Seasonal and event variations in $\delta^{34}$S values of stream sulfate in a Vermont forested catchment: Implications for sulfur sources and cycling

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Abstract
Stable sulfur (S) isotope ratios can be used to identify the sources of sulfate contributing to streamwater. We collected weekly and high-flow stream samples for S isotopic analysis of sulfate through the entire water year 2003 plus the snowmelt period of 2004. The study area was the 41-ha forested W-9 catchment at Sleepers River Research Watershed, Vermont, a site known to produce sulfate from weathering of sulfide minerals in the bedrock. The $\delta^{34}$S values of streamwater sulfate followed an annual sinusoidal pattern ranging from about 6.5‰ in early spring to about 10‰ in early fall. During high-flow events, $\delta^{34}$S values typically decreased by 1 to 3‰ from the prevailing seasonal value. The isotopic evidence suggests that stream sulfate concentrations are controlled by: (1) an overall dominance of bedrock-derived sulfate ($\delta^{34}$S ~ 6–14‰); (2) contributions of pedogenic sulfate ($\delta^{34}$S ~ 5–6‰) during snowmelt and storms with progressively diminishing contributions during base flow recession; and (3) minor effects of dissimilatory bacterial sulfate reduction and subsequent reoxidation of sulfides. Bedrock should not be overlooked as a source of S in catchment sulfate budgets.

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1. Introduction

Predicting how ecosystems respond to changes in deposition of atmospheric sulfur (S) requires an understanding of sources and cycling of S in the terrestrial landscape. In some watersheds, S inputs and outputs are approximately balanced. Such steady-state conditions, however, do not imply that atmospheric S is simply passing through the landscape. Large reservoirs of S exist in the soil and vegetation, and these pools damp ecosystem responses to changes in S deposition. In other watersheds, S inputs and outputs are not in balance. Net sulfate export may be caused by geologic sources (Alewell et al., 1999; Bailey et al., 2004, Mitchell et al., 1986; Shanley et al., 2005), net mineralization of organic S (Driscoll et al., 1998, Likens et al., 2002, Park et al., 2003), or net sulfate desorption (Nodvin et al., 1986). Net sulfate retention may be caused by vegetation uptake (Swank et al., 1984), conversion of sulfate to organic S (Mitchell and Alewell, 2007), sulfate adsorption (Rochelle et al., 1987, Shanley and Peters, 1993, Huntington et al., 1994), or dissimilatory bacterial sulfate reduction (Krouse and Mayer, 2000). An ecosystem may be out of steady state with respect to sulfate because it is still adjusting from lower or higher deposition in the past. Isotopic studies have shown that sulfate inputs are strongly retained in the soil and suggest mean residence times of decades (Mayer

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et al., 1995, 2001), implying that ecosystem recovery from declining S deposition will be a gradual process.

In earlier work at Sleepers River, Vermont, we found that sulfate from mineral weathering dominated stream sulfate, but that atmospheric sulfate contributed as much as 50% of stream sulfate during the snowmelt peak (Shanley et al., 2005). However, stream sulfate lacked the distinctively high \( \delta^{18}O \) value of atmospheric sulfate, revealing that most atmospheric sulfate was first incorporated in organic matter and subsequently mineralized before entering the stream as pedogenic sulfate. Low recovery in streamwater of cosmogenic \(^{35}\)S (half-life 87 days), which enters the watershed in precipitation, provided independent evidence that the mean residence time of atmospheric S in the watershed was one year or more (Shanley et al., 2005).

In the current study, we extended our sampling for an entire water year, and sampled an additional snowmelt season as well. Our objectives were to answer the following questions:

1. Is bedrock-derived sulfate the dominant source of stream sulfate throughout the year?
2. Are the previously determined sulfate isotope end members during snowmelt valid during the rest of the year?
3. How do inputs of atmospheric/pedogenic sulfate during rain storms affect stream water sulfate compared to those during snowmelt?
4. Is there isotopic evidence of dissimilatory bacterial sulfate reduction?

To this end, we sampled streamwater weekly and collected multiple samples during high-flow events. We limited our spatial sampling to one stream site, based on our earlier finding that the contribution of atmospheric/pedogenic sulfate to streamflow during snowmelt was fairly similar within various sized subcatchments at Sleepers, including both forested and agricultural landscapes (Shanley et al., 2005).

