

Long-term analysis of Hubbard Brook stable oxygen isotope ratios of streamwater and precipitation sulfate

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Received: 3 August 2010 / Accepted: 13 October 2011 / Published online: 16 November 2011
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Abstract In response to decreasing atmospheric emissions of sulfur (S) since the 1970s there has been a concomitant decrease in S deposition to watersheds in the Northeastern U.S. Previous study at the Hubbard Brook Experimental Forest, NH (USA) using chemical and isotopic analyzes ($\delta^{34}\text{S}_{\text{SO}_4}$) combined with modeling has suggested that there is an internal source of S within these watersheds that results in a net loss of S via sulfate in drainage waters. The current study expands these previous investigations by the utilization of $\delta^{18}\text{O}$ analyzes of precipitation sulfate and streamwater sulfate. Archived stream and bulk precipitation samples at the Hubbard Brook Experimental

Forest from 1968–2004 were analyzed for stable oxygen isotope ratios of sulfate ($\delta^{18}\text{O}_{\text{SO}_4}$). Overall decreasing temporal trends and seasonally low winter values of $\delta^{18}\text{O}_{\text{SO}_4}$ in bulk precipitation are most likely attributed to similar trends in precipitation $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values. Regional climate trends and changes in temperature control precipitation $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values that are reflected in the $\delta^{18}\text{O}_{\text{SO}_4}$ values of precipitation. The significant relationship between ambient temperature and the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of precipitation is shown from a nearby site in Ottawa, Ontario (Canada). Although streamwater $\delta^{18}\text{O}_{\text{SO}_4}$ values did not reveal temporal trends, a large difference between precipitation and streamwater $\delta^{18}\text{O}_{\text{SO}_4}$ values suggest the importance of internal cycling of S especially through the large organic S pool and the concomitant effect on the $\delta^{18}\text{O}_{\text{SO}_4}$ values in drainage waters.

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Keywords Acid rain · Hubbard Brook ·
Precipitation · S cycling · Stable oxygen isotope ratio
($\delta^{18}\text{O}$) of sulfate · Streamwater

Abbreviations

ANC Acid neutralizing capacity
CAA Clean air act of 1970
CAAAAs Clean air act amendments of 1977 and 1990
CNIP Canadian network for isotopes in
precipitation
GNIP Global network of isotopes in precipitation

HBEF	Hubbard Brook Experimental Forest
IAEA	International atomic energy agency
ISOHIS	Isotope hydrology information system
OIPC	Online isotopes in precipitation calculator
P	Bulk precipitation/deposition
USGS	U.S. geological survey
W6	Streamwater
WISER	Water isotope system for data analysis visualization and electronic retrieval

Introduction

The emissions of sulfur dioxide (SO₂) and the subsequent formation of acidic deposition have resulted in substantial deleterious environmental effects on watersheds in the Northeastern United States including those at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire (Likens et al. 2002). In the U.S., the 1970 Clean Air Act (CAA) was passed to regulate SO₂ and other industrial emissions into the atmosphere. Subsequent amendments to this act (CAAs) were sanctioned and implemented in 1977 and 1990 resulting in substantial decreases in SO₂ emission and the atmospheric deposition of sulfate in Eastern North America (Clair et al. 1995; Dillon et al. 1997; Mitchell et al. 2001; Stoddard et al. 1999). These decreases in deposition have resulted in lower sulfate concentrations, and decreased fluxes, in drainage waters from forested ecosystems in the Northeastern U.S. (Driscoll et al. 1995; Likens et al. 2002; Likens and Bormann 1995; Mitchell et al. 2011).

Abiotic and biotic cycling of sulfur (S) increases the residence time of S within ecosystems. This cycling results in a time lag of ecosystem response to declines in S deposition. Internal ecosystem biotic or abiotic cycles and releases of sulfate are responsible for this time lag (Shanley et al. 2005). Sulfur may be stored in forest soils and partly controlled by adsorption and desorption processes in the mineral soil which keep the concentrations of sulfates in soil and soil water in equilibrium (Driscoll et al. 1998; Zhang et al. 1999). Sulfur can be stored in inorganic or organic forms after assimilation and cycling by forest and forest floor biota. On average in Northeastern U.S. watersheds, about 80% of S is stored in organic forms within the forest floor and mineral soil with smaller amounts stored as inorganic sulfate, mostly within the mineral soil

