



Identifying sources of stream water sulfate after a summer drought in the Sleepers River watershed (Vermont, USA) using hydrological, chemical, and isotopic techniques

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ABSTRACT

In many forested headwater catchments, peak SO_4^{2-} concentrations in stream water occur in the late summer or fall following drought potentially resulting in episodic stream acidification. The sources of highly elevated stream water SO_4^{2-} concentrations were investigated in a first order stream at the Sleepers River watershed (Vermont, USA) after the particularly dry summer of 2001 using a combination of hydrological, chemical and isotopic approaches. Throughout the summer of 2001 SO_4^{2-} concentrations in stream water doubled from ~ 130 to $270 \mu\text{eq/L}$ while flows decreased. Simultaneously increasing Na^+ and Ca^{2+} concentrations and $\delta^{34}\text{S}$ values increasing from $+7\text{‰}$ towards those of bedrock S ($\sim +10.5\text{‰}$) indicated that chemical weathering involving hydrolysis of silicates and oxidation of sulfide minerals in schists and phyllites was the cause for the initial increase in SO_4^{2-} concentrations. During re-wetting of the watershed in late September and early October of 2001, increasing stream flows were accompanied by decreasing Na^+ and Ca^{2+} concentrations, but SO_4^{2-} concentrations continued to increase up to $568 \mu\text{eq/L}$, indicating that a major source of SO_4^{2-} in addition to bedrock weathering contributed to peak SO_4^{2-} concentrations. The further increase in SO_4^{2-} concentrations coincided with an abrupt decrease of $\delta^{34}\text{S}$ values in stream water SO_4^{2-} from maximum values near $+10\text{‰}$ to minimum values near -3‰ . Soil investigations revealed that some C-horizons in the Spodosols of the watershed contained secondary sulfide minerals with $\delta^{34}\text{S}$ values near -22‰ . The shift to negative $\delta^{34}\text{S}$ values of stream water SO_4^{2-} indicates that secondary sulfides in C-horizons were oxidized to SO_4^{2-} during the particularly dry summer of 2001. The newly formed SO_4^{2-} was transported to the streams during re-wetting of the watershed contributing $\sim 60\%$ of the SO_4^{2-} during peak concentrations in the stream water. Thereafter, the contribution of SO_4^{2-} from oxidation of secondary sulfides in C-horizons decreased rapidly and pedogenic SO_4^{2-} reemerged as a dominant SO_4^{2-} source in concert with decreasing SO_4^{2-} concentrations in spring of 2002. The study provides evidence that a quantitative assessment of the sources of stream water SO_4^{2-} in forested watersheds is possible by combining hydrological, chemical and isotopic techniques, provided that the isotopic compositions of all potential SO_4^{2-} sources are distinctly different.

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1. Introduction

Sulfate is often a major anion in stream water in forested headwater catchments impacted by air pollution and elevated SO_4^{2-} concentrations in stream water have been shown to contribute to acidification events (Mitchell, 2005; Wigington et al., 1996). The seasonal dynamics of SO_4^{2-} concentrations in stream water vary between watersheds dependent upon whether SO_4^{2-} from atmospheric sources or from chemical weathering is the dominant source of stream water SO_4^{2-} . In many cases SO_4^{2-} concentrations

in stream water decrease during snowmelt events (Shanley et al., 2005), but increase significantly in the fall (Eimers and Dillon, 2002; Mitchell et al., 2006, 2008). In particular, after periods of extended drought increased SO_4^{2-} concentrations and acidity are widely observed phenomena (e.g. Bayley et al., 1992; Clark et al., 2005). The Sleepers River watershed in Vermont (USA) is one example of a catchment in which peak SO_4^{2-} concentrations in stream water have been regularly observed in the fall since 1992 (Fig. 1). Fall concentration peaks of stream water SO_4^{2-} usually exceed average annual SO_4^{2-} concentrations by a factor of two. In 2001, after a particularly dry summer, peak stream water SO_4^{2-} concentrations exceeded average SO_4^{2-} concentrations of $146 \mu\text{eq/L}$ by a factor of 4 (Fig. 1). Previous studies have compared

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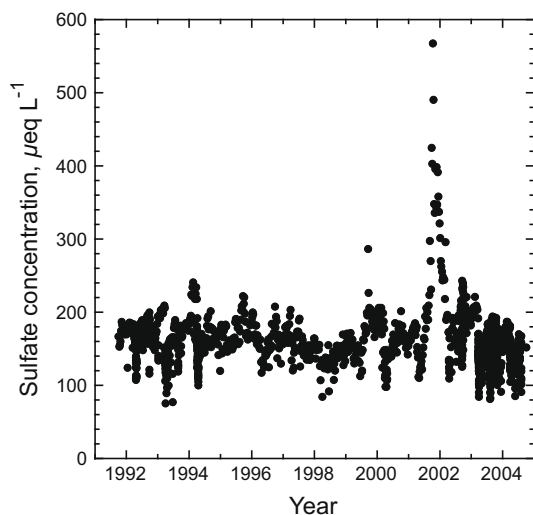


Fig. 1. Sulfate concentrations in stream water at W-9 weir in the Sleepers River watershed, Vermont, USA, from 1992 to 2004 based on weekly and event sampling.

the SO_4^{2-} dynamics at Sleepers River versus Archer Creek (Adirondack Mountains of New York state) and Cone Pond (White Mountains of the state of New Hampshire) and suggested that S-bearing minerals are major contributors to SO_4^{2-} in surface waters especially under baseflow conditions (Bailey et al., 2004). Detailed studies using both radioactive and stable S isotopes have also established the potential importance of these mineral S sources (Shanley et al., 2005, 2008). The sources contributing to peak SO_4^{2-} concentrations in stream water associated with changing watershed wetness in the fall are, however, still unclear.

