

Tracing sources of streamwater sulfate during snowmelt using S and O isotope ratios of sulfate and ^{35}S activity

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Abstract. The biogeochemical cycling of sulfur (S) was studied during the 2000 snowmelt at Sleepers River Research Watershed in northeastern Vermont, USA using a hydrochemical and multi-isotope approach. The snowpack and 10 streams of varying size and land use were sampled for analysis of anions, dissolved organic carbon (DOC), ^{35}S activity, and $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of sulfate. At one of the streams, $\delta^{18}\text{O}$ values of water also were measured. Apportionment of sulfur derived from atmospheric and mineral sources based on their distinct $\delta^{34}\text{S}$ values was possible for 7 of the 10 streams. Although mineral S generally dominated, atmospheric-derived S contributions exceeded 50% in several of the streams at peak snowmelt and averaged 41% overall. However, most of this atmospheric sulfur was not from the melting snowpack; the direct contribution of atmospheric sulfate to streamwater sulfate was constrained by ^{35}S mass balance to a maximum of 7%. Rather, the main source of atmospheric sulfur in streamwater was atmospheric sulfate deposited months to years earlier that had microbially cycled through the soil organic sulfur pool. This atmospheric/pedospheric sulfate (pedogenic sulfate formed from atmospheric sulfate) source is revealed by $\delta^{18}\text{O}$ values of streamwater sulfate that remained constant and significantly lower than those of atmospheric sulfate throughout the melt period, as well as streamwater ^{35}S ages of hundreds of days. Our results indicate that the response of streamwater sulfate to changes in atmospheric deposition will be mediated by sulfate retention in the soil.

Introduction

Trends and patterns of sulfate concentrations in streamwater have received much attention for several decades because sulfate plays a dominant role in the anthropogenic acidification of surface waters (Reuss and Johnson 1986; Likens and Bormann 1995; Driscoll et al. 2001; Likens et al. 2002). In recent years attention in the USA and Europe has focused on how stream sulfate responds to decreases in atmospheric deposition of sulfate (Stoddard et al. 1999; Clow

and Mast 1999). Trend detection in surface waters may be confounded by the presence of sulfate produced by weathering of sulfur-containing minerals in the watershed bedrock (Turk et al. 1993; Mayer et al. 1995a; Alewell et al. 1999; Bailey et al. 2004). Rochelle et al. (1987) concluded that sulfate was in approximate balance in many ecosystems in glaciated areas of eastern North America, but more recent studies have found that the amount of sulfate exported in drainage waters exceeds atmospheric inputs, suggesting the importance of an internal sulfur source (Driscoll et al. 1998; Alewell et al. 1999; Mitchell et al. 2001a, b; Likens et al. 2002). Accounting for geologic sulfate sources is essential in analyzing the response of sulfate in streamwater to changes in atmospheric deposition.

Sulfur may be retained in a catchment by adsorption, mineral precipitation, uptake, and assimilatory or dissimilatory bacterial sulfate reduction (BSR). These abiotic and biotic processes can result in a substantial residence time of sulfur in soils (Mayer et al. 1995b; Alewell 2001; Novak et al. 2001), causing a lag in streamwater response to changes in atmospheric sulfate inputs.

Stable isotope ratios of sulfur ($^{34}\text{S}/^{32}\text{S}$) have been used to assess the relative contributions of atmospheric, pedospheric, and lithospheric sulfur to streamflow (e.g. Krouse and Grinenko 1991; Mitchell et al. 1998). The $\delta^{34}\text{S}$ values of mineral sulfur vary widely (Nielsen et al. 1991), sometimes even within a small geographic area (Bailey et al. 2004). In some areas, the $\delta^{34}\text{S}$ values of atmospheric S also vary and this variation has been used to apportion S sources (Alewell et al. 2000; Mast et al. 2001). In the northeastern USA, however, $\delta^{34}\text{S}$ values of sulfate in atmospheric precipitation are often quite consistent, and average near 5‰ (Mitchell et al. 1998). If $\delta^{34}\text{S}$ values of precipitation and bedrock are uniform within each source but distinct from one another, and isotope fractionation effects during sulfur transformations are minimal, then $\delta^{34}\text{S}$ values of sulfate in streamwater may be used to quantify atmospheric and weathering sources of S. Isotopic approaches provide constraints on the pools, cycling, and residence time of sulfate that may be applied in models that predict ecosystem response to changes in atmospheric input (Gbondo-Tugbawa et al. 2002).

Atmospheric sulfur contains a small quantity of the cosmogenic radioactive isotope ^{35}S (half-life 87 days). Detectable ^{35}S in streamwater indicates the presence of S deposited from the atmosphere within the last 1–2 years (Michel and Naftz 1995; Sueker et al. 1999; Michel et al. 2000). If the decrease in specific activity of ^{35}S (mBq per mg SO_4) from precipitation to streamflow is due solely to radioactive decay, it may be used to estimate an average age of streamwater sulfate, and thus to assess how rapidly S cycles through a catchment (Michel et al. 2000). However, specific ^{35}S activity may be diluted by ^{35}S -free sulfate generated from mineral weathering, resulting in an older apparent age of atmospheric S unless the non-atmospheric component is subtracted before the calculation.

Much of the atmospheric sulfate entering a watershed is retained in the soil and vegetation. Although $\delta^{34}\text{S}$ values and ^{35}S activity help to distinguish atmospheric and geologic S sources and to estimate ecosystem residence time of S, they usually provide only limited information on S cycling in the soil

(Mitchell et al. 2001a; Novak et al. 2001). For estimating the contributions of these soil S sources, $\delta^{18}\text{O}$ values of sulfate (Mayer et al. 1995b; Kester et al. 2003) and more recently $\delta^{17}\text{O}$ values of sulfate (Bao et al. 2001; Lee et al. 2001; Johnson et al. 2001) have proved especially useful. Atmospheric sulfate is enriched in ^{18}O because it derives some of its oxygen atoms from atmospheric O_2 , which has a $\delta^{18}\text{O}$ value of $+23\text{‰}$ (Kroopnick and Craig 1972). When atmospheric sulfate undergoes assimilatory bacterial sulfate reduction and re-oxidation in the soil, the distinctive high $\delta^{18}\text{O}$ value is lost and reset to a lower $\delta^{18}\text{O}$ value (e.g. Mayer et al. 1995b) because some oxygen atoms in the sulfate are replaced by oxygen from soil water with negative $\delta^{18}\text{O}$ values (Krouse and Mayer 2000). These processes typically have only a small effect on the $\delta^{34}\text{S}$ values of sulfate unless dissimilatory bacterial sulfate reduction occurs (Mitchell et al. 1998). The various processes affecting the isotopic composition of sulfate are depicted in Figure 1.

At Sleepers River in northern Vermont, USA, Hornbeck et al. (1997) reported that sulfate export in streamwater was greater than two times atmospheric inputs during 1992–1994, suggesting a geologic S source. From a regional survey, Bailey et al. (2004) reported that Sleepers River had an elevated S content in bedrock (7.9 mg S kg^{-1}) with a relatively high $\delta^{34}\text{S}$ value ($+8.5\text{‰}$, significantly higher than the average $\delta^{34}\text{S}$ value of precipitation, $+5.6\text{‰}$). Three base-flow stream samples had sulfate $\delta^{34}\text{S}$ values of $+7.3$, $+9.1$, and $+10.5\text{‰}$, closely bracketing the value of the bedrock sample. These initial analyses suggested that isotopic source apportionment of sulfate would be possible at Sleepers River, leading to the current study.

