

Hydrologic processes controlling sulfate mobility in a small forested watershed

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Abstract. Hydrologic controls on sulfate mobility were investigated in a forested catchment in the Georgia Piedmont using a watershed mass balance approach. Variations in annual sulfate export were governed primarily by differences in runoff rather than by differences in sulfate deposition or in total annual precipitation. However, 2 years with similar total runoff had substantially different sulfate export. A residual analysis indicated that a shift in the concentration-discharge relationship accounted for 72% of the difference in sulfate export and that a change in the pattern of discharge accounted for the remainder of the difference. Stream water sulfate concentrations reflected past hydrologic conditions. Concentrations at the same discharge were higher following an extended dry period than following average periods. The elevation in stream water sulfate concentrations following dry periods persisted for several months. The influence of rainfall patterns on sulfate export underscores the need for long-term records to adequately characterize the acidification status of the watershed and to understand trends in water quality.

Introduction

Processes controlling sulfate mobility in forest ecosystems are important in determining watershed sensitivity to acidic deposition [Reuss and Johnson, 1986; Galloway *et al.*, 1983]. Watersheds dominated by soils that retain a majority of atmospherically deposited sulfate along principal hydrologic flowpaths are considered less sensitive to acidification over periods of several decades than ones that do not. Atmospherically deposited sulfur has been responsible for acidification of surface waters [National Research Council, 1986; Sullivan *et al.*, 1990] and soils [Ronse *et al.*, 1988; Billet *et al.*, 1990; Björnstad, 1991; Johnson *et al.*, 1991; Kylenstierna and Chadwick, 1991] in sensitive environments in northern temperate regions.

Sulfur is involved in numerous reactions that can influence its net retention or release. Sulfur retention has traditionally been considered as principally a mineral adsorption process [Singh, 1984; Reuss and Johnson, 1986]. Sulfur can also be incorporated into soil organic matter [David and Mitchell, 1987; Strickland *et al.*, 1986; Schindler *et al.*, 1986] or taken up by plants through roots or by stomatal uptake [Murphy and Sigmon, 1990; Goldan *et al.*, 1988]. The potential for S uptake by plants generally does not exceed 10% of total ecosystem retention [Turner *et al.*, 1990] and is usually important only where sulfate loading is low. Under anoxic conditions sulfate may be microbially reduced to sulfide and combine with Fe^{2+} to form monosulfides and FeS_2 [Berner, 1984]. These sulfides are reactive and may oxidize during dry periods and be leached during storms to produce episodic increases in stream water sulfate concentrations [Seip *et al.*, 1985; Kirchner *et al.*, 1992]. Alumino-sulfate precipitation and dissolution has also been proposed as a mechanism controlling sulfate concentrations in surface water, but

Reuss and Johnson [1986] concluded that it is unlikely that either alunite or basaluminite control the solubility of Al or sulfate in soils affected by acid deposition.

Less attention has been directed toward hydrologic control of sulfate transport that integrates the net effects of all mechanisms governing sulfur retention and release. One way to assess hydrologic control on stream water sulfate concentrations is to compare concentration-discharge relationships between sites. For some sites in the northeastern United States and Canada little variation in sulfate concentration with variation in hydrologic conditions has been reported [Likens, 1977; Haines *et al.*, 1989], and relatively small increases have been reported between preepisode and peak episode conditions for other watersheds in this region [Wigington *et al.*, 1990]. Increases in sulfate concentration with increasing discharge reported for some watersheds in the northeastern United States may be a direct result of acidic precipitation and wash-off of dry deposition, preferential elution during melting of a snowpack, or storm water drainage through acidified surface horizons [Wigington *et al.*, 1990]. Several studies conducted in the northeastern United States reported decreasing sulfate concentrations with increasing discharge [Schofield *et al.*, 1985; Swank and Waide, 1988; Schaefer *et al.*, 1990; Murdoch and Stoddard, 1992]. Decreasing sulfate concentration with increasing discharge generally is attributed to dilution during storms or snowmelt. In some watersheds, a direct concentration-discharge relationship has been reported for both seasonal and episodic variations in discharge [Lynch and Corbett, 1989; Shriner and Henderson, 1978; Buell and Peters, 1988; Seip *et al.*, 1989]. In such watersheds the direct relationship is thought to be a result of water draining through more acidified surface soil flowpaths under high discharge conditions. The acidified surface soil horizons have substantially higher equilibrium surface concentrations than soils in deeper flowpaths which have a much larger sulfate adsorption capacity.

Two recent studies have reported linkages between hydro-

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logic conditions and sulfate mobilization and transport. *Lynch and Corbett* [1989] suggested that the direct concentration-discharge relationship they observed could be explained by temporary storage of sulfate during the growing season when evapotranspiration greatly reduced runoff. Hydrologic conditions that increased the areal extent of the saturated zone contributed to storm water drainage during the dormant season, and resulted in mobilization and transport of stored sulfate. An extreme case of storage and remobilization was recently reported for the Plastic Lake catchment in Ontario, Canada. Following four successive drought years, during which streamflow ceased for 3–4 months, stream water sulfate concentrations were highly elevated and remained high for several months [*Kirchner et al.*, 1992]. However, at the Plastic Lake catchment, there was no relationship between discharge and sulfate concentration.

The objective of this study was to examine hydrologic control of sulfate mobility in a sulfate-retaining, southeastern United States forested catchment using a mass balance approach. The emphasis of the analysis is on the linkage between inter- and intraannual variations in precipitation and watershed chemical response. Many studies have provided model predictions of watershed acidification with alternate sulfur deposition scenarios, but those studies generally do not consider uncertainties associated with climate variability. The importance of precipitation amount and distribution may be accentuated in the southeastern United States where high evapotranspiration exerts much greater control on runoff than in the northeastern United States and Canada.

Site Description

The Panola Mountain Research Watershed (PMRW) is a 41-ha catchment in the Georgia Piedmont near Atlanta, Georgia (84°10'W, 33°37'N) (Figure 1). The maximum altitude in the watershed is 279 m above sea level, and the relief is 55 m. The catchment is 93% forested, and the remaining 7% consists of a 3-ha granite outcrop which includes extensive lichen and moss communities as well as some small islands of herbaceous and woody vegetation. The bedrock is dominated by Panola granite [*Atkins and Higgins*, 1980] which intrudes older surrounding country rock of the Clairmont Formation, an amphibolite-rich biotite gneiss matrix [*Higgins et al.*, 1988]. A more comprehensive site description and characterization of data records have recently been published [*Huntington et al.*, 1993].

The forest consists of even-aged deciduous or mixed deciduous and coniferous stands and a smaller proportion of predominantly coniferous stands. The communities on mesic sites are dominated by *Carya tormentosa* (mockernut hickory), *Carya glabra* (pignut hickory), *Quercus rubra* (northern red oak), *Quercus alba* (white oak), and *Liriodendron tulipifera* (tulip poplar) [*Carter*, 1978; *Skeen et al.*, 1980]. The dominant coniferous species is *Pinus taeda* (loblolly pine) which occurs mainly in more xeric environments and in an early successional stand. The forest composition and age structure reflect past land use and periods of agricultural abandonment [*Nelson*, 1957; *Brender*, 1974]. The forests in this part of the Piedmont were first settled and extensively cleared in the early 1800s [*Brender*, 1974]. Subsistence farming was replaced with cotton production after 1893. The

use of poor farming practices and steep slopes resulted in extensive erosion, causing substantial loss of topsoil and gullying [*Brender*, 1974]. Currently, at PMRW, deciduous and mixed forest stands are present in areas abandoned in the early 1900s, whereas a smaller coniferous stand is in an area that was farmed as recently as the early 1960s.

