SEASONAL SULFATE DEPOSITION AND EXPORT PATTERNS FOR A SMALL APPALACHIAN WATERSHED

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Abstract. Sulfate deposition and exports from 1988–92 were analyzed for a small headwater catchment in north-central West Virginia. Annual sulfate inputs, estimated by applying throughfall-adjusted ratios to bulk deposition values, and outputs were approximately equal for the five years. Annual mean throughfall-adjusted deposition and export loads were 55.78 and 55.48 kg ha^{-1}, respectively. While these results indicate the watershed has reached sulfate equilibrium relative to current deposition levels, seasonal sulfate accumulations and deficits were evident. Deposition and exports averaged 5.61 and 2.49 kg ha^{-1} mo^{-1}, respectively, during the growing season, and 3.69 and 5.22 kg ha^{-1} mo^{-1} during the dormant season. Sulfur accumulated within the soil during the growing season because inputs of wet and dry sulfur deposition were high while outputs were negligible. The latter was due largely to the lack of runoff resulting from high evapotranspirational demands. By contrast, net sulfate losses occurred during dormant seasons, primarily due to high runoff, even though inputs declined during this season. Researchers working on other watersheds have interpreted similar input/output patterns to mean that sulfate accumulated during the growing season is the source of sulfate exported during the dormant season. However, radioisotopic evidence from a companion study on this watershed showed that some labeled sulfate applied to the watershed more than a year earlier was still present in the organic and mineral soil layers at the point of application (with some as soluble sulfate), and in soil water dispersed throughout the watershed. Its presence indicates that dormant season exports can originate from sulfate deposited over longer periods than just the previous growing season or even previous year. Volume-weighted concentrations in soil leachate suggest that dormant-season sulfate losses resulted from progressive depletion of the anion through the soil profile. During the fall and early winter, soluble sulfate was depleted in the upper soil horizons; in later winter, depletion occurred in the lower horizons.

Keywords: inputs, outputs, seasonal accumulations, seasonal deficits, soil leachate

1. Introduction

Sulfur (S) loadings to the eastern United States are among the highest in the nation (National Atmospheric Deposition Program, 1992) due to dry and wet deposition of sulfate (SO_4) and dry deposition of sulfur dioxide (SO_2) (National Atmospheric Deposition Program, 1987; National Acid Precipitation Assessment Program, 1993). Sulfur dioxide deposition tends to be more important at sites close to major sources of SO_2 emission, while sulfate deposition is more important at more remote sites. Wet sulfate deposition occurs by precipitation scavenging – that is, sulfate particles are removed from the atmosphere by precipitation as it falls

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to earth. Dry sulfate deposition occurs by impaction of fine-aerosol sulfate, sedimentation of coarse-particle sulfate, and sulfur dioxide sorption (which is oxidized to sulfate) by plant stomata (Lindberg, 1992). Washoff of dry-deposited sulfate from vegetation surfaces is important in forests because the extensive surface area of canopies increases inputs relative to nonforested areas (Smith, 1981; Lindberg, 1992).

Sulfur can be retained within a catchment by vegetative uptake, immobilization via assimilation into microbial cells (Randlett *et al*., 1992), incorporation into organic matter, and physical adsorption onto soil colloids. Since sulfur requirements by forest vegetation are 5–25 kg ha^{-1} yr^{-1} and most of this need is obtained from recycling, annual net retention of 'new' sulfur by vegetation is modest, typically less than 5 kg ha^{-1} yr^{-1} (Reuss and Johnson, 1986). Immobilization and adsorption are considered the most important retention mechanisms; however, their degrees of importance vary with the biogeochemical character of the watershed (Randlett *et al*., 1992). For example, when substrate availability and soil moisture are conducive to microbial activity, immobilization will be high (Strickland *et al*., 1987); thus, in temperate climates, immobilization rates typically vary with season (Williams, 1967; Swank *et al*., 1985). Adsorption is controlled predominantly by pH, sulfate concentrations, the types and concentrations of other anions and cations within soil solution, and the character of the colloidal surfaces present (Harward and Reisenauer, 1966).

Non-retained sulfate ions are leached to surface waters and groundwater, and are accompanied by base or acid cations depending upon the chemical composition of the deposition and the buffering status of watershed soils. While the soils are in base-cation buffering state, sulfate pairs with base cations during leaching. When the predominant cation in deposition is H^+, the base cation supply can become exhausted over time, and the buffering status changes to an aluminum-buffering system. Charge pairing and sulfate leaching proceeds with acid cations, particularly aluminum, after which soil and water acidification can occur (Kennedy, 1986; Hendershot *et al*., 1991).

Watershed hydrology can have a substantial influence on the behavior and rates of sulfate movement within and from soils (Johnson and Henderson, 1979; Schnabel *et al*., 1991). The objective of this paper was to examine annual and seasonal sulfate deposition and exports in relation to watershed soil moisture and runoff patterns. In addition, changes in soil leachate chemistry with depth in the soil profile are analyzed to provide insight into patterns of sulfate depletion over time.