The objective of this study was to provide new information on catchment S cycling and dynamic variations of S sources during a hydrologic event using a hydrochemical and multi-isotope approach. We chose to study snowmelt because it is a hydrologically active time when 50% of the annual streamflow typically occurs in a 6-week period. Our approach was to analyze the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of sulfate and cosmogenic ^{35}S activities in the snowpack, groundwaters, and surface waters to evaluate the relative contribution of different S sources and the residence time of atmospherically derived S in the catchment. We also applied hydrograph separation using $\delta^{18}\text{O}$ values of water to evaluate the relative contributions of “new” and “old” water to discharge and the relation between new water and sulfate concentrations and isotopic composition.

Methods

Site description

Sleepers River Research Watershed (Figure 2) in northeastern Vermont, USA, was established in 1958 by the U.S. Department of Agriculture, Agricultural Research Service, and is now operated by the U.S. Geological Survey (USGS). Sleepers River was the site where the saturation-excess overland flow theory of

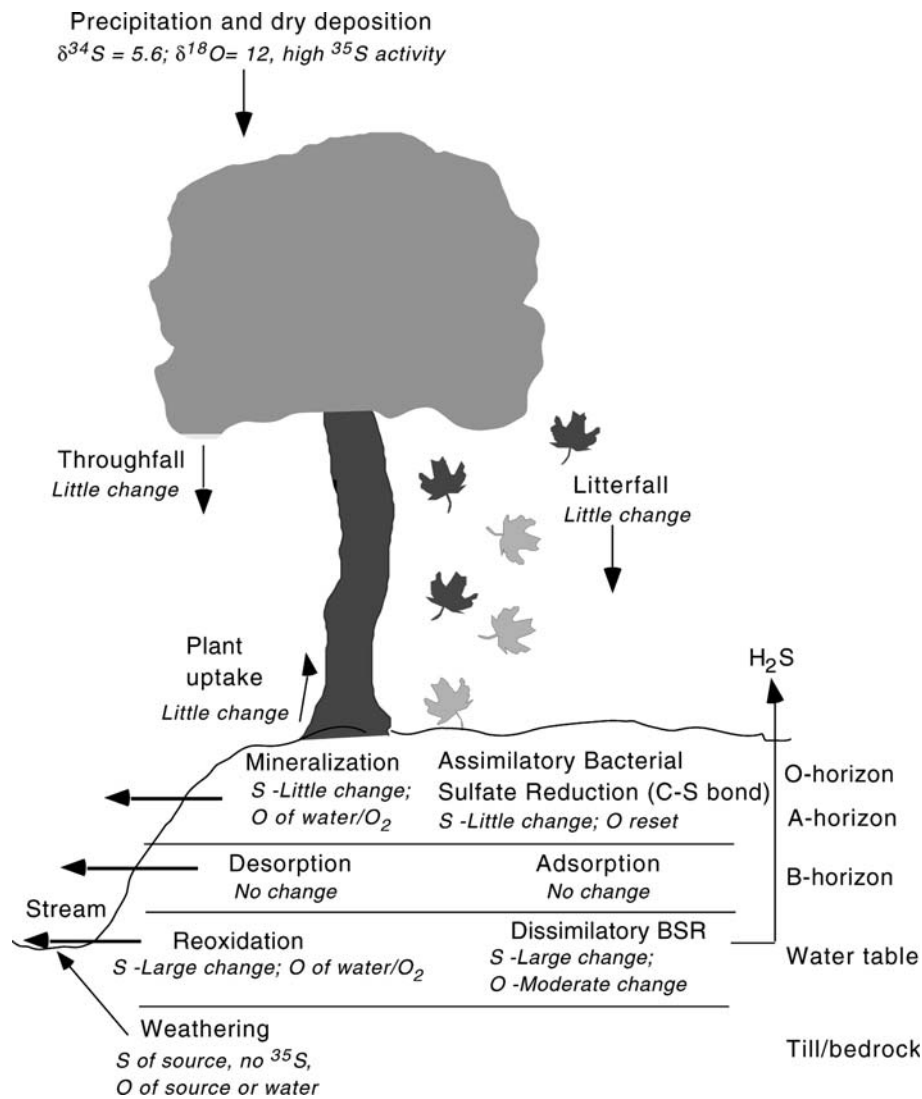


Figure 1. Sulfur cycling in a forested ecosystem and resultant changes (in italics) in S and O isotope ratios of sulfate. BSR means bacterial sulfate reduction. The isotope ratio values are given for typical precipitation in northeastern USA. Processes within the regolith are paired horizontally at the approximate depth in the system where they are most prominent. In general the process on the right immobilizes aqueous sulfate and the process on the left makes it available for aqueous transport, though in the case of dissimilatory BSR the sulfide may remain mobile, either in gas or aqueous phase. Also, this latter process often occurs near the surface in saturated areas. Activity of cosmogenic ^{35}S (half-life 87 days) is highest in deposition, zero in weathering sources, and anywhere in between within the soil zone depending on S residence time.

streamflow generation was developed by Dunne and Black (1970a, b; 1971). Their work formed the basis for recent research on streamflow generation processes using chemical and isotopic approaches (Kendall et al. 1999; Shanley et al. 2002a). The 11,125-ha basin contains several gaged watersheds of various size and land cover (Shanley et al. 2002a). This study was conducted primarily within the 41-ha forested W-9 catchment and its tributary subcatchments, but samples were also taken from the 59-ha agricultural W-2, and the larger mixed land use watersheds W-3 (836 ha) and W-5 (11,125 ha).

The Sleepers River watershed is underlain primarily by the Waits River Formation, a calcareous granulite interbedded with sulfidic micaceous phyllites and biotite schists (Hall 1959; Bailey et al. 2004). The bedrock is mantled with one to several meters of silty basal till derived mostly from the Waits River Formation. The calcareous lithology generates high-pH calcium bicarbonate sulfate waters throughout the Sleepers River watershed.

Field sampling

The study period encompassed the late winter and spring snowmelt of 2000, from late February to late April. We collected 3–12 samples from each of 10 streams draining watersheds with areas from 2 to 11,125 ha, at the same times and sites as samples collected for another study (Shanley et al. 2002b). We also sampled 3 groundwater seeps and 4 shallow wells screened within the till (1.5-m screens, maximum depth 3 m) within one day of peak snowmelt (4 to 5 April). Stream sampling included a premelt sample before the hydrograph rise, and then focused on high flows from both radiational melt and rain-on-snow events. Samples were taken from the centroid of flow in 10-L collapsible polyethylene (PE) containers for determination of ^{35}S activity and in 1-L PE bottles for determinations of the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of sulfate. A 500-ml PE bottle was filled for major anion and DOC analysis. Samples for analysis of $\delta^{18}\text{O}$ of water were collected in 16-ml glass vials with conical polyseal caps. Meltwater was collected from snowmelt lysimeters to use as the atmospheric end member in isotopic hydrograph separation (Shanley et al. 2002a). Depth-integrated snowpack samples were collected by removing an approximately 0.2×0.2 m column from the wall of an excavated pit with a lexan shovel into a large PE container. Four open-field snowpack samples were taken near the W-9 catchment on 23 February (just prior to a minor thaw) and two additional samples were taken on 22 March (just prior to the onset of the main melt sequence) for determination of sulfate concentrations, $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of sulfate, and ^{35}S activity (22 March only).