1.1. Site description

Sleepers River W-9 is a 41-ha catchment forested with second-growth Northern Hardwoods dominated by *Acer saccharum* (sugar maple), *Fraxinus americana* (white ash), and *Betula alleghaniensis* (yellow birch), with less than 5% conifer, *Picea rubens* (red spruce) and *Abies balsamea* (balsam fir) (Fig. 1). It was selectively logged in 1929. Elevation ranges from 519 to 671 m. The bedrock is a calcareous phyllite interbedded with sulfidic mica phyllites and biotite schists (Hall, 1959; Bailey et al., 2004). There is up to 3 m of dense basal till with high fine silt content, developed from the local bedrock. Soils are inceptisols, spodosols and histosols developed to 500 to 700 mm depth. The low permeability till supports sustained base flow and gives rise to numerous small wetlands in the hummocky topography. The bedrock and till generate well-buffered Ca-bicarbonate-sulfate streamwater (Shanley et al., 2004). Precipitation is evenly distributed throughout the year and averages 1300 mm with about 25% falling as snow. Spring snowmelt dominates the annual hydrograph, but the peak flow can occur at any time of the year. Mean annual temperature is 4.6 °C.

2. Methods

The study was conducted from September 2002 through October 2003, encompassing Water Year 2003 (which began 1 October 2002), with additional sampling for a few weeks before and during the 2004 snowmelt. During the dormant season (October through May), precipitation and throughfall samples for S isotopic analysis were collected using 1.2-m×1.2-m troughs constructed as a shallow “V” and lined with polyethylene sheeting. The troughs were gently sloped to drain into large polyethylene buckets. The precipitation collector was in a forest clearing and the throughfall collector was
under a mature A. saccharum (sugar maple), the dominant tree species in the catchment. Collection intervals were irregular but approximately monthly, and samples represented all precipitation between collections. During the latter part of the growing season (July to October), we sampled precipitation in the same manner but we sampled throughfall by an alternate method. On 4 occasions, we collected 3 weekly throughfall samples, each of which was pooled from eight 20-cm funnel collectors within a specific forest type. These 3 samples represented the diversity of canopy species in the catchment. During Water Year 2003, stream samples from the W-9 outlet were collected manually every week, and with automatic samplers triggered by a rise in stage during selected high-flow events. Several stream samples were also collected during the 2004 snowmelt, mostly at high flow.

An aliquot of each sample was filtered (0.45 µm) and shipped on ice to a laboratory at the State University of New York, College of Environmental Science and Forestry for analysis of anions by ion chromatography (IC) and cations by inductively coupled plasma emission spectrophotometry (ICP). For isotope analyses, 10 l (precipitation and throughfall) or 1 l (stream) samples were dripped through anion exchange (ICP). For isotope ratio determinations, stable isotope ratios in precipitation and throughfall δ34S, corresponding values from common collection periods (n = 9) were often quite different (Fig. 2). Five of the paired values differed by less than 0.4‰, but the other four pairs differed by 1.2 to 3.5‰. Among the latter, the δ34S values of throughfall sulfate were higher in two cases and lower in the other two cases than δ34S values of precipitation. No seasonal pattern in δ34S values was apparent for either precipitation or throughfall. For the period in which throughfall was obtained from the distributed collectors, δ34S values among the three plots were similar, with a standard deviation of 0.6‰ or less for all four dates (Table 1).

3.2. Surface water: 2003 water year

δ34S values in weekly stream water sulfate samples followed a distinct seasonal pattern, decreasing from nearly 8‰ in early fall to 6.5‰ in winter, reaching a minimum of 6.2‰ during snowmelt, then increasing through the spring and summer to a peak of 10.3‰ near the end of summer (Fig. 3). δ34S values then returned to values in the 8 to 9‰ range, similar to the start of the water year. For several months in summer and fall, stream δ34S values exceeded 8‰, the value previously used for the bedrock weathering end member based on winter base flow conditions (Shanley et al., 2005). Storm-flow samples and weekly samples that coincided with high flow had δ34S values that deviated from the smooth seasonal pattern.