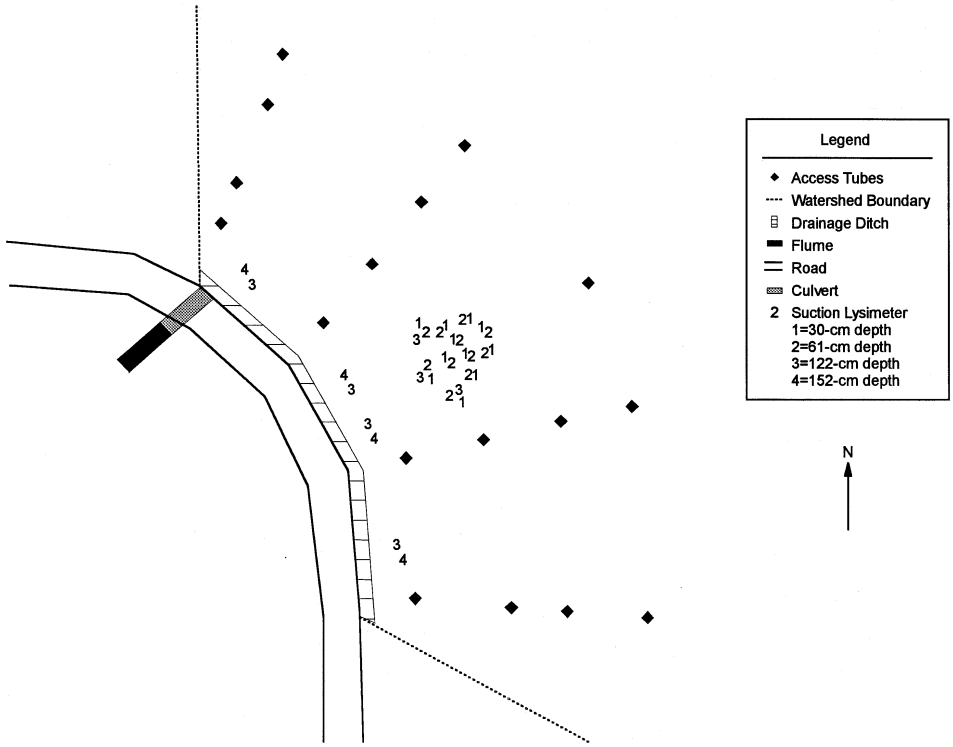

Figure 1. Schematic of the lower one-third of SH5 showing watershed features, access tube locations, and suction lysimeter locations and depths.

2. Methods

2.1. Study Area

The study was conducted on a 1.7-ha watershed, called SH5, on Pheasant Mountain, Tucker County, West Virginia (79°44′50″ W, 39°5′25″ N). Along with a larger watershed, of which it is a part, the timber on SH5 was harvested to a minimum stump diameter of 35.6 cm between May 1986 and February 1987. The current stand on SH5 consists of Allegheny mixed hardwoods dominated by chestnut oak (*Quercus prinus* L.) and red maple (*Acer rubrum* L.).

SH5 faces southwest and in bounded at the top and bottom by a ridge and road cut, respectively. Elevations in the watershed range from 670–716 m, and the slope averages about 40%. The dominant soil on SH5 is an Ernest silt loam (fine-loamy, mixed, mesic Aquic Fragiudult) underlain by acidic sandstones and shales of the Chemong geologic formation. It has a fragipan at a depth of 66 cm (Edwards, 1994). Ernest soils are moderately well drained and common along drainages and in headwater areas in the Appalachians (Losche and Beverage, 1967).

2.2. Sampling and Analysis

SH5 has no perennial or intermittent surface stream channels; drainage is entirely subsurface and was captured in a bedrock-lined ditch along the road cut. Discharge was diverted through a culvert under the road into a 0.3-m H-type flume (Figure 1) where it has been measured continuously since 1988 with a Belfort 5-FW-1 water-level recorder. Water samples were collected each Tuesday from May 1988 through October 1991 by grab sampling from a permanent sampling point in the drainage ditch, just above the culvert.

A companion sulfur movement study was begun on SH5 in November 1991 (Edwards, 1994). At that time, grab sampling from the drainage ditch was terminated, and from November 1991 through April 1993 stream water was sampled at the flume outlet using a Coshocton wheel proportional sampler. Approximately 0.65% of the total weekly flow was diverted to a 220-L plastic storage tank. Each Monday, a 1-L sample was collected from the tank, and then the tank was emptied (Edwards, 1994).

Meteorological data and precipitation samples were collected each Tuesday from a weather station located about 305 m east of SH5 at an elevation of 731 m. Weekly precipitation totals were measured with a standard 20.3-cm-diameter manual rain gauge. Bulk precipitation, which includes precipitation deposition and gravity-controlled particle deposition (Ulrich, 1983), was collected continuously in open containers (Eaton *et al*., 1980; Lindberg *et al*., 1985). From May to October, bulk collectors constructed of a 20.3-cm-diameter polyethylene funnel connected by looped Tygon tubing to a 1-L polyethylene bottle were used; this system minimized evaporative losses. From November to April, open NADP-type polyethylene buckets (Bigelow and Dossett, 1988) were used to avoid snow bridging. Weekly snowfall amounts did not exceed the bucket's capacity. Clean collectors were placed in the field every Tuesday at the time of sample collection.

Soil leachate was collected with suction lysimeters from November 1991 to December 1992 to determine sulfate concentrations. Suction lysimeters were located throughout the lower one-third of the watershed at depths of 30, 61, 122, and 152 cm (Figure 1). The maximum rooting depth in this watershed is approximately 45 cm. Eleven 30- and 61-cm-deep lysimeters, seven 122-cm-deep lysimeters, and four 152-cm-deep lysimeters were used. A 55-centibar vacuum was placed on each lysimeter every Friday, and samples were extracted the following Monday. Lysimeters were installed more than four months prior to the first sample collection to minimize installation effects, which were not evident based upon subsequent soil water chemical analyses.

Water samples were handled and analyzed for sulfate using EPA-approved protocols (Edwards and Wood, 1993) at the USDA Forest Service's Timber and Watershed Laboratory at Parsons, WV, about 16 km north of SH5. Samples were filtered through 0.45-μm filters and analyzed by ion chromatography. Prior to analysis, samples were stored at 4 °C.

