Biogeochemistry **44:** 281–299, 1999.

Sources of stream sulfate at the Hubbard Brook Experimental Forest: Long-term analyses using stable isotopes

C. ALEWELL[1,*], M.J. MITCHELL[1], G.E. LIKENS[2] & H.R. KROUSE[3]
[1]*S.U.N.Y., College of Environmental Science and Forestry, Syracuse, New York 13210, USA;* [2]*Institute of Ecosystem Studies, Millbrook, New York 12545, USA;* [3]*The University of Calgary, Department of Physics and Astronomy, Calgary, Alberta, T2N 1N4, Canada (*Current address: BITÖK, Universität Bayreuth, Dr.-Hans-Frisch-Str.1-3, 95440 Bayreuth, Germany)*

Accepted May 26 1998

Key words: isotopes, mass balances, precipitation, sulfur, watersheds

Abstract. Sulfur deposition in the northeastern U.S. has been decreasing since the 1970s and there has been a concomitant decrease in the SO_4^{2-} lost from drainage waters from forest catchments of this region. It has been established previously that the SO_4^{2-} lost from drainage waters exceeds SO_4^{2-} inputs in bulk precipitation, but the cause for this imbalance has not been resolved. The use of stable S isotopes and the availability of archived bulk precipitation and stream water samples at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire provided a unique opportunity to evaluate potential sources and sinks of S by analyzing the long-term patterns (1966–1994) of the $\delta^{34}S$ values of SO_4^{2-}. In bulk precipitation adjacent to the Ecosystem Laboratory and near Watershed 6 the $\delta^{34}S$ values were greater (mean: 4.5 and 4.21, respectively) and showed more variation (variance: 0.49 and 0.30) than stream samples from Watersheds 5 (W5) and 6 (W6) (mean: 3.2 and 3.7; variance: 0.09 and 0.08, respectively). These results are consistent with other studies in forest catchments that have combined results for mass balances with stable S isotopes. These results indicate that for those sites, including the HBEF, where atmospheric inputs are ≤ 10 kg S ha^{-1} yr^{-1}, most of the deposited SO_4^{2-} cycles through the biomass before it is released to stream water. Results from W5, which had a whole-tree harvest in 1983–1984 showed that adsorption/desorption processes play an important role in regulating net SO_4^{2-} retention for this watershed-ecosystem. Although the isotopic results suggest the importance of S mineralization, conclusive evidence that there is net mineralization has not yet been shown. However, S mass balances and the isotopic result are consistent with the mineralization of organic S being a major contributor to the SO_4^{2-} in stream waters at the HBEF.

Introduction

Biogeochemical research during the last thirty years has improved considerably our understanding of S cycling in forest ecosystems. However, important questions remain unresolved that hinder our ability to understand and predict how changing atmospheric S inputs will affect S loses from forest ecosystems (e.g., Johnson & Mitchell 1998). Since the late 1960s, anthropogenic emissions have been declining in eastern North America. This decreasing S deposition in forest ecosystems has resulted in decreasing concentrations and fluxes of SO_4^{2-} in drainage waters in the northeastern US (Driscoll et al. 1995; Likens 1992; Likens & Bormann 1995) and Europe (Wright et al. 1993; van Dijk et al. 1992). Despite these decreases SO_4^{2-} output from forest ecosystems via drainage waters exceeds SO_4^{2-} input in bulk precipitation in the northeastern U.S. (Likens et al. 1990; Likens & Bormann 1995). Possible sources for this additional S output include dry deposition, weathering of S minerals, reoxidation of reduced S, desorption of previously adsorbed inorganic SO_4^{2-} and mineralization of organic S. Mitchell et al. (1992a) suggested that desorption of SO_4^{2-} that had accumulated during periods of higher S deposition may have contributed to the additional SO_4^{2-} draining from the B horizon of a northern hardwood site in the Adirondack Mountains of New York. The potential of such reversible SO_4^{2-} desorption has been shown to be an important mechanism in both laboratory (Harrison et al. 1989) and field (Rustad et al. 1996) experiments including roof exclusion experiments in Europe (Hultberg 1992; Alewell et al. 1997). However, using a modeling approach Driscoll et al. (1998) has suggested that SO_4^{2-} adsorption/desorption reactions cannot account for the changing patterns of SO_4^{2-} concentrations in surface waters of the northeastern US. Likens et al. (1990) proposed that dry deposition is the source for this additional S in drainage waters using a watershed mass balance approach at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire. For wetland and lake regions the possible release of re-oxidized S has been suggested as an important S source to drainage waters (Dillon & LaZerte 1992).

Identifying the source of the S which is currently in excess of S inputs from wet deposition is a major concern to scientists as well as to policy makers. If dry deposition were the major source for this additional output of SO_4^{2-}, reductions in anthropogenic S emissions from the combustion of fossil fuels would result in a direct decrease in SO_4^{2-} losses in stream waters. Moreover, it has been found that annual changes in SO_2 emissions explains only a portion ($r^2 = 0.5$ to 0.7) of the temporal patterns of wet or bulk deposition (Butler & Likens 1991; Likens 1992) suggesting that other factors may also affect this relationship. If there is a major source of SO_4^{2-} in the soil, the effect of anthropogenic emission reduction would be delayed and/or decreased. A delay in the response of S cycling and streamwater output to decreasing S emissions has been predicted by various models of SO_4^{2-} desorption (e.g., Church et al. 1990; Rochelle & Church 1987; Anonymous 1995). If a major internal SO_4^{2-} source (e.g., weathering of S minerals, net mineralization of organic S) were to exist in the soil, the impact of emission reductions would be diminished or delayed in proportion to the contribution of this internal source to SO_4^{2-} losses in surface waters (Johnson & Mitchell 1998).

The analysis of the stable isotopes of S provides a powerful tool for studying various aspects of the biogeochemical flux and cycling of this element (Krouse & Grinenko 1991). The use of stable isotopes in evaluating the S biogeochemistry of forest ecosystems has been reviewed recently by Mitchell et al. (1998). The isotopic composition in forest ecosystems is controlled by isotopic composition of sources (i.e., atmospheric deposition and mineral weathering) and isotopic discrimination during S transformations. Only biological processes, especially dissimilatory SO_4^{2-} reduction, cause major shifts in $\delta^{34}S$ values under natural environmental conditions (Krouse & Grinenko 1991). Dissimilatory SO_4^{2-} reduction, which occurs under anaerobic conditions, results in marked fractionation between the enriched ($> \delta^{34}S$) SO_4^{2-} reactant and the depleted ($< \delta^{34}S$) sulfide product, because bacteria generally prefer the lighter ^{32}S. Recent studies have also suggested some small preference for ^{32}S during immobilization and mineralization (Fuller et al. 1986b; Krouse et al. 1991; Zhang et al. 1998).

The purpose of our study was to investigate the S cycle of forest ecosystems in the northeastern US by analyzing the $\delta^{34}S$ values in archived bulk precipitation and stream water samples collected from 1966–67 through 1993–94 water years at the HBEF. Evaluating this long-term record of $\delta^{34}S$ values should provide new information on the sources of S contributing to the SO_4^{2-} in the drainage waters at the HBEF.