Soils are predominantly Ultisols developed in colluvium and residuum intergrading to Inceptisols developed in colluvium, recent alluvium, or in highly eroded landscape positions. Smaller areas of Entisols, developed in alluvium, occur along stream banks and in a small, poorly drained floodplain near the confluence of three tributaries near the watershed outlet. Typical profiles range from 0.6 to 1.6 m of soil over saprolite of variable thickness. The depth of saprolite typically ranges from 0 to 5 m over Panola Granite and 5 to 20 m over the Clairmont Formation. The soils at PMRW are similar to other soils of the southeastern United States, which generally have high sulfate adsorption capacities because of their high clay sesquioxide content. Substantial net sulfur retention has been reported in watershed studies at PMRW [*Shanley*, 1989] and at other sites in the southeastern United States [*Rochelle et al.*, 1987; *Buell and Peters*, 1988; *Shriner and Henderson*, 1978].

The long-term mean annual precipitation for Atlanta, Georgia, 20 km west of PMRW, is 124 cm, >98% of which is rain [*U.S. Department of Commerce*, 1931, 1961, 1991]. Frontal storms occur in winter (December through March), and thunderstorms occur in spring and summer. Mean annual temperature is 16.3°C. Prevailing winds are from the northwest. Streamflow is flashy, and time from maximum rain intensity to peak streamflow is typically ≤40 min [*Shanley*, 1989]. Mean annual runoff measured in much larger watersheds in the surrounding Piedmont area is 40.6 cm [*Carter and Stiles*, 1983], which corresponds to a water yield of 33%.

Methods and Measurements

Deposition Measurements

Descriptions of the methods used to estimate sulfur fluxes to and within the PMRW watershed have been reported elsewhere [*Meyers et al.*, 1991; *Shanley and Peters*, 1993; *Cappellato et al.*, 1993]. Precipitation volume was measured using replicate tipping bucket rain gauges (0.254 mm resolution). Measurements of precipitation volume were verified with independent estimates using a recording weighing bucket rain gauge and three 10-cm diameter standard rain gauges. Precipitation samples were collected as weekly composites and on a storm basis using two Aerochem Metrics, Inc. model 301 wetfall/dryfall automatic collectors. Sulfate and Cl concentrations in precipitation were measured by ion chromatography. One collector was sampled weekly and another collector was sampled on a storm basis. Concentration and flux calculations were based primarily on the weekly collections and the storm-based collector was used as a backup. The weekly based collector was located in a clearing about 1 km from the watershed, and the storm-based collector was located on the granite outcrop within the watershed (Figure 1). Wet deposition sulfur flux was calculated from the product of sulfate concentration in precipitation times the appropriate precipitation volume measured using the tipping bucket. Coverage was >99.6% over the study period for measurement of precipitation volume and

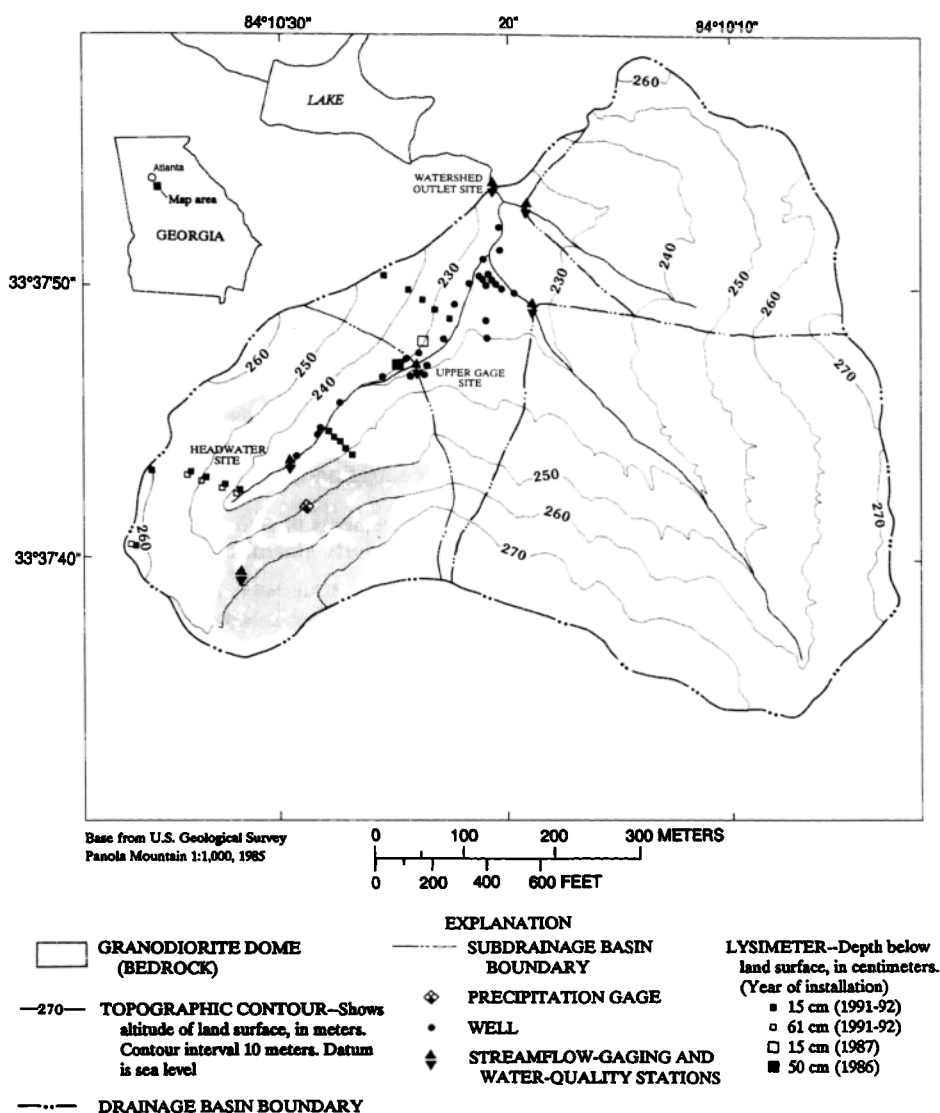


Figure 1. Map of the study area showing locations of stream water gaging, stream water quality sampling, precipitation gaging, precipitation sampling, wells, and lysimeters at the Panola Mountain Research Watershed in the southern Piedmont near Atlanta, Georgia.

sulfate concentration. Annual precipitation, runoff, and sulfur flux were computed based on water years (WY) for the period October through September.