Isotopic and chemical analyses

Samples for ^{35}S activity determination were dripped through ion exchange resin columns in the field. The ^{35}S columns and water samples for $\delta^{18}\text{O}$ analysis

were shipped to the USGS isotope lab in Menlo Park, CA. Sulfate was eluted from the columns and analyzed for ^{35}S as described in Michel et al. (2000). Replicate precision averaged 0.71 mBq l^{-1} or 0.12 mBq/mg SO_4 (C.V. 33%). The $\delta^{18}\text{O}$ of water was determined with a precision of $\pm 0.05\text{‰}$. Samples for anion analysis were filtered ($0.45 \mu\text{m}$) and chilled, and shipped to the USGS in Boulder, CO, where they were analyzed by ion chromatography. Samples for DOC were filtered ($0.7\text{-}\mu\text{m}$ glass fiber) to amber glass vials and analyzed by ultraviolet persulfate oxidation with infrared detection at the USGS laboratory in Troy, NY.

Samples for determining the stable isotope composition of sulfate were dripped through separate ion exchange columns in the field laboratory, and columns were sent to the Isotope Science Laboratory (ISL) at the University of Calgary (Alberta, Canada). In Calgary the sulfate was eluted from the column and precipitated as BaSO_4 by adding a BaCl_2 solution. The filtered, washed and dried BaSO_4 was converted to sulfur dioxide (SO_2) in an elemental analyzer and swept with a He stream into an isotope ratio mass spectrometer (VG Prism II) for isotope ratio determinations. For oxygen isotope analyses on SO_4^{2-} , BaSO_4 -oxygen was converted to CO at 1450°C in a pyrolysis reactor (Finnigan TC/EA). The resultant gas was subsequently swept with a He stream into a mass spectrometer (Finnigan MAT delta plus XL) for isotope ratio determinations in continuous-flow mode (CF-IRMS). Stable isotope ratios are reported in the usual δ notation in permil with respect to the international standards V-CDT for sulfur isotope measurements and V-SMOW for oxygen isotope measurements. Precision (standard deviation on replicate analyses) averaged 0.26‰ for $\delta^{34}\text{S}$ values and 0.53‰ for $\delta^{18}\text{O}$ values of sulfate.

Mixing models

$\delta^{18}\text{O}$ of water

Snowmelt is an ideal time for isotopic separation of streamflow into event and pre-event water and the method has been successfully applied at Sleepers River (Shanley et al. 2002a). As in past studies, streamwater was separated into old and new water with a standard two-component $\delta^{18}\text{O}$ mixing model using the varying composition of meltwater from the lysimeters for the new water signal and a constant pre-melt base flow for the old water signal.

$\delta^{34}\text{S}$ of sulfate

We applied a two-component sulfate-S source separation to differentiate atmospheric from mineral-derived sulfate. This separation requires three conditions: (1) a constant known $\delta^{34}\text{S}$ value for atmospheric sulfate; (2) a constant known $\delta^{34}\text{S}$ value for sulfate from mineral weathering that is different from that of the atmospheric source; and (3) processes that fractionate sulfur isotopes such as dissimilatory bacterial sulfate reduction do not occur.

We used snowpack $\delta^{34}\text{S}$ for the atmospheric end member and stream base flow $\delta^{34}\text{S}$ for the mineral end member, giving a 2–3‰ difference between atmospheric and stream base flow $\delta^{34}\text{S}$ values of sulfate that was small but sufficiently distinct to satisfy condition (2). The fraction of atmospheric S in streamwater was given by:

$$S_{\text{ATM}} = (\delta^{34}\text{S}_{\text{BF}} - \delta^{34}\text{S}_{\text{SW}}) / (\delta^{34}\text{S}_{\text{BF}} - \delta^{34}\text{S}_{\text{SP}}) \quad (1)$$

where subscripts ATM = atmosphere, SW = streamwater, BF = streamwater at base flow, and SP = snowpack.

$\delta^{18}\text{O}$ of sulfate

The $\delta^{18}\text{O}$ of sulfate was treated identically to the $\delta^{34}\text{S}$ of sulfate, assuming two-component mixing and using an equation analogous to equation 1.

^{35}S activity

The specific activity of ^{35}S (mBq per mg SO_4) data were analyzed in two ways. In the first approach, we attributed all of the ^{35}S activity in streamwater to the melting snowpack (and subsequent rainfall). This would yield a maximum contribution from the snowpack as any remaining ^{35}S activity from aged atmospheric sulfur would be attributed to the snowpack. Mixing fractions were calculated as for $\delta^{34}\text{S}$ above, with the simplification that the ^{35}S activity at baseflow is zero so the analogous equation reduces to:

$$S_{\text{NEW}} = (\alpha^{35}\text{S}_{\text{SW}} / \alpha^{35}\text{S}_{\text{SP}}) \quad (2)$$

where S_{NEW} is the fraction of new atmospheric S in streamwater and α refers to the specific ^{35}S activity. The second approach was to calculate the apparent age of stream sulfate assuming simple radioactive decay of ^{35}S in precipitation:

$$A = T_{1/2} \ln(\alpha^{35}\text{S}_{\text{SP}} / \alpha^{35}\text{S}_{\text{SW}}) \quad (3)$$

where A is mean streamwater sulfate age in days and $T_{1/2}$ is the half-life of ^{35}S (87 days). After the atmospheric fraction of streamwater sulfate was determined by Equation (1), its specific ^{35}S activity was recomputed and Equation (3) was re-applied to compute the age of the atmospheric fraction of stream sulfate.

Results

Hydrology

Water Year 2000 (October 1999 through September 2000) at Sleepers River featured the typical autumn flow increase with some high flow events, followed by recession to winter base flow as precipitation was stored in the snowpack

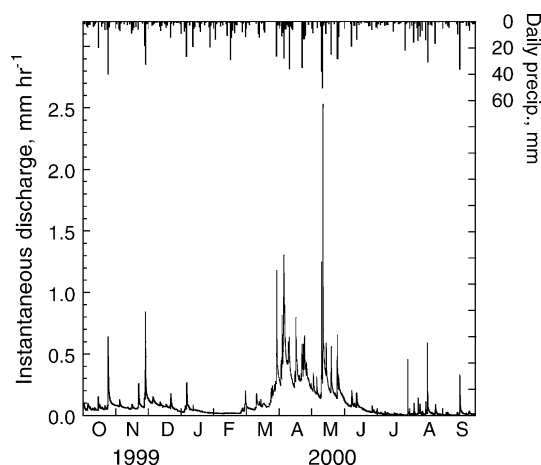


Figure 3. Daily precipitation amount and continuous stream discharge hydrograph for the 2000 water year at the 41-ha W-9 catchment at Sleepers River (Figure 2).

(Figure 3). Snowmelt in March and April clearly dominated the annual hydrograph. In 2000 the snowmelt recession lasted well into June, extended by above-average rainfall in April and May. The summer of 2000 was dry, with the lowest flow of any of the nine summers on record to that point, though there were occasional moderate peak flows from thunderstorms in August and September.