Sulfur isotope ratios constitute a valuable tracer for the origin and fate of S in the environment (Krouse and Grinenko, 1991). Throughout the last four decades, numerous case studies have been conducted to assess the sources of SO_4^{2-} in rivers and streams. Generally, dissolved SO_4^{2-} in stream water can be of atmospheric origin, can be mobilized from soils or wetlands, or can be of lithospheric origin. In industrialized countries, the majority of the S in atmospheric SO_4^{2-} deposition is of anthropogenic origin (e.g. Benkovitz et al., 1996). $\delta^{34}\text{S}$ values between -1‰ and $+6\text{‰}$ were found to be characteristic for atmospheric SO_4^{2-} deposition in Europe and North America (Alewell et al., 2000; Cortecchi and Longinelli, 1970; Herut et al., 1995; Mizutani and Rafter, 1969b; Moerth and Torsander, 1995; Wadleigh et al., 1994; Wakshal and Nielsen, 1982). The O isotope composition of atmospheric SO_4^{2-} is dependent on the oxidation conditions in the atmosphere and the $\delta^{18}\text{O}$ value of the moisture involved in the oxidation of precursor compounds such as SO_2 . Comprehensive reviews on the relevant oxidation mechanisms and the associated isotope effects have been provided by Holt and Kumar (1991) and Van Stempvoort and Krouse (1994). In temperate regions, $\delta^{18}\text{O}$ values between $+5\text{‰}$ and $+17\text{‰}$ are typical for SO_4^{2-} in atmospheric deposition (e.g. Cortecchi and Longinelli, 1970; Rafter and Mizutani, 1967), with the lower values observed in winter and the higher values associated with summer precipitation.

Upland soils usually have $\delta^{34}\text{S}$ similar to those of SO_4^{2-} in atmospheric deposition since the deposited SO_4^{2-} is rapidly immobilized with negligible isotope fractionation (Trust and Fry, 1992). Soil SO_4^{2-} formed via mineralization also has $\delta^{34}\text{S}$ values similar to those of atmospheric deposition, but markedly lower $\delta^{18}\text{O}$ values. During the oxidation of C-bonded S compounds, four new O atoms are incorporated into the newly formed SO_4^{2-} ion with the majority of the O derived from water with negative $\delta^{18}\text{O}$ values (Mayer et al., 1995). Hence, $\delta^{18}\text{O}$ values between 0‰ and $+5\text{‰}$ are typical

for soil SO_4^{2-} and make it isotopically distinct from SO_4^{2-} in atmospheric deposition.

Lithospheric S occurs commonly in sedimentary rocks, either as sulfate minerals (gypsum, anhydrite, etc.) in evaporite deposits or as reduced inorganic S in minerals such as pyrite, which are common in shales and many other rock types. The isotopic composition of evaporite sulfate deposited throughout Earth's history has been summarized by Claypool et al. (1980) and more recently by Strauss (1997). Typical $\delta^{34}\text{S}$ values range between 35‰ (late Precambrian and Cambrian) and 8‰ (Permian). The respective $\delta^{18}\text{O}$ values for evaporite sulfate vary between $+7\text{‰}$ and $+20\text{‰}$ dependent upon geological age (Claypool et al., 1980). Reduced inorganic sedimentary S compounds vary from $\delta^{34}\text{S}$ values below -20‰ to values exceeding $+15\text{‰}$ (e.g. Migdisov et al., 1983; Strauss, 1999). The $\delta^{34}\text{S}$ value of SO_4^{2-} generated via oxidation of reduced inorganic S is often similar to that of the precursor minerals, since there tends to be only minor S isotope fractionation during oxidation (Price and Shieh, 1979). The O isotope ratios of SO_4^{2-} generated by sulfide oxidation are generally lower than those of SO_4^{2-} from evaporitic or atmospheric sources. Similar to the mineralization process in soils, four oxygen atoms are incorporated into the newly formed SO_4^{2-} during the oxidation of sulfide minerals with the O derived from H_2O and atmospheric O_2 . The proportion of water and atmospheric O_2 incorporated into the SO_4^{2-} molecule is dependent on whether the reaction occurs abiotically or biologically under reducing or oxidizing conditions (e.g. Balci et al., 2007; Taylor and Wheeler, 1994; Taylor et al., 1984). Regardless of the exact stoichiometry, SO_4^{2-} derived from oxidation of sulfide minerals often has a distinct isotopic composition with comparatively low $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values.

Many watersheds contain wetlands and riparian zones in which reducing conditions prevail throughout most of the year, facilitating the occurrence of bacterial (dissimilatory) SO_4^{2-} reduction (BSR). It has been well known for more than five decades that the light isotope ^{32}S is preferentially metabolized during BSR (e.g. Harrison and Thode, 1958; Mizutani and Rafter, 1969a) due to isotope effects associated with individual steps in the dissimilatory SO_4^{2-} reduction pathway (Rees, 1973). Hence, the produced H_2S usually has $\delta^{34}\text{S}$ values that are $20\text{--}40\text{‰}$ more negative than those of the metabolized SO_4^{2-} . Since reaction of H_2S to form sulfide minerals proceeds with negligible isotope fractionation, sulfide minerals formed as a result of BSR under reducing conditions in wetlands and riparian zones are usually characterized by negative $\delta^{34}\text{S}$ values (Mitchell et al., 2006, 2008).

Previous studies attempting to identify the sources of stream water SO_4^{2-} using stable isotope techniques were often hampered by the fact that the isotopic compositions of potential SO_4^{2-} sources in the watershed such as bedrock derived S or soil S were not well characterized. In addition, isotope measurements on stream water SO_4^{2-} were often conducted infrequently (e.g. once/season or once/year). Hence potential variations in the relative contributions from different sources to stream water SO_4^{2-} dependent on hydrological conditions would not have been detected. The objective of this study was to identify the sources that contributed to the anomalous extended high SO_4^{2-} concentration peak in the stream water and quantify their respective contributions at the Sleepers River watershed in Vermont, USA, in the fall of 2001. Such a high concentration in surface water SO_4^{2-} was not found in previous studies at Sleepers River (Mitchell et al., 2008; Shanley et al., 2005, 2008). The objective was achieved by determining the isotopic composition of stream water SO_4^{2-} on a weekly basis combined with a detailed isotopic characterization of S pools that constitute potential SO_4^{2-} sources including S-bearing minerals of bedrock, sulfides in reducing soils or wetlands, foliage, forest floor and mineral soil horizons. A better knowledge of watershed SO_4^{2-} sources to stream water will enhance understanding of how landscapes respond to decreasing

deposition of atmospheric SO_4^{2-} and future climate conditions with potentially more droughts.