Dry deposition was estimated using an inferential technique involving the direct measurement of ambient SO_2 and sulfate aerosols using a filter pack and estimation of deposition velocities using meteorological and vegetation data [Hicks *et al.*, 1991; Meyers *et al.*, 1991]. Dry deposition at PMRW also was estimated using throughfall measurements during the period June 1986 to November 1989 to validate the inferential technique [Cappellato *et al.*, 1993]. Throughfall measurements have been shown to correspond very closely to independent estimates of wet plus dry deposition because they include gaseous and aerosol forms that impact canopies and are washed off during storms [Joslin and Wolfe, 1992; Lindberg and Garten, 1988]. Sulfur inputs in dry deposition to the forest floor and coarse particulate ($>1 \mu\text{m}$) deposition to the canopy were not considered in this study. Coarse particulate sulfate aerosol deposition at

PMRW was estimated using the method of Lindberg and Lovett [1985] to be about 10% of total atmospheric deposition during a 2-year period [Cappellato *et al.*, 1993]. Deposition to the forest floor is reported to be about 15% of total deposition [Meyers and Baldocchi, 1993], but is sensitive to surface wetness and proportions of gaseous, fine particulate, and coarse particulate forms.

Stream Water Discharge and Sulfate Export Measurements

Stream water stage was measured at the watershed outlet (Figure 1) using a compound, sharp-crested 90° V-notch weir and a continuously recording float-counterweight mechanism that was connected to a high-precision potentiometer and data logger (0.3 mm resolution); accuracy of the stage measurements was within 3 mm. Stage was recorded every 5 min except during storms when it was recorded every 1 min. Stream water was sampled manually each week throughout the study period and during selected storms between Octo-

ber 1985 and October 1988 using stage-actuated automatic samplers. Stream water samples were collected immediately upstream of the weir where the stream was gauged. Stream water was also sampled at the upper gauge and headwater sites along the tributary in the drainage area containing the granite outcrop (Figure 1). Streamflow at these sites is ephemeral with sustained flow occurring only under wet conditions in winter or spring. The upper gauge site was sampled weekly, when flowing, throughout the study and during selected storms between October 1985 and October 1988. The headwater site was sampled intermittently throughout the study and during selected storms in water years 1991 and 1992.

Mass flux is ideally calculated as the integral of the product of discharge and concentration. However, because sulfate concentration was not measured continuously, the sulfate flux Φ was estimated as

$$\Phi \approx \int Q(t)(C'(Q^*(t), D) + \varepsilon(t)) dt \quad (1)$$

where $Q(t)$ is the instantaneous discharge, $C'(t)$ is the estimated concentration from a regression model, $Q^*(t)$ is the 1-hour running average discharge, D is the day of year, and $\varepsilon(t)$ is a piecewise linear function constructed from the model residuals so that the sum of $C'(t)$ and $\varepsilon(t)$ equaled the observed stream water concentration at every point when it was measured. The concentration-discharge relationship was modeled using a hyperbolic function (Figure 2) [Johnson *et al.*, 1969] to eliminate transformation biases that might arise if a logarithmic model was used [Cohn *et al.*, 1989]. The 1-hour average discharge was found to improve the fit of the model over the use of the instantaneous discharge because this averaging reduces the effects of hysteresis in the concentration-discharge relationship. Seasonal variations in concentration were fit using sine and cosine functions. The coefficient of determination (R^2) for this model was 0.735; all coefficients were significant at the $p = 0.01$ level.

The integral in (1) was numerically evaluated using the extended trapezoidal rule [Press *et al.*, 1986] to calculate daily mass fluxes. The time step used in the integration was halved repeatedly until the difference in the solution between iterations was <1%. A minimum of five iterations (17 equally spaced evaluations per day) was implemented to ensure that short duration events entered the calculations.

The integrand in (1) can be expanded into its two parts, so that Φ may be divided into the flux arising from the concentration-discharge model (Φ_M) and the flux from the model residuals (Φ_ε); that is,

$$\Phi = \int Q(t)C'(Q^*(t), D) dt + \int Q(t)\varepsilon(t) dt = \Phi_M + \Phi_\varepsilon. \quad (2)$$

If the model is well-posed, that is, the residuals meet the usual assumptions of normality and independence Φ_ε would be expected to be small relative to Φ_M . Furthermore, the integral of the absolute value of the residuals

$$\Phi_{|\varepsilon|} = \int Q(t)|\varepsilon(t)| dt \quad (3)$$

would be inversely related to the R^2 of the model. For example, if Φ_ε is much less than $\Phi_{|\varepsilon|}$, the model is well-posed

and has an R^2 less than 1.0. Alternatively, if Φ_ε is approximately the same magnitude as $\Phi_{|\varepsilon|}$, the model suffers from a systematic lack of fit, such as a change in the concentration-discharge relation over time. The residuals would tend to be all positive or all negative, rather than being evenly distributed around zero.

When the average sulfate concentration (that is, the sulfate flux divided by the water flux) differs between years, the relative contribution of Φ_M and Φ_ε to this change lends insight into why the change occurred. Because Φ_M incorporates the concentration-discharge model, a change in Φ_M reflects any hydrologic differences between the years (for example, more water flowing out of the catchment at higher discharge). Alternately, a change in Φ_ε indicates a change in the concentration-discharge model, either a change in the variation explained (if $\Phi_{|\varepsilon|} \gg \Phi_\varepsilon$) or a systematic shift in the concentration-discharge relation (if $\Phi_{|\varepsilon|} \approx \Phi_\varepsilon$).

Measurements of Soil Solution and Groundwater Chemistry

Soil solution was collected at two sites with $\approx 1 \text{ m}^2$ stainless steel zero tension pan lysimeters installed at 50- and 15-cm depths beginning in December 1986 and August 1987,

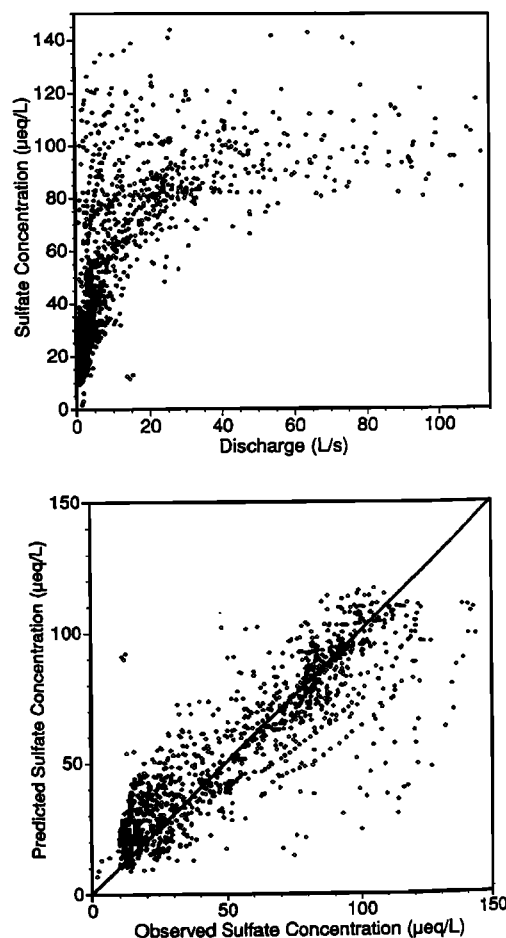


Figure 2. Relationships between (top) stream water SO_4^{2-} concentration and discharge and (bottom) observed versus predicted stream water SO_4^{2-} concentration for all samples collected at the Watershed Outlet Site at Panola Mountain Research Watershed between October 1985 and September 1992.