The winter of 2000 was relatively mild with below-average snowfall. The peak snow water equivalent (SWE) ranked 33 among 43 years of record from 1960 to 2002 (Shanley et al. 2002c). The winter was also unusual in that it lacked a major thaw, but several minor warm-ups periodically reduced the snow water equivalent and produced moderate streamflow. The main melt sequence began in late March (Figure 4). Flow progressively increased with a series of diurnal melts, culminating in two rain-on-snow events, 22 mm on 28 March and 29 mm on 4 April. These two storms generated the highest flows of the melt period (1.2 and 1.3 mm h⁻¹, respectively, in W-9, the headwater catchment), and isotope sampling focused on these and subsequent snowmelt peaks. These snowmelt peaks were less than those of most previous years, e.g., a 2.0 mm h⁻¹ peak in 1996 (Kendall et al. 1999).

Solute chemistry

The sulfate concentration in the snowpack was 12 µeq l⁻¹ at its maximum SWE of 199 mm on 23 February, just before a late winter thaw. On 22 March SWE was 169 mm and the sulfate concentration had decreased to 6.2 µeq l⁻¹. Sulfate concentration in streamwater varied inversely with

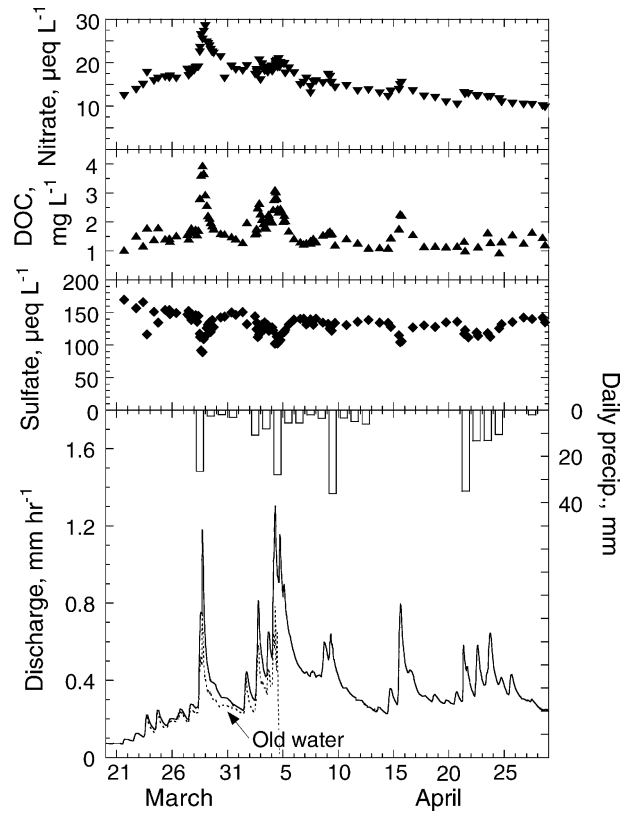


Figure 4. Daily precipitation with continuous hydrograph and hydrograph separation using $\delta^{18}\text{O}$ of water during the main 2000 snowmelt period, with sulfate, DOC, and nitrate concentrations. Isotopic hydrograph separation was not possible after isotopically heavy rain fell on April 4.

Table 1. Sulfate mass balance at w-9 for water years 1992–1994 and for water year 2000; sulfate and ^{35}S mass balance at w-9 for the 2000 snowmelt period.

	Units	Input	Output	Ratio
Water year 1992–1994 (Hornbeck et al. (1997))	$\text{meq m}^{-2} \text{ year}^{-1}$	45.1	106.9	2.37
Water year 2000	$\text{meq m}^{-2} \text{ year}^{-1}$	48.1	131.3	2.73
2000 snowmelt: 22 March–29 April	meq m^{-2}	9.1	41.4	4.55
^{35}S , 2000 snowmelt, 25 March–4 April	mBq m^{-2}	473*	157	0.33

*363 mBq m^{-2} from snowpack; 110 mBq m^{-2} from rainfall during this period, assuming same ^{35}S concentration as snowpack.

discharge ($r^2 = 0.52$, $p < 0.0001$) during snowmelt, decreasing from $170 \mu\text{eq l}^{-1}$ at base flow to $90 \mu\text{eq l}^{-1}$ at peak melt (Figure 4). In contrast to sulfate, nitrate and DOC concentrations increased sharply during melt

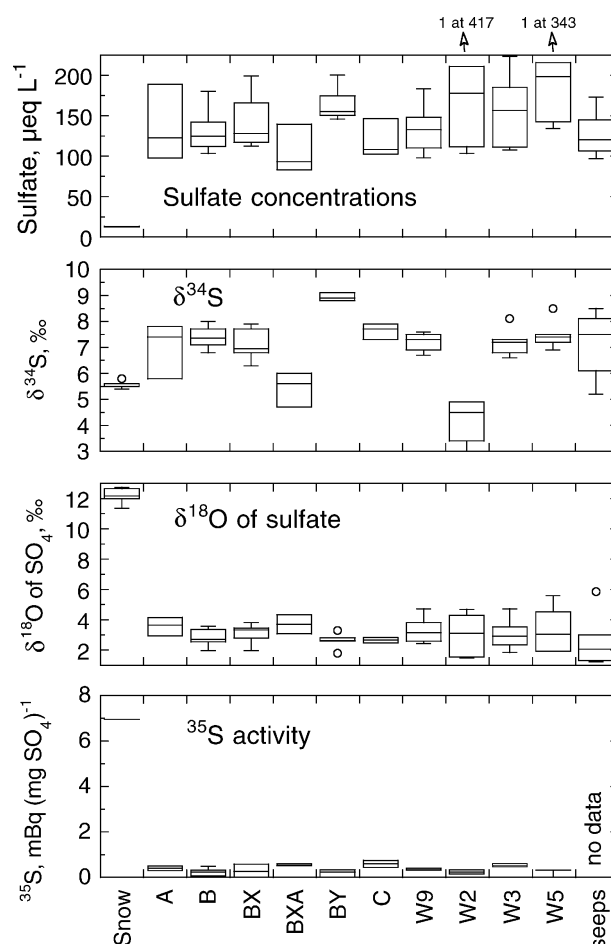


Figure 5. Boxplot of sulfate concentrations, $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulfate, and ^{35}S activities for snow, 10 streams, and groundwater (seep) samples during the 2000 snowmelt.

episodes (Figure 4). Nitrate concentration increased from $12 \mu\text{eq l}^{-1}$ during pre-melt to a maximum of $28 \mu\text{eq l}^{-1}$ during the first major snowmelt peak on 28 March, after which it gradually decreased to $10 \mu\text{eq l}^{-1}$ by the end of the melt period, with progressively lower concentration peaks during subsequent flow peaks. DOC concentration increased from 1.0 mg l^{-1} during pre-melt to its maximum of 4.1 mg l^{-1} , also during the 28 March peak. Unlike nitrate, DOC continued to increase significantly in response to flow increases throughout the melt. For water year 2000, sulfate output in streamwater was 2.7 times the input in wet (bulk) deposition (Table 1). During the snowmelt period alone, sulfate export was more than four times the input.

*Isotopic compositions**Snowpack*

Snowpack sulfate on 23 February had $\delta^{34}\text{S}$ values near $+5.6\text{‰}$ and $\delta^{18}\text{O}$ values near $+12\text{‰}$. On 22 March, after minor thawing, the snowpack had nearly identical $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values (Figure 5). Sulfate in two meltwater samples collected near the end of snowmelt in late April had somewhat lower $\delta^{34}\text{S}$ values of 4.2 and 5.0‰ , and a slightly higher $\delta^{18}\text{O}$ value (measured on one sample only) of 13.5‰ . The ^{35}S activity of the Sleepers River snowpack on 22 March was 6.9 mBq/mg SO_4 .

