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Stable sulfur isotopic biogeochemistry of the Hubbard Brook Experimental Forest, New Hampshire

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Abstract. In natural ecosystems, differences often exist in the relative abundance of stable S isotopes (δ^{34}S) that can provide clues as to the source, nature, and cycling of S. Values of δ^{34}S in precipitation, throughfall, soils, soil solution, and stream waters were measured at the Hubbard Brook Experimental Forest (HBEF), New Hampshire. Values of δ^{34}S in precipitation and throughfall were similar to each other but differed seasonally. Precipitation δ^{34}S values were higher in the dormant season [δ^{34}S = 5.9±0.6‰ (17)] [Mean+SE(N)] than in the growing season [δ^{34}S = 5.0±0.6‰ (40)] but throughfall growing-season values were higher [δ^{34}S = 5.6±0.6‰ (68)] than for the dormant season [δ^{34}S = 4.9±0.7‰ (9)]. Different tree species did not affect throughfall δ^{34}S values. In soil solution, δ^{34}S values were higher in the growing season (δ^{34}S = 8.9±2.8‰; 8.8±1.7‰; and 4.0±0.6‰ for Oa, Bh, and Bs horizons, respectively) than in the dormant season (δ^{34}S = 5.6±1.5‰; 3.7±2.4‰; and 3.4±1.2‰ for Oa, Bh, and Bs horizons, respectively). These seasonal differences in δ^{34}S were probably caused by biological isotopic fractionation. The δ^{34}S values in streams were generally 2‰ lower and more variable than those in precipitation and throughfall, suggesting fractionation and/or different isotopic sources in the soil.

Introduction

Stable isotopes of S can be used for tracing the cycling of S within ecosystems (Krouse & Grinenko, 1991). The use of stable isotopes in evaluating the S biogeochemistry of forested ecosystems has been reviewed by Mitchell et al. (1998). There are two different approaches: (1) following the fate of added S with an isotopic composition distinct from other pools and sources of S; or (2) evaluating differences in the natural abundance of S constituents within an ecosystem. This latter natural abundance approach may be used to evaluate a wide range of biogeochemical processes.

The S isotopic composition of an ecosystem component is controlled by essentially two factors: the isotopic composition of sources (in combination with mixing ratios) and isotopic discrimination during transformations. These factors may result in substantial variation in natural abundances of S isotopes with δ^{34}S values typically ranging from -40 to $+40$‰ (Krouse & Grinenko 1991). Much of the differences in S isotopic composition among materials can be attributed to large kinetic isotope effects in microbially mediated S transformations of which the dissimilatory sulfate reduction is most important. There is also some evidence that other processes such as microbial immobilization and emissions of biogenic S gases may change the isotopic composition of S pools (Mitchell et al. 1997).

There have been relatively few studies which have examined the natural isotopic composition of S compounds in forest catchments (Mitchell et al. 1998). Here, we will focus on the Hubbard Brook Experimental Forest (HBEF) which has been a focal point of biogeochemical research using small watersheds for 34 years (Likens & Bormann 1995). At this same site, Fuller et al. (1986) previously examined the isotopic composition of organic and inorganic S fractions in the soil as well as SO_4^{2-} in soil water and surface waters. Their analysis was done in Watershed 5 of the HBEF before whole tree harvesting in the winter of 1983–1984. The isotopic composition of SO_4^{2-} extracted from the soil (both adsorbed and soluble forms) generally corresponded to that of SO_4^{2-} in soil solutions obtained by lysimeters. These inorganic soil SO_4^{2-} pools tended to have higher δ^{34}S values than those of organic S. The reason for the lower δ^{34}S in the organic constituents was not known, but it has since been suggested that the formation of the organic S occurred over a long period (Mitchell et al. 1989) dating from the end of the last glaciation some 14,000 yr BP (Likens & Davis 1975; Davis et al. 1985). Low δ^{34}S values of organic S have also been documented for a site in the Black Forest of Germany (Mayer et al. 1995a).

Fuller et al. (1986) also measured concentrations of SO_4^{2-} and δ^{34}S values of SO_4^{2-} along an elevational gradient in soil and stream water during one year at the HBEF. Sulfate concentrations and δ^{34}S values both decreased at lower elevations. The higher SO_4^{2-} concentrations in the upper elevations may have been due partly to a somewhat greater abundance of conifers which are effective collectors of dry deposited S (Lindberg et al. 1986; Hultberg & Likens, 1992; Mitchell & Lindberg, 1992; Hultberg et al. 1994). The reason for the change in δ^{34}S values was not known, but Fuller et al. (1986) suggested that it might have been due to (1) differential contributions of S from weathering of minerals with distinctive δ^{34}S compositions, (2) isotopic fractionation between SO_2 and HSO_3^- in the atmosphere and differences in the relative contribution of dry and wet deposition with elevation and (3), most likely, the increasing contribution to sulfate reduction processes with decreasing elevation due to an increase in the contribution of saturated zones.