Streamwater sulfate sampled during storms consistently had lower δ34S values, typically deviating 1 to 3‰, and as much as 5‰ during two storms in September 2002, from the general seasonal pattern (Fig. 3). In the September 2002 storms, δ34S values decreased below 5.6‰, the value previously used as the precipitation end member (Shanley et al., 2005). This 1 to 5‰ range in δ34S values of streamwater sulfate within individual storms exceeded the range during the entire 2000 snow melt. The overall range in δ34S values of streamwater sulfate for the water year was 6.4‰ (4.0 to 10.4‰), with much greater temporal variability compared to our earlier snowmelt study (Shanley et al., 2005).

Table 1 – Average throughfall sulfate δ34S-values and standard deviations for collections made from 3 plots on each sampling date

<table>
<thead>
<tr>
<th>Date</th>
<th>δ34S</th>
<th>Std. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/28/03</td>
<td>4.52</td>
<td>0.48</td>
</tr>
<tr>
<td>9/24/03</td>
<td>5.35</td>
<td>0.13</td>
</tr>
<tr>
<td>10/1/03</td>
<td>6.21</td>
<td>0.36</td>
</tr>
<tr>
<td>10/16/03</td>
<td>5.73</td>
<td>0.61</td>
</tr>
</tbody>
</table>
3.3. Storm of 15 September 2002

Following 7 weeks of well below average precipitation, an intense convective storm on 15 September 2002 deposited 51 mm rain in 1 h, causing a sharp peak in discharge (Fig. 4). Sulfate concentrations varied inversely with discharge and were diluted by nearly 50% at peak flow compared to pre-storm values. The \( \delta^{34}S \) value of streamwater sulfate at base flow prior to the storm was 9.0‰. Stream sulfate \( \delta^{34}S \) values decreased rapidly to 5.3‰ with the initial hydrograph rise, then continued to decrease more gradually to 4.5‰ through the hydrograph peak and well into the recession limb of the hydrograph. At 2 h after peak flow, when discharge had receded to 10% of the storm peak, sulfate concentration had nearly returned to its pre-storm value, but the stream sulfate \( \delta^{34}S \) value remained low at 4.6‰. Nitrate and DOC concentrations (not shown) increased several fold and peaked slightly after the hydrograph peak. Nitrate concentrations remained high through the recession. Similarly to sulfate, base cation concentrations (not shown) decreased with increasing flow but returned more gradually to pre-storm concentrations than sulfate (Fig. 4).

3.4. Snowmelt in 2003 and 2004

The 2003 and 2004 snowmelt periods had considerably less runoff than the 2000 snowmelt (Shanley et al., 2005). The 2003 snowmelt had one large peak of 1.3 mm h\(^{-1}\), similar to the 2000 peak, whereas the 2004 snowmelt was prolonged but flow never exceeded 0.5 mm h\(^{-1}\) (Fig. 5). In 2000, stream sulfate \( \delta^{34}S \) values decreased from 8.0‰ prior to melt to 6.8‰ at peak snowmelt, which represented a shift from a predominantly bedrock-derived sulfate source to an approximately equal mixture of bedrock and atmospheric/pedogenic sources. During the 2003 melt peak, \( \delta^{34}S \) values decreased from 7.2 to 6.5‰, though some greater decreases occurred during two earlier small peaks (Fig. 5). During the 2004 melt, stream sulfate \( \delta^{34}S \) values decreased only from 7.4 to 7.1‰, remaining virtually constant within the analytical uncertainty. In contrast to the muted isotopic response, sulfate concentration decreased from 180 to 105 µeq l\(^{-1}\) in 2004, only slightly less than the 50% dilution for the other two snowmelt periods.