(Johnson and Mitchell 1998; Mitchell et al. 1992). Because the overall S budget at the HBEF is unbalanced, it has been suggested that HBEF watersheds and others within the region, are releasing stored S in surface water. Sulfur stored during past periods of high S inputs (prior to and soon after the passing of the CAA and CAAs) are released during the current period of reduced S deposition (Likens et al. 2002; Mitchell et al. 1992, 2011). Mitchell and Likens (2011) have shown that with decreasing amounts of atmospheric deposition of S the annual variation in the discrepancies in the S mass balances of the HBEF watersheds is becoming increasingly controlled by watershed wetness and hence climatic factors.

Four sources have been identified potentially contributing to S imbalances in watersheds in the Northeastern U.S. and Eastern Canada: (1) an underestimate in dry deposition inputs (Edwards et al. 1999; Likens et al. 1990, 2002); (2) the weathering of S-containing minerals (Baron et al. 1995; Likens et al. 2002); (3) the mineralization of organic S in soil (Driscoll et al. 1998; Likens et al. 2002); and (4) the desorption of adsorbed sulfate from soils (Driscoll et al. 1995; Likens et al. 2002). The latter three S sources are all enhanced by greater watershed wetness (Mitchell and Likens 2011).

Stable isotopes are widely used in ecosystem analyzes to help evaluate complex biogeochemical relationships (e.g., Peterson and Fry 1987). In investigations of the S cycle in watersheds analyzing the stable isotopic ratios of oxygen (O) and S in sulfate has provided valuable insights about the sources and transformations of S (Mayer et al. 1995; Mitchell et al. 1998, Novák et al. 2005a, b).

Sulfur cycling studies at the HBEF have included the utilization of stable S isotope ratios (e.g., Alewell et al. 1999). Likens et al. (2002) provide a comprehensive analysis of S biogeochemistry at HBEF suggesting that S mineralization provides ~60%, sulfate adsorption and desorption processes provide ~37%, and dry deposition underestimates provide a very small portion of sulfate to the S mass imbalance. Alewell et al. (1999) using $\delta^{34}\text{S}$ measurements on historical precipitation and drainage water samples concluded that most of the S deposited from the atmosphere cycles through forest and soil biota. Seasonal patterns in $\delta^{34}\text{S}$ values of streamwater sulfate were especially evident when comparing the growing and dormant seasons, as biological activity (both

vegetative and microbial) are reduced by factors, such as temperature, in the dormant season (Zhang et al. 1998). No previous studies at the HBEF have investigated $\delta^{18}\text{O}$ values of sulfate.

The evaluation of stable O isotopes of sulfate provides further information on the importance of S processing including mineralization of organic forms of S. Conservative transport of atmospherically deposited sulfate through the soil and water-unsaturated zone would not alter the isotopic composition of sulfate and hence sulfate from atmospheric deposition and sulfate in drainage water should be isotopically identical. Also, sulfate adsorption and desorption proceed with no substantial isotope fractionation (Van Stempvoort et al. 1990). During S mineralization of organic carbon-bonded S, however, four new O atoms are incorporated into the newly formed SO_4^{2-} (Mayer et al. 1995). Since the majority of this O is derived from soil water with typically negative $\delta^{18}\text{O}$ values, mineralization of organic S results in distinctive O isotope ratios of the newly formed sulfate causing substantial differences between the $\delta^{18}\text{O}$ values of precipitation sulfate versus drainage water sulfate (Mitchell et al. 1998; Novák et al. 2007; Shanley et al. 2005; Van Stempvoort et al. 1990). Consequently, sulfate derived by mineralization involving organic forms of S has a lower $\delta^{18}\text{O}$ value compared to that of atmospherically deposited sulfate.

One objective of our study was to distinguish better, the sources of sulfate in streamwater at the HBEF by investigating a long-term dataset of stable O isotopes of sulfate in streamwater and precipitation. Another objective was to evaluate the oxygen isotopic values in HBEF precipitation sulfate over time and to identify any temporal trends that may be attributed to atmospheric S conversion processes.