TABLE I

Precipitation and runoff characteristics from water year 1988 to 1992 (Water years begin May 1 and end April 30)

Water year	Precipitation	Runoff	Runoff/Precipitation
	cm		
1988	135.76	85.09	0.63
1989	158.27	102.92	0.65
1990	162.10	86.08	0.53
1991	116.69	58.93	0.51
1992	119.10	57.57	0.48
Mean	138.38	78.12	0.56

Deposition and exports were calculated by applying the sulfate concentrations to the total precipitation and total discharge for the week ending on the day of sample collection. The precipitation amounts used were those measured in the rain gauge, because the gauge provided more accurate and precise totals than the bulk collector (Brakensiek *et al*., 1979).

Soil samples were collected by horizon on February 7, 1994, at three locations at the base of the watershed to characterize the sulfate status. The samples were composited by horizon, air dried, passed through 2-mm sieves, and analyzed for soluble and adsorbed sulfate (Johnson and Todd, 1983) at the University of Maine, Department of Plant, Soil, and Environmental Sciences. Additional samples were taken within the interior of the watershed in 1992 by depth for a companion study (Edwards, 1994). The analytical results were very similar to those taken for this study; thus, results for this study (presented later) are considered to be representative of the overall watershed sulfate status.

Soil moisture also was measured at 17 locations fitted with access tubes in the lower one-third of the watershed (Figure 1). Measurements were made with a Troxler model 3321 nuclear depth moisture gauge. Soil moisture was measured at depths of 30, 61, 91, and 122 cm twice a week at each of the 17 locations.

3. Results and Discussion

3.1. HYDROLOGIC RELATIONSHIPS

SH5 received an average of 138 cm of precipitation annually (Table I), with fairly even distribution throughout the year. Annually, runoff averaged about 78 cm and constituted about 56% of precipitation (Table I). Runoff is concentrated primarily within the dormant season due to high evapotranspirational demands during the

TABLE II

Sulfate inputs in bulk precipitation and outputs in runoff, by water year for SH5

Water year	Sulfate outputs	Sulfate inputs	Outputs-inputs
	kg ha^{-1}		
1988	57.32	40.23	17.09
1989	72.32	51.73	20.59
1990	59.20	43.50	15.70
1991	39.97	38.72	1.25
1992	63.95	35.53	28.42

growing season. Runoff and the runoff/precipitation ratio may be somewhat greater now than before the 1986–87 selective harvesting because of the reduction in leaf area and, thus, transpirational demand. However, the annual runoff/precipitation ratio has decreased every year since 1988, so the watershed appears to be returning to preharvest runoff conditions.

Water years 1991 and 1992 were the driest years of those measured, though the two years were similar (Table I). Precipitation was about 15% below the 1988–92 average and runoff was about 25% below the average (Table I). Runoff was only about 50% of precipitation for 1991 and 1992.

3.2. DEPOSITION/EXPORT ANALYSES

For all years of analyses, sulfate outputs were greater than bulk deposition inputs (Table II). However, exports cannot exceed inputs unless (1) sulfate deposition has declined and current conditions reflect desorption associated with reaching new steady-state conditions (Rochelle and Church, 1987; Reuss and Johnson, 1986), (2) there is a sulfur-generating source within the watershed, for example, highly weatherable S-containing minerals, or (3) inputs of dry deposition have been underestimated by bulk deposition measurements (Rochelle and Church, 1987; Christophersen and Wright, 1980).

Analyses of several factors at this site indicate that the excess outputs were due primarily to underestimation of the dry sulfate component (Edwards, 1994). Bulk sampling of precipitation in known to underestimate sulfate dry deposition (Helvey and Kunkle, 1986) because submicron particles and aerosols (<10 μm diam.) are under sampled since they are only minimally influenced by gravity (Galloway and Parker, 1980). Ratios of bulk/total deposition for sulfate ranged from 0.4–0.7 for a wide range of forested sites in the United States and Norway (Lindberg, 1992).

Throughfall measurements provide good estimates of total sulfate deposition to forested catchments (Lindberg, 1992). Although throughfall inputs were not mea-

sured for this study, they were measured previously nearby (6 km) on the Fernow Experimental Forest (Helvey and Kunkle, 1986). Their data show that for each of the three monitored years (1981–83), ratios for throughfall/bulk sulfate inputs were consistent, averaging 1.33. Therefore, to estimate total deposition more accurately for this study, sulfate inputs in bulk precipitation were multiplied by 1.33 (Table III).

Because small decreases in sulfate deposition have been reported for some sites in the eastern United States (Council on Environmental Quality, 1989), and such a change could affect the throughfall/bulk ratio, an analysis was done to check for temporal changes in sulfate deposition for SH5. There was a slight decrease in bulk sulfate deposition between 1981 and 1992 based upon data from the weather station near SH5 (unpublished data). However, the decrease appears to be largely controlled by high deposition inputs in 1985, which was a year of very high precipitation. Excluding 1985 data indicated no significant temporal change in sulfate deposition. Consequently, temporal changes in the throughfall/bulk deposition ratio are expected to have been minimal.

The factor of 1.33 may overestimate SO_4 deposition for SH5 because Helvey and Kunkle (1986) used an unthinned 70-year-old mixed hardwood stand. The greater canopy surface likely in the 70-year-old stand should have resulted in greater dry deposition scavenging, but the higher elevation of SH5 may have offset some of that difference (Swank and Waide, 1988; Lindberg, 1992). However, we believe that this factor is reasonable based upon correction values reported for neighboring states (Cosby *et al*., 1985; Dow, 1992).

Using the estimated total SO_4 deposition, sulfate inputs to SH5 nominally exceeded outputs for all years except 1991 (Table III), but the differences for all years are not substantial and can be explained in terms of the errors associated with precipitation, bulk deposition, and output measurements, and the estimated correction factor (Christophersen and Wright, 1981). Thus, for 1988–90 and 1992, inputs effectively equaled outputs, indicating that the watershed has reached equilibrium relative to current deposition levels (Lynch and Corbett, 1989), though some retention appears to have occurred in 1991. In 1991, total sulfate deposition (Table III) was about 11 kg ha^{-1} greater than sulfate output.

