

USE OF STABLE ISOTOPE RATIOS FOR EVALUATING SULFUR SOURCES AND LOSSES AT THE HUBBARD BROOK EXPERIMENTAL FOREST

M. J. MITCHELL^{1*}, B. MAYER², S. W. BAILEY³, J. W. HORNBECK³,
C. ALEWELL⁴, C.T. DRISCOLL⁵ and G.E. LIKENS⁶

¹SUNY-ESF, Syracuse, NY 13210, U.S.A.; ²University of Calgary, Calgary, Alberta, T2N 1N4, Canada; ³USDA Forest Service, Northeastern Research Station, Durham, NH 03824, U.S.A.;

⁴BITÖK, Universität Bayreuth, 95440 Bayreuth, Germany; ⁵Syracuse University, Syracuse, NY 13244, U.S.A.; ⁶Institute of Ecosystem Studies, Millbrook, NY 12545, U.S.A.

(* author for correspondence, e-mail: mitchell@mailbox.syr.edu)

Abstract. Anthropogenic S emissions have been declining in eastern North America since the early 1970s. Declines in atmospheric S deposition have resulted in decreases in concentrations and fluxes of SO_4^{2-} in precipitation and drainage waters. Recent S mass balance studies have shown that the outflow of SO_4^{2-} in drainage waters greatly exceeds current S inputs from atmospheric deposition. Identifying the S source(s) which contribute(s) to the discrepancy in watershed S budgets is a major concern to scientists and policy makers because of the need to better understand the rate and spatial extent of recovery from acidic deposition. Results from S mass balances combined with model calculations and isotopic analyses of SO_4^{2-} in precipitation and drainage waters at the Hubbard Brook Experimental Forest (HBEF) suggest that this discrepancy cannot be explained by either underestimates of dry deposited S or desorption of previously stored SO_4^{2-} . Isotopic results suggest that the excess S may be at least partially derived from net mineralization of organic S as well as the weathering of S-bearing minerals.

Keywords: atmospheric deposition, organic S, S budgets, stable isotopes, watersheds, weathering

1. Introduction

1.1. ROLE OF SULFATE IN SURFACE WATER ACIDIFICATION

Sulfate (SO_4^{2-}) is the major anion in acidic precipitation and in surface waters with low acid neutralizing capacity (ANC) affected by acidic deposition. Sulfate, in the form of sulfuric acid, is the major source of acidity contributing to the acidification of surface waters in the northeastern U.S.A. (Likens *et al.*, 1977; Driscoll, 1991). Although biogeochemical research during the last thirty years has improved considerably our knowledge of S cycling in forest ecosystems, important questions remain unresolved that hinder our ability to understand and predict how changing atmospheric S inputs will affect S losses from forest ecosystems (*e.g.*, Johnson and Mitchell, 1998). It has generally been assumed that SO_4^{2-} in low ANC surface waters is derived from atmospheric deposition, and that inputs of SO_4^{2-} to glaciated watersheds in the northeastern U.S. are transported relatively conservatively with drainage waters resulting in approximately balanced input/output S budgets (Galloway *et al.*, 1983; Likens *et al.*, 1990; Rochelle *et al.*, 1987; Church *et al.*, 1989). Since the early 1970s, anthropogenic emissions and S



deposition have been declining in eastern North America and are expected to continue to decrease at least until 2010 (Likens *et al.*, 2000a). This decrease in S deposition has resulted in decreases in SO_4^{2-} concentrations in surface waters in the northeastern U.S.A. (Likens, 1992; Driscoll *et al.*, 1995; Likens and Bormann, 1995). However, a complete accounting of S inputs, outputs and internal transfers within watersheds is necessary to evaluate fully those processes that regulate the changes in surface water SO_4^{2-} concentrations.

1.2. WATERSHED SULFUR MASS BALANCES

Currently in the northeastern U.S., many watersheds are exporting more S than can be accounted for by atmospheric deposition (Mitchell *et al.*, 1996; Driscoll *et al.*, 1998). Identifying the source of the S which is currently in excess of S inputs from total (wet and dry) deposition is a major concern to scientists as well as to policy makers. Although good estimates of wet deposition are available, dry deposition is much more difficult to quantify. If underestimated dry deposition is 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 more direct decrease in SO_4^{2-} losses in stream waters assuming conservative SO_4^{2-} transport. Annual changes in SO_2 emissions may explain, however, only a portion ($r^2 = 0.5$ to 0.7) of the temporal patterns of wet or bulk S deposition (Butler and Likens, 1991; Likens, 1992; Likens *et al.*, 2000ab) suggesting that other factors may also affect this relationship.

A delay in the response of S cycling and streamwater output to decreasing S emissions due to the desorption of previously deposited SO_4^{2-} has been predicted by various models (*e.g.*, Galloway *et al.*, 1983; Church *et al.*, 1989; Rochelle *et al.*, 1987; Anonymous, 1995). If a major internal SO_4^{2-} source (*e.g.*, weathering of S-bearing minerals, net mineralization of organic S) occurs within watersheds, the impact of emission reductions would be diminished or delayed in proportion to the contribution and nature of this internal source to SO_4^{2-} losses in surface waters (Johnson and Mitchell, 1998).