Groundwater

Sulfate at seven groundwater sites in the W-9 catchment sampled during peak melt had a median $\delta^{34}\text{S}$ value of 7.5‰ (range of $5.2\text{--}8.5\text{‰}$). The median $\delta^{18}\text{O}$ value of sulfate was 2.0‰ (range of $1.2\text{--}3.0\text{‰}$ with one exception of 5.9‰) (Figure 5). Groundwater was not sampled for ^{35}S activity.

Streamwater

In eight of the ten streams, pre-melt base flow $\delta^{34}\text{S}$ values were between 7.3 and 8.9‰ . In seven of these eight streams, $\delta^{34}\text{S}$ values decreased (by 0.1 to 2.0‰), toward the atmospheric value of 5.6‰ , at peak snowmelt (Table 2). Stream C was the exception in that its $\delta^{34}\text{S}$ value shifted away from the atmospheric value (increased) during the 28 March event, despite having at that time the highest streamwater ^{35}S activity measured in the entire study (Table 2). The stream draining the 2-ha BXA catchment (Figure 2) maintained $\delta^{34}\text{S}$ values similar to the snowpack throughout the melt. The BXA stream is the outlet to a swamp and flows only during snowmelt. At W-2, the small agricultural catchment, $\delta^{34}\text{S}$ values remained lower than atmospheric sulfate throughout the melt.

The $\delta^{18}\text{O}$ values of streamwater sulfate were much lower than those of the snowpack and varied little spatially or temporally (Figure 5). The median sulfate $\delta^{18}\text{O}$ values for the 10 streams ranged narrowly between 2.5 and 4.0‰ , and the absolute range for all stream samples was $1.5\text{--}5.5\text{‰}$, compared to a value of 12‰ for snowpack sulfate (Figure 5).

Except for some of the pre-melt samples, minor amounts of ^{35}S were present in all streamwater samples. The absolute range among the 26 stream samples analyzed was $0.0\text{--}0.75$ mBq/mg SO_4 with a median of 0.34 mBq/mg SO_4 . The ^{35}S activities were highest during the early snowmelt peaks.

*Mixing models**Old and new water*

Based on hydrograph separation using oxygen isotope ratios of water, old water dominated the rising limb of the overall melt hydrograph (Figure 4),

Table 2. Summary of $\delta^{34}\text{S}$ values, source separation results, and ^{35}S ages for the 10 streams sampled during the 2000 snowmelt (Figure 2).

Site	Catchment area (ha)	Forest cover, %	n for $\delta^{34}\text{S}$	Atmospheric $\delta^{34}\text{S}$ (‰)	Base flow $\delta^{34}\text{S}$ (‰)	Peak flow $\delta^{34}\text{S}$ (‰)	Flow-weighted mean atmospheric contribution, %	Atmospheric contribution at peak, %	Discharge at peak, mm h^{-1}	n for ^{35}S	Youngest ^{35}S age, days	Youngest ^{35}S age of atmospheric component, days
W-9	40.5	100	7	5.6	7.5	6.7	26	42	1.26	3	358	184
A	16.9	100	4	5.6	7.8	5.8	61	91	0.71	2	332	320
B	12.9	100	12	5.6	8.0	6.8	30	50	0.59	5	335	248
BX	5.1	100	6	5.6	7.9	6.3	50	70	0.90	3	311	218
BXA	2.0	100	4	5.6	4.7	6.0	(a)	(a)	nc	3	308	nc
BY	3.4	100	5	5.6	8.9	8.8	3	3	0.20	3	381	(b)
C	8.1	100	3	5.6	7.3	7.9	(a)	(a)	nc	2	280	nc
W-2	59	29	7	5.6	4.1	4.9	(a)	(a)	nc	2	380	nc
W-3	836	67	7	5.6	8.1	6.6	43	60	1.05	3	338	244
W-5	11125	67	7	5.6	8.5	6.9	42	55	0.75	1	385	310

nc, not computed.

N is number of samples analyzed. Atmospheric contribution calculated using $\delta^{34}\text{S}$ assuming two-component binary mixing of snow (atmospheric end member) and base flow (geologic end member). Flow-weighted average computed for all samples during active melt period. Stream discharge reported is that at time of maximum atmospheric contribution. ^{35}S age computed first considering all sulfur present, then considering only atmospheric component based on $\delta^{34}\text{S}$ separation.

(a) Calculation of atmospheric component not possible, insufficient isotopic separation or illogical results.

(b) Small atmospheric component yields negative age.

consistent with past findings at Sleepers River (Shanley et al. 2002a). Coincident with peak flow events, the new water fraction reached 40% on 28 March and 50% on 4 April. The rainfall on 4 April had an unusually high $\delta^{18}\text{O}$ value, confounding any subsequent isotopic separation between groundwater and atmospheric water during this snowmelt.

$\delta^{34}\text{S}$

Because of concerns about spatial variability of sulfate sources in groundwater and the limited groundwater sampling area, we used the isotopic composition of sulfate in pre-melt base flow of each stream as an integrated signal representing the geologic sulfate source. We illustrate the $\delta^{34}\text{S}$ source separation approach for Stream B (Figure 2), for which we had the most sulfate isotope analyses (12). The $\delta^{34}\text{S}$ value of Stream B streamwater was 7.5‰ at base flow in February. On 25 March, early in the main melt sequence, the stream $\delta^{34}\text{S}$ value had increased to 8.0‰ but ^{35}S still was not detectable, indicating negligible

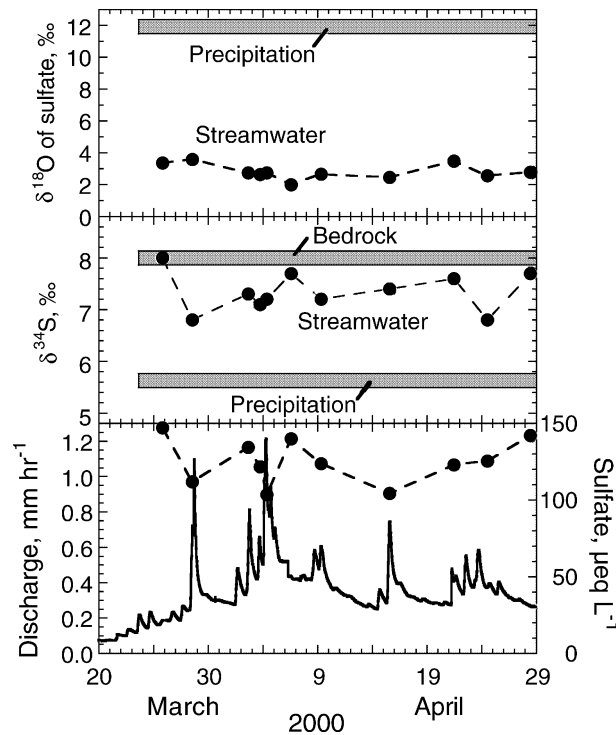


Figure 6. Snowmelt hydrograph with stream sulfate concentrations and temporal patterns of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of streamwater sulfate at Stream B within the W-9 catchment. Horizontal stippled bars represent end member values of atmospheric-derived and mineral-derived $\delta^{34}\text{S}$ and atmospheric $\delta^{18}\text{O}$ of sulfate used in the mixing models.

input of atmospheric S to the stream. Hence we assigned 8.0‰ as the $\delta^{34}\text{S}$ end member signal from weathering of S-containing minerals. The $\delta^{34}\text{S}$ value of the snowpack, 5.6‰, was assumed to represent the sulfur isotope composition of the atmospheric end member. These end member $\delta^{34}\text{S}$ values provide a 2.4 ± 0.5 ‰ separation for determining mixing ratios for sulfate in Stream B based on this simple two-source mixing model.