2. Study area

The study was conducted in Sleepers River W-9, a 41-ha catchment forested with second-growth Northern Hardwoods and <5% conifers (Fig. 2). Elevation ranges from 519 to 671 m above sea level. The bedrock is the Waits River formation, 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 contents, developed from the local bedrock. Soils are Inceptisols, Spodosols and Histosols developed to 50–70 cm depth. The till supports sustained base flow and gives rise to numerous small wetlands in the hummocky topography. The bedrock and till generate a well-buffered Ca– HCO_3 – SO_4 stream water (Shanley et al., 2004). Annual precipitation is evenly distributed and averages 1300 mm with about 25% as snow. Spring snowmelt dominates the annual hydrograph, but the peak flow can occur at any time of year. Mean annual temperature is 4.6 °C (Shanley et al., 2004).

3. Materials and methods

Stream stage was measured electronically at 5-min intervals with a potentiometer driven by a float in a stilling well adjacent to the pool behind a 120° V-notch weir. Stage was converted to discharge using an empirical rating. Stream water was routinely sampled at the W-9 weir on a weekly basis with samples from June 5, 2001 to May 7, 2002 considered for this paper. All samples were sent to the USDA Forest Service laboratory in Durham, NH, for analysis by inductively coupled plasma spectrometry (ICP) for major cations, ion chromatography (IC) for major anions, and by a Shimadzu analyzer for DOC. Bulk precipitation amount data were obtained from long-term records available for this site.

One liter samples for determining the stable isotope composition of SO_4^{2-} in stream water were dripped through anion exchange columns (Bio-Rad Polyprep, AG 1X-8) near the field site. In the Isotope Science Laboratory at the University of Calgary, SO_4^{2-} was eluted from the column using 3 M HCl and precipitated as BaSO_4 by adding a BaCl_2 solution. The filtered, washed and dried BaSO_4 was subsequently used for determining the S and O isotope ratio of SO_4^{2-} .

Nine representative bedrock samples were obtained from various outcrops in the Sleepers River watershed and analyzed for the concentrations and isotopic compositions of different S compounds. The rock samples were collected with a hammer and chisel. A saw was used to slab specimens and to separate

unweathered interior sections from a weathered rind, identified by pitting and oxide staining. Samples were subsequently crushed to a fine power in a Spex Industries shatterbox.

Leaves and needles from red spruce, white ash, yellow birch, sugar maple and American beech were obtained, and litter samples were collected and dried and ground prior to analyses. A soil sampling pit was hand dug near the base of the watershed. Samples were collected by genetic horizon, air-dried and sieved to remove particles greater than 2 mm. pH was measured in 0.01 M CaCl_2 . Sub-samples were obtained and analyzed for the concentrations and isotopic compositions of different S compounds.

Total S concentrations were determined both gravimetrically (see below) and with a LECO analyzer with the results agreeing within the uncertainty of the measurements ($\pm 10\%$). Total S in leaves and litter material was converted to SO_4^{2-} by Parr bomb oxidation (Siegfriedt et al., 1951) and subsequently precipitated as BaSO_4 for S isotope analyses (Mayer and Krouse, 2004).

In order to assess the chemical and isotopic compositions of S pools that may constitute sources of stream water SO_4^{2-} , several S compounds were extracted from bedrock, mineral soil, and wetland samples for chemical and isotopic analyses. Total S was extracted by soaking the samples overnight in open beakers in a fume hood with concentrated HNO_3 and liquid Br_2 and subsequent heating to dryness (Zhabina and Volkov, 1978). The generated SO_4^{2-} was dissolved in dilute HCl and, after removing undissolved matter by filtration, the SO_4^{2-} -containing solution was transferred into a beaker, where BaSO_4 was precipitated by addition of BaCl_2 solution. On a separate sample, acid volatile S (AVS), acid-soluble SO_4^{2-} (ASS), and Cr-reducible S (CRS) were sequentially extracted from sedimentary material using an extraction scheme slightly modified from Rice et al. (1993), the latter based on methods described in Zhabina and Volkov (1978) and Canfield et al. (1986).

To determine AVS, widely believed to represent mono-sulfide minerals, between 5 and 20 g of wet sediment was placed in a reaction vessel and attached to a distillation apparatus modified after Tuttle et al. (1986). The reaction system was de-oxygenated by a stream of N_2 for 30 min to establish anaerobic conditions. AVS was then extracted by introducing 40–80 mL 6 M HCl under a continuous stream of N_2 . The released H_2S was swept by the carrier gas into a trap with 0.1 M cadmium acetate solution, where CdS precipitated. After 25 min at room temperature, the reaction vessel was heated to 70 °C for 15 min. Thereafter, the acetate trap was removed from the distillation apparatus and CdS was converted to Ag_2S by adding ~20 mL 0.1 M AgNO_3 solution. The Ag_2S precipitate was subsequently filtered, air-dried, weighed, and stored for isotopic analysis. The remaining 6 M HCl was separated from the sediment sample and acid-soluble SO_4^{2-} (ASS) was precipitated by addition of BaCl_2 solution. ASS contains all soluble SO_4^{2-} , acid-soluble mineral SO_4^{2-} , as well as SO_4^{2-} that was formed via sulfide oxidation at the lithosphere-atmosphere interface at outcrops in the watershed. The produced BaSO_4 was also filtered, air-dried, weighed, and stored for isotopic analysis.