The objective of this research was to expand the evaluation of natural abundance of S isotopes in precipitation, throughfall, soil, soil solutions, and streams at the HBEF and use this information for evaluating some aspects of the biogeochemistry of S.

Site description

The Hubbard Brook Experimental Forest in the White Mountain National Forest in New Hampshire (43°56′ N, 71°45′ W) has been the site of ecological and biogeochemical research since 1963 (Likens & Bormann 1995). This research was conducted east of Norris Brook within the Norris Brook Watershed at the HBEF at an elevation of about 350 m. The soils of the Norris Brook Watershed are mostly well drained, sandy loam Spodosols (Typic Fragiorthods) that developed in sandy till (Christ et al. 1995).

In this northern hardwood forest, the overstory was dominated by American beech (*Fagus grandifolia*), with yellow birch (*Betula alleghaniensis*), sugar maple (*Acer saccharum*), red maple (*Acer rubrum*), and smaller amounts of hemlock (*Tsuga canadensis*), red spruce (*Picea rubens*), balsam fir (*Abies balsamea*) and white ash (*Fraxinus americana*) also present.

Methods

Bulk precipitation and throughfall

Two racks, each with three bulk precipitation collectors, were installed in a cleared, open site behind the Robert S. Pierce Ecosystem Laboratory in July 1991. Collectors were similar to those used by Eaton et al. (1973) except 2-L plastic bags, instead of 2-L glass bottles, were used as reservoirs. A rack in a cleared area in Watershed 6 (W6) was used for sampling precipitation events. Six racks of throughfall collectors were also installed near the soil solution study plots (described below) in July 1991. Four of the racks were located under beech, one under hemlock, and one under a sugar maple canopy.

Precipitation in the cleared sites and throughfall were collected immediately after each precipitation event ($\geq$ 0.25 mm of precipitation bounded by 6 hours dry periods before and after collection). Event precipitation samples at W6 were collected from October 3, 1991 to November 30, 1992. These samples were not part of the long-term record for the HBEF (Likens &

Bormann 1995) as collection and analytical procedures were different. Event precipitation from the open site behind the Robert S. Pierce Laboratory and event throughfall from the lysimeter plot area were collected from August 5, 1991 to August 1, 1992. Samples were divided into growing and dormant season collections for statistical analyses. The growing season was defined as May 1 through September 30 and approximated the time from bud break to leaf abscission. The remaining seven months constituted the dormant season. During the dormant season funnels were replaced with 76 L (20-gallon) buckets for collection of snow. Bulk precipitation and throughfall samples were collected monthly during the dormant season. Frozen samples were melted over night at room temperature and any debris (e.g., leaf litter) removed by hand.

Soil solution

In the Norris Brook Watershed in the summer of 1988 zero-tension lysimeters (Driscoll et al. 1988) were installed in fourteen plots (6 × 8 m) that had been previously selected to avoid large boulders and wetland. An excavated pit in each plot was used for the upslope installation of a pair of lysimeters underneath the Oa, Bh and Bs horizons, respectively. Pits were backfilled after installation (Christ et al. 1995).

Soil solutions were sampled monthly from June 5, 1990 to November 27, 1992 (Christ et al. 1995). Volumes were determined and the samples transported in clean polyethylene bottles to the laboratory in Syracuse, N.Y. for analysis.

Surface water

Samples from Norris Brook and a small stream which is the western tributary to Mirror Lake were obtained at the same time as when the lysimeter solutions were collected. Samples from Hubbard Brook were taken about 0.5-km south from the Robert S. Pierce Ecosystem Laboratory. Watershed 6 and Watershed 1 stream samples were collected monthly from July 1991 through December 1992. For the latter two watersheds, samples were obtained directly above the gauging weirs. Sample handling was the same as for soil solutions.

Soils

Soil samples were collected during May 21–22, 1991, and June 9–11, 1992. A section of the forest floor was cut away, and a 50-cm long core of mineral soil collected with a 5-cm diameter PVC pipe and divided by horizons. At least 300 g of soil for each horizon were needed for the S isotopic analyses. All soil samples were sealed in plastic bags, returned to the laboratory in Syracuse, and kept frozen until further processing. Soil samples were freeze dried and ground in a "coffee grinder" to ensure homogeneity prior to analyses.