Near the peak of the March 28 rain-on-snow event, $\delta^{34}\text{S}$ values in Stream B decreased from 8.0‰ to 6.8‰ (Figure 6), a shift one-half of the way toward the atmospheric composition. The mixing model (Equation 1) therefore suggests that at peak discharge, 50% of the sulfur in streamwater originated from mineral weathering and 50% originated from atmospheric sources. After increasing to greater than 7.0‰ during the subsequent recession, $\delta^{34}\text{S}$ values again shifted toward the atmospheric end member during a small diurnal melt on 3 April and the 4 April rain-on-snow event. After a multi-day recession following this event, the $\delta^{34}\text{S}$ value increased to 7.7‰, nearly back to the base flow value of 8.0‰. During a series of subsequent small diurnal and rain-on-snow peaks, $\delta^{34}\text{S}$ values fluctuated between 7.1 and 7.6‰, except for a late diurnal peak on 24 April when streamwater $\delta^{34}\text{S}$ matched its lowest value of 6.8‰.

The $\delta^{34}\text{S}$ values of streamwater sulfate tended to vary inversely with stream discharge; as discharge increased, $\delta^{34}\text{S}$ values decreased so the calculated percentage of atmospheric sulfur in streamwater increased (Figure 6). Also, the percentage of atmospheric sulfur in streamflow approximately tracked the percentage of new water in streamflow. Although only five samples for $\delta^{34}\text{S}$ were collected during the interval before 4 April when hydrograph separation was possible, they revealed a positive but weak relation ($r^2 = 0.54$, $p = 0.15$) between percentage of atmospheric sulfur and percentage of new water, approximately along the 1:1 line.

For the 7 streams where source separation was possible during snowmelt, the calculated maximum contribution of atmospheric S to streamwater sulfate occurred at or near the early snowmelt peak during the rain-on snow events of March 28 and April 4. The median peak atmospheric S contribution was 55% and ranged from 3 to 91% (Table 2). With the exception of a single high and a single low value, the range was 42–70%. For all streamwater samples for which an atmospheric S contribution could be calculated using this isotope ratio approach ($n = 33$), the grand flow-weighted mean atmospheric S contribution was 41% (Table 2).

$\delta^{18}\text{O}$ of sulfate

In contrast to the relatively small 2–3‰ separation in end member $\delta^{34}\text{S}$ values of sulfate, there was a large 9–10‰ separation in end member $\delta^{18}\text{O}$ values of sulfate. Also in contrast to $\delta^{34}\text{S}$ patterns, there was no discernable shift of streamwater sulfate $\delta^{18}\text{O}$ values toward the $\delta^{18}\text{O}$ value of atmospheric sulfate during the melt event (Figure 6). Therefore, the mixing model was not applied.

³⁵S activity and sulfur age

If we assume that the sole source of ³⁵S to streamwater was new atmospheric sulfate (the melting snowpack plus new rain, which we assumed to have the same ³⁵S concentration as the snowpack), then the contribution of snowpack sulfate to streamwater sulfate (Equation 2) was no more than 7% at any one time, reaching this maximum during the 28 March event. Alternatively, we could assume that ³⁵S was contributed by both new and previously deposited atmospheric sulfur and calculate a mean sulfur age (Equation 3). The ³⁵S ages during snowmelt had a rather narrow range from 280 to 385 days among the 10 streams. If the geologic sulfate, which contains no ³⁵S, is subtracted from the streamwater sulfate based on results from the source apportionment using $\delta^{34}\text{S}$ values, the range of minimum ages of the remaining atmospheric S decreased to 184–320 days. The grand mean of ³⁵S ages ($n = 23$) for all streams was 372 days; for cases where an unambiguous atmospheric S component could be calculated ($n = 15$), the mean ³⁵S age of atmospheric S in streamwater was 287 days (Table 2). Note that computed ages are *minimum* mean ages, as any S older than 1–2 years has lost most of its radioactive ³⁵S and is indistinguishable from ~one-year old S.

As snowmelt progressed, the activity of ³⁵S tracked the $\delta^{34}\text{S}$ values of sulfate in Stream B in an inverse manner, suggesting a shift to younger sulfate as the atmospheric sulfate component in streamwater increased. Although only five samples for ³⁵S were collected in Stream B, the relation between $\delta^{34}\text{S}$ values and ³⁵S activity in streamwater sulfate was strong and highly significant ($r^2 = 0.81$, $p = 0.03$). At the peak ³⁵S activity during the 28 March event, the minimum mean age of the atmospheric sulfur component was 248 days.

Uncertainty in the $\delta^{34}\text{S}$ mixing model

There are two sources of uncertainty in the mixing model results – analytical uncertainty and uncertainty of end member values. For the $\delta^{34}\text{S}$ model, the analytical uncertainty (standard deviation of replicate analyses) was 0.26‰. For the atmospheric end member (snowpack), temporal variability was negligible and spatial variability (standard deviation of four replicates) was 0.15‰. Assessing uncertainty in the geologic end member (base flow) was more problematic, as usually only one sample was taken per site. However, one could argue that all of the small streams draining a common lithology and till within the forested headwater W-9 catchment should have a common geologic end member. Using these base flow values (except that from the atmospherically influenced BXA) as a measure of geologic $\delta^{34}\text{S}$ variability, we computed a standard deviation of 0.55‰. Although this is a substitution of spatial variability for the desired temporal variability, note that the two pre-melt samples collected at stream B had a similar $\delta^{34}\text{S}$ difference of 0.5‰. Applying the total analytical and end member composition uncertainty using the method of Genereux (1998), the uncertainty in the computed S source percentages from the $\delta^{34}\text{S}$ separation at Stream B ranged from 20 to 28% over the melt

hydrograph. This high uncertainty stems principally from the narrow separation of the end members.

Discussion

We used a combined hydrologic, chemical, and isotopic approach to assess sources of sulfate during snowmelt. Collectively, four isotopic indicators that each track a somewhat different aspect of sulfur cycling and/or hydrologic behavior of the catchment build a framework for understanding sulfate dynamics in Sleepers River streamwater. In the following sections we discuss solute dynamics, atmospheric and geologic sulfur sources, evidence for pedogenic sulfate, and finally we link the discussion together with a conceptual model of sulfur cycling. Note that in the discussion of sources, sulfur and sulfate are purposely distinguished, as sulfate from one source may be formed with sulfur from another (e.g. pedogenic sulfate formed with atmospheric sulfur).