The residual sample was subjected to Cr reduction in order to extract elemental S and disulfide (pyrite) S. Chromium-reducible S (CRS) was extracted in the same distillation apparatus that was used for the AVS determination. Sediment samples were boiled under a continuous stream of N_2 with 40–60 mL 1 M CrCl_2 solution and 20 mL 6 M HCl (Canfield et al., 1986; Tuttle et al., 1986). Reduced inorganic sedimentary S compounds such as FeS_2 and S^0 were released concomitantly as H_2S and carried by the N_2 stream into a CdAc trap, where CdS precipitated. After 90 min, the CdAc trap was removed from the distillation apparatus and CdS was converted to Ag_2S as described above. The Ag_2S precipitate was dried, weighed, and stored for subsequent isotopic analysis.

The concentrations of various S compounds in the soil and rock samples were determined gravimetrically, utilizing the quantities

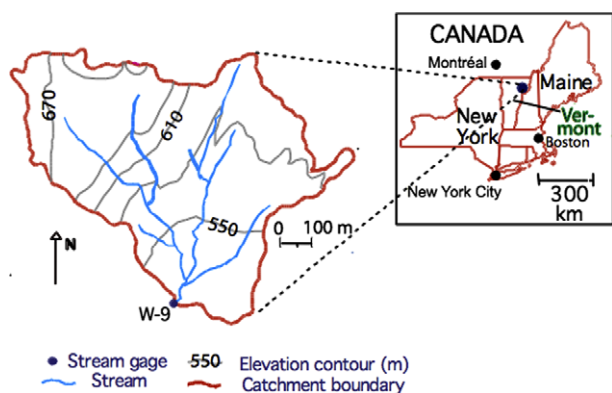


Fig. 2. Location and site map for Sleepers River watershed W-9.

of recovered Ag_2S or BaSO_4 and the known sample weights. Concentration of residual S comprising mainly organic S compounds was calculated as:

$$S_{\text{residual}} = S_{\text{total}} - \text{AVS} - \text{ASS} - \text{CRS}$$

Concentration-weighted average $\delta^{34}\text{S}$ values were determined for various C horizon and bedrock S compounds.

The isotopic compositions of total S, AVS, ASS, CRS, and stream water SO_4^{2-} were determined by converting BaSO_4 or Ag_2S into SO_2 in an elemental analyzer (EA 1500) coupled to a mass spectrometer (VG Prism II) in continuous-flow mode (Giesemann et al., 1994). For O isotope analyses on stream water 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 standard δ notation in ‰ with respect to the international standards V-CDT for S isotope measurements and V-SMOW for O isotope measurements. Sulfur isotope data were calibrated with the international reference materials IAEA-S1 ($\delta^{34}\text{S} = -0.3$) and IAEA-S2 with an assigned $\delta^{34}\text{S}$ value of +22.6‰. The reproducibility for S isotope measurements on aqueous SO_4^{2-} was better than ± 0.3 ‰. The overall reproducibilities of extractions, gas preparations, and mass spectrometric analyses for S isotope determinations on sedimentary AVS, ASS, CRS and total S determined by duplicate analyses, were typically ± 0.5 ‰ or better. Oxygen isotope measurements on SO_4^{2-} were calibrated with the international reference materials NBS 127 ($\delta^{18}\text{O} = 8.7$ ‰), IAEA-SO5 ($\delta^{18}\text{O} = 12.0$ ‰), and IAEA SO6 ($\delta^{18}\text{O} = -11.0$ ‰). The analytical precision for $\delta^{18}\text{O}$ measurements on SO_4^{2-} was ± 0.5 ‰.

4. Results

4.1. Bedrock sulfur

Sulfur concentrations and $\delta^{34}\text{S}$ values of various S compounds in 13 different sub-samples from nine rock specimens are summarized in Table 1. Granulites and quartzites were characterized by low total S concentrations of less than 550 $\mu\text{g/g}$. In the weathered samples (sample code ending with W) most of the S was present in the acid-soluble fraction while S in the fresh bedrock samples (F) occurred predominantly in the Cr-reducible form. $\delta^{34}\text{S}$ values of total S for granulites and quartzites varied between 1.8‰ and 8.3‰

Table 1
Contents and isotopic ratios of total sulfur, acid volatile sulfur (AVS), acid-soluble sulfate (ASS), chromium-reducible sulfur (CRS), and residual sulfur for granulites and quartzites (upper part) and schists and phyllites characteristic for bedrock in the Sleepers River watershed. Sample codes ending with F indicate fresh bedrock samples whereas W indicates weathered bedrock samples. Average S contents and concentration-weighted average $\delta^{34}\text{S}$ values for the various sulfur compounds in the different rock types are also given.

Sample code	Rock type	Total S ($\mu\text{g g}^{-1}$)	$\delta^{34}\text{S}_{\text{total}}$ (‰)	AVS ($\mu\text{g g}^{-1}$)	ASS ($\mu\text{g g}^{-1}$)	CRS ($\mu\text{g g}^{-1}$)	Residual ($\mu\text{g g}^{-1}$)	$\delta^{34}\text{S}_{\text{AVS}}$ (‰)	$\delta^{34}\text{S}_{\text{ASS}}$ (‰)	$\delta^{34}\text{S}_{\text{CRS}}$ (‰)
1SR2-F	Calcareous granulite	160	8.3	26	15	86	33	10.5	7.7	3.4
1SR2-W	Calcareous granulite	330	7.5	0	318	0	12	–	10.0	–
1SR4-F	Calcareous granulite	80	1.8	0	18	53	9	–	–	–
1SR5-F	Calcareous granulite	170	3.1	2	124	39	5	–	4.7	0.0
1SR5-W	Calcareous granulite	520	7.8	0	472	282	0	–	10.0	5.4
1SR6-F	Calcareous granulite	140	6.5	38	59	283	0	10.2	8.4	6.2
2SR4-F	Quartzite	70	5.5	0	43	1	26	–	5.4	–
2SR4-W	Quartzite	530	7.0	0	281	1	248	–	7.1	–
	Average	250	6.8	8	166	93		10.3	8.5	4.8
1SR3-F	Cross-biotite schist	9940	7.9	5606	105	1802	2427	7.3	6.8	8.0
1SR1-F	Cross-biotite schist	1930	8.9	0	264	1065	601	–	8.1	7.4
1SR1-W	Cross-biotite schist	3750	5.9	0	3430	29	291	–	6.5	–
1SR7-F	Cross-biotite schist	3720	11.6	405	299	2158	858	12.5	10.4	11.4
1SR8-F	Phyllite	13,010	13.8	9927	7	1556	1520	13.6	12.5	11.7
	Average	6470	10.5	3188	821	1322		11.4	6.9	9.8