Preparation for isotopic analyses

Solutions – Samples were stored at 1 °C, filtered using Whatman® GF/C filters and then passed through an anion exchange column (Dowex-1® resin with 25–50 mesh, Cl^- form) at a maximum flow rate of 20 ml min^{-1}. A 5% HCl solution was passed through the column at a maximum flow rate of 100 ml min^{-1} to elute the adsorbed SO_4^{2-}. The eluant was neutralized with a concentrated NaOH solution and SO_4^{2-} precipitated with $BaCl_2$. The precipitate was collected onto Metrical® membrane filters (0.45-μm pore) and dried at 60 °C. At least 1 mg of S was the minimum mass required for isotopic determination and thus solutions from replicated collectors often had to be combined to obtain sufficient amounts of S.

Soil – Approximately 10 g of organic soil and 30 g of mineral soil (freeze-dried) were required to yield 1 mg of S for measurement of $\delta^{34}S$. A solution of 15 mmol phosphate (Na_2HPO_4) buffer solution was used to extract inorganic SO_4^{2-}. After shaking for an hour, the slurry was centrifuged at 2000 rpm for 30 minutes. The supernatant then was decanted to a 1000-ml beaker and neutralized with concentrated NaOH solution. The soil residue from the phosphate extraction was saved for analysis of ester sulfate. Sulfate in the neutralized solution was precipitated with $BaCl_2$. The precipitate was collected onto Metrical® membrane filters and kept frozen before chemical reduction to ensure sample purity. The $BaSO_4$ collected on the membrane filter from phosphate extraction and ester sulfate in the soil residue were separately reduced to H_2S with a mixture of hydriodic acid using a modified (500-ml flask) Johnson-Nishita digestion-distillation apparatus (Landers et al. 1983). The H_2S was precipitated with Zn acetate and collected onto the 0.45-μm membrane filters and oven-dried at 105 °C.

Isotopic analysis

All the $BaSO_4$ collected from solutions and ZnS samples from soil were sent to the Stable Isotope Laboratory at the University of Calgary, Alberta, Canada for ^{34}S determination using mass spectrometry.

Stable isotope ratios of S in $BaSO_4$ and ZnS were determined on a mass spectrometer built around a Micromass 602 analyzer (Krouse & Case 1981). Sulfur isotope ratios are expressed in the standard $\delta^{34}S$ notation: $\delta^{34}S$ (l) = $[(R_{sample}/R_{standard}) - 1] \times 1000$, where R_{sample} and $R_{standard}$ refer to the $^{34}S/^{32}S$ abundance ratio of the sample and the internationally accepted standard troilite (FeS) from the Canyon Diablo meteorite, respectively. $(NH_4)_2SO_4$ with $\delta^{34}S = -3.0‰$ (N = 25; SE = 0.1) was used as an intra-laboratory analytical standard.

Results and discussion

Bulk precipitation

Sulfate concentration in precipitation was greater during the growing season versus the dormant season at the Robert S. Pierce Ecosystem Laboratory site (Table 1). The absence of seasonal differences at the open site at W6 may have been due to the smaller number of samples analyzed. Higher SO_4^{2-} concentrations in summer precipitation have been reported elsewhere for the northeastern USA and been attributed to both the greater use of fossil fuels and more rapid conversion of sulfur dioxide to SO_4^{2-} during the summer compared to the winter (Mitchell et al. 1992; Sisterson et al. 1990; Venkatram et al. 1990). The $\delta^{34}S$ values also varied with season (Table 1). At the W6 site, the mean $\delta^{34}S$ value for precipitation was higher in the dormant season (5.9‰; range 4.5 to 7.4‰; N = 7) than the growing season (4.9‰; range 1.7 to 8.0‰; N = 16). A similar pattern was found at the Robert S. Pierce Ecosystem Laboratory site with a higher average $\delta^{34}S$ value in the dormant season (5.9‰; range 3.0 to 12.7‰; N = 10) than in the growing season (5.1‰; range 1.1‰ to 5.7‰; N = 24). A similar seasonal trend in precipitation $\delta^{34}S$ values was found by Nriagu and Coker (1978) in comparing 19 sampling sites across the Laurentian Great Lakes region with higher values in the winter ($\delta^{34}S = 6.4 \pm 0.98‰$) than the summer ($\delta^{34}S = 2.9 \pm 1.0‰$). They suggested that the seasonal differences in $\delta^{34}S$ values were due, in part, to changes in the relative amounts of the atmospheric S compounds derived from biogenic and anthropogenic sources. In summer, biogenic S released from soils and wetlands is characteristically depleted in ^{34}S (Grey & Jensen 1972; Nriagu et al. 1987; Nriagu & Krouse 1992), decreasing $\delta^{34}S$ values in precipitation.

