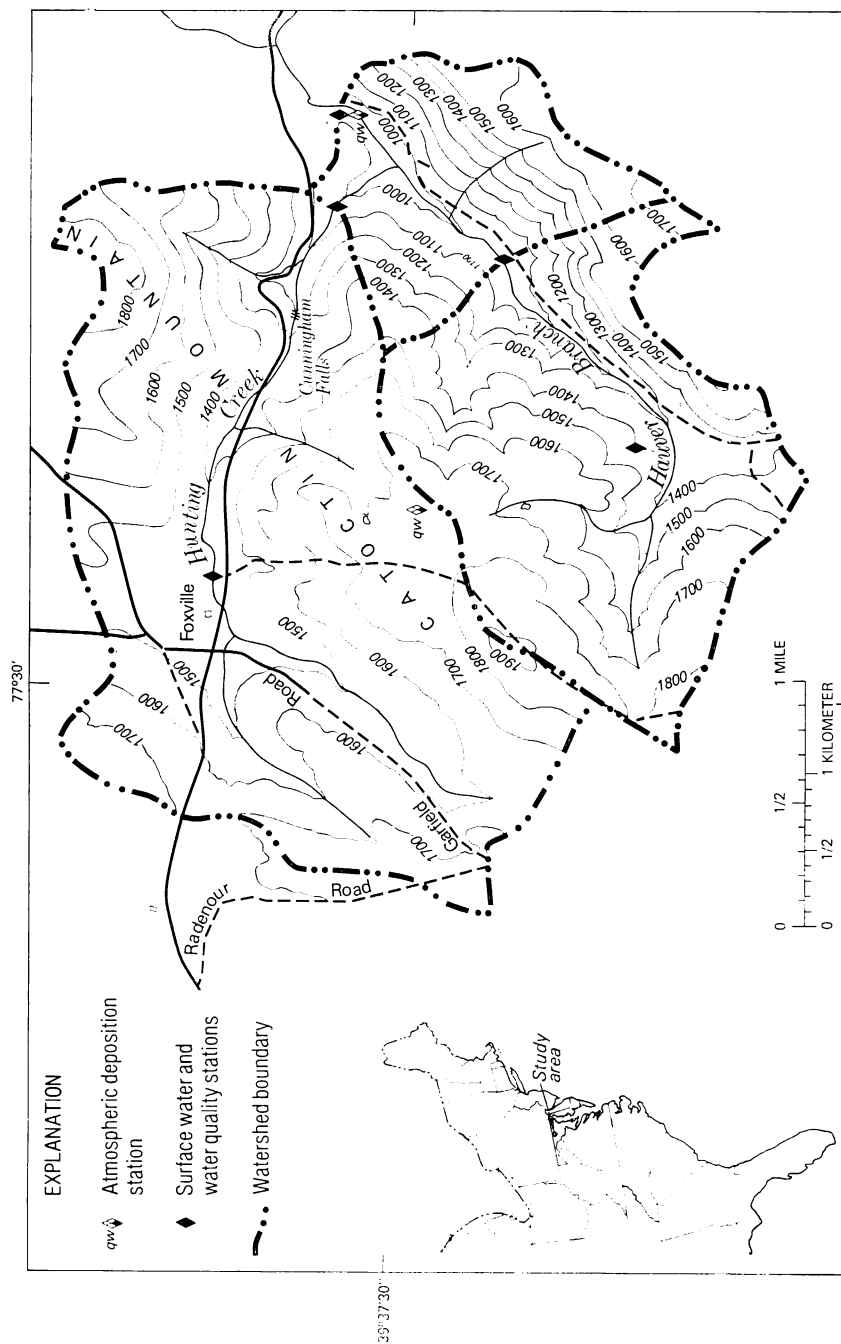


Fig. 1. Location of study watersheds and sampling sites for atmospheric deposition and stream water.

record is 12°C, identical with the data from the earlier period of record (1891-1944).

The velocity and direction of winds are highly variable from hour to hour. The average velocity is lowest in August and highest in March. The prevailing wind direction is from the northwest from October to April and from the southwest during May through September.

Geology

The Catoctin Mountains in Maryland are underlain by a thick sequence of interbedded greenstone and sedimentary rocks known as the Catoctin Formation of Precambrian Age. This formation underlies the Lower Cambrian sedimentary rocks in the Blue Ridge province of northern Virginia, Maryland, and southern Pennsylvania, and unconformably overlies Precambrian granitic rocks. The original Catoctin lavas were basaltic and appear to have been normal plateau basalts (Reed, 1955). These lavas have subsequently been altered to greenstone by low-grade regional metamorphism. The major minerals in the greenstone are chlorite, epidote, albite, and actinolite, with small amounts of quartz and calcite. Accessory minerals are magnetite, ilmenite, hematite, and sphene (Stose and Stose, 1946; Reed, 1964). The greenstone commonly is amygdaloidal, and the vesicles are filled with secondary minerals such as quartz, epidote, and chlorite with lesser amounts of calcite, jasper, and orthoclase feldspar. A well-developed joint and fracture system serves as the principal pathway for movement of water through the rock. Joint and fracture surfaces are lined commonly with the same secondary minerals found in the amygdules such as calcite. The watersheds of Hauver Branch and Hunting Creek are developed on lava flows within the Catoctin Formation.

Soils.—The major soils derived from weathering of the Catoctin Formation in Frederick County, Md., belong to the Highfield Series—a group of medium textured, well developed, and generally well-drained soils (Matthews, 1956). In the watersheds studied, these soils range in depth from 0 to 150 cm, depending upon their location. Bedrock exposure is common on steep slopes. A large part of each of the watersheds is mapped as rough and stony ground, and the thickest soils occur in the valley bottoms. The A horizon of these soils is generally a porous loam and has soil slurry pH values (1:1 soil/water) ranging from 5.2 to 5.8. The subsoil (B horizon) ranges from 5.0 to 5.8 in slurry pH, contains large rock fragments, and commonly has a high content of iron oxyhydroxides. The substratum is saprolitic, being derived from and grading into the metabasalt. The thickness of the saprolite is highly variable depending upon location in the watershed. Saprolite thickness ranges from zero to about 1.5 m. Drainage of some of the flood plain and valley bottom soils is poor, creating saturated conditions in those areas during periods of heavy rainfall.

Hydrology.—Precipitation during the years 1982 and 1983 covered in this report show very different distributions from the averages cited above (fig. 2A and B). There are large seasonal fluctuations in each of these years, and nearly 60 percent more rain fell in 1983 than in 1982. In 1982,

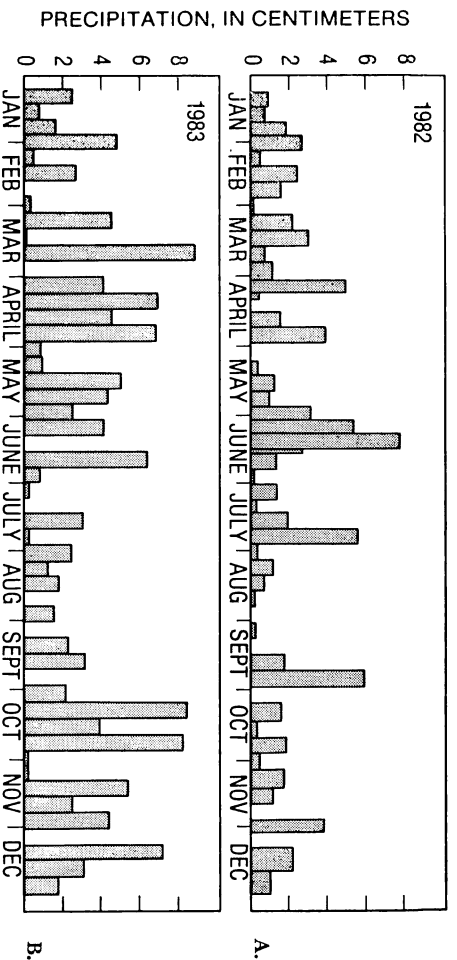


Fig. 2. Distribution of weekly precipitation amounts during 1982 and 1983.

a dry year, the watersheds received 95 cm of precipitation; nearly 70 percent of this fell in the first 6 months, which were followed by a dry summer and fall. In contrast, 1983 was an unusually wet year with 147 cm of precipitation. One third fell in the spring quarter, and an equal amount fell in the fall quarter following a dry summer (table 1).