with a concentration-weighted mean value of 6.8‰ ($n = 8$). The $\delta^{34}\text{S}$ values of the individual S compounds were typically within 3‰ of the $\delta^{34}\text{S}$ value of total S. Schists and phyllite samples were characterized by substantially higher total S concentrations ranging between 1930 and 13,010 $\mu\text{g/g}$, with most of the S occurring in acid volatile, acid-soluble, and Cr-reducible forms. The $\delta^{34}\text{S}$ values of total S in the schist and phyllite samples ranged from 5.9‰ to 13.8‰ with a concentration-weighted mean value of 10.5‰ ($n = 5$). The rock sample with the highest total S concentration, a phyllite, had the highest $\delta^{34}\text{S}_{\text{total}}$ value of 13.8‰. The $\delta^{34}\text{S}$ values of the individual S compounds in the schist and phyllite samples were generally within ± 4 ‰ of those for total S.

4.2. Plant and soil sulfur

Total S concentrations in leaves and needle samples averaged 1201 ± 355 $\mu\text{g/g}$ and $\delta^{34}\text{S}$ values of total S were 4.2 ± 0.5 ‰ ($n = 11$) (Table 2). Sulfur concentrations and $\delta^{34}\text{S}$ values of various soil S compounds are summarized in Table 3. A forest floor sample was characterized by a total S concentration of 2000 $\mu\text{g/g}$ and by a $\delta^{34}\text{S}_{\text{total}}$ value of 6.1‰, while E and B horizons had total S concentrations of less than 350 $\mu\text{g/g}$ and $\delta^{34}\text{S}_{\text{total}}$ values ranging between 0‰ and 4‰. Most of the S was contained in the residual fraction representing predominantly organic S compounds. In contrast, C-horizons had total S concentrations ranging from less than 700 to up to 11,850 $\mu\text{g/g}$ and $\delta^{34}\text{S}_{\text{total}}$ values between -6 ‰ and

Table 2
Contents and isotopic ratios of total sulfur in foliage of various trees in the Sleepers River watershed.

Forest type	Tree type	Total S ($\mu\text{g g}^{-1}$)	$\delta^{34}\text{S}_{\text{total}}$ (‰)
Rich hardwoods	White ash	2121	4.4
Rich hardwoods	Yellow birch	1210	3.5
Rich hardwoods	Sugar maple	1068	4.8
Spruce/fir	Red spruce	1436	5.1
Spruce/fir	Red spruce	852	4.2
Rich hardwoods	Sugar maple	1281	4.4
Rich hardwoods	Yellow birch	1084	4.5
Poor hardwoods	Yellow birch	1049	3.5
Rich hardwoods	American beech	785	4.7
Poor hardwoods	American beech	1194	3.7
Poor hardwoods	Sugar maple	1128	3.8
	Average	1201 ± 355	4.2 ± 0.5

Table 3

Soil horizons, depth, pH and contents and isotopic ratios of total sulfur, acid volatile sulfur (AVS), acid-soluble sulfate (ASS), chromium-reducible sulfur (CRS), and residual sulfur for soil horizons of a characteristic spodosol from toeslope near the weir of W-9 in the Sleepers River watershed (SR01VT). Average S contents and concentration-weighted average $\delta^{34}\text{S}$ values for the various sulfur compounds in the C horizon samples are also given.

Soil horizon	Depth (cm)	pH	Total S ($\mu\text{g g}^{-1}$)	$\delta^{34}\text{S}_{\text{Total}}$ (‰)	AVS ($\mu\text{g g}^{-1}$)	ASS ($\mu\text{g g}^{-1}$)	CRS ($\mu\text{g g}^{-1}$)	Residual ($\mu\text{g g}^{-1}$)	$\delta^{34}\text{S}_{\text{AVS}}$ (‰)	$\delta^{34}\text{S}_{\text{ASS}}$ (‰)	$\delta^{34}\text{S}_{\text{CRS}}$ (‰)	$\delta^{34}\text{S}_{\text{Residual}}$ (‰)
Oa	3–10	3.8	2000	6.1	0	473	0	1527	–	6.7	–	6.5
E	10–13	3.6	130	2.3	0	9	0	121	–	4.1	–	2.3
Bs	13–25	4.4	310	3.6	0	179	16	115	–	7.2	–4.1	–3.9
BC	25–38	4.8	230	0.4	0	34	119	77	–	5.2	0.2	–
Cd	38–61	5.9	130	–6.2	4	20	24	82	–1.9	0.0	–10.0	–
C	61–81	3.0	11,850	–22.1	6	4052	6429	1363	–14.9	–22.0	–21.3	–21.6
C	81–102	6.8	1550	–28.7	2	236	940	372	–6.5	–31.0	–28.0	–26.4
C	114–127	7.5	640	–16.1	4	10	331	295	–3.4	–18.3	–20.2	–15.7
C	140–152	7.5	520	–9.1	5	31	409	75	0.9	–18.5	–25.5	–6.1
C horizon average			2938	–21.9	4	870	1627	437	–5.7	–22.4	–22.2	

–29‰ with a concentration-weighted mean value of –21.9‰ ($n = 5$). Most of this S occurred in Cr-reducible and acid-soluble form and was characterized by $\delta^{34}\text{S}_{\text{CRS}}$ and $\delta^{34}\text{S}_{\text{ASS}}$ values ranging from 1‰ to –31‰. The C horizon sample with the highest S content at a soil depth of 61–81 cm also had the lowest pH value of 3.0 (Table 3).