Table 1. Selected Annual Hydrologic, Deposition, and Concentration Measurements at the Panola Mountain Research Watershed From October 1985 to September 1992

Water Year	Rainfall, cm	Runoff, cm	Water Yield, %	Precipitation Sulfate Concentration,* $\mu\text{eq L}^{-1}$	Stream Water Sulfate Concentration,* $\mu\text{eq L}^{-1}$	Sulfur Input Wet, kg ha^{-1}	Sulfur Input Dry, kg ha^{-1}	Sulfur Input Total, kg ha^{-1}	Sulfur Export, kg ha^{-1}	Sulfur Export,† %
1986	76	15.3	20.2	47.0	28.4	5.72	5.82	11.6	0.70	6.00
1987	113	31.5	27.9	46.4	57.4	8.38	5.62	14.0	2.90	20.7
1988	100	17.8	17.9	47.8	42.8	7.64	5.10	12.8	1.22	9.55
1989	131	25.0	19.1	36.4	49.5	7.62	4.67	12.3	1.98	16.1
1990	133	55.5	41.7	39.1	53.1	8.32	4.94	13.3	4.72	35.5
1991	137	35.4	25.8	44.6	41.6	9.78	6.18	15.9	2.36	14.8
1992	119	30.4	25.4	31.5	34.3	6.00	6.24	12.2	1.67	13.7
Mean	116	30.1	26.1	41.2	43.9	7.64	5.51	13.2	2.22	16.6

*Volume-weighted annual average sulfate concentrations.

†Sulfur export as a percentage of total sulfur inputs.

respectively (Figure 1). The lysimeters were installed laterally into the upslope side of soil pits parallel to the land surface. Soil solution drained freely through polyvinyl chloride (PVC) tubing into polyethylene bottles. Soil solution was sampled sequentially during all storms from the time of lysimeter installation through October 1988, and on a fixed-interval (weekly) basis thereafter. Volume-weighted mean concentrations were computed from samples collected during storms so that soil solution chemistry could be compared by year.

The analysis in this paper uses the 5-year record from the two lysimeters described above; however, we are confident that they are representative of the soil solution chemistry of the watershed more generally, since we have compared them with many more lysimeters that have a shorter record (1.5-years). Beginning in January 1992, soil solution was also sampled from 13 additional zero tension lysimeters ($\approx 0.06 \text{ m}^2$ PVC) at 15-cm depth and 4 additional porous cup tension lysimeters at each of 15-, 30-, and 61-cm soil depths (Figure 1). Comparisons of the solution chemistry between the two lysimeters used in the long-term analysis and the newer lysimeters over the period of overlap indicates that the mean sulfate concentration of all lysimeters is within 25% of the two lysimeters at each corresponding depth (data not shown).

Groundwater was sampled monthly from 26 wells installed near the stream channel. Wells were screened from the bottom of the well for 0.6–1.5 m into saprolite and soil, depending upon thickness of the regolith. Water was pumped from the wells until approximately three well volumes were withdrawn before sample collection. Under drier conditions, wells were pumped dry, and samples were collected after recharge was sufficient to allow sampling.

Results and Discussion

Precipitation and Sulfur Deposition

During the study annual precipitation ranged from 76 to 137 cm and averaged 116 cm (Table 1). Precipitation for water years 1986 and 1988 was in the lowest quartile ($< 106 \text{ cm}$), as computed from a continuous 123-year record of precipitation for Atlanta, Georgia, 20 km west of PMRW [U.S. Department of Commerce, 1931, 1961, 1991]. In no

water year was precipitation in the highest quartile ($> 141 \text{ cm}$). Except for the two dry years precipitation ranged from the 32nd to the 70th percentiles which will be referred to as "average" precipitation.

The long-term annual precipitation distribution in Atlanta is bimodal with peaks in March and July. For the 123-year record average monthly precipitation was $\sim 12 \text{ cm}$ from December through April and $\sim 9 \text{ cm}$ from May through November [U.S. Department of Commerce, 1931, 1961, 1991]. The distribution of precipitation measured at PMRW for the study period has been somewhat different with peaks during the periods January through March and July through September; each of these periods had an average monthly precipitation of ~ 10 – 12 cm . There was a substantial variation in the intraannual temporal distribution of precipitation between years at PMRW.

The rate of sulfur deposition at PMRW ranged from 12 to $16 \text{ kg ha}^{-1} \text{ yr}^{-1}$, which is comparable to that reported at other low elevation sites in the Eastern United States and one half to one third of that observed for high elevation sites in the central and southern Appalachian Mountains and parts of the Ohio River Valley [Lindberg and Lovett, 1992]. Wet deposition of sulfur ranged from 5.7 to $9.8 \text{ kg ha}^{-1} \text{ yr}^{-1}$, and dry deposition ranged from 4.7 to $6.2 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (Table 1). Wet sulfur deposition exhibited seasonal variation that had a peak in June through August (Figure 3). The temporal pattern in dry deposition was very similar to the temporal pattern of wet deposition [Meyers et al., 1991].

Temporal Pattern of Stream Water Sulfate Concentration

Sulfate concentrations in streamwater generally exhibited seasonality, with highest concentrations during the period January through April, and lowest concentrations during the period July through October (Figure 3). This seasonal pattern is consistent with the direct concentration-discharge relationship because streamflow is highest in winter and spring. The seasonal pattern at PMRW contrasts with several other intensively studied watersheds where little seasonal variation is normally observed [Likens, 1977; Gunn and Keller, 1986; Haines et al., 1989]. A review of regional watershed concentration-discharge relationships [Wigington et al., 1990] indicates that in most systems where sulfur inputs and outputs are nearly in balance, there is little

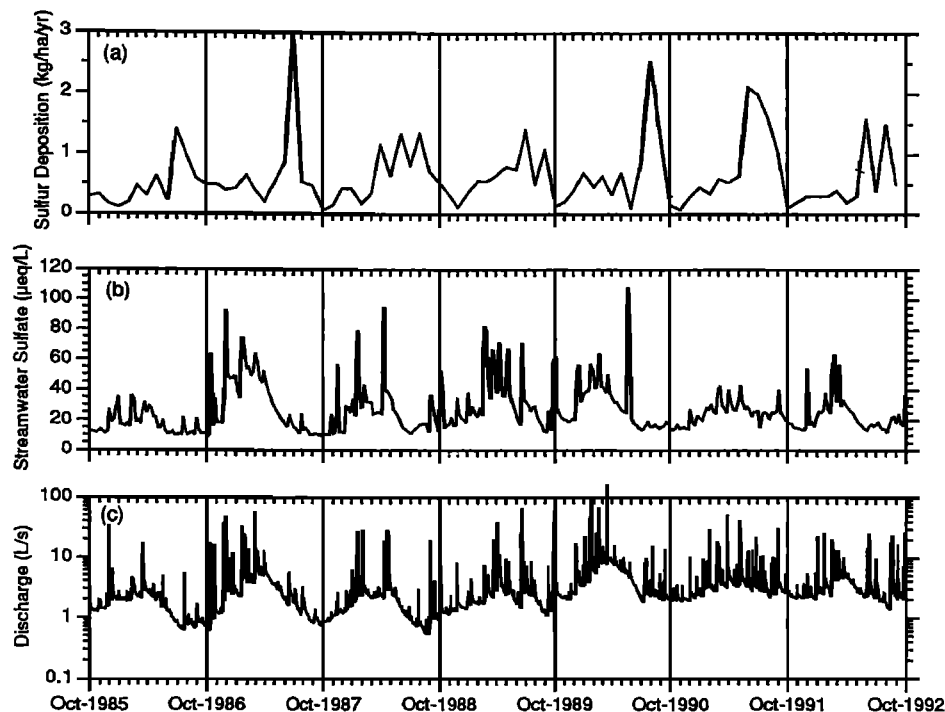


Figure 3. Variation in (a) monthly wet deposition of sulfate, (b) weekly measured streamwater sulfate concentrations, and (c) average daily stream discharge at the Panola Mountain Research Watershed from October 1985 to September 1992.