Methods

Site description

The HBEF is located in the southern portion of the White Mountains of New Hampshire (USA). The landscape is characterized as till-mantled glacial valleys, and has a humid continental climate, with an annual mean precipitation of about 140 cm, 25–35% of which is snow. Most soils at the HBEF have been described as well drained Spodosols of a sandy loam

texture, with a well-developed organic layer, and average depth of 60 cm (Likens and Bormann 1995). The study site is underlain by Devonian quartz mica schist and quartzite of the Littleton formation. The schist contains feldspar, an aluminosilicate, which is a primary mineral and weathers slowly (Bailey et al. 2004). The vegetation is characteristic of Northern hardwood forests; the mid and higher elevations are dominated by some softwood species (Likens and Bormann 1995). Timber harvesting occurred between 1915 and 1917; the forests have recovered and dominant species today are yellow birch (*Betula alleghaniensis*), American beech (*Fagus grandifolia*), and sugar maple (*Acer saccharum*). On average hardwoods comprise ~80–90%, and softwoods ~10–20% of the forests.

Portions of the HBEF are separated into experimental watersheds. Watershed 6 (W6) is the biogeochemical reference watershed. W6 has an area of 13.2 ha, the elevation of this watershed ranges from 549–792 m, and the watershed faces Southeast (Likens and Bormann 1995).

HBEF archive sampling

Streamwater at W6 has been sampled weekly, since 1963. Samples are collected ~10 m upstream from the stream gauging station. Bulk deposition/precipitation samples at Rain Gauge 11 (RG11) in W6 were also collected weekly. Both streamwater and precipitation samples were analyzed for sulfate. After analysis the remaining samples have been stored in plastic bottles in the archive building with temperature control (to keep from freezing) at the HBEF. Sulfate is isotopically and chemically stable under ambient temperature conditions. For further information on the use of these archived samples for isotopic $\delta^{34}\text{S}$ analyzes of sulfate see Alewell et al. (1999).

For the current study, the period sampled for the W6 weekly archived streamwater (W6) and bulk deposition (P) was from 1968 to 2004 for a total of 36 years. At the HBEF, the archived subsampling policy allows only 10% of each archived sample to be removed. Therefore ~10% of the remainder of each archived weekly sample was subsampled (~10–40 ml per sample). In order to create a seasonal composite sample with a sufficient amount of sulfate for isotopic analyzes, 10% of each weekly sample was added to the composite sample. Because only 10% of each archived sample

could be sampled, it was not possible to create a weighted seasonal streamflow/precipitation sample; a weighted sample would have required larger volumes to be taken from periods of high flow, and less from periods of low flow, but archived samples are only up to 1 l in volume. The weekly subsamples were composited into four samples per year (Winter: Dec. 1–Feb. 28/29; Spring: March 1–May 31; Summer: June 1–Aug. 31; Fall Sept. 1–Nov. 30). These samples were then analyzed for sulfate concentrations and stable O isotope ratios ($\delta^{18}\text{O}$) of sulfate. In order to evaluate the effect of storage on the solute concentrations of the samples, seasonal mean concentrations calculated using original data were compared to the concentrations in the current study. The seasonal mean concentration calculation used was a simple average and was not a volume-weighted mean concentration.

Chemical and isotopic analysis

The sulfate and chloride concentration of samples with sufficient volumes were analyzed in duplicate by ion chromatography using a Dionex ICS-2000 with AS40 Automated Sampler at the SUNY-ESF Biogeochemistry Laboratory. After ion chromatographic analysis, water samples were prepared for isotopic analysis. Samples were passed through Bio Rad[®] strong anion exchange resin columns, which retained the sulfate anion, and these were sent for analysis at the University of Calgary Isotope Science Laboratory. The same laboratory was used previously in the Alewell et al. (1999) HBEF stable S isotopic study. Sulfate was eluted from ion exchange columns using 15 ml of a 3 M solution of HCl. To this eluent a 10% solution of BaCl_2 was added and $\text{BaSO}_4(\text{s})$ was precipitated (Mayer and Krouse 2004). The samples were then filtered using a small filtration apparatus and Millipore 0.45- μm HA[®] membrane filters containing nitrocellulose. The samples with very small amounts of $\text{BaSO}_4(\text{s})$ were filtered using Whatman Nuclepore track-etch[®] membrane 25 mm, 0.4- μm titanium filters in order to prevent biased O isotope ratio measurements via accidental introduction of cellulose to the samples from scrapping the cellulose filters. This method of sulfate isolation for isotopic analysis was the best suited for relatively low concentrations of sulfate as needed for our study (Kendall and Caldwell 1998).