The growing season $\delta^{34}S$ values in precipitation SO_4^{2-} measured in the current study were also similar to $\delta^{34}S$ values (range -1.6 to +7.6l) reported for precipitation at Bear Brook Watershed in eastern Maine (Stam et al. 1992), but higher by about 2‰ than the $\delta^{34}S$ values previously reported by Fuller et al. (1986) in bulk precipitation ($\delta^{34}S$ range +2.3 to +3.0‰) and by Saltzman et al. (1983) in SO_4^{2-} aerosols ($\delta^{34}S$ range from +0.8 to +3.5‰) at the HBEF. If biogenic S sources were contributing proportionately more to S deposition due to a decline in anthropogenic S emissions (Likens 1992; Driscoll et al. 1995), then a decline and not an increase in $\delta^{34}S$ values in precipitation would be expected. However, we currently do not have accurate information

Table 1. δ^{34}S (‰) values and SO_4^{2-} concentrations in bulk precipation and throughfall at the Hubbard Brook Experimental Forest during 1991–1992.

Site/Seasons[6]	N	δ^{34}S (SE)	δ^{34}S Range	SO_4^{2-} (μmol L^{-1})
Bulk Precipitation				
W6 open				
Growing Season	16	4.9 (0.4)	1.7 to 8.0	29.5 (3.4)
Dormant Season	7	5.9 (0.7)	4.5 to 7.4	29.5 (5.1)
Robert S. Pierce Ecosystem Laboratory Site Open				
Growing Season	24	5.1 (0.7)	1.1 to 5.7	28.5 (2.8)
Dormant Season	10	5.9 (0.5)	3.0 to 12.7	24.0 (0.9)
Throughfall				
Growing Season				
Beech #1	12	6.1 (0.6)	3.7 to 9.7	31.5 (1.5)
Beech #2	12	5.2 (0.6)	0.9 to 7.9	30.5 (4.2)
Beech #3	12	5.6 (0.7)	1.1 to 9.3	32.0 (3.0)
Beech #4	11	5.9 (0.7)	1.7 to 8.8	28.0 (2.5)
Hemlock	11	5.2 (0.5)	3.0 to 7.7	38.5 (3.5)
Sugar Maple	10	5.6 (0.4)	4.0 to 8.2	28.5 (5.1)
Dormant Season				
plot 18 (beech)	5	5.1 (0.8)	2.5 to 7.6	24.0 (7.8)
plot 20 (maple)	4	4.8 (0.5)	3.4 to 5.6	29.0 (11.2)

The growing season was definedd as May 1 through September 30 and approximated the time from bud break to leaf abscission. The remaining seven months constituted the dormant season.

on the relative contributions of various isotopic sources of S to draw any firm conclusions about long-term changes of the δ^{34}S values in precipitation.

Throughfall

The δ^{34}S values in throughfall did not differ significantly ($p>0.05$) under the three tree species (Table 1). The mean δ^{34}S values ranged from 5.2‰ under hemlock to 6.1‰ under beech in the growing season, and from 4.8‰ under sugar maple to 5.1‰ under beech in the dormant season. The hemlock throughfall tended to have the lowest δ^{34}S value, and the highest concentration of SO_4^{2-}. Also the δ^{34}S values tended to be lower in the dormant season compared to those in the growing season. Throughfall δ^{34}S values measured in the current study were similar to the δ^{34}S values (range −0.7 to +7.5‰) in throughfall SO_4^{2-} at Bear Brook Watershed (Maine) (Stam et al. 1992).

There was no significant difference ($p>0.05$) between the δ^{34}S values measured in throughfall and precipitation (Table 1). While the dormant season δ^{34}S values in precipitation tended to be higher than those in the growing season, the opposite was true for the δ^{34}S values in the throughfall. Also, in the growing season the δ^{34}S values in throughfall were in general higher than the δ^{34}S values in the precipitation (Table 1). It has been shown that dry deposition of S contributes to throughfall SO_4^{2-} fluxes (Lindberg & Garten 1989; Lovett et al. 1992). Thus, differences between precipitation and throughfall δ^{34}S values could have been due to canopy alterations including the contribution of dry deposition of S with a different isotopic composition than that of precipitation.

Soil solution

Sulfate δ^{34}S values ranged from -1.6 to 18.1, -4.0 to 14.4 and -1.7 to 8.5 in Oa, Bh, and Bs horizon solutions, respectively (Figure 1). In general, there was no difference between δ^{34}S values in Oa solution and those in Bh solution. The δ^{34}S values in the Bs solution were, in general, less variable than those in the Oa and Bh solutions. Variances of the mean δ^{34}S concentrations were 24.7, 34.5, and 7.5 for Oa, Bh and Bs horizons, respectively. The variation in soil solutions δ^{34}S values were much greater than that for precipitation and throughfall indicating that this variation was due to soil effects and not differences due to inputs from the atmosphere.