relation between streamflow and sulfate concentration. In systems that retain substantial proportions of atmospherically deposited sulfate, such as PMRW, sulfate concentration in stream water frequently increases with discharge [Shriner and Henderson, 1978; Buell and Peters, 1988; Shanley and Peters, 1993]. The Leading Ridge One (LRO) catchment in Pennsylvania is an exception because sulfate inputs and outputs are nearly in balance, but there is a well-defined positive concentration-discharge relationship [Lynch and Corbett, 1989].

Increasing sulfate concentrations during storm flow at PMRW are accompanied by rapid decreases in alkalinity that are characteristic of episodic acidification [Shanley and Peters, 1993]. Episodic acidification of streams in the northeastern United States (where watersheds generally exhibit no net annual sulfate retention) is due to dilution, as low alkalinity water is routed through surface horizons to the stream [Galloway et al., 1987; Molot et al., 1989] and generally is not accompanied by an increase in sulfate concentrations in stream water [Wigington et al., 1990].

The seasonal pattern of stream water sulfate concentrations at PMRW was in contrast to the pattern of wet and dry sulfur deposition that peaked during June through August (Figure 3). Lynch and Corbett [1989] reported a similar difference in temporal patterns between deposited and streamwater concentration at the LRO watershed in central Pennsylvania [Lynch and Corbett, 1989]. The inverse patterns in deposition and stream water sulfate concentrations at these two watersheds representing both nonsulfate retaining (LRO) and sulfate retaining (PMRW) watersheds strongly suggests that intraannual variations in stream water sulfate concentration are controlled by seasonal hydrologic

conditions which, in turn, control flowpaths rather than by deposition directly.

Runoff and Sulfate Export

Variations in the amount and distribution of precipitation during years controlled the quantity and distribution of runoff. The distribution of rainfall was particularly important because of the high potential evapotranspiration (ET) at this site. The majority of runoff was generated during the period January through May under conditions of low ET and wet conditions (Figure 3). Annual runoff ranged from about 15 to 56 cm, and water yield ranged from about 18 to 42% over the study period (Table 1). Water years 1990 and 1991 had similar total precipitation but there were about 35 cm of runoff in WY1991 compared to 56 cm in WY1990. During the period January 1 through March 15, >60 cm of precipitation occurred in WY1990 compared to <20 cm during the same period in WY1991 (Figure 4). Precipitation during the dormant season in WY1990 generated more runoff than equivalent precipitation during the growing season in WY1991 because of ET during the growing season. Evapotranspiration is highly variable in this environment as demonstrated by the ~63 cm of ET in WY1991 compared with ~33 cm in 1990. These results indicate that water is normally limiting at PMRW and that potential runoff during the growing season is limited by high ET.

Annual variations in sulfate export were more closely related to annual runoff than to precipitation or sulfur deposition (Figure 5). Annual net sulfur export ranged between 6.00 and 35.5% of total atmospheric deposition to the canopy (Table 1). The lowest annual net sulfur export occurred in the driest years (WY1986 and WY1988). During

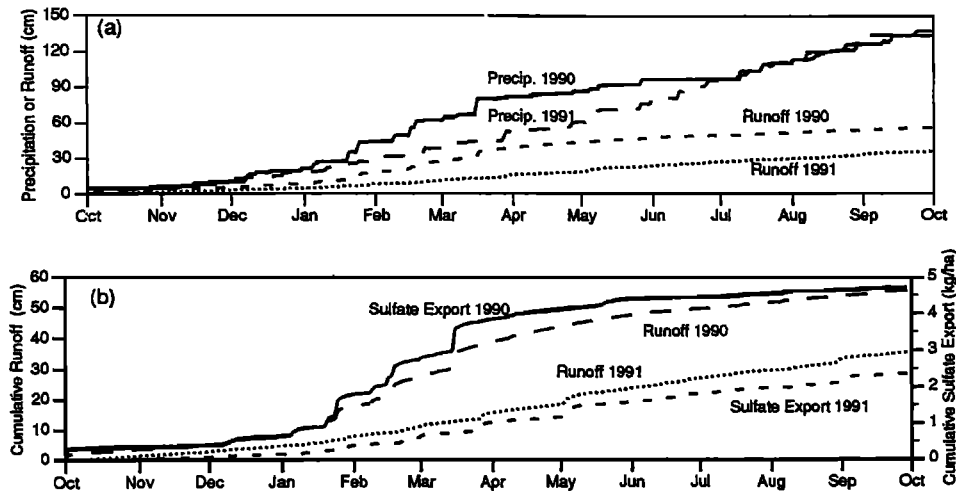


Figure 4. Cumulative (a) precipitation and runoff and (b) sulfate export and runoff for water years (October to September) 1990 and 1991 at the Panola Mountain Research Watershed.

the other 5 years of the study, sulfur retention was not correlated with precipitation (Figure 5). For example, water-years 1990 and 1991 had similar total precipitation, but sulfur export as a percentage of total sulfur deposition was 35.5%

in WY1990, compared with 14.8% in WY1991. Sulfate export from the watershed tracked runoff very closely during both WY1990 and WY1991 (Figure 4), indicating that in these years, sulfate export was directly proportional to runoff, despite seasonal differences in precipitation. On an annual average basis the watershed retained 83% of all sulfur deposited.

Variations in sulfate export between years having similar total runoff were explained by differences in the pattern of discharge and changes in the concentration-discharge relation. In water years 1987 and 1992 there were similar amounts of precipitation and runoff but there was substantially more sulfate exported in WY1987 (Figure 6). The temporal pattern of discharge and sulfate export in WY1987 indicated that three distinct periods in November 1986, January 1987, and February 1987 generated large amounts of runoff and sulfate export (Figure 6). In WY1987 more runoff occurred at higher discharges than in WY1992 (Figure 7); for example, ~24% of all runoff in WY1987 occurred at discharges ≥ 20 L/s compared with ~13% in WY1992. Runoff at higher discharges in WY1987 transported more sulfate than runoff in WY1992 as a result of the direct concentration-discharge relationship (Figure 2). The direct concentration-discharge relationship observed at PMRW is thought to be a result of variation in flowpath [Shanley and Peters, 1993; Hooper et al., 1990]. Under higher discharge, water draining sulfate-rich and base-poor soil horizons contributes proportionately more sulfate to streamflow.