Data from streams draining similar watersheds in this area indicate that about 55 percent of the incident precipitation leaves as stream discharge (James, Simmons, and Strain, 1984). In 1982, stream discharge of both Hauver Branch and Hunting Creek was 50 percent of precipita-

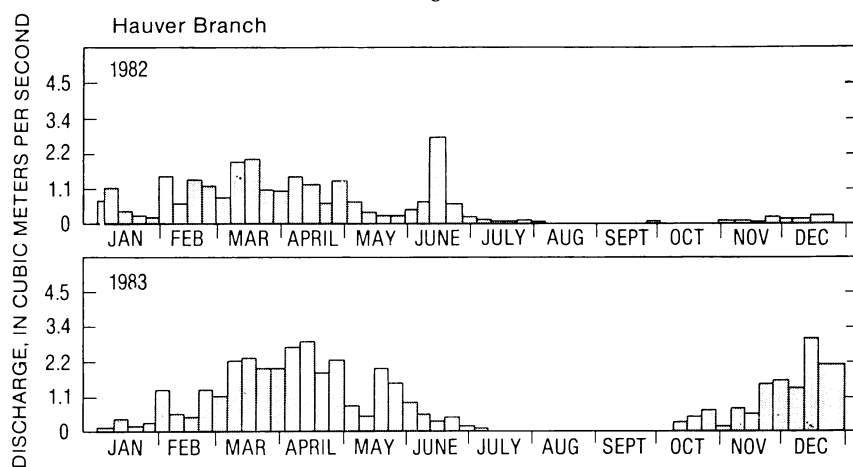
TABLE 1
Seasonal water budgets for Hauver Branch and Hunting Creek watersheds during 1982 and 1983. [All values expressed in liters $\times 10^8$ and rounded to nearest tenth]

Period	1982		1983	
	Precipitation	Stream	Precipitation	Stream
Hauver Branch Watershed				
January-March	10.2	13.0	16.5	12.9
April-June	19.5	10.1	26.8	15.1
July-September	11.3	0.7	10.5	0.4
October-December	8.6	1.1	27.6	11.0
	49.6	24.9	81.4	39.4
Hunting Creek Watershed				
January-March	19.2	21.5	30.9	22.2
April-June	36.5	19.1	50.2	30.2
July-September	21.1	3.0	19.6	1.1
October-December	16.0	2.8	51.8	28.6
	92.8	46.4	152.5	82.1

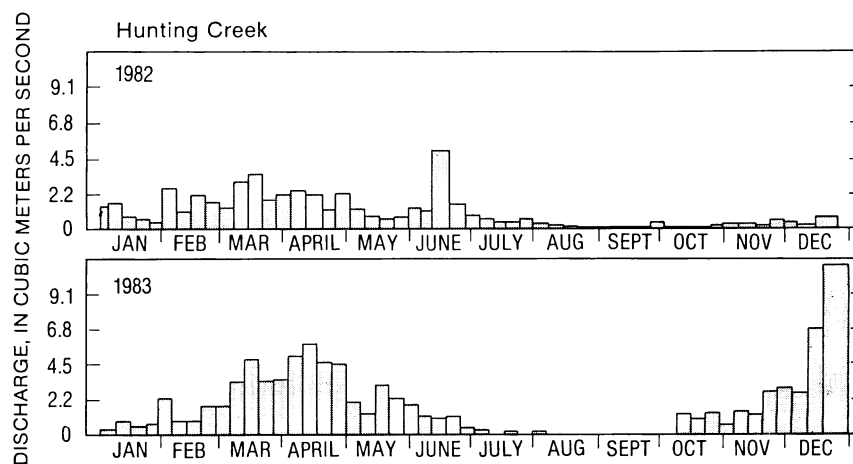
tion input. In 1983, discharge of Hauver Branch was 48 percent and of Hunting Creek 54 percent of precipitation. It is surprising that the precipitation-discharge relationship remains nearly constant in view of the 60-percent difference in total precipitation between these 2 yrs.

Hunting Creek and Hauver Branch displayed large seasonal fluctuations in discharge in 1982 and 1983 (fig. 3A and B). The differences in flow are largely related to rainfall, temperature, antecedent soil-moisture conditions, and biological activity. In these watersheds, the highest discharge usually occurs in the spring during heavy rainfall; however, because of the unusually wet autumn in 1983, about one-third of the total discharge for that year occurred in November and December.

Fig. 3



A. Distribution of weekly discharge data for Hauver Branch.



B. Distribution of weekly discharge data for Hunting Creek.

The seasonal effects of temperature and biological activity on water balance can be seen in table 1. During the first quarter of the year (January-March), most of the precipitation falling on the watersheds is discharged as streamflow. In the first quarter of 1982 following a dry summer and fall, both basins discharged slightly more water as streamflow than entered as precipitation. This water must have been supplied from ground-water storage. Water-level data from an observation well in the study area show that the water table declined about 3 m during this period. In the second quarter of the year, average daily temperature begins to rise, and vegetation enters an active growth period. Only about 50 percent of the precipitation input leaves as stream discharge. In the third quarter of the year (1982), temperature reaches its maximum, vegetation is fully developed, and only a small percentage of incident precipitation leaves as stream discharge. In the fourth quarter, temperature decreases, biological activity slows down, and an increasing amount of precipitation input leaves the watershed as stream discharge.

Precipitation falling in the watersheds rapidly infiltrates into the soil during most of the year. Overland flow has occasionally been observed during the winter months when the top few centimeters of the soil are frozen and in areas that have steep slopes.

Residence time for water in the soil and saprolite is highly variable depending upon location in the study area and other factors such as antecedent moisture conditions. Ground water moves principally through joints, along cleavage planes, or other irregular fracture zones (Fauth, 1977). Wells located in the Catoctin Formation have yields ranging from 0.3 L/s to about 0.63 L/s.

METHODS

In the years 1982-1983, precipitation samples were collected on a weekly schedule. Ninety samples were collected during this period using an Aerochem metrics Model 301¹ atmospheric deposition collector, the same type of collector used at stations participating in the National Trends Network and the National Atmospheric Deposition Program (NADP). Two collectors were placed in the study area to investigate variability in the chemistry of precipitation with elevation difference. One collector is located in the center of the study area at an elevation of 530 m, and another collector is located on the eastern boundary of the study area at an elevation of 287 m (fig. 1). The volume of wet deposition is measured at each collection site using a weighing bucket rain gage. Chemical analyses for major ions along with volume measurement of the wet deposition are used to calculate the deposition input to the study area.

In the years 1982-1983, stream-water samples were collected at weekly intervals at a fixed point on each stream near the gaging station. One hundred and two samples were collected during this period. The volume of surface-water outflow from the watersheds was measured by continuously gaging the two streams. Discharge data were generated from rating

¹ Mention of trade names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

curves developed from periodic current meter measurements according to methods described in Buchanan and Somers (1969). The accuracy of the daily discharge values are reported to be within 10 percent (James and others, 1984).

Chemical analyses of major ions and dissolved silica along with volume measurement of the stream water provide the streamflow output from each watershed. Sampling according to a weekly time series has been shown to be an effective method for obtaining accurate annual budgets for major constituents in precipitation and stream water (Likens and others, 1977).

Specific conductance, pH, alkalinity, and temperature were measured in the field. All stream samples and precipitation samples (provided there was sufficient volume) were filtered through 0.10 μm membrane filters. These samples were stored in dark plastic bottles, chilled to 4°C, and analyzed for sulfate, nitrate, and chloride by ion chromatographic techniques.

An aliquot from each sample was analyzed for alkalinity by an automatic incremental titration method and gran plot analysis. Samples to be analyzed for major cations, silica, and selected trace metals were preserved by depressing the pH to <2 with concentrated ultrapure nitric acid. Calcium, sodium, magnesium, and potassium were analyzed by atomic absorption spectrophotometric methods (Skougstad and others, 1979). Silica was determined colorimetrically according to the method of Skougstad and others (1979). In general, cation-anion balances for precipitation analyses were within 15 percent and for stream analyses within 10 percent.

RESULTS AND DISCUSSION

Seasonal Mean Concentrations of Dissolved Constituents in Precipitation and Stream Water

There are distinct differences between the chemical composition of the incoming precipitation and the stream water leaving each watershed. For precipitation collected in 1982 and 1983, sulfate and nitrate were the major anions and hydrogen the principal cation. For stream water and a small number of ground-water samples, bicarbonate was the major anion, and calcium and magnesium were the principal cations.

Precipitation chemistry.—A comparison of paired data collected at the two precipitation stations for 1982 and 1983 revealed that there is no significant difference in the concentrations of major dissolved ions in weekly samples of precipitation at different elevations (287 and 530 m above mean sealevel). However, the concentrations of SO_4^{2-} , and NO_3^- were generally higher (although not statistically significant) at the lower station. The source of this variation is not known. A similar effect was noted at sites located in the Hubbard Brook Experimental Forest, but no definite source could be identified in that study (Likens and others, 1977). Because of the essential identity of precipitation chemistry between the two stations, only data from the station located in the center of the study area are presented in this report (fig. 1).

Seasonal trends in concentrations of certain constituents in precipitation are apparent from the data of figure 4A and B. Highest sulfate and hydrogen-ion concentrations in precipitation occur in the summer, whereas highest nitrate concentrations generally occur during the winter months. These data are consistent with other studies in the northeastern United States (Bowersox and De Pena, 1980; Galloway and Likens, 1981).