For all years of record, discharge explained a much larger portion of the variation in sulfate outputs ($R^2 = 0.92$) than precipitation explained in throughfall-adjusted inputs ($R^2 = 0.21$). This difference has been reported elsewhere (Lindberg, 1992; Lynch and Corbett, 1989; Christophersen and Wright, 1981). Output calculations are dominated by discharge, while a significant component of input calculations is dominated by dry deposition and, thus, is uncoupled from the hydrologic flux.

On an annual basis, SH5 apparently has reached equilibrium with respect to sulfate inputs and outputs, but net sulfate accumulations and deficits do occur on a seasonal basis. Generally, inputs exceeded outputs throughout the growing season (May 1-October 31); inputs consistently exceeded outputs from July through Sep-

TABLE III

Sulfate outputs and throughfall-adjusted inputs by month and water year. Net = outputs – inputs

Month	1988			1989			1990			1991			1992		
	Output	Input	Net	Output	Input	Net	Output	Input	Net	Output	Input	Net	Output	Input	Net
	kg ha^{-1}														
May	6.82	6.95	–0.13	14.04	10.80	3.24	8.21	7.40	0.81	1.06	2.98	–1.92	6.92	10.13	–3.21
June	0.67	3.79	–3.12	7.74	3.06	4.68	1.85	4.68	–2.83	0.22	5.97	–5.75	0.40	3.32	–2.92
July	0[a]	9.33	–9.33	2.40	8.90	–6.50	3.19	7.02	–3.83	0.05	3.80	–3.75	0.21	5.61	–5.40
August	0[a]	4.75	–4.75	1.77	12.05	–10.28	0.21	4.30	–4.09	0[a]	7.43	–7.43	0.52	3.21	–2.69
September	3.04	7.97	–4.93	3.16	7.19	–4.03	0.52	7.43	–6.91	0.29	8.15	–7.86	0.01	2.23	–2.22
October	0.53	1.30	–0.77	7.01	4.05	2.96	3.83	1.45	2.38	0[a]	2.46	–2.46	0[a]	0.57	–0.57
November	6.45	2.83	3.62	5.50	3.50	2.00	1.39	2.28	–0.89	0.61	1.79	–1.18	0.30	2.80	–2.50
December	3.05	1.44	1.61	2.32	0.93	1.39	6.21	3.16	3.05	10.47	2.67	7.80	9.64	3.33	6.31
January	8.48	4.12	4.36	12.68	4.79	7.89	10.44	3.87	6.57	1.88	1.45	0.43	4.72	2.21	2.51
February	12.84	4.39	8.45	6.53	2.83	3.70	7.00	3.28	3.72	8.73	2.91	5.82	4.44	1.93	2.51
March	10.38	2.98	7.40	3.19	2.89	0.30	8.74	4.76	3.98	12.48	6.24	6.24	13.87	6.12	7.75
April	5.05	3.65	1.40	6.00	7.77	–1.77	7.61	8.22	–0.60	4.19	5.66	–1.47	7.54	5.80	1.74
Total	57.31	53.50	3.81	72.34	68.76	3.58	59.20	57.85	1.35	39.98	51.51	–11.53	48.57	47.26	1.31
% Dec. to Mar. Contr.	60.60	24.20		34.20	16.60		54.70	26.00		83.90	25.80		67.30	28.60	

[a] Runoff for the month = 0, therefore, outputs = 0.

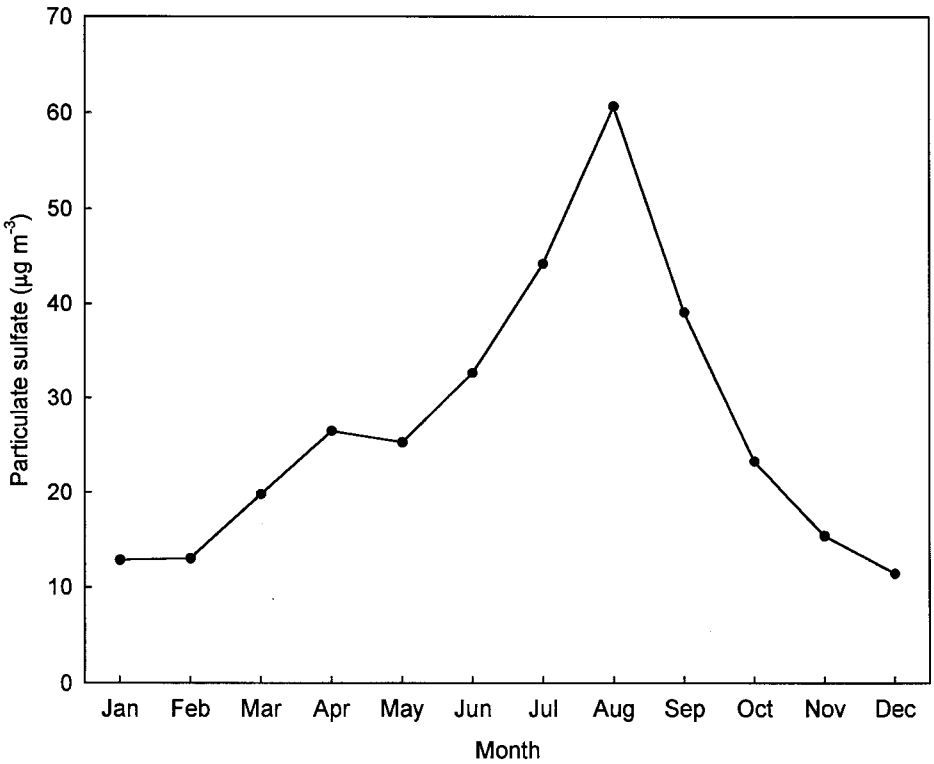

Figure 2. Particulate sulfate concentrations determined from EPA National Dry Deposition Network for Parsons, West Virginia site (unpublished 1990 data).

tember (Table III). Sulfate inputs exceeded outputs not only because runoff was low during the growing season, but also because absolute inputs tended to be highest for this period. Precipitation amounts remain high during the growing season in this region, and concentrations of atmospheric sulfate particulates are simultaneously highest during the growing season (Figure 2), accounting for these large inputs. Evapotranspirational demands are sufficient to significantly reduce or effectively eliminate summer discharge.