In soil solution, δ^{34}S values were higher in the growing season (δ^{34}S = 8.9±2.8‰; 8.8±1.7‰; and 4.0±0.6‰ for Oa, Bh, and Bs horizons, respectively) than in the dormant season (δ^{34}S = 5.6±1.5‰; 3.7±2.4‰; and 3.4±1.2‰ for Oa, Bh, and Bs horizons, respectively). The seasonal difference in δ^{34}S may be the result of biological utilization of SO_4^{2-} in the ecosystem. If SO_4^{2-} were taken up from soil solutions during the growing season with preferential utilization of ^{32}S, the δ^{34}S of SO_4^{2-} remaining in solution would increase. Although there is some evidence that assimilation by some plants discriminates against ^{34}S resulting in lower δ^{34}S values (-1 to -2‰) (Krouse et al. 1991), it is generally believed that most biological assimilation of SO_4^{2-} results in little isotopic fractionation (Kusakabe et al. 1976). It has also been suggested that microbial mineralization and immobilization processes may be important in affecting the isotopic composition of organic S resulting in high (+3.6‰ enrichment) and low (-1‰ depletion) δ^{34}S values for ester sulfates and carbon-bonded S, respectively (Mayer et al. 1992). Thus, if these organic S pools are mineralized this could cause differences in δ^{34}S values of SO_4^{2-} in the soil solution.

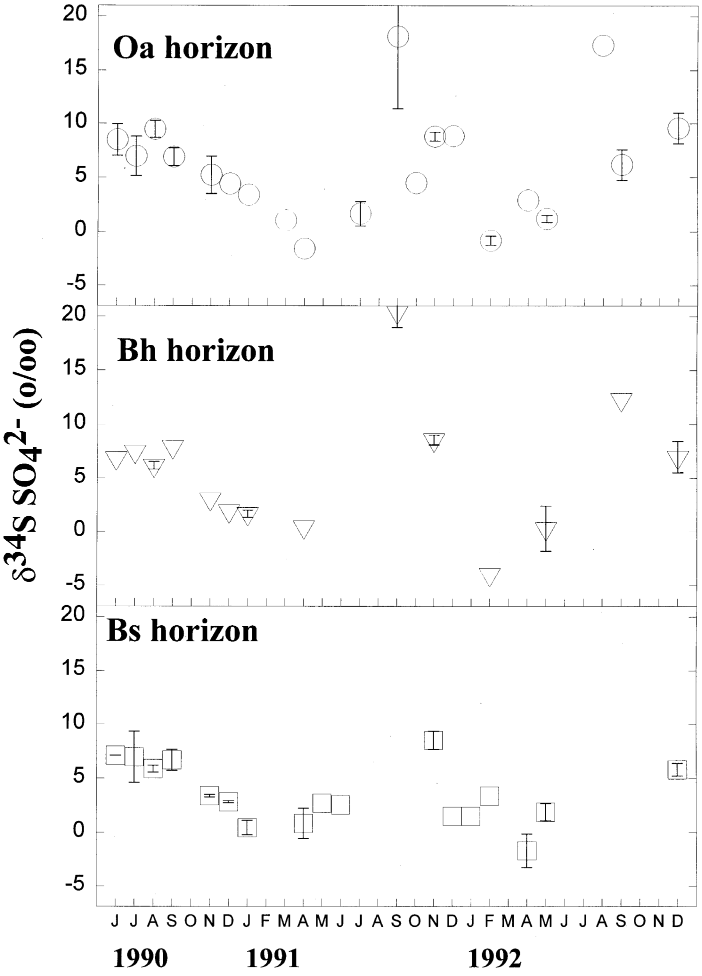

Figure 1. Mean monthly δ^{34}S SO_4^{2-} values in soil solutions of Oa, Bh, and Bs horizons in the Norris Brook Watershed at the Hubbard Brook Experimental Forest (HBEF). Vertical bars are standard errors.

Soil

The δ^{34}S values of extracted SO_4^{2-} and ester sulfate varied among horizons and years (Figure 2). Soil sampled in June 1992 generally had lower δ^{34}S values for extractable SO_4^{2-} than that in May 1991 (Figure 2). These differences in δ^{34}S values between years in extractable SO_4^{2-} in the forest floor (0.3‰) were less than differences in the Bh (3.0‰) and Bs (1.4‰) horizons. The δ^{34}S values in soil ester sulfate also varied with horizon as well as