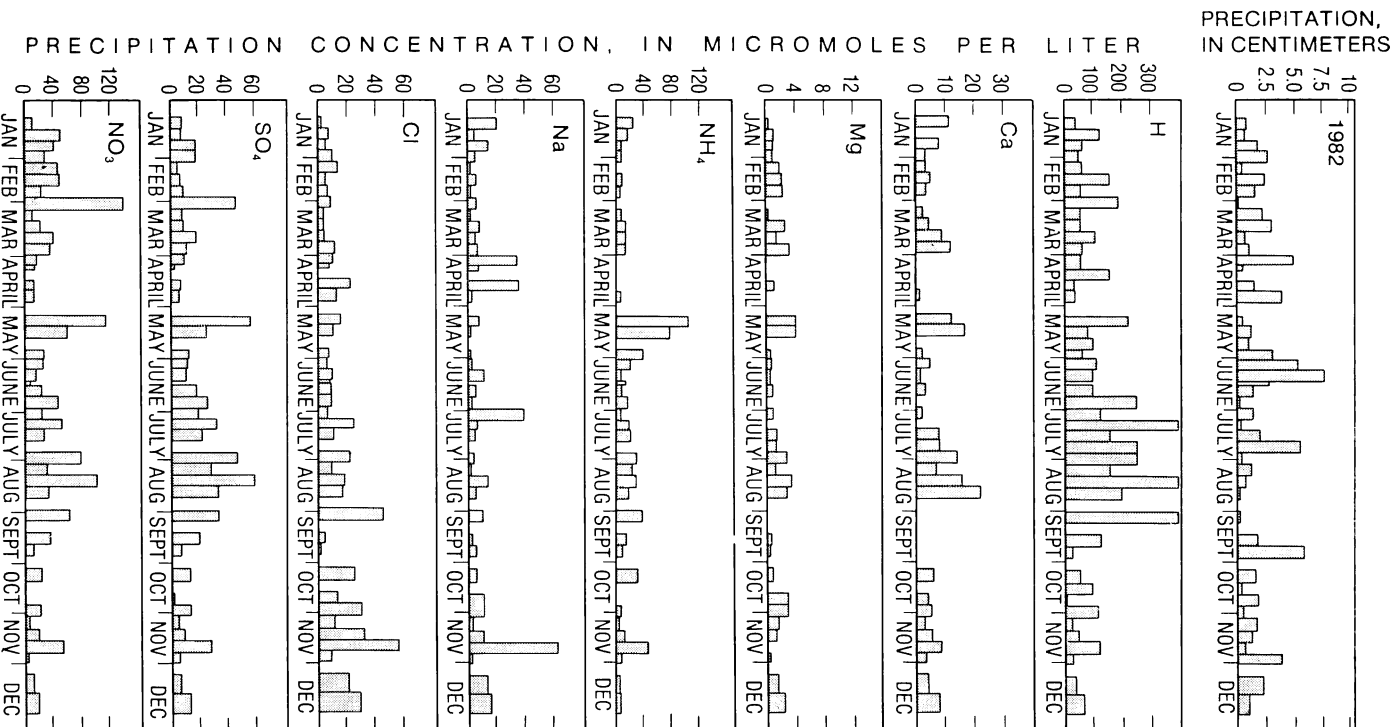
Chloride and sodium concentrations in precipitation fluctuate seasonally (fig. 4A). In 1982, the highest values for chloride and sodium were during the fall, whereas in 1983, chloride values were highest in the summer, and sodium values were highest in the fall (fig. 4B). The higher values for these two ions may be related to sea-salt distribution by the regional atmospheric circulation pattern. Some storms in the fall track from a northeasterly direction, and sea-salt may be incorporated in these storm patterns. The overall Cl:Na ratio for 1982, 1.1:1, is less than the corresponding ratio of 1.8:1 for seawater. This suggests there are additional sources of sodium in the study area precipitation. A similar observation was made during an earlier study located about 80 km east of the study area (Cleaves, Fisher, and Bricker, 1974) and also was reported by the Hubbard Brook study in New Hampshire (Likens and others, 1977). Gambell and Fisher (1966) reported ratios of less than 1.8:1 for stations located in southeastern Virginia and eastern North Carolina. They attributed soil dust as the source for the excess of sodium to chloride. In contrast, the overall chloride to sodium ratio was 2.1:1 in 1983. This ratio, along with the higher chloride concentration during the summer, was surprising considering that the majority of summer storms originate from a westerly (inland) direction. Hydrochloric acid is a frequent component of air pollution and may have contributed to the elevated chloride levels (Gorham, 1961).

Stream-water chemistry.—Streams draining both watersheds have similar chemical compositions that vary seasonally. The major dissolved ions in stream water are calcium, magnesium, and bicarbonate. These ions along with aqueous silica are the principal dissolved constituents derived from weathering reactions of minerals in the bedrock.

The differences between the composition of the incoming precipitation and the stream water leaving each watershed are striking (figs. 5A and B and 6A and B). No bicarbonate (alkalinity) was found in precipitation, whereas seasonal volume-weighted mean concentrations of bicarbonate in stream water ranged from 210 to 440 $\mu\text{moles/L}$ for Hauer Branch (fig. 5A and B) and from 250 to 600 $\mu\text{moles/L}$ for Hunting Creek (fig. 6A and B) in 1982 and 1983. Hydrogen and ammonium ions (1982 data) are depleted in stream water relative to precipitation indicating that these ions are consumed in biogeochemical reactions in the watersheds.

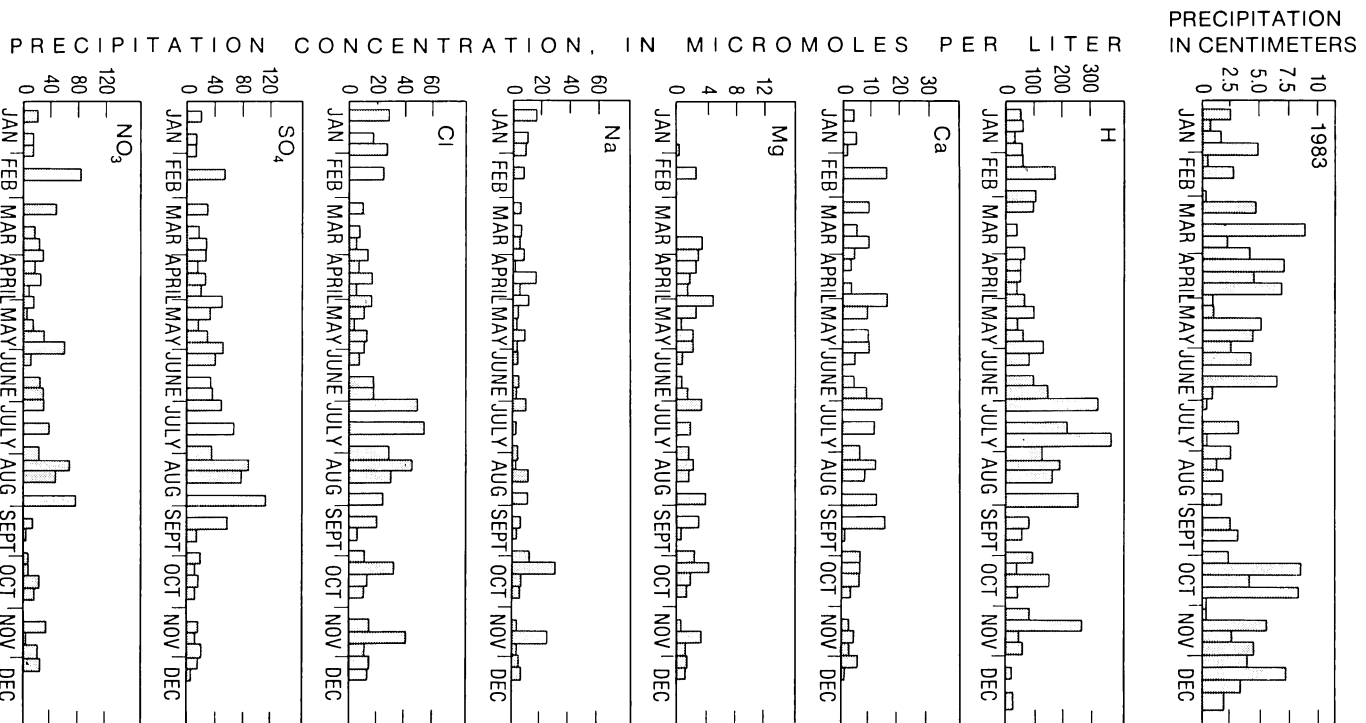
Stream discharge was sampled weekly for analysis of major dissolved constituents in 1982 and 1983 (figs. 5A and B and 6A and B). Within a week after the first snowfall in 1982, it became apparent that salt used on roads in the watersheds was entering the streams in runoff. The State of

Fig. 4



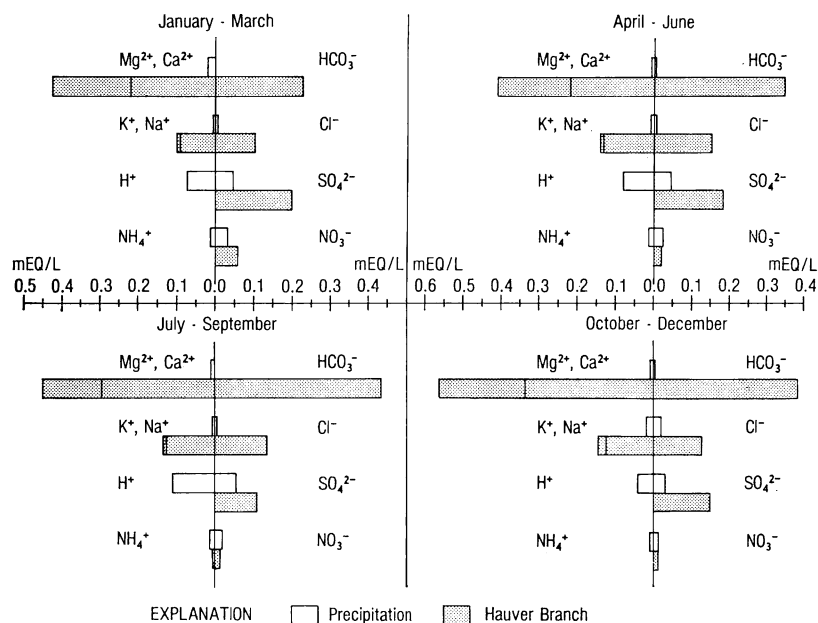
A. Weekly volume and concentration of major dissolved ions in precipitation for 1982.