Site description

This study was conducted at the HBEF in the White Mountains of central New Hampshire (43°56′ N, 71°45′ W). Watersheds 6 (W6: area 13.1 ha, elevation 540 to 800 m) and 5 (W5: area 22.5 ha, elevation 490 to 775 m) are adjacent catchments with steep slopes and southerly aspects. W6 is the biogeochemical reference watershed at the HBEF. Most soils in these two watersheds are Typic Haplorthods and Fragiorthods of the Tunbridge-Lyman, Berkshire, Skerry, and Becket series (Huntington et al. 1988). W5 was commercially whole-tree harvested from the autumn of 1983 to the spring of 1984. Forest vegetation is predominantly northern hardwoods with American beech (*Fagus grandifolia* Ehrh.), yellow birch (*Betula alleghani-*

ensis Britt.), and sugar maple (*Acer saccharum* Marsh.) at lower and middle elevations with red spruce (*Picea rubens* Sarg.), balsam fir [*Abies balsamea* (L.) Mill], and white birch [*Betula papyrifera* var. *cordifolia* (Marsh.) Regel] at the higher elevations of W5 and W6 (Bormann et al. 1990).

Methods

At both W5 and W6, stream samples are collected weekly just above the weirs which are used for measuring stream flow. In the open site adjacent to the Robert S. Pierce Ecosystem Laboratory (rain gauge 22) at 253 m and near Watershed 6 (rain gauge 11) at 549 m, weekly bulk precipitation samples were collected and processed using procedures described by Likens et al. (1967) and Buso et al. (1998). Sulfate in stream water and bulk precipitation were analyzed from June 1964 to June 1972 spectrophotometrically using barium chloride titration/thorin endpoint method and from June 1972 to December 1976 with automated colorimetric (barium sulfate, methyl thymol blue) method, and from December 1976 by ion chromatography (IC) (Buso et al. 1998).

Sampling of the archived samples at HBEF

Archived solutions, which had been stored in clean polyethylene bottles, collected from 1966 through 1994 from W5 (stream water), W6 (stream water and bulk precipitation) and rain gauge 22 (bulk precipitation, only from 1982–1994) were sampled. The policy of the Hubbard Brook Ecosystem Study is to allow each approved request to sample no more than 10% of the volume of the archived samples. To yield sufficient SO_4^{2-} for the stable isotope analysis, weekly samples of the solutions were subsampled and combined to form composited half-year samples divided into "summer" (June 1 through November 30) and "winter" (December 1 through May 31) samples that encompass the water year that begins on June 1 and ends on May 31 of the next calendar year.

These composited water samples then were analyzed for SO_4^{2-} with ion chromatography and for Na^+ with atomic adsorption spectroscopy at SUNY-ESF. Sulfate in the solutions was precipitated as $BaSO_4$ by adding $BaCl_2$ and the S isotopic composition of the $BaSO_4$ measured on-line with an elemental analyzer coupled to an isotope ratio mass spectrometer.

The isotopic composition of samples is expressed using the δ^{34}S notation defined as:

$$\delta^{34}\mathrm{S}(‰) = \left[\frac{(^{34}\mathrm{S}/^{32}\mathrm{S})_{sample}}{(^{34}S/^{32}S)_{standard}} - 1\right] \times 10^3$$

where ‰ (per mil) is parts per thousand and $^{34}S/^{32}S$ is the ratio of the number of ^{34}S atoms to the number of ^{32}S atoms in the sample or standard. The historical international standard is troilite (FeS) from the Cañon Diablo meteorite for which the $^{34}S/^{32}S$ ratio is 1/22.22. Precision of the $\delta^{34}S$ measurement was 0.8‰.

Storage effects on $\delta^{34}S$ values

Because solution samples were stored for up to three decades with little temperature control except the prevention of freezing, storage effects need to be considered. To estimate storage effects on SO_4^{2-} in solution the "new" SO_4^{2-} and Na^+ concentrations were compared with the "original" SO_4^{2-} and Na^+ concentrations that had been determined before samples were archived. Only samples taken after December 1978 (when IC was used for SO_4^{2-} analyses) were used in this comparison to avoid any potential confounding factors associated with differences in analytical techniques. It has been shown that IC is the most precise and accurate method for measuring SO_4^{2-} in stream and soil waters (Searle 1979; Alewell 1993). The regression of the "new values" of SO_4^{2-} and Na^+ taken after 1977 against the values of the "original" samples indicated that these two measurements were in agreement: new-SO_4^2 [μmol l^{-1}] = 0.93 original-SO_4^2 [μmol l^{-1}] + 8.3 ($R^2 = 0.93$) and new-Na [μmol l^{-1}] = 1.07 original-Na [μmol l^{-1}] − 0.82 ($R^2 = 0.96$). These differences between the "new" and "original values" could be due to differences among the laboratories where the "new" and "original" values were measured. The absence of any marked change in the concentrations in the stored water samples also indicates that it is highly unlikely that there would have been any change due to storage of the $\delta^{34}S$ values of SO_4^{2-} in solution. The only process that would result in substantial change in $\delta^{34}S$ values would be dissimilatory SO_4^{2-} reduction that would only occur under anaerobic conditions which did not occur during the storage of these samples.

Statistical analysis

Summer and winter SO_4^{2-} concentrations were calculated using volume-weighted weekly values from bulk precipitation and stream collections. All data were analyzed with SAS. The test for normal distribution was done with PROC UNIVARIATE and normality was rejected when $Prob<w$ was <0.05. Since not all data sets were normally distributed, tests for significant differences between independent groups were done with the Wilcoxon Rank Sum Test (PROC NPAR1WAY). Tests were performed at the 5% significance level.

Results and discussion

Patterns of δ^{34}S values and sulfate concentrations in bulk precipitation and stream water

In bulk precipitation at HBEF (Figure 1) there were distinct differences ($p < 0.05$) in the δ^{34}S values in SO_4^{2-} between summer and winter as well as variation from 1967 through 1994. Previous work at HBEF (Zhang et al. 1998) as well as other areas in the North America (Nriagu et al. 1987; Nriagu & Krouse 1992) have also found lighter δ^{34}S values in the summer than the winter. There were also greater concentrations of SO_4^{2-} in precipitation during the summer compared to the winter (Figure 2) as has been reported previously (Likens & Bormann 1995; Mitchell et al. 1992c; Sisterson et al. 1990; Venkatram et al. 1990). There were no significant differences ($p > 0.05$) between the δ^{34}S values in bulk precipitation near W6 and at the open site near the Ecosystem Laboratory (Figure 1).

Stream water δ^{34}S values from W6 were slightly (0.5l), but significantly different ($p < 0.05$) from W5 (Figure 1). The ability to detect this statistical difference results from the small variation in the δ^{34}S values in the respective streams of each watershed (Table 1a) and the large number of samples analyzed ($n \leq 54$). The δ^{34}S values of stream SO_4^{2-} have smaller variances and ranges than the δ^{34}S values of bulk precipitation (Table 1a). There were two unusually high δ^{34}S values in bulk precipitation (Ecosystem Laboratory in summer 1984 and Watershed 6 in the winter of 1985) (Figure 1). If these two values are not included in the analyses the variations and ranges are reduced but the overall patterns and statistical differences are still present. The most important result, moreover, is that for the exception of the winter 1980 the stream δ^{34}S values are always lighter than those in precipitation during any one year (Figure 1).