4. Discussion

Precipitation and throughfall sulfate each had similar ranges of \( \delta^{34}S \) values, with the mean only slightly higher (by 0.4‰) for precipitation, consistent with other studies reporting minimal differences. Novak et al. (2001) reported about 1‰ lower \( \delta^{34}S \) in throughfall sulfate compared to precipitation, whereas Zhang et al. (1998) reported \( \delta^{34}S \) values of throughfall that were slightly higher than precipitation in summer and slightly lower than precipitation in winter. The discrepancies between \( \delta^{34}S \) in throughfall and precipitation sulfate (as much as 3.5‰; Fig. 2) on some sampling dates were enigmatic. The few \( \delta^{34}S \) values higher than 7‰ were still within the range of up to 8‰ reported at Hubbard Brook, NH (Zhang et al., 1998) or 9‰ reported at an Ontario, Canada site (Hesslein et al., 1988), and may indicate slightly elevated contributions of marine sulfate in these precipitation events. In general, our results are in agreement with other measurements of \( \delta^{34}S \) values of precipitation sulfate in this region (Alewell et al., 2000; Wadleigh et al., 1996), and tend to validate our atmospheric
suggests that the measurement of δ lower prior to the 2003 and 2004 snowmelts compared to the 8 slight decrease in its atmospheric sulfate caused a dilution of stream sulfate and a (Fig. 5). During snowmelt, soil water sulfate and possibly direct uptake, immobilization, and subsequent mineralization (Shanley et al., 2005). Increased pedogenic sulfate contributions are responsible for decreasing the base flow δ34S values of streamwater sulfate from near 5‰ in the fall to between 6 and 7‰ in winter (Fig. 3). Winter base flow δ34S values were notably lower prior to the 2003 and 2004 snowmelts compared to the 5‰ previously used as the bedrock value during the 2000 snowmelt (fig. 5). During snowmelt, soil water sulfate and possibly direct atmospheric sulfate caused a dilution of stream sulfate and a slight decrease in its δ34S values, but thereafter the increasing dominance of groundwater caused stream sulfate concentrations and δ34S values to increase steadily throughout the summer months. The decreases in δ34S values that occurred during snowmelt and rain storms resulted from inputs of pedogenic and atmospheric sulfate isotopically depleted in 34S relative to the sulfate in groundwater that supplied base flow.

The δ34S values of streamwater sulfate of -10‰ are notably higher than the previously determined weathering end member value of 8.0‰ (Shanley et al., 2005) and the value of 8.5‰ previously reported for total S in Sleepers River bedrock (Bailey et al., 2004). More extensive recent measurements suggest a higher δ34S value for bedrock-derived sulfate. Bedrock units with elevated total S contents between 600 and 13,000 mg kg⁻¹ were all characterized by elevated δ34S values between 6 and 14‰. The S-content weighted average δ34S value of total S in bedrock was 10.3‰ (n = 14), virtually equal to the maximum values observed in streamwater sulfate. The δ34S values of streamwater sulfate progressively increased in summer and early fall as bedrock-derived sulfate increasingly dominated and pedogenic sulfate contributions gradually diminished.

Dissimilatory BSR would also tend to increase δ34S values of streamwater sulfate in summer and early fall. As sulfate is reduced in anoxic stream sediments and riparian soils, the produced sulfide is depleted in 34S and the remaining sulfate becomes progressively enriched in 34S (Krouse and Mayer, 2000). Removal of sulfate by this process would tend to lower sulfate concentrations in streamwater. Instead, sulfate concentrations consistently increased throughout the summer and were highest during late summer and early fall (Fig. 3) when dissimilatory BSR effects would be expected to peak. However, seasonal variations in the relation between stream sulfate concentration and discharge (Fig. 6A) suggest an influence of dissimilatory BSR.

In winter and spring, stream sulfate concentration had a strong log-linear relation (r² = 0.97) to stream discharge (Fig. 6A), suggesting simple two-source mixing between lithogenic and pedogenic sulfate. During these seasons, low temperatures should minimize any effect of dissimilatory BSR on δ34S values of streamwater sulfate. The summer points all plot below this line, i.e. for a given discharge the sulfate concentration is lower, suggesting removal by dissimilatory
BSR (although in-stream uptake by biota cannot be ruled out). The fall points plot on either side of the winter/spring line. Fall points below the line reflect continued BSR from summer into early fall, whereas fall points above the line reflect release of sulfate derived from reoxidation of the product sulfides and/or release of accumulated pedogenic sulfate by rising water tables and fall flushing events (Fig. 6A).