Fig. 4 (continued)

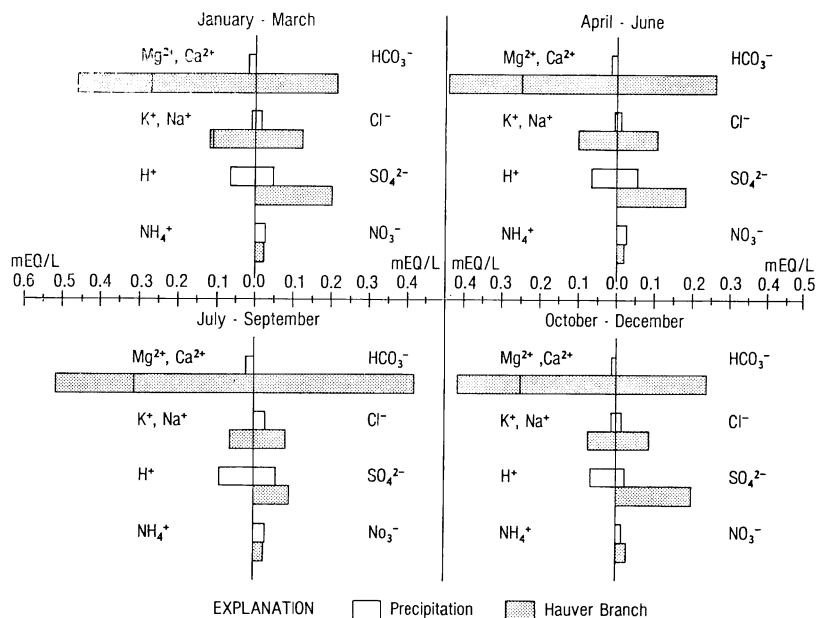


B. Weekly volume and concentration of major dissolved ions in precipitation for 1983.

Fig. 5

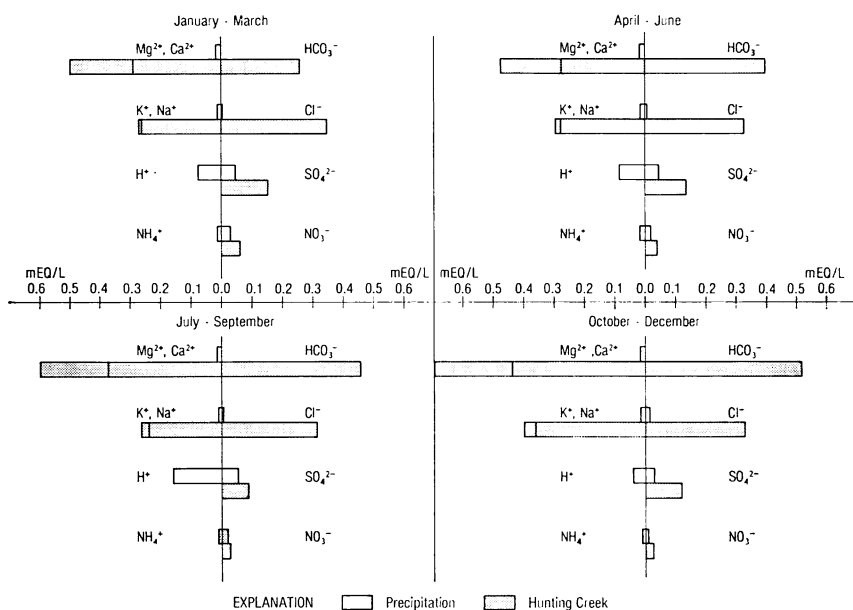


A. Seasonal volume-weighted concentrations of major ions in precipitation and in Hauver Branch stream water for 1982.

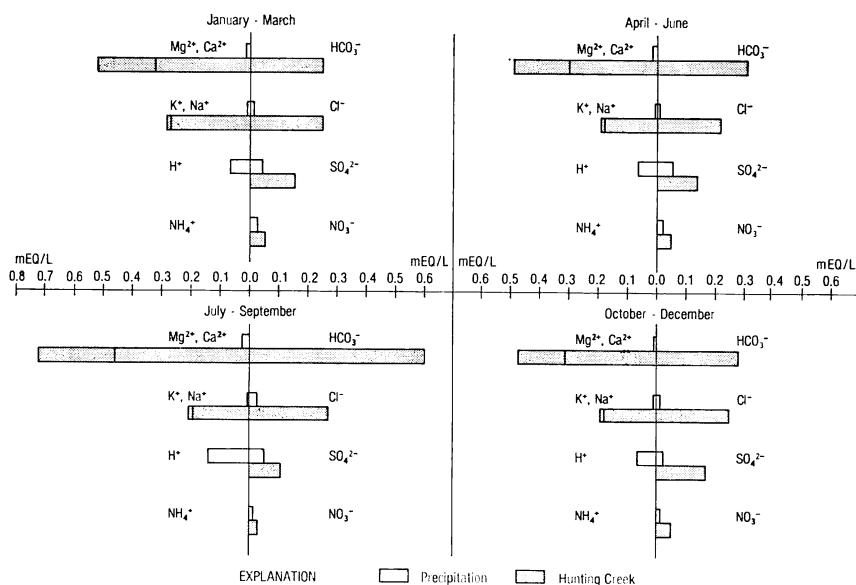


B. Seasonal volume-weighted mean concentrations of major ions in precipitation and in Hauver Branch stream water for 1983.

Fig. 6



A. Seasonal volume-weighted mean concentrations of major ions in precipitation and in Hunting Creek stream water for 1982.



B. Seasonal volume-weighted mean concentrations of major ions in precipitation and in Hunting Creek stream water for 1983.

Maryland uses halite and sand mixed with small amounts of calcium chloride to control ice on State Route 77, the major road through Hunting Creek watershed (fig. 1). A mixture of sand, calcium chloride, and halite is used on roads in Cunningham Fall State Park. These soluble salts dissolve and are rapidly transported through the watersheds to the streams. In a matter of days after application, elevated concentrations of chloride, calcium, and sodium are detected in the streams.

The concentration of sulfate ion is enriched in stream water relative to precipitation in both watersheds for 1982 (figs. 5A and 6A) and for 1983 (figs. 5B and 6B). Dry deposition of aerosol sulfur species and (or) neutral sulfate salts may be a major source for this enrichment (see below).

In general, the weekly concentrations of calcium, magnesium, and silica in stream water draining both watersheds do not seem to be related to changes in discharge. Figures 7A and B and 8A and B show the typical lack of correlation of concentration with discharge observed during the study. A three-orders-of magnitude range in discharge in 1982 (fig. 7A and B) produced only a very small change in weekly concentrations of silica, magnesium, and calcium. Bicarbonate values show a definite increase during the beginning of May through the end of October coinciding with the growing season for vegetation.

Chemical weathering has had a large impact on the composition of the streamflow. The principal products of chemical weathering, calcium, silica, magnesium, and bicarbonate, make up the majority of the total dissolved solids in the stream water draining both watersheds. Several explanations may account for the lack of correlation between discharge and the concentrations of these species: (1) the dissolution of the various mineral species by incoming water may be relatively fast, allowing waters with short residence times to reach rapidly chemical "equilibrium" with minerals in soils, saprolite, and bedrock; (2) the flow system is such that the residence time is relatively long and insures adequate time for equilibration with minerals in soil, saprolite, and bedrock. Water may be stored in streambank areas for considerable lengths of time before being released to the stream by increased infiltration of soil water; (3) the stream chemistry is a result of a combination of the two previous explanations at different locations along the stream reach. Other detailed watershed studies have found that the residence time of water is a function of both the amount of water flowing through the system (discharge) on the day of sampling and the position along the channel (Johnson and others, 1981).

Geochemical Budget

The geochemical budget of a watershed may be formulated as: *input* (materials contributed to the watershed by atmospheric deposition, by mineral weathering reactions, and by other watershed processes such as decomposition of biomass) = *output* (materials leaving the watershed in stream discharge, materials stored in the ground-water reservoir, and materials taken up by the biomass). Input/output loads for major dissolved constituents have been measured for the Hauver Branch and Hunting Creek watersheds for calendar years 1982 and 1983. These loads (table 2A,

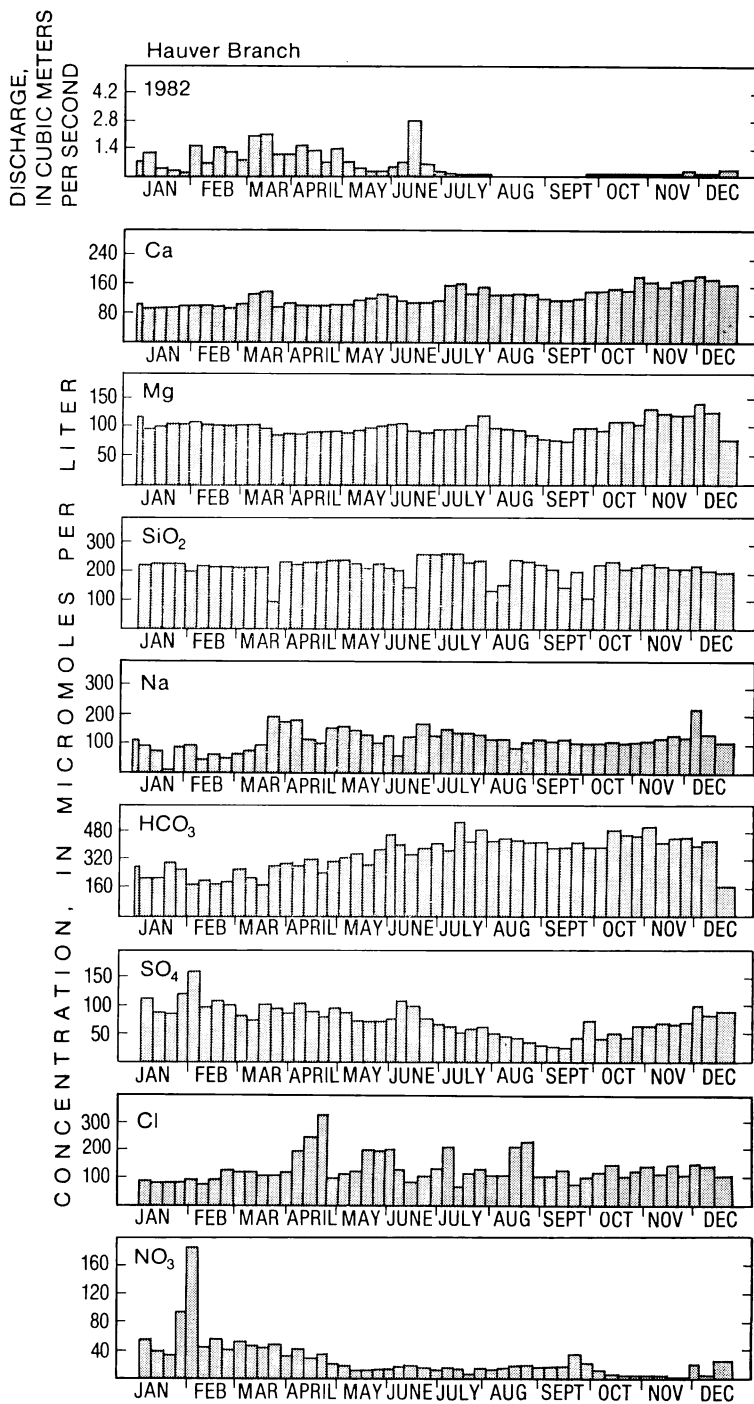
B, C, and D) form the basis for interpreting the watershed reactions that control the water chemistry of the streams.