The use of mass balances for evaluating the S cycle has recently been reviewed by Evans *et al.*, (1997). Several mass balance watershed studies in the northeastern U.S. have shown that stream outflow of SO_4^{2-} exceeds S inputs from wet or bulk deposition and estimates of dry deposition based on net throughfall or inferred from measured air concentrations and the application of a deposition velocity model (Mitchell *et al.*, 1996; Driscoll *et al.*, 1998). Mitchell *et al.* (1992) suggested that desorption of SO_4^{2-} that had previously accumulated in soil during periods of higher S deposition may have contributed to the elevated SO_4^{2-} draining from the B horizon of a northern hardwood site in the Adirondack Mountains of New York, U.S.A. Such reversible SO_4^{2-} desorption has been shown to be an important mechanism regulating drainage SO_4^{2-} loss 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). Using model calculations, however, Driscoll *et al.* (1998) found that SO_4^{2-} adsorption/desorption reactions cannot completely account for the changing patterns of SO_4^{2-} concentrations in surface waters of the northeastern U.S.A. For wetland and lake regions the oxidation and mobilization of previously reduced S have been suggested as an important S source to drainage waters in both North America (Dillon and LaZerte, 1992) and Europe (Alewell and Novak, 2000). Thus, new approaches are needed to elucidate the processes contributing to elevated S leaching losses, beyond direct atmospheric deposition.

1.3. UTILIZATION OF THE STABLE ISOTOPIC RATIOS OF SULFATE

Stable isotopic ratios provide a powerful tool for studying the biogeochemical flux and cycling of S (Krouse and 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 S composition in forest ecosystems is controlled by isotopic contribution of S sources (*i.e.*, atmospheric deposition, mineral weathering, net mineralization of organic S) and isotopic discrimination during S transformations. Such processes can influence the $\delta^{34}\text{S}$ values of SO_4^{2-} in soil and drainage waters (Alewell and Giesemann, 1996; Alewell and Novak, 2000). Although many S conversions (*e.g.*, adsorption, desorption, precipitation) proceed with no isotopic selectivity, some studies have found some preference for ^{32}S during immobilization and mineralization (Fuller *et al.*, 1986; Krouse *et al.*, 1991; Zhang *et al.*, 1998). Dissimilatory SO_4^{2-} reduction, which occurs under anaerobic conditions, results in marked fractionation between the ^{34}S enriched SO_4^{2-} reactant and the ^{34}S depleted sulfide product, because bacteria preferentially metabolize the lighter ^{32}S (Krouse and Grinenko, 1991).

There have been a few studies conducted on forest catchments in Europe and eastern North America that have combined S mass balances and stable S isotopic investigations. Experimental additions with distinctive isotopic S signatures have been used successfully to identify and quantify S fluxes in watersheds and forest soils (Legge and Krouse, 1992; Mayer *et al.*, 1992, 1993, 1995; Morgan, 1992; Giesemann *et al.*, 1995; Mörtz and Torssander, 1995; Prietzel *et al.*, 1995; Mitchell *et al.*, 1998). Natural abundances of S isotopes have also been used to infer information on S cycling relationships (Mitchell *et al.*, 1998). However, further research is clearly needed on the use of S isotopic ratios to evaluate the biogeochemistry of S, including discrepancies in S mass balances.

2. Sulfur Biogeochemistry at the Hubbard Brook Experimental Forest

2.1. BACKGROUND

The understanding of S biogeochemistry has been a major focus of research at the

HBEF and a comprehensive monograph of this research is in preparation (Likens *et al.*, 2000b). Research at the HBEF has included evaluations of the effects of various forest harvesting practices on S losses (Likens *et al.*, 1970; Dahlgren and Driscoll, 1994; Likens and Bormann, 1995; Mitchell *et al.*, 1989; Zhang *et al.*, 1999). One of the most important findings of these studies was that pH-dependent SO_4^{2-} adsorption plays a pivotal role in explaining temporal patterns in SO_4^{2-} concentrations and fluxes in drainage waters (Fuller *et al.*, 1987; Nodvin *et al.*, 1988). With the removal of vegetation there is a decrease in N demand allowing excess mineralized NH_4^+ to be available for nitrification that acidifies soil water. The lowering of pH results in a marked increase in soil SO_4^{2-} adsorption and as vegetation recovers and pH increases this adsorbed SO_4^{2-} may be desorbed.