Solute dynamics

During snowmelt at Sleepers River, rain and meltwaters cause large increases in streamflow. Past studies at Sleepers River have shown that DOC and nitrate concentrations increase with increasing flow as surficial soil horizons are flushed during snowmelt (Titus et al. 1995; Shanley et al. 2002b). In contrast, Ca and other solutes derived from weathering are diluted by meltwater. Sulfate has a mineral weathering source as well as an atmospheric/pedogenic source, thus could exhibit both dilution and flushing. Sulfate concentration in streamwater did in fact dilute by nearly 50% during snowmelt (Figure 4). However, the relative dilution was somewhat less for sulfate than it was for Ca and the other base cations (Shanley et al. 2004). The potential sulfate dilution is partly counteracted by a labile pool of pedogenic sulfate in the upper soil, which is flushed by infiltrating meltwater and by rising water tables during snowmelt.

Atmospheric and geologic sulfur sources

Atmospheric component

In the source separation we assumed that the snowpack $\delta^{34}\text{S}$ value of $+5.6\text{‰}$ represents the atmospheric end member. Given our results showing that much of the atmospheric sulfur in streamwater pre-dates the snowpack, the representativeness of this end member becomes an important issue. Based on other regional determinations (Stam et al. 1992; Zhang et al. 1998; Alewell et al. 2000) and also on a USA compilation (Newman et al. 1991), a $\delta^{34}\text{S}$ value of 5.6‰ appears to be broadly representative of atmospheric sulfate. In a European study, Novak et al. (2001) cautioned that $\delta^{34}\text{S}$ values in throughfall were on average 1‰ lower than

those of precipitation, but Zhang et al. (1998) found seasonal reversals of this relation at Hubbard Brook, NH. Our snowpack samples were collected within the forested W-9 watershed, but given that the forest is 85% deciduous, there should be minimal alteration by the canopy during winter.

Cosmogenic ^{35}S is an excellent tracer of young atmospheric sulfate. Globally, the production of cosmogenic ^{35}S is fairly uniform in space, whereas the deposition of sulfate is highly variable. Thus ^{35}S activities normalized to sulfate mass tend to increase with decreasing sulfate deposition. The ^{35}S activity of 6.9 mBq/mg SO_4 measured in the Sleepers River snowpack on 22 March was intermediate between reported activities in snowpacks in a region of low S deposition, the Rocky Mountains (21 mBq/mg SO_4 (Sueker et al. 1999) and 60 mBq/mg SO_4 (Michel et al. 2000)) and in precipitation at an area of high S deposition in central Europe (2–6 mBq/mg SO_4 (Novak et al. 2004)). Although the snowpack at the Vermont site is prone to sulfate elution during periodic midwinter thaws, elution should not affect the ^{35}S activity as expressed per unit mass of sulfate. The snowpack develops over a 4–5 month period thus some of its ^{35}S decays, but its activity at the start of snowmelt is the effective initial (zero-age) activity of atmospheric inputs during snowmelt.

Geologic component

The $\delta^{34}\text{S}$ separation hinges on the assumption that base flow represents the geologic end member. Clearly geologic S is important, based on the 2.7 ratio of S exports to inputs calculated for this study year, which agrees closely with an earlier 3-year average of 2.4 reported by Hornbeck et al. (1997). Both ratios used sulfate input in bulk deposition, which underestimates dry deposition. Dry deposition of S was not measured at our site, but has been estimated at 21% of total S deposition for the Arbutus Watershed in the Adirondacks, New York (Park et al. 2003) and 21% of bulk deposition at Hubbard Brook, New Hampshire (Likens et al. 2002). The presence of primary sulfides (as opaque minerals) is well-documented in the Waits River formation (Hall 1959), and Bailey et al. (2004) also isolated secondary sulfate minerals.

The $\delta^{34}\text{S}$ values of stream sulfate at base flow were generally within 1‰ of the $\delta^{34}\text{S}$ value of 8.5‰ measured in one sample of Waits River bedrock (Bailey et al. 2004). Base flow at the small agricultural W-2 catchment had a much lower base flow $\delta^{34}\text{S}$ value of 4.1‰, possibly due to different $\delta^{34}\text{S}$ values of its bedrock or to past fertilizer use. However, the narrow range of base flow $\delta^{34}\text{S}$ values of sulfate, at least among streams within the W-9 catchment, suggests that a $\delta^{34}\text{S}$ value near 8.0‰ (allowed to vary for individual stream base flows) is a robust end member value for mineral-derived sulfate. On the other hand, four of the seven streams within W-9 had detectable ^{35}S in these base flow samples, indicating that some atmospheric sulfur was present. Small amounts of meltwater from the minor mid-winter thaws could have caused this ^{35}S signal without appreciably altering $\delta^{34}\text{S}$ values of streamwater sulfate.

Evidence for pedogenic sulfate formation

Three lines of evidence support the importance of pedogenic sulfate formed from atmospheric sulfur in this ecosystem. The first argument uses the $\delta^{18}\text{O}$ values of sulfate. Despite an overall contribution of 41% atmospheric sulfur to streamwater sulfur during snowmelt (Table 2), the $\delta^{18}\text{O}$ values of streamwater sulfate were consistently lower than, and did not shift toward, those of atmospheric sulfate (Figures 5 and 6). This finding suggests that atmospheric sulfate is assimilated by soil microbes, with the end result that the high atmospheric $\delta^{18}\text{O}$ value of sulfate is reset to a lower value typical of pedogenic sulfate (Mitchell et al. 1998) (Figure 1).

The shift of the atmospheric sulfate $\delta^{18}\text{O}$ signal to lower values within the soil has been previously noted (Mayer et al. 1995a, b). Even in areas where soil is thin or absent, such as the alpine/subalpine zone of the Rocky Mountains, only a limited atmospheric sulfate $\delta^{18}\text{O}$ signal propagates through the landscape (Johnson et al. 2001; Kester et al. 2003). Mayer et al. (1995a) showed a progressive decrease in the $\delta^{18}\text{O}$ values of sulfate in soil solution with depth, indicating that the immediate source of sulfate was mineralization of C-bonded sulfur. The resetting of the atmospheric $\delta^{18}\text{O}$ signal of sulfate is similar to the resetting of the atmospheric $\delta^{18}\text{O}$ signal of nitrate at the Sleepers River site (Kendall et al. 1995) and elsewhere (Kendall 1998; Campbell et al. 2000; Mayer et al. 2001a; Burns and Kendall, 2002).

The second line of evidence for pedogenic sulfate formation is provided by the ^{35}S patterns. The low ^{35}S activities in streamflow relative to the snowpack suggest that most of the atmospheric sulfur appearing in streamflow was older than the current year's snowpack. Regardless whether the ^{35}S activity in streamwater is attributed solely to new atmospheric sulfate inputs (Equation 2) or to atmospheric/pedogenic sulfate with a range of ages (Equation 3), the ^{35}S patterns indicate that most of the incoming atmospheric S resides for a considerable time in the soil zone. The computed ages of 184–320 days probably reflect a mixture of young sulfate in rain and snowmelt with atmospheric/pedogenic sulfate of varying age. Much of the pedogenic sulfate in streamwater likely formed from atmospheric sulfur deposited at an earlier time (Mayer et al. 2001b). As noted previously, based on ^{35}S activities (Equation 2), the direct contribution of snowpack sulfate to stream sulfate never exceeded 7%. This result is consistent with the sulfate $\delta^{18}\text{O}$ results, in that such a small contribution may not be enough to cause a detectable shift in $\delta^{18}\text{O}$ values of streamwater sulfate.