Comparisons of stream water sulfate concentrations between years during periods of comparable discharge suggested that the pattern discharge alone could not explain differences in sulfate concentration and export between years. A comparison of stream water sulfate concentrations at the same time of year and during periods of comparable flow during water years 1987 and 1992 indicated that sulfate concentrations were higher in WY1987 throughout the period December to May (Table 2). The differences in sulfate concentration were greatest in December and diminished until concentrations were equivalent in July and August.

The relative importance of discharge compared with a change in the concentration-discharge relationship itself was assessed by separating the integral for sulfate flux (Φ) into

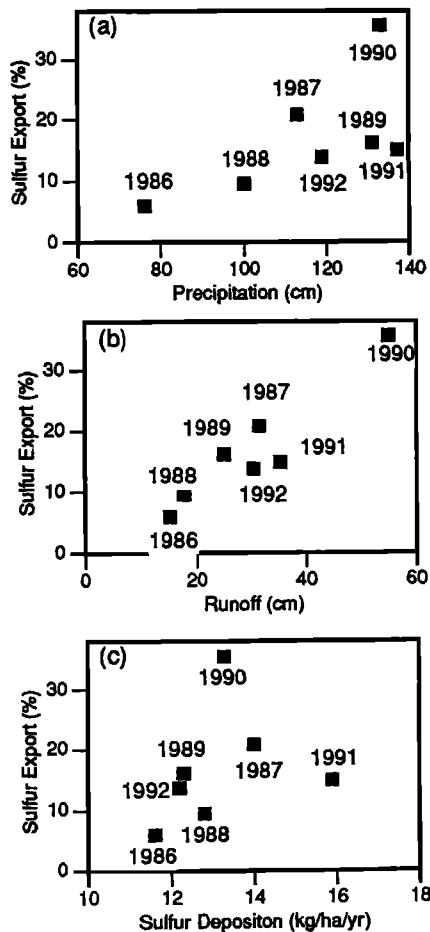


Figure 5. Relationships between total annual sulfate export and (a) total annual precipitation, (b) total annual runoff, and (c) total annual sulfur deposition at the Panola Mountain Research Watershed.

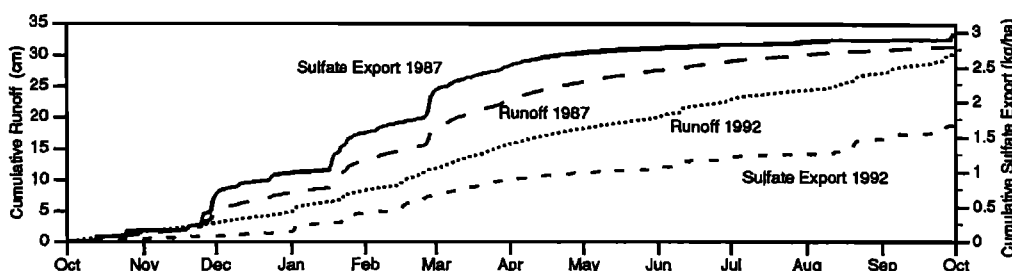


Figure 6. Cumulative runoff and sulfur export for water years (October to September) 1987 and 1992 at the Panola Mountain Research Watershed.

flux arising from the concentration-discharge model (Φ_M) and (Φ_e) residual components (equation (2)). This separation indicated that only 28% of the difference in sulfate export between water years 1987 and 1992 could be explained by higher discharge in WY1987 (Table 3). It was evident that there had been a shift in the concentration-discharge relationship when Φ_e and the integral of the absolute value of the residuals ($\Phi_{|e|}$) were compared. During water years 1986 through 1989 both Φ_e and $\Phi_{|e|}$ were relatively small compared to Φ indicating a well-posed model with no obvious bias. After WY1989, Φ_e was consistently large and approximately equal to $\Phi_{|e|}$, which indicated a bias toward overprediction of sulfate flux and hence a shift in the concentration-discharge relationship.

Atmospheric deposition of sulfur may also explain a part of the difference in stream water sulfate concentrations between water years 1987 and 1992. There was ~15% more total sulfate deposition in WY1987 than in WY1992, but sulfate export (kilograms per hectare) was 74% higher in WY1987 than in WY1992 (Table 1), which suggests that deposition can only explain a small part of the observed differences. Over the 7-year record the relationship between total sulfur deposition and sulfur export was quite weak (Figure 5), suggesting a stronger role for hydrologic controls.

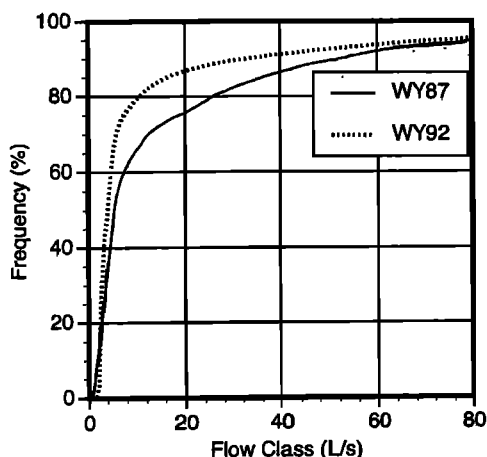


Figure 7. Cumulative density function for discharge for water years 1987 and 1992 showing the proportion of total runoff discharged at flows less than or equal to those shown along the abscissa.

Temporal Trends in Soil and Stream Water Sulfate Concentration

The shift in the concentration-discharge relationship may be explained by a decrease in sulfate concentrations in soil solutions. Sulfate concentrations in soil solutions collected at 15- and 50-cm depths generally were $\geq 200 \mu\text{eq L}^{-1}$ from July 1987 through October 1988 (Figure 8). Sulfate concentrations in soil solutions declined from October 1988 through January 1990. After January 1990, concentrations at 15 and 50 cm remained relatively constant at 110 and $150 \mu\text{eq L}^{-1}$, respectively. The decrease in soil solution sulfate concentrations occurred primarily in WY1989, which was a year of average precipitation following a period in which two out of three years had below-average precipitation (Table 1). Sulfate concentrations in soil solution remained low for an extended period of average precipitation from WY1990 through WY1992. Lower sulfate concentrations ($120\text{--}150 \mu\text{eq L}^{-1}$) in soil solution at the 50-cm depth during the first half of WY1987 (Figure 8) may reflect above average precipitation during 3 of the preceding 4 years [United States Department of Commerce, 1991]. Soil solution sulfate concentrations at PMRW are substantially higher than stream water concentrations because stream water is composed of a mixture of soil solution having relatively high sulfate concentration and groundwater having very low sulfate concentration [Shanley and Peters, 1993; Hooper et al., 1990].