There have also been extensive analyses of the role of S in surface water acidification. Research at the HBEF was one of the earliest studies to document the occurrence and deleterious impacts of “acid rain” (Likens *et al.*, 1972; Likens and Bormann, 1974; Likens, 1989). Studies on the mass balances of S at the HBEF have demonstrated the relative importance of wet and dry deposition. For example, Likens *et al.* (1990) proposed that dry deposition could account for the differences between bulk S deposition and S losses in drainage waters using a watershed mass balance approach at the HBEF. Lovett *et al.* (1992) compared three approaches to estimating dry deposition of S at the HBEF. These methods included: 1) an inferential method, 2) measurements of net throughfall S and, 3) the discrepancy in watershed mass balances of S. These three methods showed large differences in estimates of dry deposition of S, with the watershed mass balance approach giving substantially higher values than the other two. Possible sources for this additional S output, besides underestimates of dry deposition, include an underestimate of weathering of S-containing minerals, reoxidation of previously reduced and stored S, desorption of previously adsorbed inorganic SO_4^{2-} and mineralization of organic S. Alewell *et al.* (1999) presented S mass balances for a

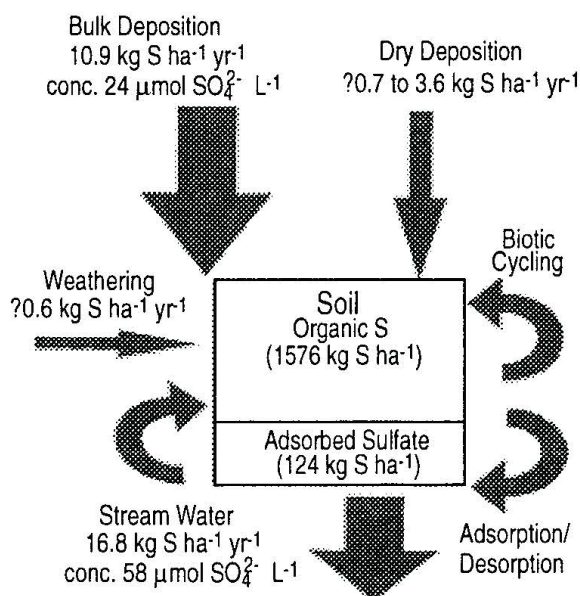


Figure 1. Sulfur pools and fluxes for an undisturbed watershed at the Hubbard Brook Experimental Forest, White Mountains, New Hampshire, U.S.A. Fluxes with “?” values have high uncertainty (After Alewell *et al.*, 1999).

period of 29 years. These results suggested that an internal source of S was necessary to account for the SO_4^{2-} in stream water (Fig. 1). However, this mass balance approach does not allow precise quantification of the relative importance of dry deposition, net organic S mineralization and S mineral weathering to account for discrepancies in the S budget.

2.2. SULFUR ISOTOPE STUDIES

Fuller *et al.* (1986) examined the isotopic composition of S including both organic and inorganic fractions in the soil as well as S in soil water and surface waters at the HBEF. This analysis was done in Watershed 5 prior to whole tree harvesting in the winter of 1983-1984 (Mitchell *et al.*, 1989). The isotopic composition of SO_4^{2-} extracted from the soil 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 $\delta^{34}\text{S}$ values than those of organic S. The reason for the lower $\delta^{34}\text{S}$ in the organic constituents was not known, but it has been suggested that the formation of the organic S occurred over a long period starting from the last glaciation (see also Mitchell *et al.*, 1989). Low $\delta^{34}\text{S}$ values of organic S have also been documented for other sites as discussed previously.

Values of $\delta^{34}\text{S}$ in precipitation, throughfall, soils, soil solution, and stream waters at the HBEF were evaluated further by Zhang *et al.* (1998). Values of $\delta^{34}\text{S}$ in precipitation and throughfall SO_4^{2-} were similar to each other but differed seasonally. The mean precipitation $\delta^{34}\text{S}$ value was higher in the dormant season (5.9‰) than in the growing season (5.0‰) but the throughfall growing-season value was higher (5.6‰) than for the dormant season (4.9‰). In soil solutions, $\delta^{34}\text{S}$ values of SO_4^{2-} were higher in the growing season (8.9, 8.8, and 4.0‰ for Oa, Bh, and Bs horizons, respectively) than in the dormant season (5.6, 3.7, and 3.4‰ for Oa, Bh, and Bs horizons, respectively). Zhang *et al.* (1998) suggested that these seasonal differences in $\delta^{34}\text{S}$ were probably caused by biological isotopic fractionation due to immobilization and mineralization. The $\delta^{34}\text{S}$ values of SO_4^{2-} in streams were generally 2‰ lower and more variable than those in precipitation and throughfall, suggesting either isotopic fractionation during transformation and/or the contribution of SO_4^{2-} from a different source with a lower $\delta^{34}\text{S}$ value.