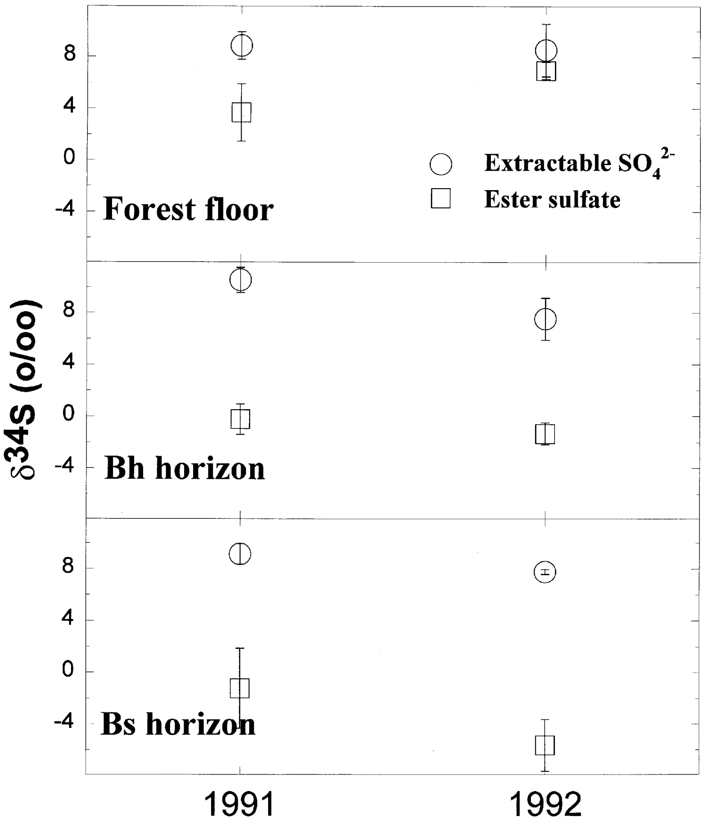

Figure 2. δ^{34}S values in extractable sulfate and ester sulfate of Oa, Bh, and Bs horizons in the Norris Brook Watershed of the HBEF. Vertical bars are standard errors.

between sampling years (Figure 2). In 1992, the δ^{34}S value for ester sulfate in the forest floor was higher than that in 1991, but the δ^{34}S values of this fraction of Bh and Bs horizons were lower than those in 1991, especially in the Bs horizon (−5.7‰ in 1992 and −1.3‰ in 1991). The soil conditions at the time of sampling may have affected the δ^{34}S values.

In 1991 samples were collected in the early growing season when soils were generally cool and wet whereas 1992 samples were collected when leaves had developed fully. The mean air temperatures for the May 1991 and June 1992 sampling were 13.3 and 15.2 °C, respectively. The current and proceeding soil conditions would affect S fluxes and possibly affect the δ^{34}S values of extractable SO_4^{2-} and ester sulfate.

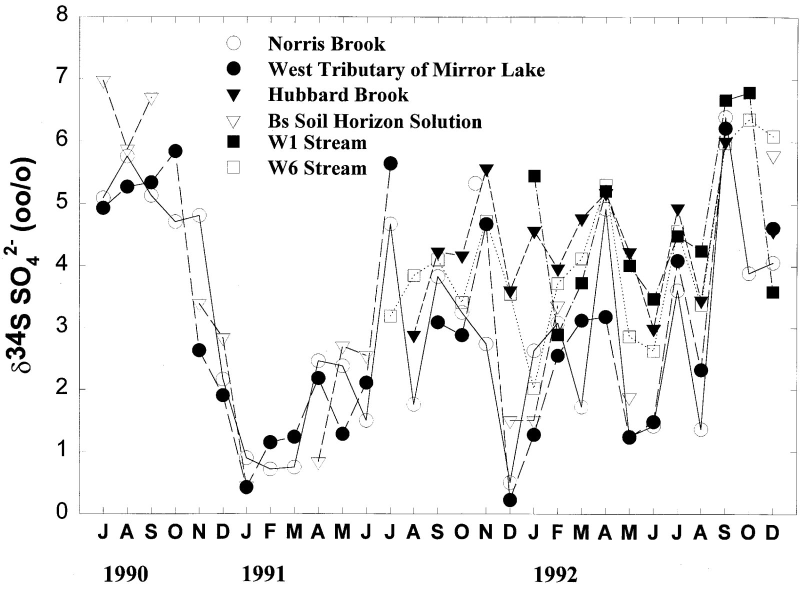

Figure 3. δ^{34}S SO_4^{2-} values in streams and Bs horizon solutions at the Hubbard Brook Experimental Forest.