4.3. Precipitation sulfate

Initially, the isotopic composition of SO_4^{2-} in precipitation was assessed based on analyses of pre-melt snow cores and snow melt-water samples collected in 2000 that yielded a $\delta^{34}\text{S}$ value of +5.6‰ and a $\delta^{18}\text{O}$ value of 12‰ (Shanley et al., 2005). Subsequently, bulk precipitation and throughfall were sampled periodically between September 2002 through October 2003 and similar $\delta^{34}\text{S}$ values were observed with an average of 5.8‰ ($n = 9$) for bulk precipitation and an average of 5.5‰ for throughfall (Shanley et al., 2008).

4.4. Stream discharge and sulfate, calcium and sodium concentrations

During the summer of 2001 SO_4^{2-} concentrations in stream water doubled from 130 to 270 $\mu\text{eq/L}$ with a concomitant increase of Ca^{2+} and Na^{+} concentrations while flows decreased from <0.0089 mm/h to <0.0009 mm/h (<1 L/s to <0.1 L/s) (Fig. 3). During re-wetting of the watershed in late September and early October,

flow increased to <0.0044 mm/h (<0.5 L/s) and sulfate concentrations continued to increase to a peak of more than 550 $\mu\text{eq/L}$, while Ca^{2+} and Na^{+} concentrations decreased. Subsequently, flows continued a general increase while SO_4^{2-} concentrations gradually decreased reaching levels below 200 $\mu\text{eq/L}$ by April 2002, while Ca^{2+} and Na^{+} concentrations remained low.

The $\delta^{34}\text{S}$ values of stream water SO_4^{2-} initially increased from 7.3‰ in June 2001 to ~10‰ in August and early September 2001 (Fig. 4), when stream flow reached a minimum (<0.0009 mm/h). With the re-wetting of the watershed and the further increase of SO_4^{2-} concentrations in stream water, $\delta^{34}\text{S}$ values decreased rapidly reaching a minimum value of –3.0‰ coincident with the maximum SO_4^{2-} concentration of 568 $\mu\text{eq/L}$ on October 9, 2001. Subsequently, $\delta^{34}\text{S}$ of stream water SO_4^{2-} increased asymptotically towards a value of 6‰ as SO_4^{2-} concentrations decreased to less than 200 $\mu\text{eq/L}$. The $\delta^{18}\text{O}$ values of stream water SO_4^{2-} remained relatively constant with values between 1‰ and 4‰ throughout the observation period.

5. Discussion

Hydrological, chemical and isotopic patterns were used to quantify the sources of stream water SO_4^{2-} . $\delta^{34}\text{S}$ values in stream water SO_4^{2-} plotted against SO_4^{2-} concentrations (Fig. 5) revealed a triangular pattern indicating that at least three distinct sources

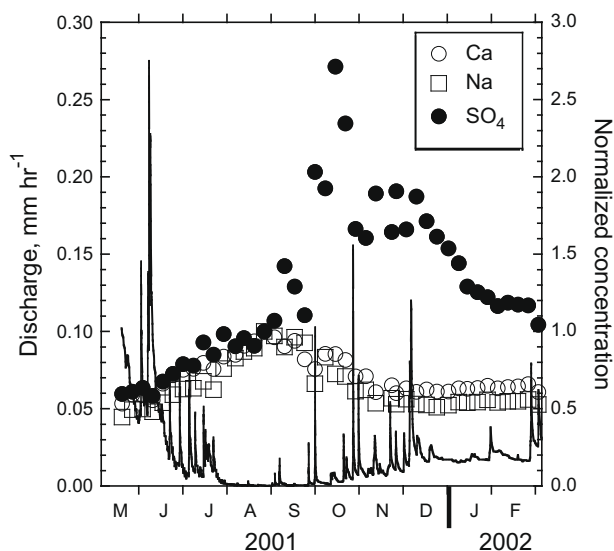


Fig. 3. Discharge and weekly SO_4^{2-} , Na and Ca concentrations at W-9 weir between May 2001 and February 2002.

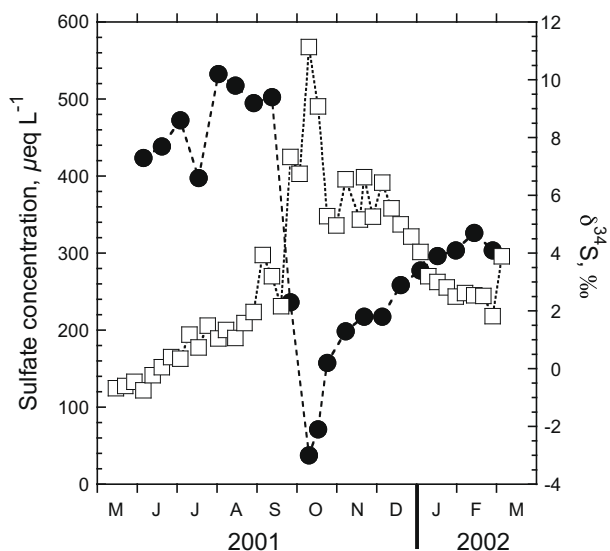


Fig. 4. Sulfate concentrations (open squares) and $\delta^{34}\text{S}$ values of SO_4^{2-} (full circles) at W-9 weir between May 2001 and March 2002.