The availability of archived bulk precipitation and stream water samples at the HBEF provided a unique opportunity to evaluate potential sources and losses of S by analyzing the long-term patterns (1966–1994) of the $\delta^{34}\text{S}$ values of SO_4^{2-} (Alewell *et al.*, 1999). In bulk precipitation collected adjacent to the R.S. Pierce Ecosystem Laboratory (253 m elevation) and near Watershed 6 (549 m elevation) the $\delta^{34}\text{S}$ values of SO_4^{2-} were greater (mean: 4.5 and 4.2‰, respectively) and showed more variation (variance: 0.49 and 0.30) than stream SO_4^{2-} samples collected from Watersheds 5 (W5) and 6 (W6) (mean: 3.2 and 3.7‰; variance: 0.09 and 0.08, respectively) (Fig. 2). These results were consistent with other

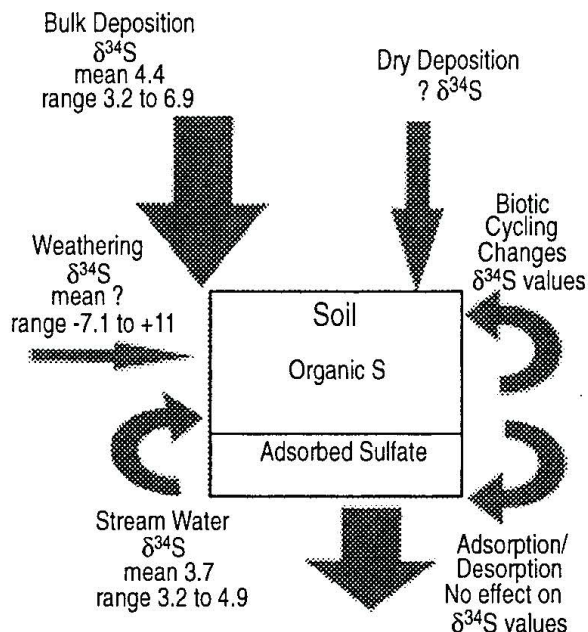


Figure 2. Sulfur isotopic composition of SO_4^{2-} of major fluxes and important processes affecting $\delta^{34}\text{S}$ values (‰) at the Hubbard Brook Experimental Forest, White Mountains, New Hampshire, U.S.A. Values with "?" have uncertainty or have not been measured (modified from Alewell *et al.*, 1999).

studies in forest catchments that have combined results for mass balances with stable S isotopes (Mayer *et al.*, 1995; Novak *et al.*, 1997; Alewell and Gehre, 1999). These results indicate that for sites, including the HBEF, where atmospheric inputs are $\leq 10 \text{ kg S ha}^{-1} \text{ yr}^{-1}$, most of the deposited SO_4^{2-} cycles through the biomass before it is released to stream water. Although the isotopic results suggest the importance of S mineralization, conclusive evidence was not available for net mineralization.

The origin of SO_4^{2-} in bulk precipitation was evaluated by Alewell *et al.* (2000) using the archived bulk precipitation samples for stable S isotopic analyses. These analyses compared the $\delta^{34}\text{S}$ values to anthropogenic SO_2 emissions, the relative contribution of sea salt aerosols (as $[\text{SO}_4^{2-}]/[\text{Na}^+]$ ratio in precipitation) and the effects of temperature and solar radiation on the long-term patterns of $\delta^{34}\text{S}$ values. The long-term pattern of $\delta^{34}\text{S}$ values in bulk precipitation SO_4^{2-} could be partly explained by the relative contribution of marine SO_4^{2-} or solar radiation effects on S transformation and isotopic discrimination. The high variability of the $\delta^{34}\text{S}$ values of various fossil fuels made it difficult to use stable S isotopes for identifying whether changes in fossil fuel utilization has affected the $\delta^{34}\text{S}$ values of SO_4^{2-} in bulk precipitation. The seasonal pattern of $\delta^{34}\text{S}$ values of SO_4^{2-} in bulk precipitation (significantly higher values in the winter than the summer) was explained by the temperature dependence of the isotopic shift during SO_4^{2-} formation in the atmosphere. A greater relative contribution of marine SO_4^{2-} during the winter may also have contributed to the higher $\delta^{34}\text{S}$ values of SO_4^{2-} in the winter. Previous investigations (*e.g.*, Nriagu and Coker, 1978; Nriagu *et al.*, 1987) may have overestimated the role of biogenic emissions in affecting the seasonal patterns of $\delta^{34}\text{S}$ values of SO_4^{2-} (Alewell *et al.*, 2000).

The isotopic analyses of SO_4^{2-} in precipitation (mean = 4.4‰ $\delta^{34}\text{S}$) and drainage water (mean = 3.7‰ $\delta^{34}\text{S}$) at the HBEF clearly show that the drainage waters are

depleted in ^{34}S by $\sim 0.7\text{‰}$ (Alewell et al., 1999). This difference was most likely due to contributions from S sources with lower $\delta^{34}\text{S}$ values and/or S isotopic fractionation. Most recently research at the HBEF has begun to focus on evaluating the relative importance of mineral weathering versus organic S mineralization in affecting the isotopic composition of drainage water SO_4^{2-} .