Conversely, sulfate exports consistently exceeded inputs from December through March each year (Table III). During this period, sulfate inputs often are lower because concentrations of atmospheric sulfate particulates decline (Figure 2). For the five periods from December to March on record, sulfate inputs accounted for an average of 24.3% of the total annual inputs (Table III). During those same months, outputs accounted for an average of 60.2% of the annual export. Thus, sulfate exports from December to March originate from more than the inputs during just those months; a significant portion originates from stored sources in the watershed.

Lynch and Corbett (1989) reported similar accumulations in the Leading Ridge watershed in central Pennsylvania, though net losses occurred from February

through May. They hypothesized that the two-reservoir model proposed in the Birkenes model (Christophersen and Wright, 1981) was applicable to the processes occurring on Leading Ridge. In the Birkenes model, catchments are separated into (1) an upper reservoir which contributes stormflow and some 'old soil water' (Christophersen *et al*., 1982) and associated ions to streams by macropore flow, and (2) a lower reservoir that contributes flow and associated ions during baseflow (Christophersen and Wright, 1981). The upper reservoir is composed of humus and the upper-most mineral soil layers, while the lower reservoir is composed of deeper mineral soil and rock layers. Retention of sulfur as sulfate typically is much less in the upper reservoir than in the lower reservoir, because sulfate retention occurs principally by nonspecific and specific adsorption onto positively-charged sites dominated by layer silicates, oxide and hydrous oxide-dominated surfaces, and organic matter (Bohn *et al*., 1985). Adsorption onto organic matter is much less common than the former two types of sites which are found primarily in deeper soil layers (Johnson and Cole, 1977; Schindler and Mitchell, 1987). Thus, sulfate is labile in the upper reservoir (Christophersen and Wright, 1981) and can be leached when precipitation and soil moisture conditions become conducive to permit macropore flow (Johnson and Henderson, 1979).

Lynch and Corbett (1989) suggested that atmospherically deposited sulfate was stored within the Leading Ridge watershed during the summer and fall when soil moisture deficits existed across the watershed. During winter and spring, soil saturation or near-saturation conditions occurred, creating periods of excess sulfate exports derived from ions stored in the upper reservoir.

If this theory holds for SH5, sulfate accumulates primarily during the growing season when inputs are high but soil moisture and discharge are low. Then during the dormant season, conditions are reversed–inputs decrease but soil moisture and flows increase, allowing stored sulfate to be transported from the watershed. This behavior is suggested for SH5 (Figure 3), and on a mass basis, soluble sulfate levels in the organic layers were much greater than adsorbed sulfate levels in those layers and much greater than the soluble or adsorbed levels in the mineral soil (Table IV).

However, radioisotopic evidence from the companion study on SH5 indicates that the presence of soluble sulfate in the organic layers and upper horizons does not mean that all of it is flushed or leached when conditions become favorable. Fifty-five weeks after $Na_2{}^{35}SO_4$ was applied during a rain event to a 0.9-m $\times$ 1.2-m plot on SH5, 0.15% of the applied ^{35}S still was present as soluble sulfur in the organic and mineral soil layers of that plot, and less than 2% of that applied was recovered in soil water and continuously-sampled watershed discharge over those 55 weeks (though some ^{35}S was thought to have been lost but unaccounted for due to isotopic dilution) (Edwards, 1994). Its detection followed two rewetting cycles (i.e., winters of 1991–92 and 1992–93). If the isotope had remained soluble during the study, particularly during dormant-season rewetting periods, and the processes described in the Birkenes model had held true, all of this soluble sulfate should have been exported earlier–probably during the first wetting cycle. However, this did not