The mean concentrations of SO_4^{2-} in the stream draining W6 and W5 were 58 and 56 μmol l^{-1}, respectively, and were similar and substantially greater than mean values of 24 and 25 μmol l^{-1} in bulk precipitation collected near W6 and the Ecosystem Laboratory, respectively. The variance in SO_4^{2-} concentrations was less for W6 than for bulk precipitation (Table 1b). This dampening of the variation of SO_4^{2-} concentration has been noted previously for a northern hardwood site and was attributed to the buffering effect of SO_4^{2-} adsorption/desorption (Mitchell et al. 1992a). The higher variance in SO_4^{2-} concentrations in the W5 stream was likely due to the effect of the whole-tree harvest on SO_4^{2-} retention as discussed further below.

The differences in both the temporal patterns and the overall means of the δ^{34}S values and SO_4^{2-} concentrations in bulk precipitation and streams suggest that there was either an additional external or internal SO_4^{2-} source

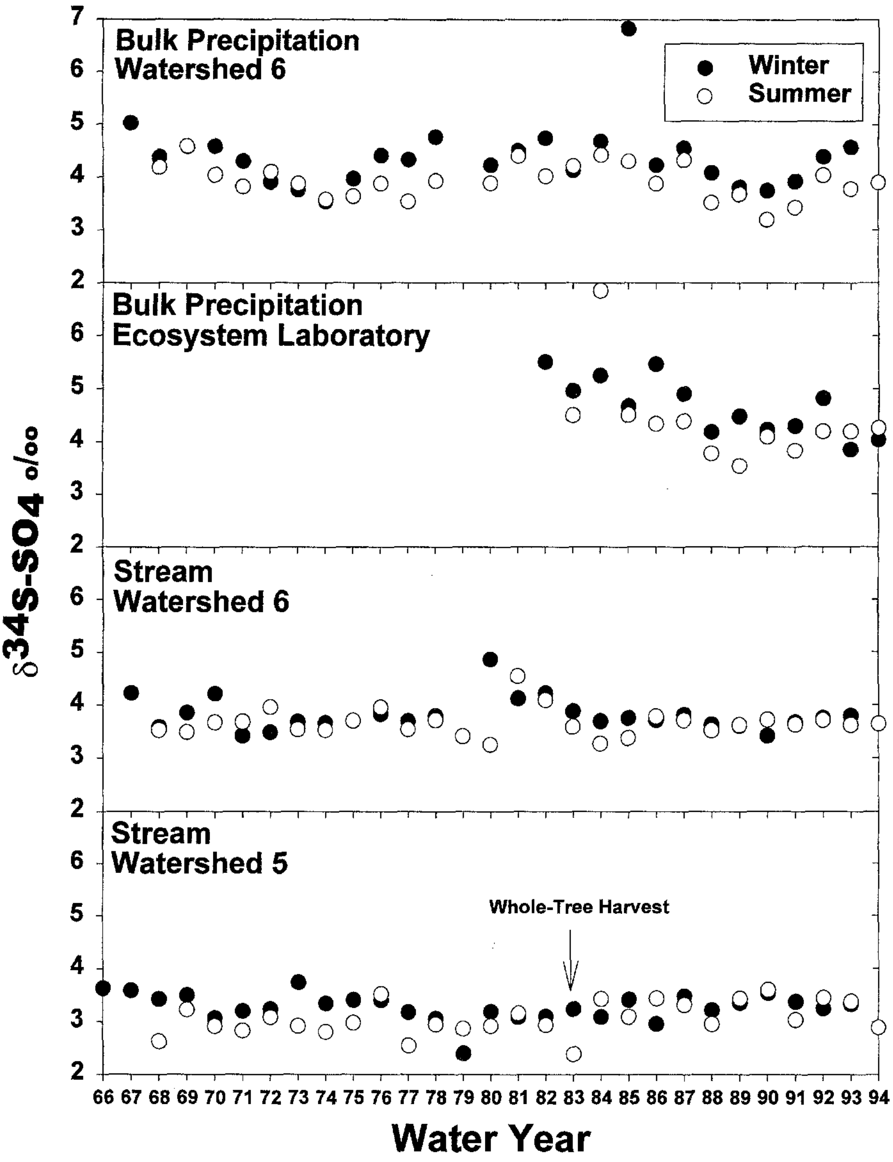

Figure 1. δ^{34}S values of SO_4^{2-}. Bulk precipitation taken near base of Watershed 6 and at open site near the Robert S. Pierce Ecosystem Laboratory. Stream samples were taken just above the weir of Watersheds 5 and 6. Archived samples were combined into summer (June 1 through Nov. 30) periods and winter (Dec. 1 through May 31) periods. Years are water years which begin on June 1 and end on May 31 of the following calendar year.