Each of the watersheds received the same atmospheric deposition inputs. Hydrogen ion loading was 0.82 kg/ha in 1982 and 1.10 kg/ha in 1983. Sulfate loading was 19.8 kg/ha in 1982 and 34.2 kg/ha in 1983. The higher loadings in 1983 reflect the increased rainfall in that year relative to 1982. These loadings correspond well with those observed by the NTN/NADP network for this region of the United States (Interagency Task Force on Acid Precipitation, 1984). Sulfate loadings above 20 kg/ha/yr have been linked to surface-water acidification and environmental damage in areas underlain by sensitive (nonreactive) bedrock types (Johnson and others, 1982; Linthurst, 1984; Kramer and Tessier, 1982). Gorham and others (1984) suggested that a lower sulfate loading of 14 to 16 kg/ha/yr may be necessary to produce pH values near 4.7, the boundary level below which damage to aquatic ecosystems occurs.

Dissolved solutes introduced in wet precipitation account for 12 to 19 percent of the load of the streams draining the watersheds (table 3). Direct measurements of dry deposition contributions to the watersheds have not been attempted, since there currently are no generally accepted methods for making such measurements. Estimates of dry deposition of sulfate range from less than 10 percent (Dasch, Cadle, and Wolff, 1984) to more than 50 percent of the total input (Lindberg and Lovett, 1985). Bischoff, Paterson, and Mackenzie (1984) evaluated wet deposition and river runoff along the east coast of the United States and estimate that, on a regional basis, 26 percent of the sulfate in river discharge cannot be accounted for in wet deposition and is derived from dry deposition.

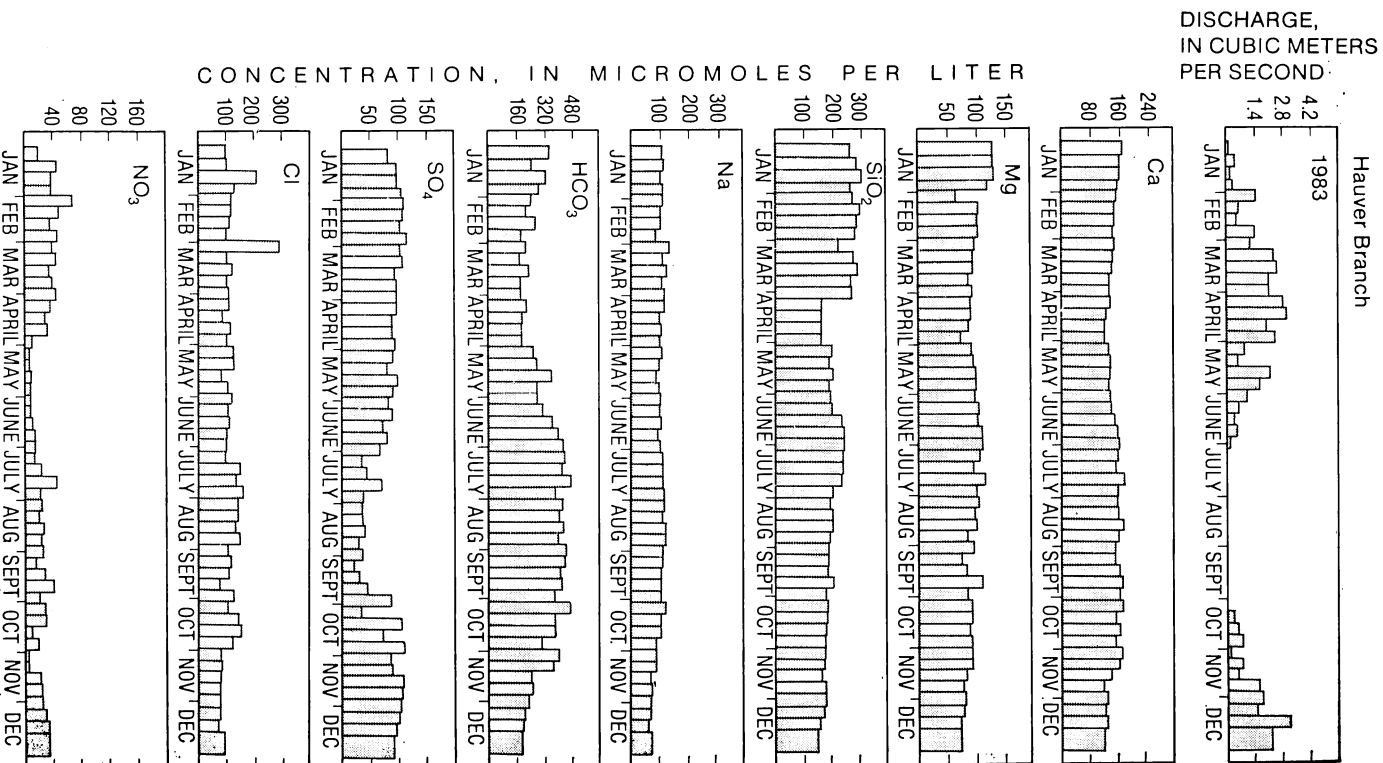
In the Catoctin watersheds, there was a 50 percent excess of sulfate in stream discharge relative to precipitation input for both years of record. There are no sources of sulfur in the watersheds (except very minor amounts of pyrite in fresh greenstone); thus we conclude that the excess sulfate in stream discharge reflects dry deposition input. Studies in western Maryland (Campbell, Scott, and Quinn, 1983) and north-central Virginia (O. P. Bricker, U.S. Geol. Survey, written commun., 1984) have found a similar enrichment of sulfate in stream discharge and have attributed this enrichment to dry deposition of sulfur species. Dry deposition of sulfur may occur in a number of different forms (gypsum, anhydrite, $(\text{NH}_4)_2\text{SO}_4$, H_2SO_4 , and gaseous SO_2 which is oxidized to SO_4^{2-} in the watershed). We have not identified the form of dry sulfur deposition to the Catoctin watersheds; however, the geochemical balance suggests that it most probably enters as gaseous SO_2 or as ammonium sulfate. If there were a significant amount of calcium associated with the sulfate (gypsum or anhydrite) the geochemical budget (after correction for road salt), instead of balancing, would show a large deficit for Ca^{+2} . Pratt and Krupa (1985) found that sulfate was the dominant component of aerosols at sampling sites in Minnesota and Wisconsin. It occurs mainly as ammonium sulfate and ammonium bisulfate in the fine particle fraction ($<2.5\ \mu\text{m}$ aerodynamic diameter). Calcium, on the other hand, constituted only a

Fig. 7



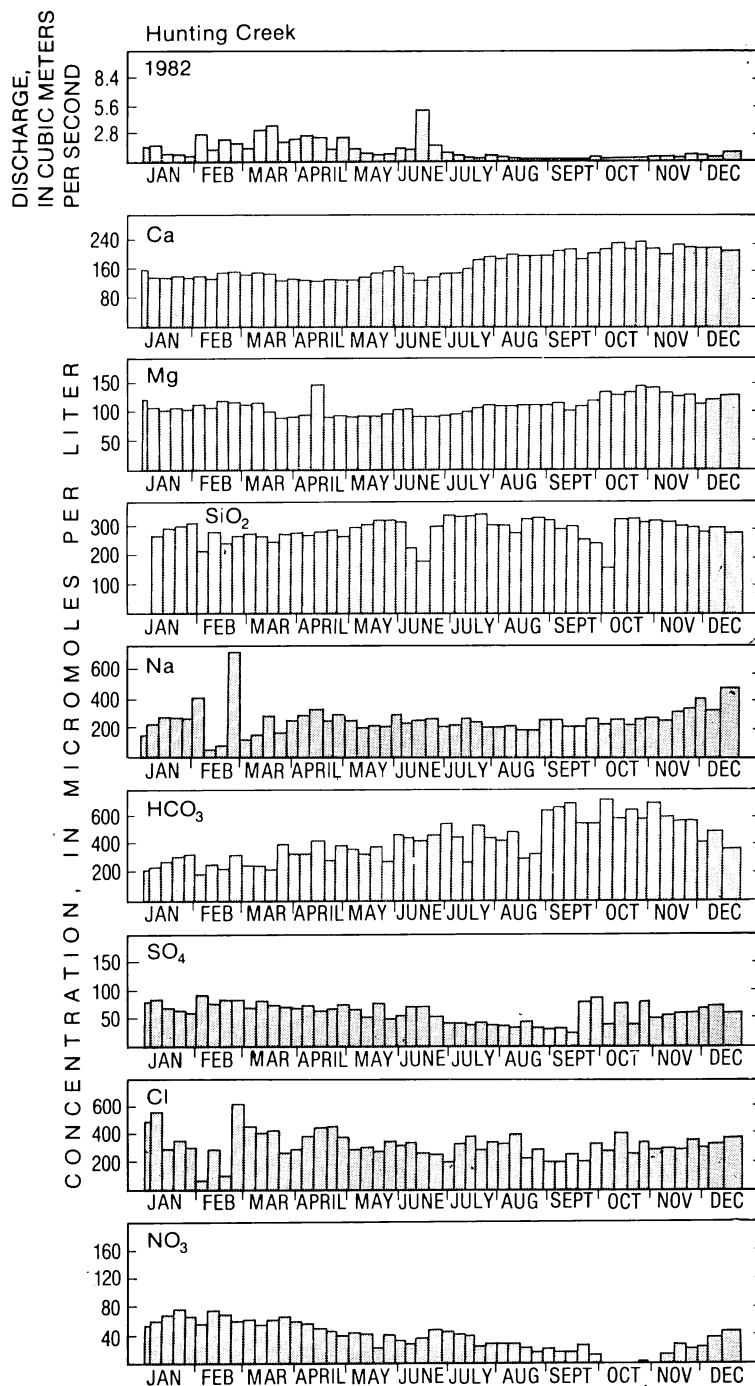
A. Weekly discharge values and concentrations of major ions and silica in Hauver Branch stream water for 1982.