Annual volume-weighted sulfate concentration in stream water (Table 1) was more variable between years than sulfate concentrations in soil solution (Figure 8) because of major differences in total runoff and discharge pattern between years. However, the annual average stream water sulfate concentration of $57.4 \mu\text{eq L}^{-1}$ in WY1987 compared

Table 2. Stream Discharge and Corresponding Sulfate Concentrations During Water Years (October to September) 1987 and 1992

Month	Flow		SO_4^{2-}	
	WY 1987, L s^{-1}	WY 1992, L s^{-1}	WY 1987, $\mu\text{eq L}$	WY 1992, $\mu\text{eq L}$
December	2.7–3.2	2.7–3.2	47–53	17–22
February	3.8–4.3	2.9–3.8	50–54	25–27
March	5.0–6.0	5.4–6.7	43–47	30–33
May	2.3–3.5	2.7–3.2	20–29	15–19
July/August	1.2–1.8	1.9–2.6	10–17	12–16

Table 3. Separation of Sulfate Flux Into Its Component Parts by Water Year

Water Year	Φ , kg ha ⁻¹	Φ_M , kg ha ⁻¹	Φ_{ε} , kg ha ⁻¹	$\Phi_{ e }$, kg ha ⁻¹
1986	0.70	0.80	-0.10	0.19
1987	2.90	2.83	0.07	0.38
1988	1.22	1.15	0.08	0.23
1989	1.98	1.98	0.00	0.58
1990	4.72	5.98	-1.26	1.39
1991	2.36	3.11	-0.75	0.76
1992	1.67	2.48	-0.81	0.81

Φ , sulfate flux calculated as $\Phi = \Phi_M + \Phi_{\varepsilon}$; Φ_M , sulfate flux arising from the concentration-discharge model; Φ_{ε} , sulfate flux arising from model residuals; and $\Phi_{|e|}$ the integral of the absolute value of the residuals.

with 34.3 $\mu\text{eq L}^{-1}$ in WY1992 indicated a change had occurred, since total runoff was similar between years and differences in discharge could explain only a small part of the difference in sulfate export.

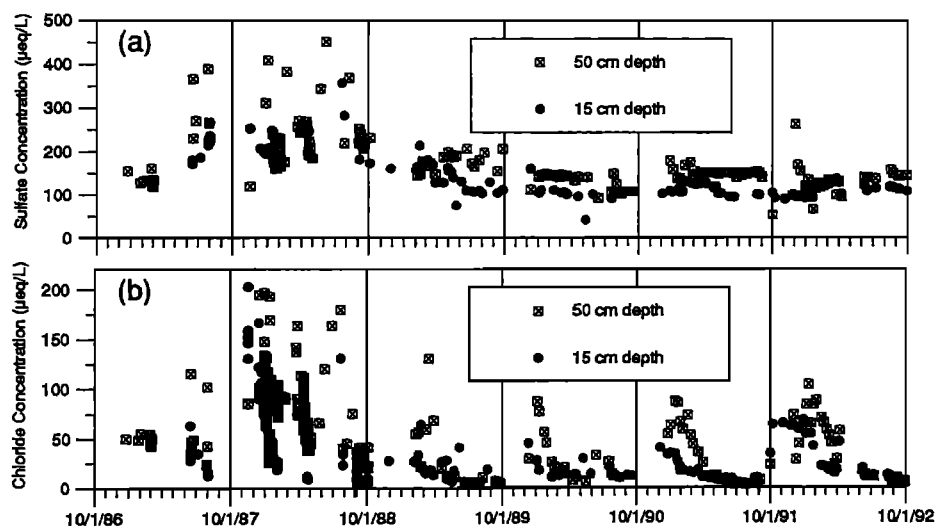
During years of average precipitation following dry years (WY1987 and WY1989), sulfate concentration in stream water was higher than at comparable flow during years of average precipitation following average years (WY1991 and WY1992) (Figure 9). The range of sulfate concentrations in stream water sampled under base flow ($\leq 7 \text{ L s}^{-1}$) decreased from 35–50 $\mu\text{eq L}^{-1}$ to 15–30 $\mu\text{eq L}^{-1}$ between 1987 and 1992 (Figure 9). Comparisons of sulfate concentrations in stream water between years are most valid for periods of equivalent discharge because concentration is strongly related to discharge. The samples used in this analysis were collected on a fixed interval (weekly), and samples were collected and analyzed during 94% of weeks during the study period. Any randomly selected sampling time would tend to occur under base flow conditions because stormflow is flashy in this headwater catchment. Discharges $\leq 7 \text{ L s}^{-1}$ represent between 92 and 98% of all weekly collections during the 4 water years considered in Figure 9.

Comparisons of sulfate concentrations in stream water between years, even during periods of equivalent discharge, should be made cautiously because of a marked hysteresis in the concentration-discharge relationship during spring and fall storms at PMRW [Shanley, 1989]. Shanley [1989] found that sulfate concentrations increased rapidly with increasing flow on the ascending limbs of the hydrographs, but decreased slowly on the descending limbs. This counterclockwise hysteresis would introduce bias when comparing comparable stream discharges between years when the flows were during base flow in 1 year but on descending limbs (recessions) in another year. This bias was largely eliminated in the comparison shown in Figure 9 by restricting the comparison to samples collected weekly and to flows $\leq 7 \text{ L s}^{-1}$ because this excluded the storm samples collected during the first three years of the study.

Stream water samples collected from two additional sites located upstream from the watershed outlet also indicate that sulfate concentrations decreased during the study period. Sulfate concentrations during storms were higher at the upper gauge site between WY1985 and WY1988 than at the headwater site between WY1991 and WY1992 (data not shown). If there had been no change in surface water chemistry the headwater site would have had higher sulfate concentrations than the upper gauge site, because at the headwater site the flow is composed entirely of water draining surface soils and groundwater derived from shallow hillslopes that are only saturated during storms or for several days following storms.

Explanation for the Shift in Concentration-Discharge Relationship

The change in the concentration-discharge relationship and corresponding decrease in soil solution concentration implies that a chemical shift occurred in the soil that resulted in a decrease in mobilizable sulfate. Decreases in soil solution sulfate concentration indicate that the adsorbed sulfate pool is dynamic and is responsive to hydrologic conditions. As a conceptual model, we propose that sulfate accumulates in surface soils during dry years and soil solution concentra-

**Figure 8.** Temporal variation in soil solution (a) sulfate concentrations and (b) chloride concentrations at 15- and 50-cm depths.

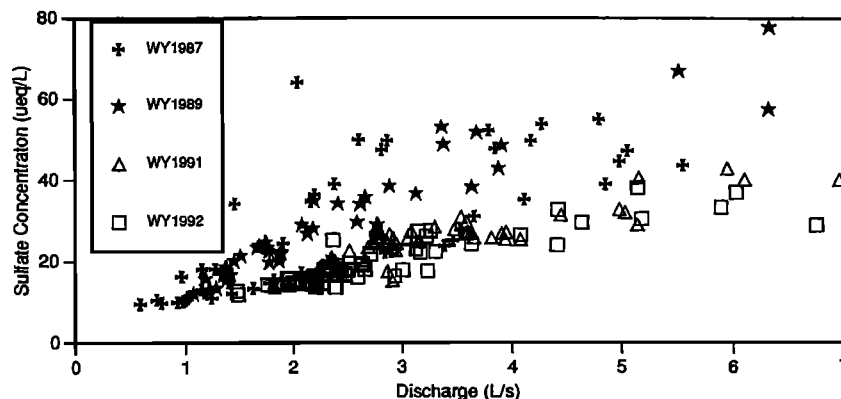


Figure 9. Stream water sulfate concentrations as a function of instantaneous discharge at flows $\leq 7 \text{ L s}^{-1}$ for samples collected weekly at the Panola Mountain Research Watershed for selected water years (October to September).

tions increase rapidly as the equilibrium between solution and solid phase shifts to higher solution and adsorbed concentrations. During subsequent years of average or above average precipitation, when flowpaths in surface soils become hydrologically active, sulfate is released as the equilibrium shifts back to lower sulfate concentrations. Lynch and Corbett [1989] also observed a carry over of atmospheric sulfur deposition between years at the LRO catchment in Pennsylvania due to antecedent periods of low precipitation and runoff. At both PMRW and LRO catchments below average precipitation and runoff leads to an accumulation of sulfate that can later be mobilized. It is noteworthy that this phenomenon was so strongly expressed at PMRW where, unlike LRO, annual sulfate retention was typically $>83\%$ of atmospherically deposited sulfur.