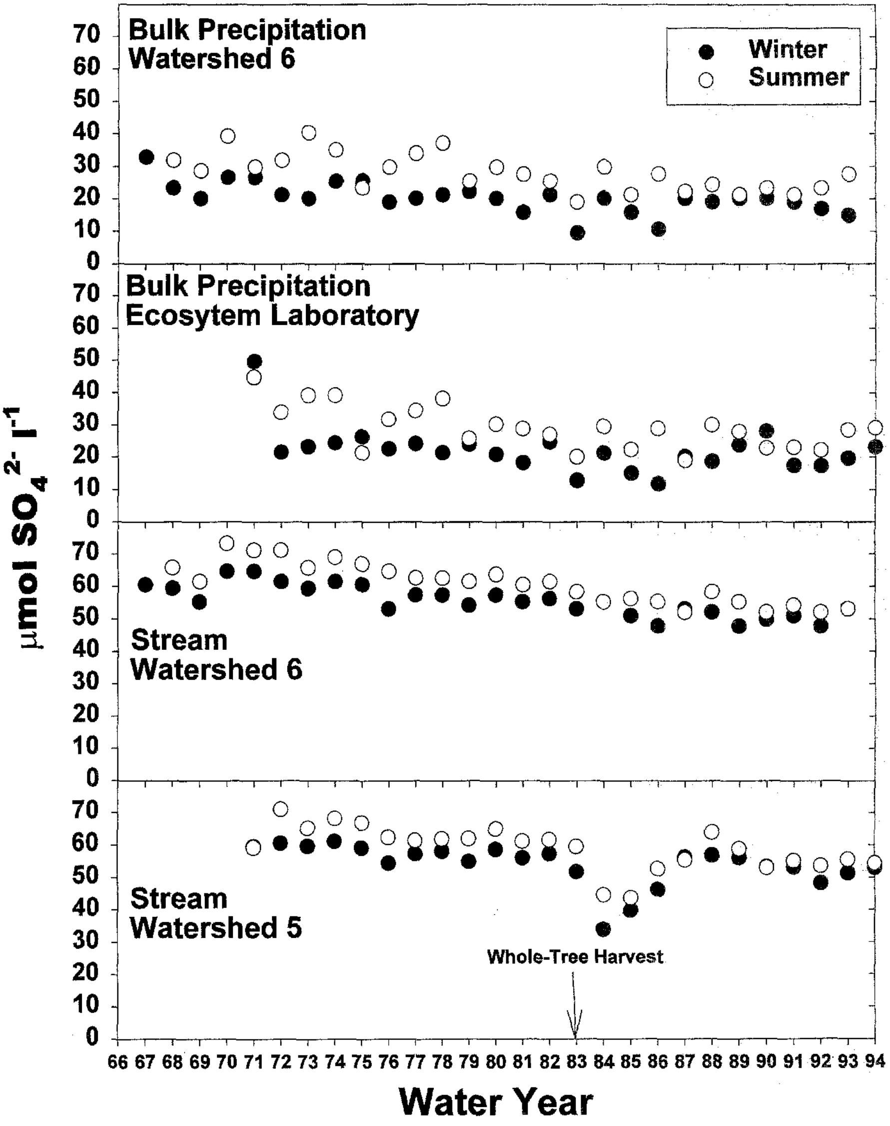

Figure 2. Concentration of SO_4^{2-} in bulk precipitation taken near base of Watershed 6 and at an open site near the Robert S. Pierce Ecosystem Laboratory. Stream samples were taken just above the weir of Watersheds 5 and 6. Archived samples were combined into summer (June 1 through Nov. 30) periods and winter (Dec. 1 through May 31) periods. Years are water years which begin on June 1 and end on May 31 of the following calendar year.

Table 1a. Statistical values of the $\delta^{34}S$ values in bulk precipitation and stream water at the HBEF.

Sample type	Location	Number of samples	$\delta^{34}S$‰ x̄	Variance	Max.–Min. (range)
Bulk precipitation	Open site adjacent to laboratory	25	4.5	0.5	6.9–3.5 (3.4)
Bulk precipitation	Adjacent to W6	53	4.2	0.3	6.8–3.2 (3.6)
Stream	W5	55	3.2	0.1	3.7–2.4 (1.3)
Stream	W6	54	3.7	0.1	4.9–3.3 (1.6)

Table 1b. Statistical values of the SO_4^{2-} concentrations in bulk precipitation and stream water at the HBEF. Sample values were obtained by volume weighting weekly values of SO_4^{2-} concentrations.

Sample type	Location	Number of samples	SO_4^{2-} μmol l^{-1} x̄	Variance	Max.–Min. (range)
Bulk precipitation	Open site adjacent to laboratory	52	25	61	50–12 (38)
Bulk precipitation	Adjacent to W6	53	24	43	40–10 (30)
Stream	W5	52	56	50	71–34 (37)
Stream	W6	52	58	39	73–48 (25)

affecting the $\delta^{34}S$ values of the streams. The differences in the $\delta^{34}S$ values of stream water may also be attributed to fractionation of S as it passes through the watershed-ecosystem.

Effects of whole-tree harvest on the sulfur budget and $\delta^{34}S$ values

It is notable that there was no detectable change in the $\delta^{34}S$ values in the stream after the whole-tree harvest of W5 (Figure 1) although marked decreases in SO_4^{2-} concentrations in stream waters were noted (Figure 2). Soil solution and stream concentrations of NO_3 and H^+ were elevated due to enhanced nitrification and SO_4^{2-} concentrations decreased due to pH dependent SO_4^{2-} adsorption (Nodvin et al. 1986, 1988; Mitchell et al. 1989). The patterns of SO_4^{2-} in solution were confirmed by quantitative increases in the adsorbed sulfate in the upper mineral horizons (Mitchell et al. 1989). The only difference in the $\delta^{34}S$ values of SO_4^{2-} in stream water was that winter values were slightly higher than summer values before the cut, thus possibly reflecting the seasonality of the atmospheric inputs. After the cut, winter and summer δ^{34}S were very similar and less variable. These results suggest that the size of the absorbed SO_4^{2-} pool was large enough to obscure any changes in the δ^{34}S values of the stream during the relatively short period (three years) when SO_4^{2-} concentrations were depressed.

Sources of sulfur to drainage waters

Sulfur budget. To evaluate the contribution of SO_4^{2-} sources, we show in Figure 3 SO_4^{2-} fluxes from 1968 through 1993 (as a summation for over 26 years) and soil S pools at the HBEF for an undisturbed watershed such as W6. The soil data were taken from the analysis of the soil S constituents before the whole-tree harvest of W5 (Mitchell et al. 1989). It was assumed that these S constituents would be similar to those of adjacent W6 due to similarity of soils, aspect, vegetation, climate etc. Bulk deposition and drainage water losses were taken from direct measurements from W6. Dry deposition estimates from HBEF have varied considerably due to different methods and the period of measurements. Based on net throughfall measurements in the 1970s dry deposition estimates as great as 4 kg S ha^{-1} yr^{-1} have been reported (Eaton et al. 1973, 1978, 1980) while more recent measurements using both net throughfall measurements as well as deposition modeling techniques have found lower deposition levels ranging from about 0.7 to 1.8 kg S ha^{-1} yr^{-1} (Lovett et al. 1996, 1997). Mineral weathering values are from Likens and Bormann (1995).

Dry deposition. A possible source for SO_4^{2-} from outside the forest ecosystem is dry deposition. It has been documented that dry deposition of S can be a substantial input to some forest ecosystems (e.g., Lovett et al. 1992; Mitchell et al. 1992b; Hultberg et al. 1994). For dry deposition to account for the lower δ^{34}S values in the streams compared with those in bulk precipitation, dry deposition δ^{34}S values would need to have been lower than those in bulk precipitation. Several studies in North America measured no significant difference between δ^{34}S values of precipitation, throughfall and stemflow (e.g., Stam et al. 1992; van Stempvoort & Wills 1991; Zhang et al. 1998). Zhang et al. (1998) also reported that δ^{34}S values of throughfall at HBEF did not differ significantly between sites with different tree species. Thus, it is unlikely that dry deposition accounts for the lower δ^{34}S values in stream water compared with atmospheric inputs. Furthermore, dry deposition effects cannot explain the dampening of the input signal of δ^{34}S as shown by the decreased variability of the δ^{34}S values of SO_4^{2-} in streams compared with bulk precipitation (Table 1). However, from 11 to 61% of the imbalance