Fig. 7 (continued)



B. Weekly discharge values and concentrations of major ions and silica in Hauver Branch stream water for 1983.

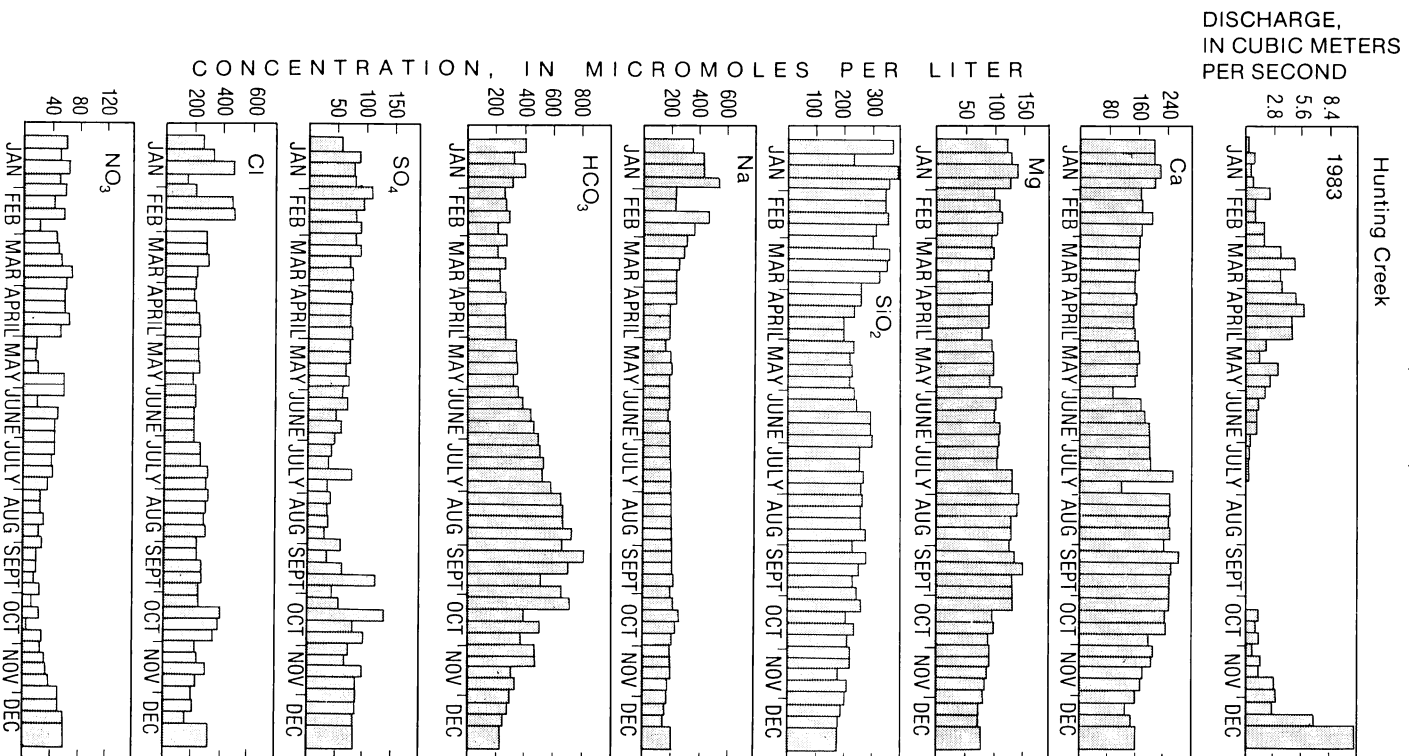
Fig. 8



A. Weekly discharge values and concentrations of major ions and silica in Hunting Creek stream water for 1982.

Fig. 8 (continued)

Hunting Creek



B. Weekly discharge values and concentrations of major ions and silica in Hunting Creek stream water for 1983.

TABLE 2
A. Seasonal and annual loads of major ions and silica in input (I) as precipitation
and in output (O) as stream water for Hauver Branch watershed, 1982

All values in moles/hectare

		H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	HCO ₃ ⁻	H ₄ SiO ₄	Total dissolved load
Jan. - Mar.	I	140.	10.8	3.09	12.9	8.57	12.0	43.3	58.5	--	--	289.
	O	0.352	260.	244.	217.	18.1	242.	233.	146.	529.	527.	2420.
Apr. - Jun.	I	283.	9.69	2.40	38.6	2.11	34.8	81.6	74.0	--	--	526.
	O	0.134	199.	175.	242.	15.0	276.	164.	44.2	625.	343.	2080.
Jul. - Sep.	I	325.	10.3	2.18	13.0	3.12	11.4	57.2	43.0	--	--	465.
	O	0.0085	17.7	12.3	15.2	1.13	15.9	15.9	1.97	52.7	20.9	154.
Oct. - Dec.	I	64.1	7.42	2.04	15.3	9.62	30.5	24.0	18.6	--	--	172.
	O	0.0124	32.9	222.	24.4	3.27	24.0	14.4	2.13	74.4	41.9	439.
Annual load	I	812.	38.2	9.71	79.8	23.4	88.7	206.	194.	--	--	1450.
	O	0.507	510.	653.	499.	37.5	558.	427	194.	1280.	933.	5090

B. Seasonal and annual loads of major ions and silica in input (I) as precipitation
and in output (O) as stream water for Hunting Creek watershed, 1982

All values in moles/hectare												
Jan. Mar.	I	140.	10.8	3.09	12.9	8.57	12.0	43.3	58.5	--	--	289.
	O	0.241	297	225.	546.	27.1	712.	160.	125.	539	575.	3210.
Apr. Jun.	I	283.	9.69	2.40	38.6	2.11	34.8	81.6	74.0	--	--	526.
	O	0.098	252	185.	508.	30.9	603.	120.	75.3	731	452	2960.
Jul. Sep.	I	325.	10.3	2.18	13.0	3.12	11.4	57.2	43.0	--	--	465.
	O	0.011	54.4	31.9	69.8	7.64	92.4	13.0	8.13	134	76.2	487.
Oct. Dec.	I	64.1	7.42	2.04	15.3	9.62	30.5	24.0	18.6	--	--	172.
	O	0.009	59.1	35.0	98.2	9.82	88.9	16.1	6.11	139	79.5	532.
Annual load	I	812.	38.2	9.71	79.8	23.4	88.7	206.	194.	--	--	1450.
	O	0.359	663.	477.	1220.	75.5	1500.	309	215.	1540.	1180.	7190.

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TABLE 2 (continued)
C. Seasonal and annual loads of major ions and silica in input (I) as precipitation
and in output (O) as stream water for Hauver Branch watershed, 1983

All values in moles/hectare

		H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	HCO ₃ ⁻	H ₄ SiO ₄	Total dissolved load
Jan. Mar.	I	195.	19.0	1.81	22.7	4.57	44.8	66.8	83.4	--	--	438.
	O	0.224	377.	267.	307.	12.4	338.	276.	118.	587.	681.	2960.
Apr. Jun.	I	312.	27.3	9.46	28.9	4.31	53.1	134.	109.	--	--	678.
	O	0.153	291.	222.	229.	10.0	238.	206.	38.1	596.	406.	2240.
Jul. Sep.	I	267.	16.9	4.13	11.3	2.78	50.5	98.2	56.5	--	--	507.
	O	0.007	10.6	6.73	7.51	0.863	8.72	3.01	1.86	28.2	13.2	80.7
Oct. Dec.	I	319.	19.3	8.03	46.9	2.58	81.2	57.2	71.7	--	--	606.
	O	0.204	249.	161.	142.	11.7	173.	195.	51.1	473.	319.	1780.
Annual load	I	1093.	82.5	23.4	110.	14.2	230.	356.	321.	--	--	2230.
	O	0.588	928.	657.	686.	35.0	758.	680.	209.	1680.	1420.	7060.