2.2.1. Contribution of the Weathering of Sulfur-Containing Minerals

Isotopic analyses may help to evaluate the relative importance of mineral weathering of S-containing minerals as a source of S to drainage waters providing that the minerals have isotopic ratios that are distinct from those of S in atmospheric deposition and soil. During the base flow period in August and September of 1998, surface water samples were collected from 56 sites including HBEF and other sites in Vermont and New Hampshire in the northeastern U.S.A. Samples were collected at base flow since at low discharge the relative contribution of mineral derived S should be at a maximum. All the samples were analyzed for $\delta^{34}\text{S}$ values of SO_4^{2-} and a subset was also analyzed for $\delta^{18}\text{O}$ values of SO_4^{2-} . These $\delta^{34}\text{S}$ values ranged from -4.3 to $+11.0\text{‰}$ (Bailey *et al.*, unpublished data). These preliminary results suggest that this range reflects differences in both mineralogical S sources and dissimilatory reduction processes. The most extreme values $\delta^{34}\text{S}$ values represent S mineralogical sources since surface waters with SO_4^{2-} concentrations $>110\text{ }\mu\text{mol}_\text{c}\text{ L}^{-1}$ deviated more from the $\delta^{34}\text{S}$ value of precipitation than those waters with lower SO_4^{2-} concentrations. Most notably the high $\delta^{34}\text{S}$ value of $+11.0\text{‰}$ was streamwater from Sleepers River, Vermont, which has different mineralogical S sources than the HBEF (Hornbeck *et al.*, 1997). For samples collected within the HBEF drainage basin, the $\delta^{34}\text{S}$ values ranged from $+1.4$ to $+5.3$ (Fig. 3). The lowest values $\delta^{34}\text{S}$ values tended to coincide

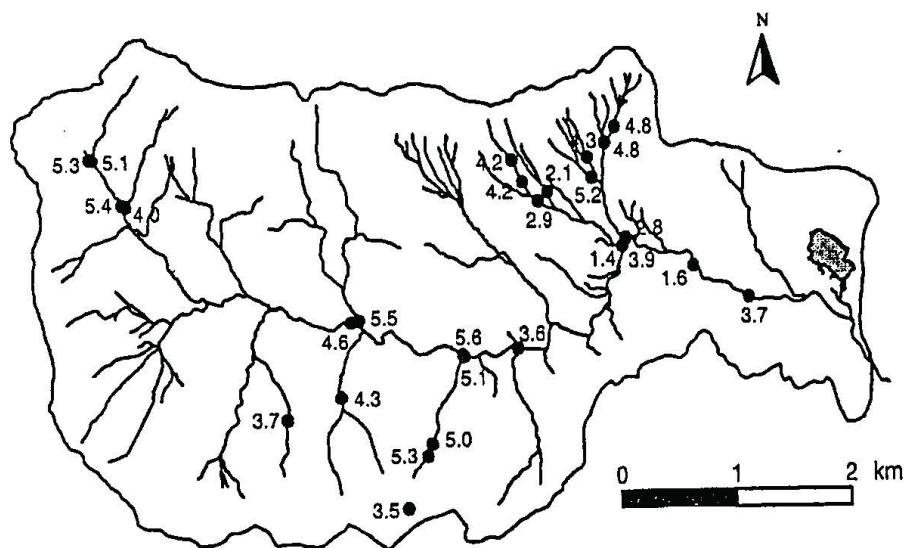


Figure 3. $\delta^{34}\text{S}$ values (‰) of SO_4^{2-} in surface waters during the base flow period (August-September, 1998) at the Hubbard Brook Experimental Forest, New Hampshire (U. S. A.) (Bailey *et al.*, unpublished data).

with areas near surface seeps and wet soils that would have conditions conducive to dissimilatory sulfate reduction that results in significant changes in the $\delta^{34}\text{S}$ values as discussed above. The low values may represent the reoxidation to SO_4^{2-} of chemically reduced sulfides that may have lower $\delta^{34}\text{S}$ values.

One of the major challenges in watershed biogeochemistry is estimating the contribution of soil and bedrock mineral weathering reactions to solute fluxes (Bricker *et al.*, 1994). Quantifying the chemical weathering of S-containing minerals that contribute SO_4^{2-} to drainage waters is a formidable task. Bedrock S concentrations are quite variable at the HBEF with values ranging from 0.2 to 0.9% (Bailey *et al.*, unpublished data), which is greater than the average S concentration (0.047%) of the continental crust (Grineko and Ivanov, 1983). Thus, the bedrock S concentrations are substantially higher than that of the soil (<2 mm fraction) which is very low (<0.001% S). Although it has not been quantified, some observations suggest that weathering of S-containing minerals is occurring at HBEF in rock fragments and shallow bedrock exposures and this weathering may be contributing to some of the discrepancy in the S mass balances. The isotopic values of some of the major mineral components at the HBEF show marked variation (whole rock samples from the Rangeley Formation in Watershed 5 = -11.5‰ $\delta^{34}\text{S}$, 0.9% S; whole rock samples from the Rangeley Formation in Watershed 9 = $+6\text{‰}$ $\delta^{34}\text{S}$, 0.2% S). Since there is a large range of isotopic values for potential weathering sources, it is not possible to assign a single value for the isotopic weathering component unless the relative importance of different weathering sources can be estimated. However, the weathering of some rocks from Watershed 5 would result in a lowering of the $\delta^{34}\text{S}$ value of SO_4^{2-} while the weathering of some rocks from Watershed 9 would result in $\delta^{34}\text{S}$ values of SO_4^{2-} that are similar to those of bulk precipitation ($\delta^{34}\text{S}$ range from 3.2 to 6.9‰; Alewell *et al.*, 1999).