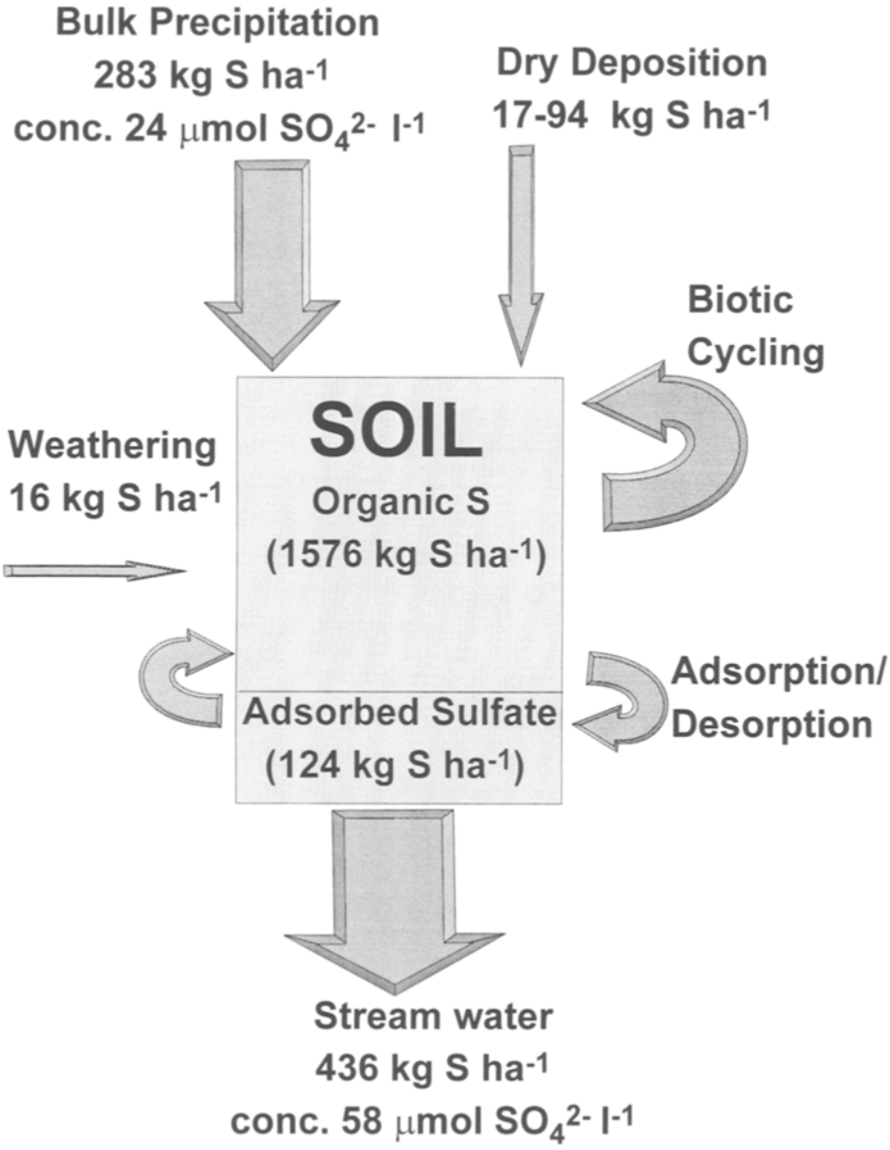

Figure 3. Summary of SO_4^{2-} concentrations, fluxes (kg S ha^{-1} for 26 years) and pools (kg S ha^{-1}) for an undisturbed watershed at Hubbard Brook Experimental Forest from 1968 through 1993. Assumptions for calculations are provided in the text.

between S inputs by bulk deposition and S losses through stream drainage may be due to dry deposition inputs (Figure 3).

Groundwater sources. Another potential source of stream SO_4^{2-} is groundwater inputs. However, none of the results from HBEF suggest that groundwater sources have any significant input to the stream waters in the experimental watersheds at this site (Likens & Bormann 1995). The absence of groundwater inputs to the streams is due to the impervious bedrock, steep slopes and small sizes that all contribute to the hydrological tight basins of these experimental watersheds.

Weathering of sulfur minerals. Another possible source for the stream SO_4^{2-} is mineral weathering. Fuller et al. (1986b) determined for bedrock at the HBEF $\delta^{34}S$ values and found −7.1 for a fine-grained diabas and +9.2 for the Rangeley (previously reported as Littleton) formation of schist bedrock. Thus, weathering of diabas minerals could have contributed to the lower $\delta^{34}S$ values in streams if this mineral were an important source of S. However, it has been suggested that mineral weathering is not an important source of S at the HBEF and may generate only about 0.64 kg S ha^{-1} yr^{-1} (Likens et al. 1990). Also, weathering reactions cannot explain the dampening of the $\delta^{34}S$ values in the streams. Thus, mass balance approaches and the isotopic results suggest that mineral weathering is not the primary source of the additional SO_4^{2-} in the streams at the HBEF.

Oxidation of previously reduced labile sulfur. Dissimilatory S reduction causes lighter $\delta^{34}S$ values in the sulfide reduction products. A reoxidation of this sulfide would result in the formation of SO_4^{2-} with relatively low $\delta^{34}S$ values that then could enter streams. Such processes have been found to be important only in watersheds for which wetlands are an important component of the landscape (Alewell et al. 1998; Dillon & LaZerte 1992). Due to the steep slopes in the experimental catchments at the HBEF, wetlands constitute $<1\%$ of W5 and W6 (G. Likens and D. Buso, personal communication) and are thus not an important features of these watersheds. Moreover, if a substantial amount of SO_4^{2-} was reduced continuously by dissimilatory processes in the catchment, stream waters should be enriched in ^{34}S compared to atmospheric inputs during the period of net dissimilatory reduction. During the current study period from 1967 through 1994, however, $\delta^{34}S$ values of SO_4^{2-} in the streams were lower than those in bulk precipitation.

Desorption of sulfate. If all of the adsorbed SO_4^{2-} were desorbed, it would account for 79% of the difference in the S input-output budgets if an adsorbed SO_4^{2-} content of 124 kg S ha^{-1} were assumed using the value obtained for W5 before the whole-tree harvest (Mitchell et al. 1989). There are no long-term data on changes in the adsorbed SO_4^{2-} content of W5, but such a large amount of desorption would not likely occur at current concentrations of SO_4^{2-} in soil solution (Mitchell et al. 1989; Nodvin et al. 1988). Also, Driscoll et al. (1998) using a modeling approach has suggested that SO_4^{2-} adsorption/desorption cannot explain the temporal patterns of SO_4^{2-} in surface water in the northeastern US including the HBEF.

Moreover, such desorption would not explain the lower δ^{34}S values of the streams since adsorption/desorption causes no isotopic discrimination (Mitchell et al. 1998). Adsorption-desorption processes, however, may play a role in dampening long-term and seasonal patterns in SO_4^{2-} concentrations and fluxes in soil solutions and streams as shown by the results from W5 at HBEF (Mitchell et al. 1989) and studies of solute flux in a hardwood forest in the Adirondack Mountains (Mitchell et al. 1992a).