D. Seasonal and annual loads of major ions and silica in input (I) as precipitation
and in output (O) as stream water for Hunting Creek watershed, 1983

All values in moles/hectare												
Jan. Mar.	I	195.	19.0	1.81	22.7	4.57	44.8	66.8	83.4	--	--	438.
	O	0.183	418.	255.	695.	32.0	630.	205.	141.	639.	793.	3810.
Apr. Jun.	I	312.	27.3	9.46	28.9	4.31	53.1	134.	109.	--	--	678.
	O	0.147	376.	234.	451.	31.2	560.	170.	120.	778.	556	3280.
Jul. Sep.	I	267.	16.9	4.13	11.3	2.78	50.5	98.2	56.5	--	--	507.
	O	0.003	19.7	11.1	16.8	2.03	23.4	4.52	0.252	51.7	21.8	151.
Oct. Dec.	I	319.	19.3	8.03	46.9	2.58	81.2	57.2	71.7	--	--	606.
	O	0.188	433.	218	492.	43.3	688.	226.	131.	777.	520.	3530.
Annual load	I	1093.	82.5	23.4	110.	14.2	230.	356.	321.	--	--	2230.
	O	0.521	1250.	719.	1660.	109.	1900.	606.	392.	2250.	1890.	10,800

TABLE 3
Atmospheric deposition contribution to total dissolved stream loads,
in percent, for the two study watersheds in 1982 and 1983

	Hauver Watershed	Hunting Creek Watershed
1982	16	12.1
1983	19	13.7

small percentage of the aerosol and was associated with crustal components in the coarse fraction. This is similar to observations on aerosol composition in the Eastern United States by Charlson and others (1978). Paces (1985) found that SO_2 is currently the major dry deposition source of sulfate to watersheds in central Europe. Rates of sulfur dioxide adsorption onto leaf surfaces and stomatal uptake have been reported by Taylor and others (1983). Garland and Branson (1977) found that in addition to surface adsorbed SO_2 , a significant fraction of internally adsorbed SO_2 is leachable from foliage as sulfate. Richter, Johnson, and Todd (1983) found up to 40 percent more sulfate in deciduous throughfall than in atmospheric deposition from open areas in the Walker Branch watershed, Tennessee. In northern Virginia, Puckett (1985, personal commun.) found an increase of 40 to 50 percent in the sulfate concentration of throughfall under mixed deciduous and coniferous canopies compared to precipitation collected in open areas.

Vegetation may affect the material balance in a watershed if the growth and decay terms are not equal or if material is removed by harvesting (Vitousek and Reiners, 1976; Likens and others, 1978; Vitousek and others, 1979; Gorham, Vitousek, and Reiners, 1979). Both Catoclin watersheds are covered by mature eastern hardwood forests. No timber harvesting has been done for at least 40 yrs. As a first approximation, we will assume that the biomass is in dynamic equilibrium. If this is not correct and if significant material is taken up from or contributed to the watershed by the biomass, it will be reflected in the geochemical budget as a surplus or deficit.

Weathering Reactions and Watershed Geochemistry

In order to quantify the chemical reactions occurring in the watershed and develop a geochemical mass balance, water chemistry data need to be integrated with mineralogical data. The major reactive minerals in the watersheds, based on petrographic examination of thin sections and field observations, are chlorite [$\text{Mg}_5\text{Al}_2(\text{Si}_3\text{O}_{10})(\text{OH})_8$] and albite ($\text{NaAlSi}_3\text{O}_8$), with smaller amounts of epidote [$\text{Ca}_2\text{FeAl}_2\text{Si}_3\text{O}_{12}(\text{OH})$], actinolite [$\text{Ca}_2(\text{Mg}_3\text{Fe}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$], and calcite (CaCO_3). Studies of greenstone in Maryland (Stose and Stose, 1946) and in Virginia (Reed, 1955) report this same assemblage of minerals. X-ray diffraction studies of the soil and saprolite show that kaolinite is a major clay mineral, although interstratified clays and vermiculite are also present. Albite appears to

weather directly to kaolinite. Chlorite first weathers to an interstratified clay, then to vermiculite, and finally to a kaolin mineral. This weathering sequence has been studied by Johnson (1964) at a locality in the Catoctin Formation to the north of our study area. Ross and Kodama (1976) simulated the first part of the weathering sequence (chlorite to chlorite-vermiculite) in the laboratory by oxidizing samples of the Catoctin greenstone from the Middletown Valley of Maryland with bromine water. Herbillon and Makumbi (1975) examined soils developed on greenstone under tropical conditions in Zaire and observed the weathering sequence chlorite to vermiculite to nontronite to kaolinite. The interstratified clays and vermiculite are metastable intermediate products in the alteration of chlorite to kaolinite, but it is the net reaction chlorite to kaolinite that appears to control the water composition. Stream-water compositions plotted on an activity diagram depicting equilibrium relations in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ suggest that kaolinite should be the stable phase in contact with this water (fig. 9). The same relation obtains in the system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. Small amounts of smectite clay are observed in some of the poorly drained flood plain soils, and hydrous iron oxides are common in the weathered material and soils.

Detailed investigation of the clay minerals is currently underway; however, this preliminary description is sufficient to provide a framework for assessing the evolution of solute composition in the watershed.

The water that reacts with the minerals in the soil and bedrock falls as precipitation charged with strong acids. In addition, biological processes in the soil contribute carbon dioxide to the soil atmosphere at concentrations well above those in the ambient atmosphere. The strong acids from precipitation, together with carbonic acid from the soil, attack minerals and release dissolved components to the water. If the aggressive agent is a strong acid, the accompanying anion (SO_4^{2-} , NO_3^- , Cl^-) will balance the base cations released. If carbonic acid is the weathering agent, bicarbonate anion will balance the cations released.

Consider the annual input versus output balance for Hauver Branch in 1982. To determine the dissolved constituents contributed by weathering reactions, the total annual load of constituents in precipitation is subtracted from the total annual load carried from the watershed by the stream. We assume that all the excess chloride in stream water, after subtracting the atmospheric input, comes from road salt. These salts contribute large quantities of sodium, calcium, and chloride to the total annual load in streams draining both watersheds. Other possible sources of chloride are fluid inclusions in the rock and dry deposition of chloride compounds. At the present time, we have no means of assessing either of these sources, and we will assume they are negligibly small. In the Hauver Branch watershed, 17 and 13 percent of the total annual load of the stream was supplied by road salt, and in the Hunting Creek watershed, 37 to 29 percent of the total annual load was furnished from road salt in 1982 and 1983, respectively. It appears that most of this chloride is flushed from the system by the end of the second quarter of the year, since, in

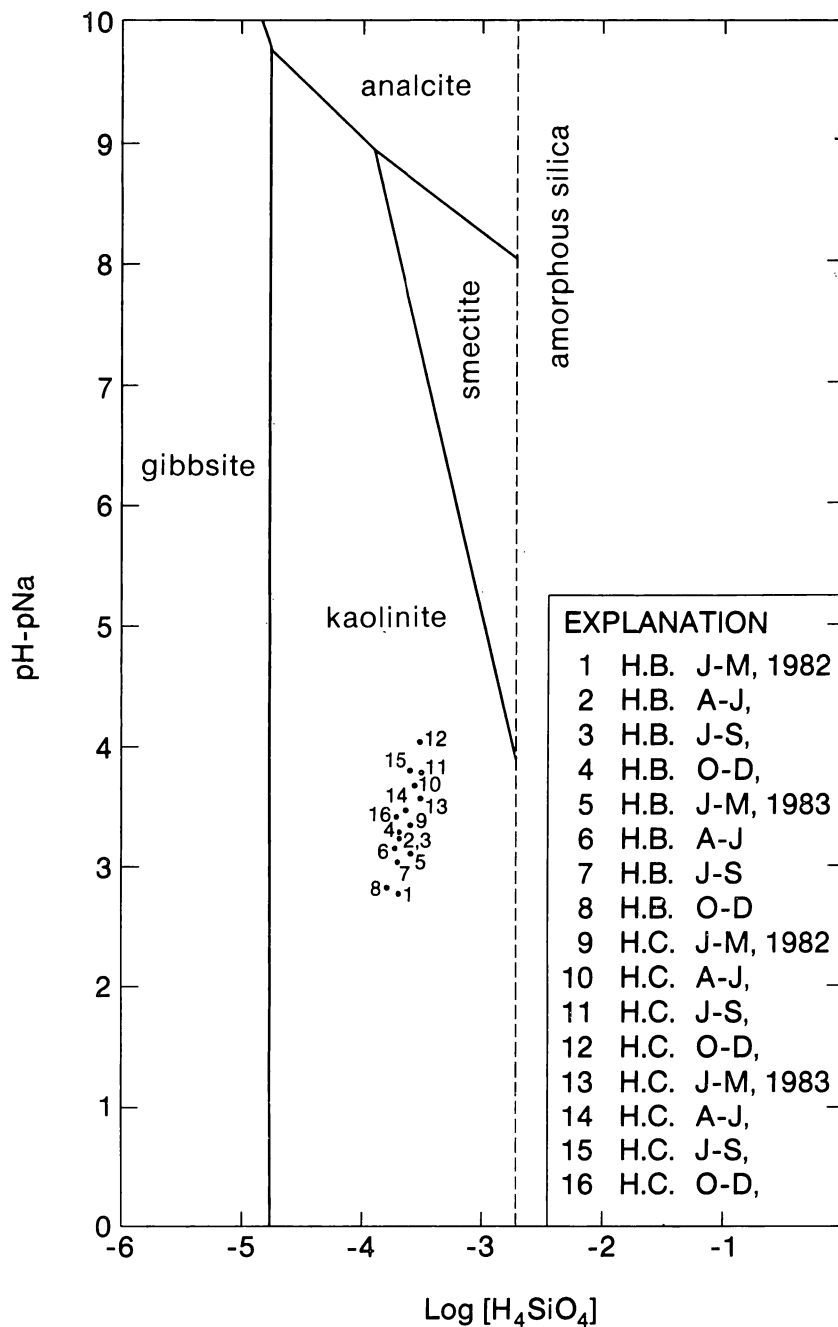


Fig. 9. Activity diagram for the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ showing the seasonal composition of water from Hauver Branch (HB) and Hunting Creek (HC) during 1982 and 1983 (modified from Drever, 1982).

the summer and early fall, the atmospheric input of chloride is closely matched by the chloride in stream discharge (table 2A, B, C, and D). Subtracting the road salt component leaves those constituents that are released or consumed within the watershed (table 4).