Streams

The δ^{34}S SO_4^{2-} values in five streams at the HBEF are presented in Figure 3. The mean δ^{34}S value of Norris Brook was 3.0‰, identical to that of the West Tributary of Mirror Lake. Similarly, the mean δ^{34}S value of 4.1‰ for Hubbard Brook was the same as for the stream draining Watershed 6. The mean δ^{34}S value for the stream draining Watershed 1 was 4.6‰ and thus higher than the δ^{34}S values for the other four streams. Since δ^{34}S values for stream SO_4^{2-} may show temporal variation, it is more appropriate to compare the Watershed 1 values with mean values from the other streams taken for the identical period. A comparison over this period results in a general increase in δ^{34}S values (4.5‰, 4.3‰, 3.0‰, and 3.0‰, for Hubbard Brook, W6 stream, Norris Brook, and West Tributary of Mirror Lake, respectively), but the δ^{34}S values for these streams were still lower than for Watershed 1.

For all five streams, δ^{34}S values of SO_4^{2-} showed temporal variation (Figure 3). Between the summer of 1990 and the spring of 1991, a distinct seasonal pattern of δ^{34}S was observed in the Norris Brook and the West Tributary of Mirror Lake: δ^{34}S values were high in the summer and low in the winter (Figure 3). This seasonal trend was also shown in soil solution data from the Bs horizon (Figure 3). However, this seasonal pattern of δ^{34}S

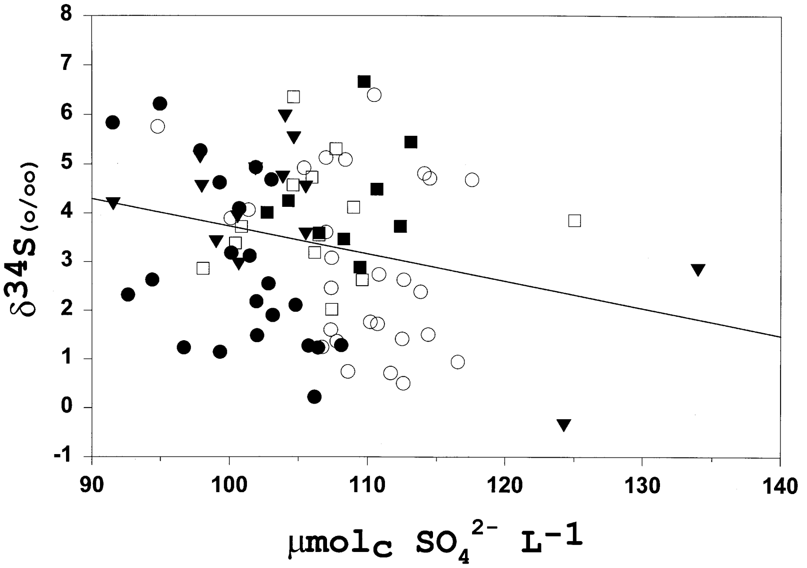

Figure 4. Sulfate concentrations versus δ^{34}S values in streams (calculated regression line). $y = -0.056X + 9.37$ ($r = 0.244$, $p<0.05$). Symbols the same as in Figure 3.

was not evident in 1992, but there was a general synchrony among streams in δ^{34}S values for all sampling times (Figure 3).

Previous work at the HBEF showed that the δ^{34}S values of SO_4^{2-} in the stream draining Watershed 5 were positively correlated with the SO_4^{2-} concentration (Fuller et al. 1986). In contrast, a negative relationship ($N = 86$, $r = -0.45$; $p<0.01$) between the δ^{34}S values and SO_4^{2-} concentrations was found for the five streams in the current study (Figure 4). A negative relationship between δ^{34}S values and SO_4^{2-} concentrations was also found in the streams of forested watersheds in Ontario, Canada (Hesslein et al. 1988).

Use of δ^{34}S values in evaluating S biogeochemistry at the HBEF

There are various sources and processes that may have affected the S isotopic composition of the surface waters at the HBEF including atmospheric inputs, weathering of minerals, plant uptake, immobilization/mineralization, and SO_4^{2-} adsorption/desorption. A general depiction of the δ^{34}S SO_4^{2-} values among ecosystem strata and between the dormant and growing season is given in Figure 5. Mass balance studies at the HBEF show that bulk precipitation inputs approximate stream water outputs assuming that dry deposition accounted for 37% of the total deposition from 1964–1987 (Likens et al.