2.2.2. Role of Biological Processes

Studies at the HBEF have suggested that the decreases in $\delta^{34}\text{S}$ values of SO_4^{2-} in drainage waters may be a result of soil processes that generate SO_4^{2-} that is depleted in ^{34}S (Zhang *et al.*, 1998; Alewell *et al.*, 1999). Such results agree with findings from Europe at sites in the northwestern Czech Republic and northeastern Bavaria, Germany, where $\delta^{34}\text{S}$ values of SO_4^{2-} in soil solutions and streams show different spatial and temporal patterns than those of precipitation or throughfall (Novak *et al.*, 1995; Alewell and Gehre, 1999). Mayer *et al.* (1995) showed that although $\delta^{34}\text{S}$ values of SO_4^{2-} in atmospheric deposition are altered only slightly in soil drainage waters, the oxygen isotopic composition ($\delta^{18}\text{O}$) 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. Other studies have reported, however, that $\delta^{34}\text{S}$ values of SO_4^{2-} from soil solution of terrestrial sites have generally lower $\delta^{34}\text{S}$ values than SO_4^{2-} in throughfall (Fuller *et al.*, 1986; Novak *et al.*, 1995; Zhang *et al.*, 1998; Alewell *et al.*, 1998, 1999; Alewell and Gehre, 1999).

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 SO_4^{2-} 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 $\delta^{18}\text{O}$ values of soil water SO_4^{2-} 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 through the organic soil pool. The importance of organic S as a SO_4^{2-} source has been shown in Europe especially for organic rich soils with relatively low amounts of adsorbed SO_4^{2-} (Alewell, 2000).

3. Research Needs for Evaluating Discrepancies in Watershed S Budgets

A full evaluation of discrepancies in the mass balances of S inputs and outputs in catchments is needed including an evaluation of the contributions of organic S mineralization and weathering of S-containing minerals (Likens *et al.*, 2000b). We suggest that a combined approach that includes the development of biogeochemical and isotopic models that predict elemental and isotopic S pools and fluxes is required. This approach will require further analyses of dry deposition inputs including information on the isotopic values of gaseous inputs (*i.e.*, SO_2). Also, more information is needed on the masses and isotopic composition of the major S pools (adsorbed SO_4^{2-} , organic S, S minerals in soil and bedrock) both within and among watersheds. Analyses of the spatial distribution of S-bearing minerals and their isotopic composition could be used to estimate weathering rates and to predict differences in the contribution of different geological S sources. Also, studies on the role of biotic processes including the effects of S mineralization/immobilization and plant uptake on isotopic fractionation would be helpful in evaluating the contribution of these processes to net loss or retention of S within catchments.

Acknowledgments

This research was supported by the National Science Foundation, U.S.A. Environmental Protection Agency, A.W. Mellon Foundation, U.S.D.A. Forest Service and the German Ministry of Education, Science, Research and Technology (Grant No. PT BEO 51-0339476). The Hubbard Brook Experimental Forest is administered by the U.S.D.A. Forest Service. This is a contribution of the Hubbard Brook Ecosystem Study. The help of P. McHale in assisting with the laboratory analyses was greatly appreciated. The help of J. Campbell in producing Figure 3 is acknowledged.