We are now in a position to examine the materials supplied by mineral weathering reactions in the watershed. The only mineral source of sodium in the watershed is albite. Although calcium, magnesium, and silica have multiple mineral sources in the watershed, the amount of each of these minerals (calcite, chlorite, albite, and actinolite) that must react is

TABLE 4
Reactions among the major minerals in greenstone; hydrogen ion from atmospheric deposition and soil generated carbonic acid from soil processes; Hauver Branch stream water 1982

(values in moles/hectare)								
Constituent	H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	HCO ₃ ⁻	H ₄ SiO ₄
Output	0.5	510.	653.	499.	37.5	558.	1280	933
Input	812.	38.	10.	80.	23.4	89.	0	0
Output-Input	-812.	472.	643.	419.	14.1	469.	1280	933
Deicing salt .75 CaCl ₂ .25 NaCl	0	176.	0	103.	14.1	469.	1280	933
Consumed or released in watershed	-812.	296.	643.	316.	0	0	1280	933

Reactions

1. $\text{NaAlSi}_3\text{O}_8 + \text{H}^+ + 9/2 \text{H}_2\text{O} \rightleftharpoons \text{Na}^+ + 1/2 \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2 \text{H}_4\text{SiO}_4$
2. $\text{CaCO}_3 + \text{H}^+ \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^-$
3. $\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 10 \text{H}^+ \rightleftharpoons 5\text{Mg}^{+2} + \text{H}_4\text{SiO}_4 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 5\text{H}_2\text{O}$
4. $\text{Ca}_2(\text{Mg}_3\text{Fe}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2 + 14 \text{H}^+ + 8 \text{H}_2\text{O} \rightleftharpoons 2 \text{Ca}^{+2} + 3 \text{Mg}^{+2} + 2 \text{Fe}^{+2} + 8 \text{H}_4\text{SiO}_4$
5. $\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$

Mass Balance Equations

1. $[\text{Na}^+] = \text{albite}$
2. $[\text{Ca}^{2+}] = \text{calcite} + 2 \text{ actinolite}$
3. $[\text{Mg}^{+2}] = 3 \text{ actinolite} + 5 \text{ chlorite}$
4. $[\text{H}_4\text{SiO}_4] = 2 \text{ albite} + \text{chlorite} + 8 \text{ actinolite}$
5. $[\text{HCO}_3^-] = \text{calcite} + [\text{H}_2\text{CO}_3]$
6. $[\text{H}^+] = \text{albite} + \text{calcite} + 10 \text{ chlorite} + 14 \text{ actinolite} - [\text{H}_2\text{CO}_3]$

minerals consumed	dissolved constituents produced		H ⁺ and H ₂ CO ₃ reacted	
albite	316	Na ⁺	316	HCO ₃ ⁻
calcite	249	Ca ⁺²	296	H ⁺
chlorite	115	Mg ⁺²	643	H ₂ CO ₃
actinolite	23.3	H ₄ SiO ₄	933	

constrained by the observed water chemistry. Enough calcite and actinolite must be consumed to provide the dissolved-calcium load of the stream, enough chlorite and actinolite must be consumed to provide the dissolved-magnesium and the remaining silica load of the stream, and enough of the minerals must react with carbonic acid to provide the observed bicarbonate load of the stream. Epidote, present in small and spatially variable amounts in the greenstone, commonly stands out in relief with quartz on weathered surfaces suggesting that it is more resistant to weathering than the other minerals in the greenstone and probably plays a negligible role in governing water chemistry. Calcite, although it is present in only small amounts, plays a major role in governing water chemistry because of its great reactivity and its localization in the hydrologic flow paths of the watersheds. If it is assumed that all the calcium is derived from the weathering of silicate minerals and none from calcite, the bicarbonate and dissolved silica will not balance.

The system can be cast in terms of five unknowns (the amounts of albite, actinolite, chlorite, and calcite weathered and the amount of H_2CO_3 consumed) and six mass balance equations (for H^+ , Ca^{2+} , Mg^{2+} , Na^+ , H_4SiO_4 , and HCO_3^-) (table 4). Any five of the mass balance equations can be used to solve for the unknowns. The solution must satisfy the sixth equation, if the fluxes are accurate and the stoichiometries properly constrained. Solution of these equations reveals that the total amounts of minerals weathered and carbonic acid consumed are a mathematically unique solution to this system of equations. There is no way to get any other amounts without changing either the reaction stoichiometries or the fluxes.

The calculations show that the major changes in chemistry can be accounted for by mineral weathering, suggesting that other processes such as ion exchange and biological activity play a secondary role, at most, in determining stream chemistry in the watersheds. A number of studies have shown that atmospheric inputs and recycling of the forest litter may account for most of the forest nutrient requirements for alkali and alkaline earth elements (Graustein and Armstrong, 1983; Art and others, 1974; Stone and Kszyszniak, 1977; Swank, 1984). Stream chemistry should then reflect mineral weathering reactions in the watershed with little or no biological overprint (Smith and Dunn, 1977; Velbel, 1984). Figure 10 shows a graphical reconstruction of the chemical composition of Hauver Branch stream water, 1982. Based on the input/output budget and the above calculations, strong acids from precipitation contributed 4.5 moles (40 percent) of H^+ and carbonic acid from soil solutions contributed 6.7 moles (60 percent) of H^+ to mineral weathering at Hauver Branch in 1982. In a study of the Astadalen watershed, southeast Norway, atmospheric deposition was found to contribute about 50 percent of the H^+ utilized in mineral weathering (Jens-Olaf Englund, 1985, personal commun.). Richter, Johnson, and Todd (1983) estimated that about 20 percent of the base cation flux from the soils of two eastern Tennessee watersheds was attributable to atmospheric inputs of strong acid. If the above scenario reasonably approximates the real system, 34 percent of the neutralization

of H^+ input from precipitation and carbonic acid was accomplished by reaction with calcite, 46 percent by reaction with albite, 17 percent by reaction with chlorite, and 3 percent by reaction with actinolite.

SUMMARY AND CONCLUSIONS

Input/output mass balances for major dissolved constituents were developed for the Hauver Branch and Hunting Creek watersheds for 1982 and 1983. Dissolved solutes introduced in wet precipitation account for 12 to 19 percent of the load of the streams draining the two watersheds. There was a 50-percent excess of sulfate in stream discharge relative to precipitation input for both 1982 and 1983. There are no sources of sulfur in these watersheds. Thus, we conclude that excess sulfate in stream discharge reflects input of dry deposition. Other studies in the mid-Atlantic region and the southeastern United States support this conclusion. There is a net export of silica, base cations (calcium, magnesium, and sodium), and bicarbonate in stream water relative to the amounts of the constituents in precipitation input. Geochemical weathering reactions of the primary and secondary minerals in the bedrock underlying the study area

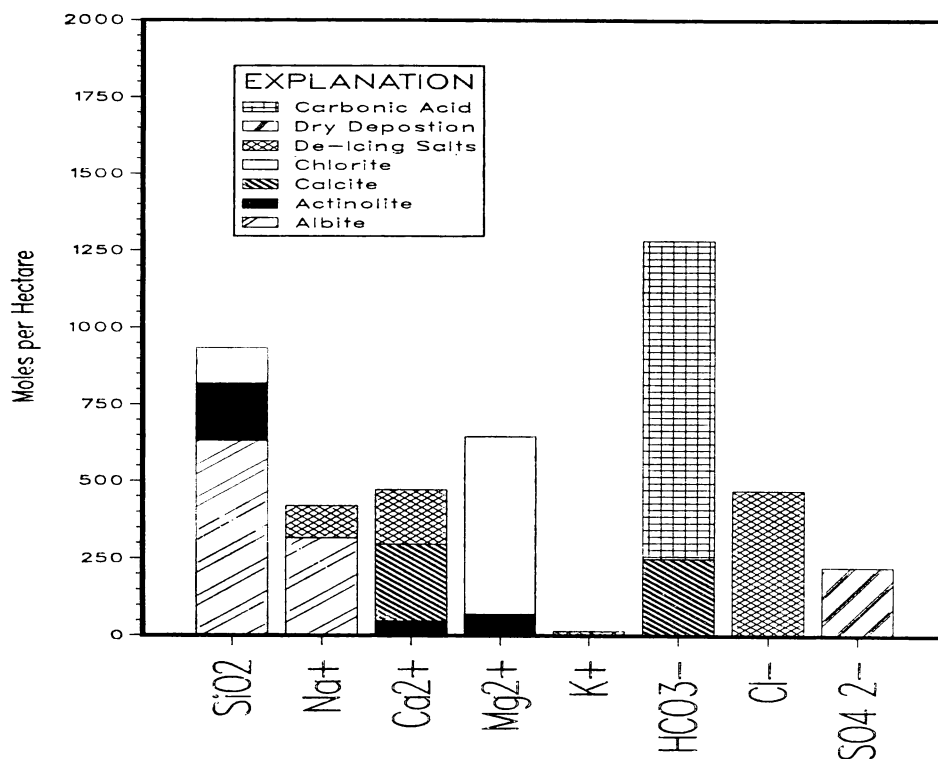


Fig. 10. Reconstruction of chemical composition of Hauver Branch stream water, 1982, from weathering of primary and secondary minerals in metabasalt, road de-icing salts, and dry deposition.

(chlorite, albite, epidote, actinolite, and calcite) account for the excess quantities of these constituents in stream water relative to incoming wet deposition to the area. Dissolution of calcite and albite account for at least 60 percent and as much as 90 percent of the neutralization of the total H^+ input from precipitation and from carbonic acid weathering. Even though calcite is present in the bedrock in extremely small amounts, it plays a major role in governing water chemistry because of its high reactivity and its location in the hydrologic flow paths in the watersheds. Other watershed processes such as constituent cycling by biomass or cation exchange appear to be of minor importance in influencing the chemistry of the streams draining both watersheds.

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