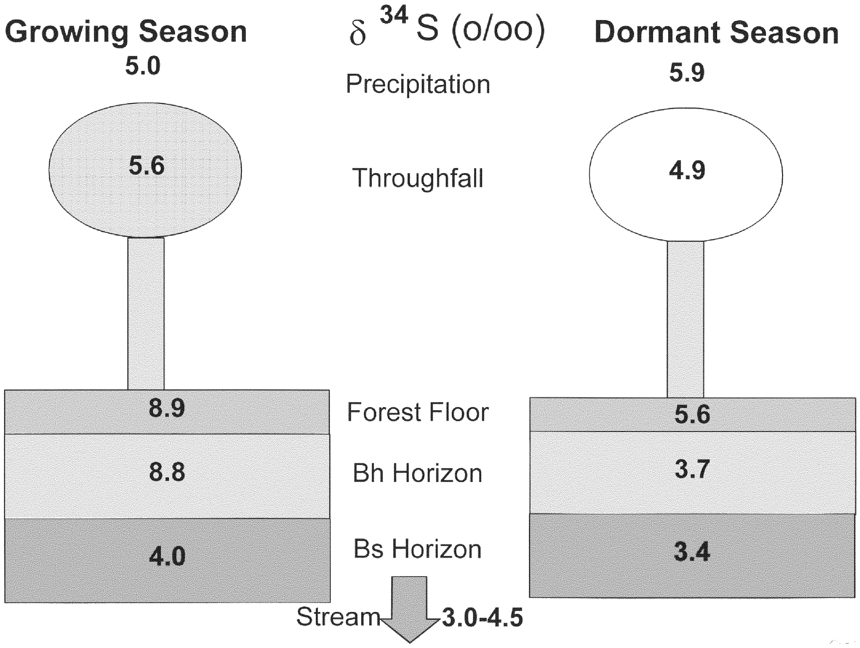

Figure 5. Generalized diagram of the δ^{34}S SO_4^{2-} values in various components of the Hubbard Brook Experimental Forest in the growing and dormant seasons.

1990). However, other studies in the northeast United States have suggested that some watersheds have been recently exhibiting net losses of SO_4^{2-} that may have been stored in the soil during periods of higher deposition (Driscoll et al. 1995; Mitchell et al. 1996).

The δ^{34}S values in streams were about 2‰ lower than those of precipitation and throughfall (Table 1; Figures 3 and 5) suggesting that there was a source of SO_4^{2-} in the soil with lower δ^{34}S values and/or isotopic discrimination processes were affecting stream SO_4^{2-} δ^{34}S values. Throughfall values were only slightly lower δ^{34}S (0.1–0.3‰) than those of precipitation. The three predominant rock types at the HBEF are Granodiorite (very low concentrations of S), Camptonite, a fine-grained diabase (δ^{34}S = −7.1l) containing small amount of pyrite, and the Upper Rangeley Formation (δ^{34}S = +9.2l), a schist bedrock of Sillimanite grade that contains pyrrhotite (Fuller et al. 1986; Barton et al. 1997). It has been generally reported that weathering of bedrock is a minor source of S to the ecosystems at the HBEF (estimated at 4% of total S input; Likens et al. 1990; Likens & Bormann 1995). However, if pyrrhotite weathering in the Upper Rangeley Formation is a significant source of S, this conclusion may need further consideration (Barton et al. 1997).

The δ^{34}S values in soil organic S have been shown to range from -5 to 4.8‰ at the HBEF (Fuller et al. 1986). Other studies have also shown that δ^{34}S values of organic S are lower than other S pools in the soil (e.g., Mayer et al. 1995a). It is likely that the mineralization of organic S was an important source of S and contributed to the lower δ^{34}S values of stream waters. Analyzing both the δ^{18}O and the δ^{34}S values of solution SO_4^{2-} in the Black Forest of Germany (Mayer et al. 1995a) also concluded that the mineralization of carbon-bonded S was an important source of SO_4^{2-} in soil solutions and streams. In contrast, it has been generally concluded that SO_4^{2-} adsorption/desorption reactions show negligible isotopic discrimination (Van Stempvoort et al. 1990; Van Stempvoort & Krouse 1994; Mayer et al. 1992, 1993, 1995b). During the dormant season at the HBEF the δ^{34}S SO_4^{2-} values of soil solution, especially in the forest floor and Bh horizon, were lower than during the growing season (Figure 5). The dormant season is responsible for most of the annual SO_4^{2-} drainage losses due to high discharge rates, especially during snow melt periods (Likens & Bormann 1995).

Isotopic studies have also shown that under experimental additions that much of the added S may be retained within forest ecosystems although there may still be significant export of S from other pools within the forest ecosystem (Mitchell et al. 1998). Results from studies at the HBEF (Nodvin et al. 1988; Mitchell et al. 1989) as well as from other forest ecosystems (Johnson & Mitchell 1997) suggest that much of the temporal and spatial patterns of solute SO_4^{2-} appear to be regulated by adsorption/desorption processes. However, studies with stable isotopes clearly indicate that the mineralization of soil organic matter with its large pool of organic S (Mitchell et al. 1992) is a substantial source of S for soil solutions and surface waters.

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