References

- Alewel, C.: 2000, *Predicting Reversibility of Acidification: the European Sulfur Story*. Proceedings of Acid Rain 2000 (This volume).
- Alewel, C. and Gehre, M.: 1999, *Biogeochemistry* **47**, 319–333.
- Alewel, C. and Giesemann, A.: 1996, *Isotopes in Environmental and Health Studies* **32**, 203.
- Alewel, C. and Novak, M.: 2000, *Environmental Pollution* (in press)
- Alewel C., Bredemeier, M., Matzner, E. and Blanck, K.: 1997, *Journal of Environmental Quality* **26**, 658.
- Alewel, C., Mitchell, M. J., Likens, G. E. and Krouse, H. R.: 1999, *Biogeochemistry* **44**, 281.
- Alewel, C., Mitchell, M. J., Likens, G. E. and Krouse, H. R.: 2000, *Journal of Environmental Quality* **29**, 759.
- Anonymous: 1995, *Acid Deposition Standard Feasibility Study Report to Congress*, United States Environmental Protection Agency, EPA 430-R-95-001a.
- Bricker, O., Pačes, T., Johnson, C. E. and Sverdrup, H.: 1994, 'Weathering and Erosion Aspects of Small Catchment Research', in B. Moldran and J. Cerny (eds.), *Biogeochemistry of Small Catchments: a Tool for Environmental Research*. SCOPE. John Wiley & Sons, Chichester, pp. 85–105.
- Butler, T. J. and Likens, G. E.: 1991, *Atmospheric Environment* **25A**, 305.
- Church, M. R., Thornton, K. W., Shaffer, P. W. et al.: 1989, *Direct/Delayed Response Project: Future Effects of Long-Term Sulfur Deposition on Surface Water Chemistry in the Northeast and Southern Blue Ridge Province*, U.S. Environmental Protection Agency, EPA/600/3-89/061, Washington, D.C.
- Dahlgren, R. A. and Driscoll, C. T.: 1994, *Plant and Soil* **158**, 262.
- Dillon, P. J. and LaZerte, B. D.: 1992, *Environmental Pollution* **77**, 211.
- Driscoll, C. T.: 1991, 'Northeast Overview', in D. F. Charles (ed.), *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies*, Springer-Verlag, NY, pp. 129–132.
- Driscoll, C. T., Postek, K. M., Kretser, W., Raynal, D. J.: 1995, *Water, Air and Soil Pollution* **85**, 583.
- Driscoll, C. T., Likens, G. E., and Church, M. R.: 1998, *Water, Air and Soil Pollution* **105**, 319.
- Evans, H. E., Dillon, P. J. and Molot, L. A.: 1997, *Hydrological Processes* **11**, 765.
- Fuller, R. D., Mitchell, M. J., Krouse, H. R. Syskowski, B. J. and Driscoll, C. T.: 1986, *Water, Air and Soil Pollution* **28**, 163.
- Fuller, R. D., Driscoll, C. T., Lawrence, G. and Nodvin, S. C.: 1987, *Nature* **325**, 707.
- Galloway, J. N., Norton, S. N. and Church, M. R.: 1983, *Environmental Science and Technology* **17**, 541A.
- Giesemann, A., Jäger, H.-J. and Feger, K. H.: 1995, *Plant and Soil* **168-169**, 399.
- Grinenko, V. A. and Ivanov, M. V.: 1983, 'Principal Reactions of the Global Biogeochemical Cycle of Sulphur', in M. V. Ivanov and J. R. Freney (eds.) *The Global Biogeochemical Sulphur Cycle*, SCOPE 19, John Wiley & Sons, Chichester, pp. 1–23.
- Harrison, R. B., Johnson, D. W. and Todd, D. E.: 1989, *Journal of Environmental Quality* **18**, 419.
- Hornbeck, J. W., Bailey, S. W., Buso, D. C. and Shanley, J. B.: 1997, *Forest Ecology and Management* **93**, 73.
- Hultberg, H.: 1992, 'Biochemical Cycling of Sulfur and its Effects on Surface Chemistry in an Acid Catchment in SW Sweden', in A. Teller, P. Mathy and J. N. R. Jeffers (eds.), *Responses of Forest Ecosystems to Environmental Changes*, Elsevier Applied Science Amsterdam, The Netherlands, pp. 677–680.
- Johnson, D. W. and Mitchell, M. J.: 1998, 'Responses of Forest Ecosystems to Changing Sulfur Inputs', in D. Maynard (ed). *Sulfur in the Environment*, Marcel Dekker Inc., New York, NY, pp. 219–262.