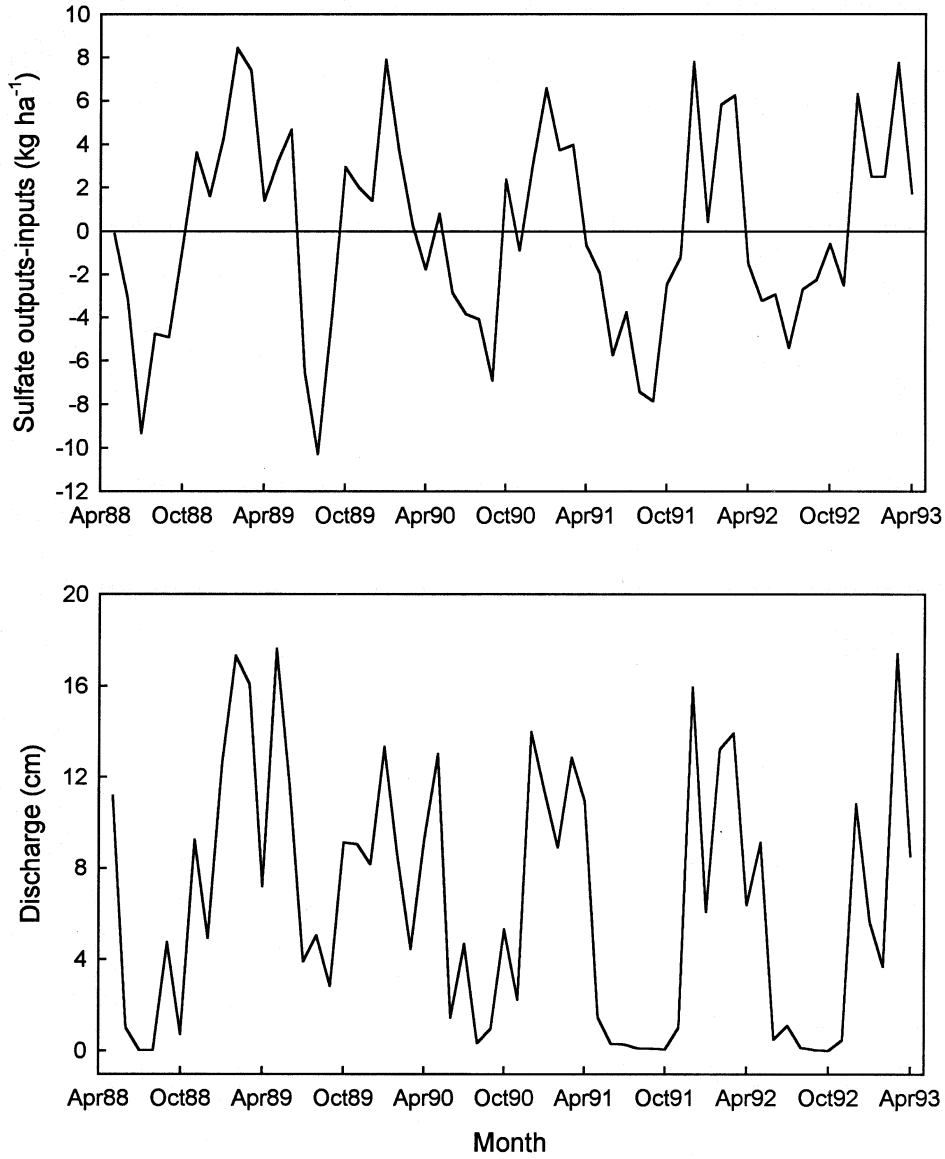

Figure 3. Net monthly sulfate fluxes (exports – deposition) (top), and total monthly discharge (bottom) from April 1988 through April 1993.

occur. No doubt, some isotope remained on the plot because the labeled sulfate went through one and perhaps many cycles of immobilization and mineralization and/or adsorption and desorption. Thus, saturated soil does not ensure the loss of all sulfate accumulated during the growing season, even on a watershed where outputs

TABLE IV
Soluble and adsorbed sulfate levels by soil horizon

Horizon	Depth	Soluble sulfate	Adsorbed sulfate
	cm	mg kg^{-1}	
Litter	3–1.5	44.3	0.00
Humus	1.5–0	40.6	0.77
E	0–3	1.00	11.0
BA	3–8	8.69	5.74
Bt1	8–20	12.7	12.9
Bt2	20–41	7.73	7.34
Bt3	41–66	6.34	6.43
Btx	66–122	3.85	6.82

equal inputs. In turn, sulfate ions in runoff are of varying ages with respect to the time they were deposited (Edwards, 1994).

3.3. Soil Leachate Responses

Soil leachate data from November 1991-November 1992 suggest that sulfate ions in watershed exports came from different soil depths over time. In autumn about the time sulfate exports began to exceed inputs, volume-weighted sulfate concentrations began to decrease in the 30- and 61-cm-deep lysimeters (Figure 4a–b). The decrease was smaller and quicker at 30 cm than in the 61-cm layer. The 122-cm layer underwent a slow initial decrease, but the rate increased sharply after most of the sulfate in the 61-cm layer had been depleted (Figure 4c). Concentration decreases in the 152-cm layer began last (Figure 4d). Sulfate concentrations in lysimeters reached a minimum for all levels in the summer, and concentrations recharged or began to recharge (depending on depth) in the fall. This pattern suggests that sulfate was exported and depleted from the upper soil layers during the first part of the fall and early winter, and subsequent sulfate losses in runoff resulted from leaching from progressively deeper layers.

The 61-cm layer appears to have been particularly influential as a source of sulfate exports on SH5. During each month for the entire year, this layer had the highest average percent volumetric soil moisture (Figure 5) and, therefore, was potentially the most hydrologically active. If this is true, the 61-cm layer also should have been the most active for exporting sulfate, which it appeared to be. Absolute concentrations in leachate decreased the most (except for a June and a July spike in the 30-cm layer) and the period during which the decreases occurred was longest in the 61-cm layer (Figure 4a-d).