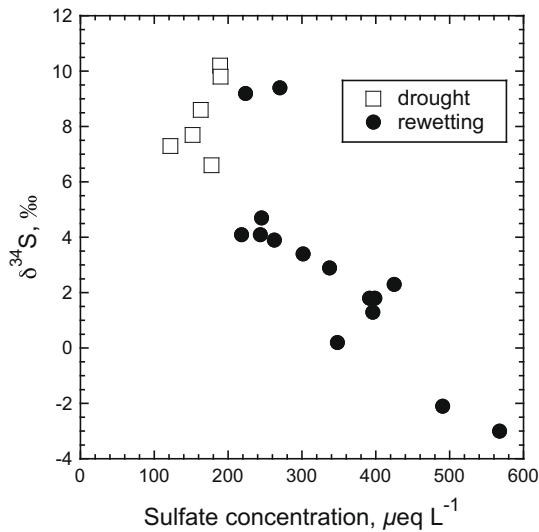


Fig. 5. $\delta^{34}\text{S}$ values of stream water SO_4^{2-} versus SO_4^{2-} concentration.

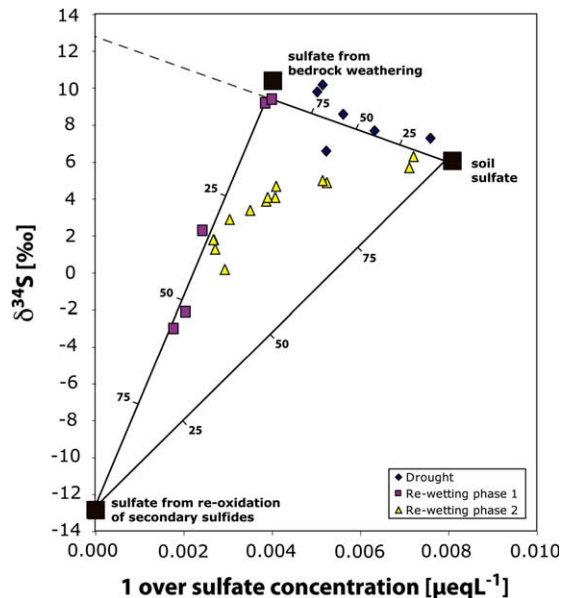


Fig. 6. $\delta^{34}\text{S}$ values of stream water SO_4^{2-} versus $1/\text{SO}_4^{2-}$ concentration.

contributed to stream water SO_4^{2-} . To assess the approximate isotopic composition of the respective end-members, $\delta^{34}\text{S}$ values of stream water SO_4^{2-} were plotted versus the inverse of SO_4^{2-} concentration (Fig. 6). On such a diagram mixing between two end-members is expected to plot on a straight line with the y-intercept indicating the $\delta^{34}\text{S}$ value of the SO_4^{2-} source responsible for elevated SO_4^{2-} concentrations (Krouse, 1980).

The initial stream water SO_4^{2-} in June of 2001 had a $\delta^{34}\text{S}$ value of 7.5‰ and a $\delta^{18}\text{O}$ value of 3.5‰ suggesting that SO_4^{2-} derived from atmospheric deposition, characterized by $\delta^{34}\text{S}$ values of 5.6‰ and $\delta^{18}\text{O}$ values of ~ 12 ‰, was not the predominant source of stream water SO_4^{2-} . $\delta^{34}\text{S}$ of stream water SO_4^{2-} collected during the drought-affected summer months between June and August of 2001 displayed a trend of increasing values with increasing SO_4^{2-} concentrations (Fig. 5) with a y-axis intercept on Fig. 6 of 12.8‰. This trend indicates contributions from two S sources: (1) soil-derived SO_4^{2-} and (2) SO_4^{2-} derived from bedrock weathering. Soil SO_4^{2-} is assumed to have $\delta^{34}\text{S}$ values of ca. 6‰ (Fig. 6) and low

$\delta^{18}\text{O}$ values as a result of oxidation of organic soil S compounds. Granulites and quartzites had an average concentration-weighted $\delta^{34}\text{S}_{\text{Total}}$ value of 6.8‰ and had generally low total S concentrations of less than 550 $\mu\text{g/g}$ and hence appear not to be major contributors to stream water SO_4^{2-} . In contrast schist and phyllites had average total S concentrations of 6470 $\mu\text{g/g}$ and are the likely major lithospheric S source. The $\delta^{34}\text{S}$ value of the SO_4^{2-} from the bedrock weathering end member obtained from Fig. 6 (12.8‰) is similar to the $\delta^{34}\text{S}$ value of total S of the phyllite sample with the highest bedrock S concentration (13.8‰, Table 1). Sulfate from bedrock weathering derives predominantly from oxidation of mono-sulfides and di-sulfides such as pyrite in the S-rich schists and phyllites with concentration-weighted $\delta^{34}\text{S}$ values of 11.4‰ (AVS) and 9.8‰ (CRS), respectively. Inspection of Fig. 5 reveals that SO_4^{2-} generated via oxidation of AVS or CRS reaches maximum $\delta^{34}\text{S}$ values between 10‰ and 11‰ representing a watershed-integrated bedrock weathering contribution. This SO_4^{2-} is also characterized by low $\delta^{18}\text{O}$ values since the O in the newly formed SO_4^{2-} is predominantly derived from water O (Balci et al., 2007). Based on these isotopic end member compositions of soil SO_4^{2-} and bedrock derived SO_4^{2-} , initial stream water SO_4^{2-} with a $\delta^{34}\text{S}$ value of 7.5‰ and a $\delta^{18}\text{O}$ value of 3.5‰ contained at least 50% soil-derived SO_4^{2-} with the remainder from bedrock weathering via oxidation of sulfide minerals in schists and phyllites (Fig. 6). Between mid-June and mid-September 2001 SO_4^{2-} concentrations in stream water doubled from ~ 130 to 270 $\mu\text{eq/L}$ while flows decreased (Fig. 3). Simultaneously Na and Ca concentrations increased (Fig. 3) and $\delta^{34}\text{S}$ increased to a maximum value of 10.2‰ (Fig. 4). Sodium and Ca are not products of sulfide oxidation but are derived from silicate weathering. The concomitant increases in solute concentrations and $\delta^{34}\text{S}$ values provide strong evidence that during baseflow conditions in the late summer of 2001 SO_4^{2-} was predominantly derived from bedrock weathering.