- Krouse, H. R. and Grinenko, V. A. (eds.): 1991, *Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment. SCOPE 43*, John Wiley and Sons, Chichester.
- Krouse, H. R., Grinenko, V. A., Grinenko, L. N. Newman, L. *et al.*: 1991, 'Case Studies and Regional Applications', in H. R. Krouse, and V. A. Grinenko (eds.), *Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment. SCOPE 43*, John Wiley and Sons, Chichester, pp. 307–422.
- Legge, A. H. and Krouse, H. R.: 1992, 'An assessment of the environmental fate of industrial sulphur in a temperate pine forest ecosystem', in *Critical Issues in the Global Environment, Vol. 5. Ninth World Clean Air Congress Towards Year 2000*, Paper 1U22B.01.
- Likens, G. E.; 1989, *Ambio* **18**, 172.
- Likens, G. E.; 1992, *The Ecosystem Approach: Its Use and Abuse. Excellence in Ecology*, Vol. 3. Ecology Institute, Oldendorf-Luhe, Germany.
- Likens, G. E. and Bormann, F. H.: 1974, *Science* **184**, 1176.
- Likens, G. E., Bormann, F. H., Johnson, N. M., Fisher, D. W. and Pierce, R. S.: 1970, *Ecological Monograph* **40**, 23.
- Likens, G. E., Bormann, F. H. and Johnson, N. M.: 1972, Acid Rain. *Environment* **14**, 33.
- Likens, G. E., Bormann, F. H., Pierce, R. S., Eaton, J. S. and Johnson, N. M.: 1977, *Biogeochemistry of a Forested Ecosystem*, First Edition, Springer-Verlag, New York.
- Likens, G. E., Bormann, F. H., Hedin, L. O. and Driscoll, C. T.: 1990, *Tellus* **42B**, 319.
- Likens, G. E. and Bormann, F. H.: 1995, *Biogeochemistry of a Forested Ecosystem*, Second Edition, Springer-Verlag, New York.
- Likens, G. E., Butler, T. J. and Buso, D. C.: 2000a, *Biogeochemistry* (in press).
- Likens, G. E., Driscoll, C. T., Buso, D. C., Mitchell, M. J., Lovett, G. M., Bailey, S. W., Siccama, T. G., Reiners, W. A. and Alewell, C.: 2000b. (In Preparation).
- Lovett, G. M., Likens, G. E. and Nolan, S. S.: 1992, 'Dry Deposition of Sulfur to the Hubbard Brook Experimental Forest: a Preliminary Comparison of Methods', in S. E. Schwartz and W. G. N. (coords). *Fifth International Conference on Precipitation Scavenging and Atmosphere-Surface Exchange. The Summer Volume (3): Application and Appraisals*, Hemisphere Publishing Corp., pp.1391–1402.
- Mayer, B., Fritz, P. and Krouse, H. R.: 1992, 'Sulphur Isotope Discrimination During Sulphur Transformations in Aerated Forest Soils', in M. J. Hendry and H. R. Krouse (eds.) *Workshop Proceedings on Sulphur Transformations in Soil Ecosystems*, 5-7 November 1992, National Hydrology Research Symposium No. 11. Saskatoon, Saskatchewan, pp. 161–172.
- Mayer, B., Fritz, P., Prietzel, J. and Krouse, H. R.: 1995, *Applied Geochemistry* **10**, 161.
- Mayer, B., Krouse, H. R., Fritz, P., Prietzel, J. and Rehfuss, K. E.: 1993, 'Evaluation of Biogeochemical Sulfur Transformations in Forest Soils by Chemical and Isotope Data', in *Tracers in Hydrology*, IAHS Publ., No. 215, pp. 65–72.
- Mitchell, M. J., Driscoll, C. T., Fuller, R. D., David, M. B. and Likens, G. E.: 1989, *Soil Science Society of America Journal* **53**, 933.
- Mitchell, M. J., Burke, M. K. and Shepard, J. P.: 1992, *Biogeochemistry* **17**, 165.
- Mitchell, M. J., Driscoll, C. T. and Raynal, D. J.: 1996, *Water, Air and Soil Pollution* **88**, 355.
- Mitchell, M. J., Krouse, C. R., Mayer, B., Stam, A. C. and Zhang, Y.: 1998, 'Use of Stable Isotopes in Evaluating Sulfur Biogeochemistry of Forest Ecosystems', in C. Kendall and J. J. McDonnell (eds.), *Isotope Tracers in Catchment Hydrology*, Elsevier, Amsterdam, pp. 489–518.
- Morgan, M. D.: 1992, *Environmental International* **18**, 545.
- Mörth, C.-M. and P. Torssander: 1995, *Water, Air and Soil Pollution* **79**, 261.
- Nodvin, S. C., Driscoll, C. T. and Likens, G. E.: 1988, *Biogeochemistry* **5**, 185.
- Novak, M., Bottrell, S. H., Groscheova, H., Buzek, F. and Cerny, J.: 1995, *Water, Air and Soil Pollution* **85**, 1641.
- Novak, M., Bottrell, S. H., Fottova, D., Buzek, F., Croscheova, H. and Zak, K.: 1997,

- Environmental Science and Technology* **30**, 3473.
- Nriagu, J. O. and Coker, R. D.: 1978, *Nature* **274**, 883.
- Nriagu, J. O., Holdway, D. A. and Coker, R. D.: 1987, *Science* **237**, 1189.
- Prietz, J., Mayer, B., Krouse, H. R., Rehfuss, K. E. and Fritz, P.: 1995, *Water, Air and Soil Pollution* **79**, 243.
- Rochelle, B. P., Church, M. R. and David, M. B.: 1987, *Water, Air and Soil Pollution* **36**, 61.
- Rustad, L. E., Fernandez, I. J., Mitchell, M. J., Nadelhoffer, K. J., David, M. B. and Fuller, R. B.: 1996, *Soil Science Society of America Journal* **60**, 1933.
- Zhang, Y., Mitchell, M. J., Christ, M., Krouse, H. R. and Likens, G.E.: 1998, *Biogeochemistry* **41**, 259.
- Zhang, Y., Mitchell, M. J., Driscoll, C. T. and Likens, G. E.: 1999, *Canadian Journal of Forest Research* **29**, 364.