The mechanism of sulfate retention is more likely to be a reversible adsorption reaction than incorporation into organic matter as has been suggested in some studies [David and Mitchell, 1987; Strickland et al., 1986; Schindler et al., 1986] because of the dynamic response of soil solution and stream water sulfate concentration to hydrologic conditions. The observed concentrations of sulfate were also too low to indicate control by precipitation and dissolution of alunite or basaluminite. Since the changes in solution sulfate concentration are evident in well-drained upland environments, microbial reduction of sulfate to sulfide under anoxic conditions, followed by oxidation during drying and release after rewetting as proposed to explain sulfate flux at Plastic Lake [Kirchner et al., 1992] also seems unlikely at PMRW.

The observed net sulfur retention throughout the study period indicates that even under the wettest conditions a majority of atmospherically deposited sulfur is not exported. Under dry conditions sulfate can be temporarily stored in surface soil horizons and later released when these flowpaths become hydrologically active. Under conditions of net sulfate release from surface soil horizons, deeper soil horizons continue to adsorb the majority of mobile sulfate. The adsorption of sulfate in lower soil horizons or saprolite is not responsive to hydrologic conditions. These results support the primary role of surface soils in the control of surface water chemistry at PMRW as proposed by Hooper and Christophersen [1992].

Within-year variation in sulfate concentration in soil solu-

tion from the 15-cm depth may illustrate another process controlling sulfate mobilization and transport. In water years 1989, 1991, and 1992 sulfate concentrations in soil solutions at 15 cm typically began increasing in February or March and peaked in March and April (Figure 8). Chloride concentrations in soil solutions at both 15- and 50-cm depths also exhibited a within-year variation in certain years having a dormant season peak but, in contrast to sulfate, the Cl peak began as early as November and reached its highest point in December or January (Figure 8). The annual peak in stream-water discharge, which corresponds to recharge of the seasonally saturated aquifer and thorough wetting of the vadose zone, typically began in December or January and reached maximum discharge in March or April (Figure 3). The lag in the onset of sulfate mobilization compared with chloride mobilization and stream water discharge may indicate more complex control than adsorption during dry conditions and desorption during subsequent wet periods. One hypothesis consistent with the observations is that during December and January macropore flow may dominate, and during February and March, after the soil is thoroughly saturated, matrix flow dominates, bringing soil solutions in contact with the bulk of the adsorbed sulfate in the soil matrix. An alternative explanation for the seasonal pattern of sulfate concentrations in soil solutions may be biological control resulting from temperature dependence of microbially mediated sulfur mineralization [Ellert and Bettany, 1992].

Decreases in stream water sulfate concentration at flows $<7 \text{ L s}^{-1}$ suggested that groundwater from seasonally saturated hillslopes would exhibit a corresponding decrease because a mixing analysis indicated that this groundwater source was a component of stream water at these flows [Hooper et al., 1990]. In contrast to observed decreases in soil solution sulfate concentration, sulfate concentration in hillslope groundwater collected at several locations (Figure 1) did not decrease over the study period (data not shown). Since sulfate concentration in hillslope groundwater did not decline the surface soil environment may play a more important role in the composition of stream water at low flows than originally modeled by Hooper et al. [1990].

Implications for Watershed Acidification Modeling

Responsiveness of both stream water chemistry and soil solution chemistry to annual variation in precipitation has implications for prediction of watershed acidification. Models of watershed acidification, such as ILWAS [Gherini *et al.*, 1985] and MAGIC [Cosby *et al.*, 1985], require calibration to measured soil chemical properties. Models that treat the soil as evolving slowly in response to chronic acidic deposition and which cannot incorporate the potential for large and rapid changes in soil solution sulfate concentrations in response to hydrologic conditions may be difficult to calibrate. For example, at PMRW, a model calibrated to soil solution sulfate concentrations following dry years would result in the selection of different sulfate adsorption parameters than a model calibrated to soil solution sulfate concentrations following years of average precipitation. Model predictions based on the higher sulfate concentrations measured during dry years would indicate more rapid watershed acidification than predicted with the model calibrated to lower soil solution sulfate concentrations.

Ideally, applications of watershed acidification models need to include a calibration period that is long enough to incorporate interannual hydrologic variation. The dynamic behavior of the surface soil, as illustrated by rapid decreases in soil solution, in contrast to the chronic accumulation of sulfate in the watershed as a whole emphasizes that models should use multiple soil layers to accurately predict water quality. Finally, because of the dependence of stream water sulfate concentrations on hydrologic conditions it is important to use time steps that are sufficiently small to incorporate variations in hydrologic conditions and routing parameters that may be masked with annual time steps. The significance of the responsiveness to hydrologic conditions is highlighted by the potential for climate change which may alter both the amount and distribution of precipitation.

Summary

Variations in annual sulfate export were controlled by total annual runoff, discharge pattern, and changes in the concentration-discharge relationship which resulted from the accumulation of sulfur during extended dry periods. Sulfate export was controlled more by runoff than atmospheric deposition of sulfur. Under conditions of similar runoff between years sulfate export was controlled by both changes in the concentration-discharge relationship and the pattern of discharge. Separating sulfate flux into components explained by the concentration-discharge model and the model residuals enabled us to determine that the concentration-discharge relationship had shifted. This technique also provided a means to quantify the relative importance of discharge versus a shift in the concentration-discharge relationship to explain differences in sulfate flux between years. The change in the concentration-discharge relationship appears to be a result of accumulation of sulfate during dry years and subsequent release during wetter years.

Hydrologic control of variations in aqueous concentrations and sulfate export indicate that the development of temporally robust concentration-discharge models for estimation of mass flux and the assessment of trends in stream-water quality and watershed sulfur retention require long-term studies. To adequately characterize watershed

response to variation in hydrologic conditions, the study period should cover a broad range of antecedent precipitation conditions. Furthermore, in watersheds such as PMRW that have a distinct concentration-discharge relationship, it is essential to sample over the entire range of discharge. Predictive models of watershed acidification should include the potential responsiveness of stream water chemistry to temporal variation in hydrologic conditions. Models should also consider the linkage between climate change and potential watershed acidification because of the responsiveness of surface soils and stream water chemistry to hydrologic variation.

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