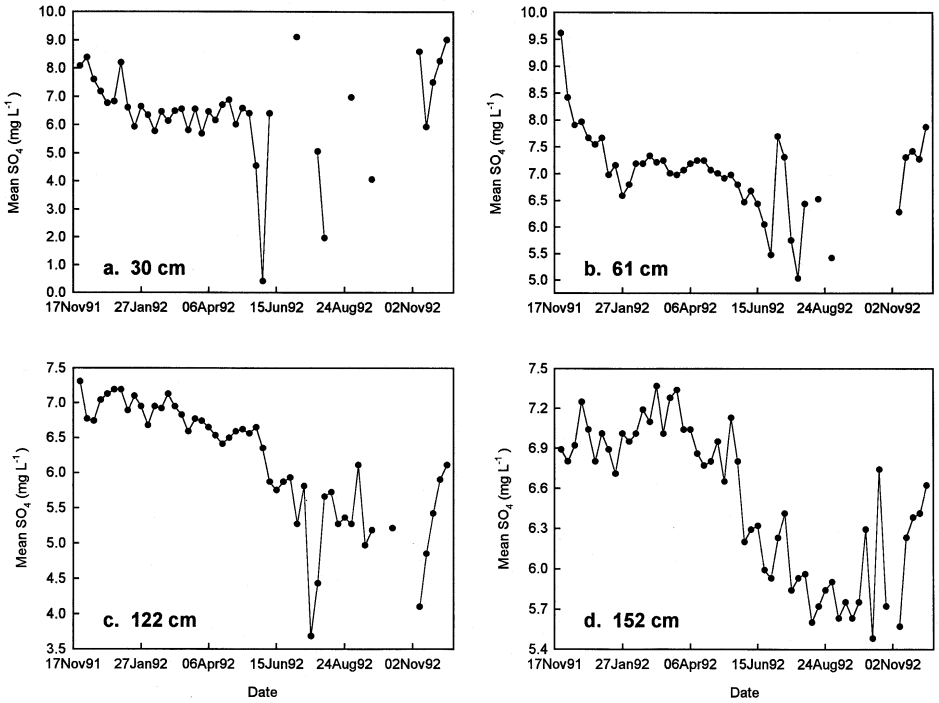

Figure 4. Volume-weighted average sulfate concentrations by collection period from suction lysimeters at depths of (a) 30 cm, (b) 61 cm, (c) 122 cm, and (d) 152 cm.

The timings of the two low spikes in the 30-cm layer (Figure 4a) correspond to samples collected just after two rain events that were the largest since the second week of soil leachate collection. Therefore, the spikes are believed to have been caused by sulfate flushing from the layer during these precipitation events. Such storm-associated losses are consistent with the Birkenes model (Christophersen and Wright, 1981).

However, on an annual basis, sulfate lost during nonstorm periods constitutes by far the largest percentage of sulfate exports in many Appalachian streams (Swistock *et al.*, 1997). A poor correlation between weekly runoff and precipitation for SH5 showed this relationship (Edwards, 1994). Thus, the more continuous, nonepisodic losses apparently originate from progressive leaching of soluble sulfate from upper soil layers through deeper ones. Longer term sulfate contributions from deep layers are consistent with current theories on streamflow generation that suggest the largest proportion of streamflow is generated by soil water draining through mesopores and micropores (Luxmore, 1981) in deeper soil layers (Jury and Fluhler, 1992).

The depletion observed should not be interpreted to mean that all soluble sulfate in any layer, including surface layers, is exported from the watershed. Evidence

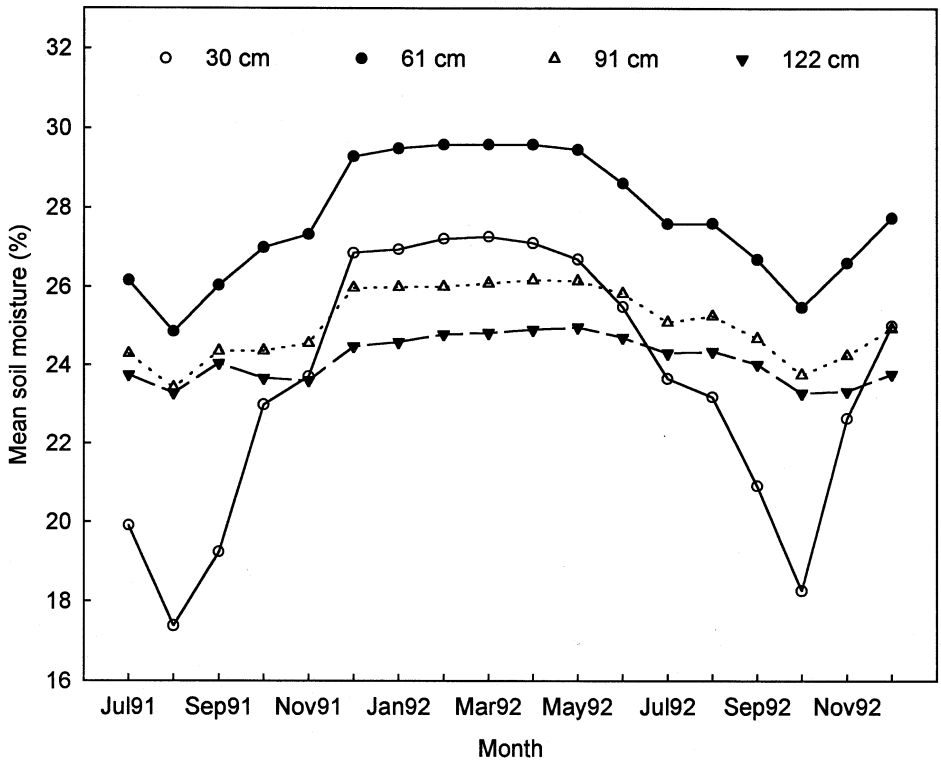

Figure 5. Mean monthly percent volumetric soil moisture by depth.

indicates that soluble sulfate can be retained within soil merely because there is insufficient moisture to move it or move it quickly (Edwards, 1994).

3.4. COMPARISONS WITH OTHER SITES

Sulfate input/output budgets have been calculated for many sites around the world. Site differences and depositional histories make generalizations about input and output levels or degrees of net retention difficult. However, within the United States, sulfate depositional inputs tend to be greater in the East than the West (Rochelle *et al.*, 1987) due to their location relative to major pollution emitters and prevailing wind directions.