Organic sulfur formation and mineralization. Organic S in the soil represents 93% of the S in the soil at HBEF (Figure 3) (Mitchell et al. 1989). This organic S consists of both ester sulfates and C-bonded S. It has been suggested that this organic S pool may represent an important source and sink for SO_4^{2-} in forest soils (Swank et al. 1984; Strickland & Fitzgerald 1984). These organic S constituents, especially the ester sulfate component, may show small increases following experimental additions of SO_4^{2-} (David et al. 1990; Mitchell et al. 1989). Detecting changes in C-bonded S, which constitutes most of the organic S in forest soils, has been very difficult to quantify, especially under field conditions, due to the large size of this pool and the heterogeneity of forest soils (Johnson & Mitchell 1998). The soil organic S pool contains more than 1500 kg S ha^{-1} at HBEF (Figure 3). If we assume that mineralization of organic S would account for the discrepancy in the S inputs compared to outputs, net mineralization would be less than 0.4% per year of the total organic S pool. Laboratory studies of HBEF soils have found rates that exceed this value (Fuller et al. 1996a; Schindler et al. 1986) but it is very difficult to extrapolate these laboratory values to natural field conditions.

Several authors in North America and Europe concluded that SO_4^{2-} transport through forest soils is rather conservative, because precipitation, soil solution and stream water of forest ecosystems have shown similar δ^{34}S values (Caron et al. 1986; Stam et al. 1992; Mayer et al. 1995). However, Mayer et al. (1995), showed that although δ^{34}S values are altered only

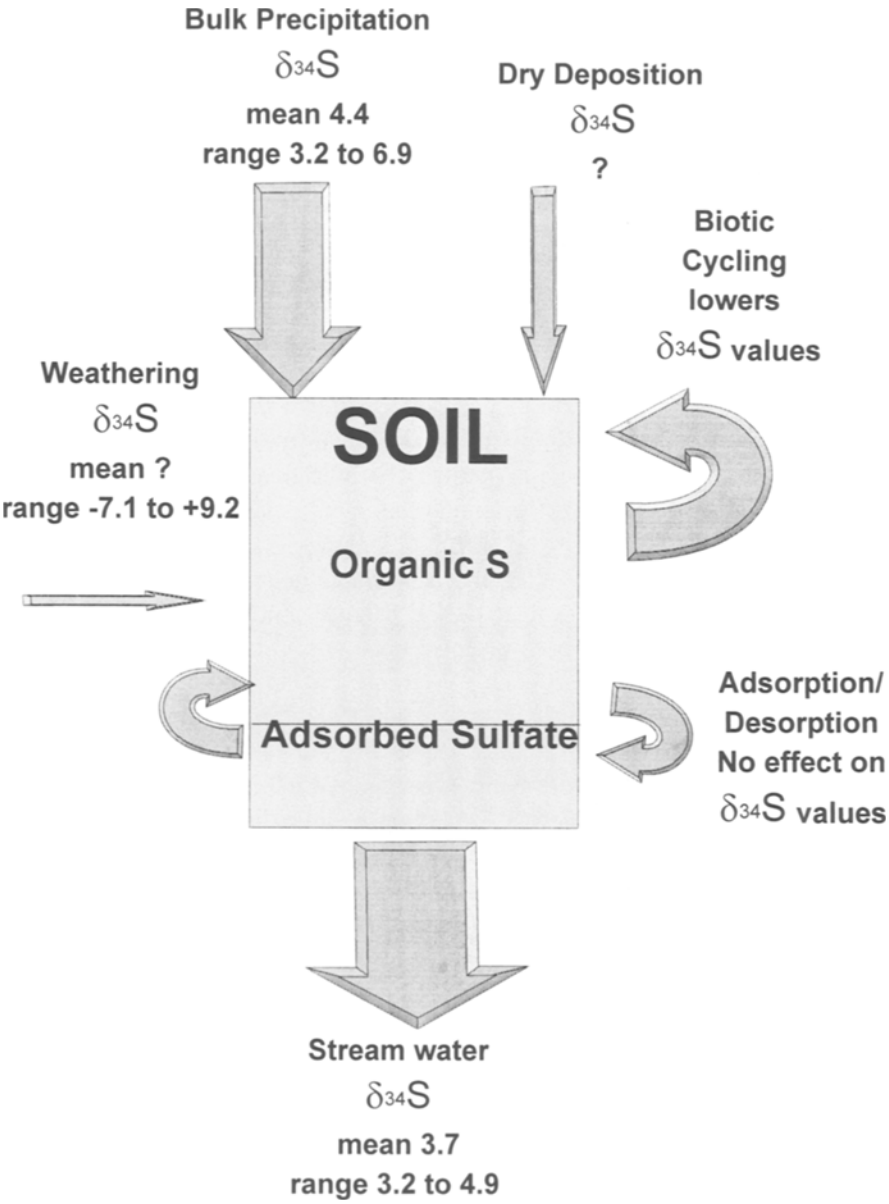

Figure 4. Summary of inputs, pools and processes that affect $\delta^{34}S$ values of SO_4^{2-} for an undisturbed watershed at Hubbard Brook Experimental Forest from 1968 through 1993. Units are ‰$\delta^{34}S$. Further information is provided in the text.

slightly, the oxygen isotopic composition (δ^{18}O) of SO_4^{2-} shows a depletion of several per mil indicating that biological processes were contributing to the SO_4^{2-} in soil solution. Studies from the HBEF (Zhang et al. 1998 and results of the present study) as well as from two sites in the northwestern Czech Republic and a site in northeastern Bavaria, Germany (Novac et al. 1995; Alewell et al. 1998) have shown that δ^{34}S values of soil solutions and streams show different spatial and temporal patterns than those of precipitation or throughfall. Moreover, δ^{34}S values of SO_4^{2-} in soil solution of terrestrial sites have generally lower δ^{34}S values than SO_4^{2-} in precipitation and throughfall (Fuller et al. 1986; Novac et al. 1995; Alewell et al. 1998; Zhang et al. 1998; data of this study). A depletion in ^{34}S of SO_4^{2-} in soil solution in comparison to SO_4^{2-} in throughfall may indicate S mineralization as a potential source, because the soil microflora prefer the lighter ^{32}S isotope. Furthermore, it has been suggested for aerobic, forest soils that the mineralization of labile organic S produces SO_4^{2-} that is more depleted in ^{34}S compared to adsorbed SO_4^{2-} or the SO_4^{2-} in soil solution (Fuller et al. 1986; Krouse et al. 1991; Zhang et al. 1998). These results are consistent with C-bonded S being depleted in ^{34}S. Mayer et al. (1995) concluded from δ^{18}O values of soil water sulfate that a considerable proportion of the SO_4^{2-} was derived from the mineralization of the C-bonded S suggesting that atmospherically derived S was cycling though the organic soil pool.