After August 21, 2001, the drought began to end with a series of small storm events. In response, over the next 2 weeks SO_4^{2-} increased to ~ 300 $\mu\text{eq/L}$ while the $\delta^{34}\text{S}$ value decreased slightly (Fig. 4), accompanied by decreasing Ca^{2+} and Na^+ concentrations (Fig. 3). After another 2 weeks of dry conditions, SO_4^{2-} concentrations in stream water decreased to 230 $\mu\text{eq/L}$. Then a series of larger storms, starting on September 25, 2001, resulted in increased flow of 0.07 mm/h (8 L/s) and a subsequent marked increase in stream water SO_4^{2-} concentrations to a maximum of 568 $\mu\text{eq/L}$ on October 9, 2001 (Fig. 3). Within these 2 weeks, the $\delta^{34}\text{S}$ value of stream water SO_4^{2-} decreased from its maximum value of ~ 10 ‰ to a minimum value of -3.0 ‰ (Fig. 4), suggesting that an additional source of SO_4^{2-} with a negative $\delta^{34}\text{S}$ value was contributing to the peak SO_4^{2-} concentrations in stream water. The $\delta^{34}\text{S}$ values of stream water SO_4^{2-} collected during this re-wetting period fall on a straight mixing line ($r^2 = 0.98$) with a y-axis intercept of -12.8 ‰ (Fig. 6), suggesting that oxidation of C-horizon sulfide constitutes an additional SO_4^{2-} source. The C-horizons had generally negative $\delta^{34}\text{S}$ values for total S ranging between -6.2 ‰ and -28.7 ‰ with the majority of the S occurring as Cr-reducible (CRS) and acid-soluble S (Table 3). The concentration-weighted average $\delta^{34}\text{S}_{\text{CRS}}$ value of -22.2 ‰ suggests that bacterial (dissimilatory) SO_4^{2-} reduction had been occurring in the C-horizons under reducing conditions and that the produced H_2S precipitated as secondary sulfide minerals resulting in total S concentrations of up to 11,850 $\mu\text{g/g}$. During the extremely dry summer of 2001 groundwater levels decreased to the lowest levels on record exposing the lower solum (e.g. 61–81 cm depth, see Table 3) to oxidizing conditions. During the re-wetting phase between September 25 and October 9, 2001, SO_4^{2-} formed via re-oxidation of secondary sulfides in the C-horizons caused low pH values (Table 3) and constituted an additional source of SO_4^{2-} that was transported to the stream, contributing significantly to peak SO_4^{2-} concentrations.

Using $\delta^{34}\text{S}$ values of +10.5‰ for the SO_4^{2-} from bedrock weathering end member and –12.8‰ for the C-horizon sulfide oxidation end member reveals that at the beginning of the re-wetting period at the end of August >90% of the SO_4^{2-} was derived from bedrock weathering (Fig. 6). By October 9, stream water SO_4^{2-} concentrations had doubled while $\delta^{34}\text{S}$ values decreased by 13‰ to –3‰ indicating that ~60% of the SO_4^{2-} was derived from re-oxidation of secondary sulfides in C-horizons, with the remainder contributed from bedrock weathering while soil SO_4^{2-} contributions were negligible. The diminishing role of SO_4^{2-} from bedrock weathering is corroborated by simultaneously decreasing Na^+ and Ca^{2+} concentrations (Fig. 3).

Between October 16, 2001 and May 7, 2002, SO_4^{2-} concentrations in stream water monotonically decreased from 491 to less than 150 $\mu\text{eq/L}$ while $\delta^{34}\text{S}$ values increased to 6.3‰. The contribution of SO_4^{2-} derived from re-oxidation of secondary sulfides in C-horizons rapidly decreased to less than 50% with SO_4^{2-} from bedrock weathering constituting again the predominant SO_4^{2-} source in November and December 2001 (Fig. 6). Thereafter, SO_4^{2-} concentrations continued to decrease and $\delta^{34}\text{S}$ values increased from +2‰ towards +6‰ (Fig. 4) indicating that SO_4^{2-} in the topsoil and upper mineral soil horizons (Table 3) progressively became the dominant SO_4^{2-} source (Fig. 6). Hence soil-derived SO_4^{2-} reemerged as a dominant SO_4^{2-} source as SO_4^{2-} concentrations decreased during further re-wetting of the watershed in spring of 2002.

6. Conclusions

Isotopic characterization of all potential SO_4^{2-} sources at Sleepers River watershed (Vermont, USA) revealed that soil SO_4^{2-} , SO_4^{2-} from bedrock weathering, and SO_4^{2-} derived from oxidation of secondary sulfides in C-horizons contributed to stream water SO_4^{2-} , with the relevant proportions dependent on hydrological conditions. Whereas soil SO_4^{2-} is a major source of stream water SO_4^{2-} during snowmelt (e.g. Shanley et al., 2005) it was found that SO_4^{2-} derived from weathering of phyllites and schist was the dominant stream water SO_4^{2-} source during baseflow conditions in the extremely dry summer of 2001. Combining hydrological, chemical and isotopic approaches showed that during the watershed re-wetting phase in October 2001, SO_4^{2-} from oxidation of secondary sulfides in the lower solum constituted an additional SO_4^{2-} source causing a doubling of the SO_4^{2-} concentrations and a decrease in stream water $\delta^{34}\text{S}$ values by 13‰ in less than one month. These results suggest the importance of hydrological wetting and drying in triggering marked changes in S biogeochemistry. Elucidating how such events alter S dynamics requires frequent chemical and isotopic analyses of stream water SO_4^{2-} , a thorough isotopic characterization of all potential SO_4^{2-} sources, and interpretation of the chemical and isotopic patterns in concert with hydrological conditions.

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