Seasonal variations in the relation of $\delta^{34}S$ values versus concentrations of sulfate in streamwater (Fig. 6B) provide additional insights. The positive relation in summer is consistent with increasing lithogenic sulfate contributions throughout the summer as flow decreases while streamwater sulfate concentration increases. Some of the fall points coincide with this trend, but the wide scatter in the relation during fall, especially the relatively high concentrations of sulfate coinciding with low $\delta^{34}S$ values, is strong evidence for release during storms of sulfate derived from reoxidation of secondary sulfides. Note the narrow range of $\delta^{34}S$ values in winter and spring. Winter sulfate concentrations overlap or exceed the highest summer sulfate concentrations, but with considerably lower $\delta^{34}S$ values of sulfate. A possible explanation is that summer and early fall is the most important time for the oxidation of sulfides in the bedrock as a result of low water tables.

The 1 to 3‰ decrease in $\delta^{34}S$ values of streamwater sulfate during storm events (Fig. 3) can generally be explained by inputs of pedogenic sulfate. But during the 15 and 27 September 2002 events, $\delta^{34}S$ values of streamwater sulfate decreased by ~5‰, to values significantly lower than $\delta^{34}S$ values of atmospheric/pedogenic sulfate (Figs. 3, 4). The isotopic patterns during these events likely reflect some input of $^{34}$S-depleted sulfate derived from reoxidation of secondary sulfides. Following drought conditions and/or in watersheds with extensive wetlands, rewetting can release large quantities of sulfate produced from the reoxidation of secondary sulfides as water tables fall and soils become aerobic (Warren et al., 2001; Eimers and Dillon, 2002; Schiff et al., 2005; Mitchell et al., 2006, in press). Interannual variations in the extent of dissimilatory BSR and reoxidation may explain the different pre-melt $\delta^{34}S$ values of streamwater sulfate in 2003 and 2004 compared to 2000, suggesting caution in assigning baseflow $\delta^{34}S$ values to the lithogenic source end member.

While dissimilatory BSR and reoxidation of the product sulfides appear to affect stream sulfate concentrations at Sleepers River at times, weathering of sulfides in bedrock is a more fundamental control on streamwater sulfate dynamics at this site. We emphasize this point because net sulfate export from a catchment is sometimes attributed to net mineralization of organic S or net sulfate desorption without first ruling out a lithogenic source. Despite relatively high atmospheric deposition of sulfate (7.2 kg ha$^{-1}$ yr$^{-1}$ as S), bedrock weathering supplies more than half of the annual sulfate export at Sleepers River (17.1 kg ha$^{-1}$ yr$^{-1}$ as S; Hornbeck et al., 1997). Even during events in which isotopic evidence suggests that sulfate formed from reoxidized secondary sulfides is flushed to streamwater, sulfate still dilutes with flow (Figs. 3, 4, 6). Mitchell et al. (in press) compared some of the fall storms in the current study to those at two other northeastern U.S. sites. During fall storms at the Archer Creek watershed in the Adirondack Mountains, New York, sulfate concentration increased with increasing flow, showing a greater importance of sulfate release from reoxidation of secondary sulfides at that site. However, even for this watershed, sulfate isotope evidence also suggested a potential bedrock weathering source (Campbell et al., 2006).

5. Conclusions

The $\delta^{34}S$ values of streamwater sulfate at Sleepers River, Vermont varied dynamically over an annual cycle with a much greater range (4.0 to 10.4‰) than previously observed during snowmelt (6.8 to 8.0‰). As in the earlier snowmelt study, lithogenic sulfate dominated in streamwater, but $\delta^{34}S$ values decreased by 1 to 3‰ during high flows due to mixing.

Fig. 6 – Seasonal relations of (A) stream sulfate concentrations to stream discharge and (B) $\delta^{34}S$ values to concentration of streamwater sulfate. Seasons were based on hydrologic shifts and accordingly were adjusted slightly from calendar dates (by no more than 10 days).
with more $^{34}$S-depleted pedogenic sulfate. Mixing of sulfate from lithogenic and pedogenic sources is the primary control on sulfate concentrations and $\delta^{34}$S values in streamwater at this site. The $\delta^{34}$S values of stream sulfate exceeding 10% in summer and fall suggest that the lithogenic end member value is higher than indicated in the earlier study, though there may be some influence of dissimilatory bacterial sulfate reduction. Reoxidation of the resulting secondary sulfides and flushing during late summer and fall storms caused decreases in the $\delta^{34}$S values of stream sulfate to below atmospheric values. This study demonstrates that careful analysis of frequently obtained hydrological, chemical, and isotopic data can yield refined insights into S cycling in watersheds.

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