Conclusions

The results from stable isotope data combined with data from SO_4^{2-} concentrations, fluxes and S pools at the HBEF clearly show that SO_4^{2-} is not a conservative anion, but rather is subject to substantial transformations between organic and inorganic S forms. The soil has a reactive S pool, which dampens the temporal variation in δ^{34}S values (Figure 4) and SO_4^{2-} concentrations of the atmospheric inputs as SO_4^{2-} passes through the watershed-ecosystem (Figure 3). The δ^{34}S values of the streams are lighter and concentrations of SO_4^{2-} greater than those of bulk precipitation suggesting the importance of organic S cycling. Most of the atmospherically deposited SO_4^{2-} is cycled through various biological processes including plant uptake, litter inputs, immobilization and mineralization (Figure 4). The relative importance of this biotic cycling of S has increased as atmospheric deposition of S has decreased. For example, litter inputs of S do not generally exceed 8 kg S ha^{-1} yr^{-1} and it has been concluded that generally less than 10 kg S ha^{-1} yr^{-1} is cycled biotically through forests ecosystems by plants and the soil microflora (Mayer et al. 1998). From 1968–1993, SO_4^{2-} inputs in bulk deposition averaged 11 kg S ha^{-1} yr^{-1} deposition suggesting that most of this input would have been subject to biotic cycling. The predominance of biotic cycling, however, cannot be generalized for some forests especially those in polluted areas of Europe that may receive over 30 kg S ha^{-1} yr^{-1} from atmospheric deposition (Johnson & Mitchell 1998) although Novak et al. (1997) suggest that even at extremely high levels (>70 kg S ha^{-1} yr^{-1}) of atmospheric deposition most of the S is cycled through the organic pools. Mineralization of S incorporated into organic matter results in the release of SO_4^{2-} into the soil solution that has a lower $\delta^{34}S$ value than atmospherically deposited S. This soil water SO_4^{2-} is subject to adsorption and desorption in the mineral soil. Adsorption/desorption processes dampen any seasonal and short-term annual variations in the drainage losses of SO_4^{2-} unless the system is highly disturbed such as occurred in the whole-tree harvest in W5 (Figure 2). Such adsorption processes may also obscure short-term changes in $\delta^{34}S$ values (Figure 1).

Stable isotopic results cannot show directly that net mineralization of organic S is occurring, but these long-term measurements of the $\delta^{34}S$ values in precipitation and throughfall suggest that mineralization of organic S is an important source of the additional S in stream waters at the HBEF. However, further studies are needed to quantify the relative contributions of mineral weathering, dry deposition and other biotic processes such as plant uptake in affecting the long term patterns of $\delta^{34}S$ values in these drainage waters.

Acknowledgments

This work was funded by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) to C. Alewell and by the National Science Foundation and the Andrew W. Mellow Foundation to G. E. Likens. The Hubbard Brook Experimental Forest is operated and maintained by the Northeastern Forest Experiment Station, US Department of Agriculture, Radnor, Pennsylvania. We would like to give special thanks to Amey Bailey and Donald C. Buso for their support of this study.

References

Alewell C (1993) Effects of organic sulfur compounds on extraction and determination of inorganic sulfate. Plant and Soil 149: 141–144

Alewell C, Bredemeier M, Matzner E & Blanck K (1997) Soil solution response to experimentally reduced acid deposition in an forest ecosystem. J. Environmental Quality 26: 658–665

Alewell C, Gehre M & Matzner E (1998) Spatial and temporal heterogeneity in a forested catchment as an indicator for biological S turnover. Biogeochemistry (in Review)

Anonymous (1995) Acid Deposition Standard Feasibility Study Report to Congress. United States Environmental Protection Agency. EPA 430-R-95-001a

Bormann FH, Siccama TG, Likens GE & Whittaker RH (1970) The Hubbard Brook Ecosystem Study: Composition and dynamics of the tree stratum. Ecological Monographs 40: 373–388

Buso DC, Likens GE & Eaton JS (1998) Long-term data on chemistry of precipitation, streamwater and lake water from the Hubbard Brook Ecosystem Study: A review of sampling protocols and analytical procedures (in prep.)

Butler TJ & Likens GE (1991) The impact of changing regional emissions on precipitation chemistry in the eastern United States. Atmospheric Environment 25A(2): 305–315

Caron F, Tessier A, Kramer JR, Schwarcz HP & Rees CE (1986) Sulfur and oxygen isotopes of sulfur in precipitation and lake water, Quebec, Canada. Applied Geochemistry 1: 601–606

Church MR, Shaffer PW, Eshleman KN & Rochelle BP (1990) Potential future effects of current levels of sulfur deposition on stream chemistry in the Southern Blue Ridge Mountains, U.S. Water, Air and Soil Pollution 50: 39–48

David MB, Fuller RD, Fernandez IJ, Mitchell MJ, Rustad LE, Vance GF, Stam AC & Nodvin SC (1990) Spodosol variability and assessment of response to acidification. Soil Science Society of America Journal 54: 541–548

Dillon PJ & LaZerte BD (1992) Response of the Plastic Lake catchment, Ontario, to reduced sulphur deposition. Environmental Pollution 77: 211–217

Driscoll CT, Postek KM, Kretser W & Raynal DJ (1995) Long-term trends in the chemistry of precipitation and lake water in the Adirondack region of New York, USA. Water, Air and Soil Pollution 85: 583–588

Driscoll CT, Likens GE & Church MR (1998) Recovery of soil and surface waters in the northeastern U.S. from decreases in atmospheric deposition of sulfur. Water Air Soil Pollution (in press)

Eaton JS, Likens GE & Bormann FH (1973) Throughfall and stemflow chemistry in a northern hardwood forest. Journal of Ecology 61: 495–508

Eaton JS, Likens GE & Bormann FH (1973) The input of gaseous and particulate sulfur to a forest ecosystem. Tellus 30: 546–551

Eaton JS, Likens GE & Bormann FH (1980) Wet and dry deposition of sulfur at Hubbard Brook. In: Hutchinson T & Havas M (Eds) Effect of Acid Precipitation on Terrestrial Ecosystems. NATO Conf. Series 1: Ecology (pp 69–75). Plenum Publishing, New York

Fuller RD, Driscoll CT, Schindler SC & Mitchell MJ (1986a) A simulation model of sulfur transformations in forested Spodosols. Biogeochemistry 2: 313–328

Fuller RD, Mitchell MJ, Krouse HR, Wyskowski BJ & Driscoll CT (1986b) Stable sulfur isotope ratios as a tool for interpreting ecosystems sulfur dynamics. Water Air and Soil Pollution 28: 163–171

Harrison RB, Johnson DW & Todd DE (1989) Sulfate adsorption and desorption in a variety of forest soils. Journal of Environmental Quality 18: 419–426

Hultberg H (1992) Biochemical cycling of sulfur and its effects on surface chemistry in an acid catchment in SW Sweden. In: Teller A, Mathy P & Jeffers JNR (Eds) Responses of Forest Ecosystems to Environmental Changes (pp 677–680). Elsevier Applied Science Amsterdam, The Netherlands.

Hultberg H, ApSimon H, Church MR, Greenfelt P, Mitchell MJ, Moldan F & Ross HB (1994) Sulphur. In: Moldan B & Cerny J (Eds) Biogeochemistry of Small Catchments: A Tool for Environmental Research. SCOPE, Chapter 10 (pp 229–254). John Wiley & Sons, Chichester

Huntington TG, Johnson CE, Johnson AH, Siccama TG & Ryan DF (1989) Carbon, organic matter, and bulk density relationships in a forested spodosol. Soil Science 148: 380–386

Johnson CE, Johnson AH & Siccama TG (1991) Whole-tree clear-cutting on exchangeable cations and soil acidity. Soil Science Society of America Journal 55: 502–508

Johnson DW & Mitchell MJ (1998) Responses of forest ecosystems to changing sulfur inputs. In: Maynard D (Ed) Sulfur in the Environment (pp 219–262). Marcel Dekker Inc., New York, New York

Krouse HR & Grinenko VA (1991). Stable Isotopes. Natural and Anthropogenic Sulphur in the Environment. SCOPE, Vol. 43. John Wiley and Sons Ltd, Chichester

Krouse HR, Stewart JWB & Grinenko VA (1991) Pedosphere and biosphere. In: Krouse HR & Grinenko VA (Eds) Stable Isotopes. Natural and Anthropogenic Sulphur in the Environment. SCOPE, Vol. 43 (pp 267–306). John Wiley and Sons Ltd., Chichester

Likens, GE (1992) The Ecosystem Approach: Its Use and Abuse. Excellence in Ecology, Vol. 3. Ecology Institute, Oldendorf-Luhe, Germany. 167 pp.