In the alpine/subalpine Loch Vale Colorado watershed, Michel et al. (2000) used ^{35}S to calculate that ~40% of stream sulfate was supplied by the current year's snowmelt. This high direct atmospheric contribution relative to that in the present study reflects greater throughput of atmospheric sulfate in this zone of thin soils and sparse vegetation. In three larger Rocky Mountain basins that extend to lower elevations, Sueker et al. (1999)

calculated ^{35}S ages that were similar to those in our study. Field experiments using amendments of ^{35}S likewise show soil retention of most of the added S in the organic soil pool (Schindler et al. 1986; Dhamala and Mitchell 1995).

The third line of evidence for pedogenic sulfate formation uses mass balance considerations. The amount of sulfate in the snowpack and subsequent rainfall was 22% of the mass of sulfate exported in streamflow during the snowmelt period (Table 1). This amount is considerably less than the 41% mean overall contribution of atmospheric S to streamwater sulfate calculated from stable S isotope ratios. The additional source of atmospheric sulfur must be S previously deposited and stored in the catchment, and may include S eluted from the snowpack during thaws earlier in the winter. Soil retention is supported by the ^{35}S mass balance; only 33% of the ^{35}S in the snowpack and subsequent rainfall could be accounted for in stream export through the peak melt period (Table 1). Collectively, the isotopic and mass balance evidence suggest that much of the atmospheric S input ultimately is exported in streamwater as pedogenic sulfate, after the atmospheric sulfate has cycled through the organic soil S pool.

Effect of soil processes on isotopic results

Sulfate adsorption

Pedogenic sulfate formed in the O and A horizons, as well as any atmospheric sulfate that passes through the forest floor, may be adsorbed in the B-horizon. This process would further increase sulfate retention times, with no change in isotopic composition.

Assimilatory bacterial sulfate reduction

The low $\delta^{18}\text{O}$ values of stream sulfate suggest assimilatory bacterial sulfate reduction followed by mineralization of C-bonded S, which would decrease the $\delta^{18}\text{O}$ value while preserving the $\delta^{34}\text{S}$ value of atmospheric sulfate. The mean ^{35}S age of greater than 200 days, dating back to the previous growing season, allows sufficient time for these conversions. From stream base flow values, it appears that a $\delta^{18}\text{O}$ value for sulfate near 2‰ can be expected from sulfur oxidation in this system (assuming sulfate minerals do not contribute), with the sulfate-oxygen contributed primarily by soil water. Despite seasonal variations in soil water $\delta^{18}\text{O}$, the $\delta^{18}\text{O}$ value of this pedogenic sulfate is likely to remain constant as it is “buffered” by the pool of adsorbed sulfate. The lack of change in the $\delta^{18}\text{O}$ value of streamwater sulfate even when atmospheric sulfur contributions reach 50% (Figure 6) suggests that atmospheric S was reduced (by assimilatory bacterial sulfate reduction) and re-oxidized within the catchment. Oxidation of C-bonded sulfur is the likely source of the stream sulfate containing the atmospheric S.

Dissimilatory bacterial sulfate reduction

Dissimilatory BSR is the lone soil process that could cause significant fractionation of sulfur isotope ratios (Figure 1), which would violate the assumptions of the mixing model. Dissimilatory BSR causes increases in the $\delta^{34}\text{S}$ of sulfate in porewaters in hyporheic zones, riparian soils, and wetlands during dry periods, potentially increasing stream $\delta^{34}\text{S}$ values while decreasing SO_4 concentrations (Alewell and Novak 2001; Eimers et al. 2004). The opposite pattern occurs when the ^{32}S -enriched sulfide product is reoxidized and flushed from soils during recharge periods, causing decreases in streamwater $\delta^{34}\text{S}$ values (Eimers et al. 2004). This latter process could operate during snowmelt flushing and thus could confound the signal of atmospheric sulfate, which also causes a decrease in $\delta^{34}\text{S}$ values of streamwater sulfate in this system. We discount the importance of dissimilatory BSR during snowmelt for two reasons: (1) this process can cause large isotope fractionations that would void the mixing model results, but the calculated atmospheric contributions from the model were reasonable and consistent with mass balances, and (2) any reduced sulfur from this process likely would have been already oxidized and flushed from the soil during fall recharge.

Conceptual model

Weathering of sulfur-containing minerals in the bedrock and till dominates the sulfate flux from Sleepers River watersheds. Based on two-component mixing using stable sulfur isotope ratios, the snowmelt period flow-weighted mean atmospheric S contribution to streamwater sulfate was 41%, consistent with the annual sulfate input/output ratio of 0.42 (Hornbeck et al. 1997). The atmospheric component consists of a small amount of atmospheric sulfate that enters the stream unaltered, and a larger fraction that enters the soil organic S pool, ultimately reaching the stream weeks, months, or years later as pedogenic sulfate.

Our results suggest a scenario in which most atmospheric sulfate undergoes assimilatory bacterial sulfate reduction and resides in the soil for months or years as carbon-bonded S, then is subsequently mineralized to sulfate (pedogenic sulfate) and flushed to the stream by meltwaters. During the initial snowmelt period, the percentage of atmospheric S in streamwater, as computed from $\delta^{34}\text{S}$, closely matched the percentage of new water as computed from the $\delta^{18}\text{O}$ values of water. Despite the match, this is not a simple matter of new (event) water conveying recently deposited atmospheric sulfate to the stream; the low ^{35}S activities indicate that most stream sulfur is several months old, and the low $\delta^{18}\text{O}$ values of streamwater sulfate show that the original atmospheric sulfate has been reduced and re-oxidized in the soil. The new water is primarily flushing this pedogenic sulfate.

Conclusions

Four isotopic indicators, hydrologic measurements, and solute chemistry were combined to elucidate sulfur biogeochemistry during snowmelt in a Vermont catchment. The two most significant findings were: (1) geologic sulfur dominates stream sulfate except at peak snowmelt when atmospheric sulfur may dominate; and (2) nearly all of the sulfate in streamwater formed from atmospheric sulfur is pedogenic, i.e. the original S–O bonds in atmospheric sulfate were broken and new sulfate was formed in the soil environment, most likely through assimilatory bacterial sulfate reduction and subsequent re-mineralization. In seven of ten watersheds of differing size and land use, distinctive $\delta^{34}\text{S}$ values of weathering and atmospheric end members enabled source separation. The maximum atmospheric/pedospheric contribution exceeded 50% for most streams during a rain-on-snow event early in the melt period, and averaged (flow-weighted) 41% for all samples ($n = 33$) during the active melt period. The pedogenic origin of stream sulfate was identified by the shift in $\delta^{18}\text{O}$ values from the distinctive high values of atmospheric sulfate to constant values that were 9–10‰ lower in stream sulfate. The percentage of atmospheric/pedospheric sulfur in streamwater (as calculated from $\delta^{34}\text{S}$) covaried with the percentage of “new water” in streamflow (as determined by the $\delta^{18}\text{O}$ of water), and covaried also with activity of the radioactive cosmogenic ^{35}S (half life 87 days), whose source is the atmosphere and is an indicator of young sulfate. However, ^{35}S ages of the atmospheric component of stream sulfate ranged from 184 to 320 days, suggesting that most of the atmospheric/pedospheric sulfur detected in streamflow was deposited well before the study snowmelt period. During the snowmelt period, the new water in snowmelt effectively flushes the pedogenic sulfate from the soil. The finding that most sulfate is mediated in the soil, and may reside in the catchment for several months to years, suggests that catchment response to changes in atmospheric S emission and deposition may be delayed.

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