By contrast, neither the magnitudes of outputs nor net retention are strongly related to region (Table V). Rochelle *et al.* (1987) hypothesized that net sulfate retention within watersheds north of the southernmost boundary of Wisconsinan glaciation is zero or negative, while sites south of the boundary tend to have some net retention. However, their model generally employed bulk deposition sulfate values rather than total or throughfall-based values; consequently, total inputs and resultant net retention (inputs-outputs) were underestimated. Data from SH5 and

TABLE V

Sulfate inputs (from throughfall or dry + wet components) and outputs from selected experimental watersheds

Site	Input	Output	Input-output	Reference
		kg ha^{-1}		
This study	55.8	55.5	0.3	
Thompson Site, WA (Douglas fir)	30.8	36.5	–5.7	Johnson *et al*., 1986
Thompson Site, WA (Red alder)	25.4	17.0	8.4	Johnson *et al*., 1986
Camp Branch, TN	46.6	20.9	25.7	Johnson *et al*., 1986
Walker Branch, TN (Chestnut oak)	95.4	55.9	39.5	Johnson *et al*., 1986
Walker Branch, TN (Yellow-poplar)	78.0	130.0	–52.0	Johnson *et al*., 1986
Peavine Hill, PA	86.8	131.0	–44.2	DeWalle *et al*., 1988
Leading Ridge, PA	35.2	39.4	–4.2	Lynch and Corbett, 1989
Fork Mountain, WV	53.0	25.1	27.9	Helvey and Kunkle, 1986
Coweeta, NC	34.9	9.4	25.5	Swank and Waide, 1988
Hubbard Brook, NH	62.8	52.6	10.2	Eaton *et al*., 1980
Birkenes, Norway	68.4	78.8	–10.4	Christophersen and Wright, 1981

other studies (Sharpe *et al*., 1989; DeWalle *et al*., 1988) show that this designation is too simple and does not hold for all sites south of the line of Wisconsinan glaciation (Table V).

The inability to make simple regional generalizations related to outputs and net accumulation is illustrated most clearly by comparing results from watersheds that are located in the same general area. For example, the yellow-poplar and chestnut oak Walker Branch sites have slightly different inputs but decidedly different outputs and net retention (Table V). Retention is occurring on the chestnut oak site, but net loss is occurring on the yellow-poplar site. Differences also exist for the Douglas fir and red alder catchments at the Thompson site (Table V), though the magnitude of differences is much less. Retention differences are attributed to soil chemistry variations at both locations (Johnson *et al*., 1986).

SH5 is located only 6 km from the Fork Mountain site (Table V) but has significantly different outputs and retention characteristics, even though inputs were similar. Approximately 50% of sulfate deposition is retained within the Fork Mountain catchment (Table V), while retention is approximately zero on SH5 (Table III).

Soil chemistry was not reported for Fork Mountain, but it appears to be significantly different than for SH5. The dominant soil series at Fork Mountain is Calvin channery silt loam (Helvey and Kunkle, 1986), which has a higher nutrient content than other soils from which net sulfate losses have been reported (DeWalle *et al*., 1988).

For many watersheds, including SH5, seasonal accumulations and deficits of sulfate are common whether net sulfate retention or loss occurs. At Birkenes in Norway, sulfate accumulations occur in the summer, but they are followed by a period of net loss in autumn during periods of heavy rains. Winter accumulation due to snowpack presence then follows. In spring, net loss again is observed as snowpacks melt (Christophersen and Wright, 1981).

Accumulation and loss patterns at Hubbard Brook correspond more closely to those shown for SH5. The year is divided into only one net accumulation period and one net loss period. At Hubbard Brook, sulfate accumulates from June through September (Likens *et al*., 1977). This period is slightly shorter than on SH5 and probably reflects the shorter transpirational period from a shorter, more-northern growing season. During the rest of the year at Hubbard Brook, exports exceed inputs, with about 52% of the sulfate output occurring from March to May (Likens *et al*., 1977).

This timing of maximum sulfate export is approximately the same for Hubbard Brook in New Hampshire, Leading Ridge in Pennsylvania (Lynch and Corbett, 1989) and Birkenes in Norway (Christophersen and Wright, 1981). Maximum export occurs later than on SH5, and probably is due to snowmelt effects. Snowpack storage of sulfate and water for the more-northern New Hampshire, Pennsylvania, and Norway sites results in delayed release of water and sulfate to runoff (Likens *et al*., 1977; Christophersen and Wright, 1981) compared to SH5. Annual snowfall totals can be quite high in the SH5 area, but prolonged snowpack accumulations are very rare (Northeastern Forest Experiment Station, 1987), and snowpack melt on SH5 is early and rapid due to its southwest aspect.

4. Conclusion

Sulfate input/output budgets were analyzed for a small Appalachian watershed for five years. Analyses showed that bulk deposition measurements could not be used to estimate sulfate inputs accurately because the dry component of sulfur was underestimated. However, adjusting the bulk loadings with throughfall estimates produced better estimates of sulfate inputs. Comparing annual throughfall-adjusted inputs to outputs indicated that the watershed has reached equilibrium with its sulfate adsorption capacity and current levels of sulfate deposition.

Seasonal accumulations and deficits of sulfate existed within each year. Sulfate accumulated during the growing season when wet and dry inputs were high but outputs were minimal due to high evapotranspirational demands. During the

dormant season, especially December through March, outputs exceeded inputs because watershed runoff was high. Similar seasonal net accumulations and net losses have been reported in other studies. In those studies, sulfate lost during periods of net export was attributed to sulfate stored during that year's period of net accumulation. However, radio-isotopic evidence on this watershed from a companion study illustrated that not all of the accumulated sulfate was lost within the year, and sulfate lost during periods of net export probably represents ions of many ages with respect to time of deposition.

Data on soil leachate chemistry suggest that sulfate losses (in discharge) during the period of net export were the result of progressive leaching of soluble sulfate from upper soil layers through deeper ones over time. While these losses were driven by soil moisture provided by precipitation, most of the sulfate discharged was not associated with subsurface flow immediately during and following precipitation events. Rather, most of the sulfate was lost due to deeper, more continuous leaching.

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