Likens GE, Bormann FH, Hedin LO & Driscoll CT (1990) Dry deposition of sulfur: A 23-year record for the Hubbard Brook Forest ecosystem. Tellus 42B: 319–329

Likens GE & Bormann FH (1995) Biogeochemistry of a Forested Ecosystem. Second Edition. Springer-Verlag, New York

Lovett GM, Scott SN, Driscoll CT & Fahey TJ (1996) Factors regulating throughfall flux in a New Hampshire forested landscape. Canadian Journal of Forest Research 26: 2134–2144

Lovett GM, Bowser JJ & Edgerton ES (1997) Atmospheric deposition to watersheds in complex terrain. Hydrologic Processes 11: 645–654

Mayer B, Fritz P, Prietzel J & Krouse HR (1995) The use of stable sulfur and oxygen isotope ratios for interpreting the mobility of sulfate in aerobic forest soils. Applied Geochemistry 10: 161–173

Mayer B, Prietzel J & Krouse HR (1998) The use of stable sulfur isotope ratios for determining retention patterns of artificially deposited sulfate in aerated forest soils. Applied Geochemistry (in press)

Mitchell MJ, Driscoll CT, Fuller RD, David MB & Likens GE (1989) Effect of whole-tree harvesting on the sulfur dynamics of a forest soil. Soil Science Society of America Journal 53: 933–940

Mitchell MJ, Burke MK & Shepard JP (1992a) Seasonal and spatial patterns of S, Ca and N dynamics of a northern hardwood ecosystem. Biogeochemistry 17: 165–189

Mitchell MJ, David MB & Harrison RB (1992b) Sulfur dynamics of forest ecosystems. In: Howarth RW, Stewart JWB & Ivanov MV (Eds) Sulfur Cycling on the Continents. SCOPE, Vol. 48, Chapter 9 (pp 215–254). John Wiley and Sons, New York

Mitchell MJ & Lindberg SE (1992c) Sulfur chemistry, deposition and cycling in forests. In: Johnson DW & Lindberg SE (Eds) Atmospheric Deposition and Nutrient Cycling in Forest Ecosystems, Chapter 5 (pp 72–149). Springer-Verlag, New York

Mitchell MJ, Krouse HR, Mayer B, Stam AC & Zhang Y (1998) Use of stable isotopes in evaluating biogeochemistry of forest ecosystems. In: Kendall C & McDonnell J (Eds) Isotope Tracers in Catchment Hydrology. Elsevier, The Netherlands (in press)

Nodvin SC, Driscoll CT & Likens GE (1986) The effect of pH on sulfate adsorption by a forest. Soil Science 142: 69–75

Nodvin SC, Driscoll CT & Likens GE (1988) Soil processes and sulfate loss at the Hubbard Brook Experimental Forest. Biogeochemistry 5: 185–199

Novac M, Bottrell SH, Groscheova H, Buzek F & Cerny J (1995) Sulphur isotope characteristics of two North Bohemian forest catchments. Water, Air and Soil Pollution 85: 1641–1646

Novak M, Bottrell SH, Fottova D, Buzek F Croscheova H & Zak K (1997) Sulfur isotope signals in forest soils of central Europe along an air pollution gradient. Environmental Science and Technology 30: 3473–3476

Nriagu JO, Holdway DA & Coker RD (1987) Biogenic sulfur and the acidity of rainfall in remote areas of Canada. Science 237: 1189–1192

Nriagu JO & Krouse HR (1992) Sulfur isotope evidence for emission of biogenic sulphur. In: Howarth RW, Stewart JWB & Ivanov MV (Eds) Sulphur Cycling on the Continents. SCOPE 48 (pp 63–66). John Wiley and Sons, Chichester

Rochelle BP & Church MR (1987) Regional patterns of sulfur retention in watersheds of the Eastern U.S. Water, Air and Soil Pollution 36: 61–73

Rustad LE, Fernandez IJ, Mitchell MJ, Nadelhoffer KJ, David MB & Fuller RB (1996) Experimental soil acidification and recovery at the Bear Brook Watershed in Maine. Soil Science Society of America Journal 60: 1933–1943

Schindler SC, Mitchell MJ, Scott TK, Fuller RD & Driscoll CT (1986) Incorporation of 35S-sulfate into organic and inorganic constituents of two forest soils. Soil Science. Society of America Journal 50:457–461

Searle PL (1979) Measurement of adsorbed sulfate in soils – Effects of varying soil:extractant ratios and methods of measurement. New Zealand Journal of Agricultural Research 22: 287–290

Sisterson DL, Bowersox VC, Myers TP, Olsen A, Vong R, Simpson JC & Mohen V (1990) Deposition Monitoring: Methods and Results. NAPAP Report 6. Government Printing Office, Washington, DC

Stam, AC, Mitchell MJ, Krouse HR & Kahl JS (1992) Stable sulfur isotopes of sulfate in precipitation and stream solutions in a northern hardwood watershed. Water Resources Research 28: 231–223

Strickland TC & Fitzgerald JW (1984) Formation and mineralization of organic sulfur in forest soils. Biogeochemistry 1: 79–95

Swank WT, Fitzgeral JW & Ash JT (1984) Microbial transformation of sulfate in forest soils. Science 223: 182–184

van Dijk HFG, Boxman AW & Roelofs JGM (1992) Effects of decrease in atmospheric deposition of nitrogen and sulfur on the mineral balance and vitality of a Scots pine stand in the Netherlands. Forest Ecology and Management 51: 207–215

van Stempvoort DR & Wills JJ (1991) Aboveground vegetation effects on the deposition and cycling of atmospheric sulfur: Chemical and stable isotope evidence. Water, Air and Soil Pollution 60: 55–82

Venkatram A, McNaughton D, Karamchandani PK, Shannon J, Fernau M & Sisterson DL (1990) Relationships Between Atmospheric Emissions and Deposition/Air Quality. NAPAP Report 8. Government Printing Office, Washington, DC

Wright RF, Lotse E & Semp A (1993) Reversibility of acidification shown by whole-catchment experiments. Nature 334: 670–675

Zhang Y, Mitchell MJ, Christ M, Krouse HR & Likens GE (1998) Stable sulfur isotopes in at Hubbard Brook Experimental Forest, New Hampshire Biogeochemistry 41: 259–275