The dried $\text{BaSO}_4(\text{s})$ (~ 0.20 mg) was packed into silver capsules. For stable O isotopic analysis, O from

sulfate was quantitatively converted to $\text{CO}(\text{g})$ at temperatures $\sim 1450^\circ\text{C}$ in a TC/EA pyrolysis reactor coupled in continuous-flow mode (CF-IRMS) to a Thermo Finnigan Mat Delta + XL. Results were corrected by using a blank capsule correction, and normalised to the VSMOW scale by using the international reference materials NBS 127 ($\delta^{18}\text{O} = 8.6\text{‰}$), IAEA SO5 ($\delta^{18}\text{O} = 12.0\text{‰}$), and IAEA SO6 ($\delta^{18}\text{O} = -11.3\text{‰}$). A laboratory standard was analyzed repeatedly within each sample set (one standard per five to ten samples) to ensure data quality. To assess the reproducibility of $\delta^{18}\text{O}$ measurements on dissolved sulfate samples we used, in addition, a “streamwater standard” obtained by collecting ~ 50 l from the Hubbard Brook main channel, and two laboratory sulfate solution “standards”: Standard 1 (A300c 212-Fisher H_2SO_4 @ 7000 ppm) and Standard 2 (VWR A SO_4^{2-} @ 1,000 ppm). At least three laboratory sulfate standards and two streamwater standards were included for every set of 50 samples. The mean and standard deviations for $\delta^{18}\text{O}_{\text{SO}_4}$ of the laboratory standards 1 and 2 were 11.8 ± 0.8 ($n = 15$) and $9.5 \pm 0.6\text{‰}$ ($n = 11$), respectively. For the Hubbard Brook “streamwater standard” the mean and standard deviation of replicate $\delta^{18}\text{O}_{\text{SO}_4}$ analyzes was $2.5 \pm 0.3\text{‰}$ ($n = 14$). The analytical uncertainty ranging from 0.3 to 0.8‰ is similar to that found in previous studies where $\delta^{18}\text{O}$ in sulfate was analyzed ($\sim 0.5\text{‰}$) at the University of Calgary (Mayer et al. 1995; Shanley et al. 2005).

Statistical analyzes

Differences between bulk deposition (P) and streamwater (W6) concentrations, trends over time, and seasonal patterns were evaluated. Statistical analysis for sulfate concentration and $\delta^{18}\text{O}_{\text{SO}_4}$ values included paired *t*-tests (Satterthwaite with unequal variances) between bulk precipitation (P) and streamwater (W6) using year as a replication (Snedecor and Cochran 1989; Yanai et al. 2005). Descriptive statistics were defined for each season within W6 precipitation and streamwater. A 4×2 factorial in a split plot design (SAS ProcMixed) was used to test for differences between W6 and P and seasons with replication or blocking by year. The main and simple effects were season and sample type (P vs. W6). Tukey–Kramer differences in least squares means tested all variations of pair wise comparisons (Lajtha et al. 2005).

Table 1 Descriptive Statistics [number of samples (*n*), mean, standard deviation (STD) and range of values] of sulfate concentrations in $\mu\text{mol SO}_4^{2-} \text{L}^{-1}$ for HBEF precipitation (RG-11) and streamwater seasonal samples for 1968 through 2004

	<i>n</i>	Mean	STD	Minimum–maximum (range)
Precipitation				
Summer	28	42.2	20.1	18.1–84.3 (66.2)
Fall	28	32.0	13.2	12.3–66.1 (53.8)
Winter	29	19.5	8.9	9.8–44.6 (34.8)
Spring	29	32.5	13.2	13.9–64.3 (50.4)
All	114	31.2	16.5	9.8–84.3 (74.5)
Streamwater				
Summer	37	63.7	14.7	37.4–95.3 (57.9)
Fall	37	65.6	15.2	42.8–101.4 (58.5)
Winter	36	61.3	11.8	41.6–82.9 (41.3)
Spring	36	57.7	12.3	28.8–85.0 (56.0)
All	146	62.1	13.8	28.8–101.4 (72.6)

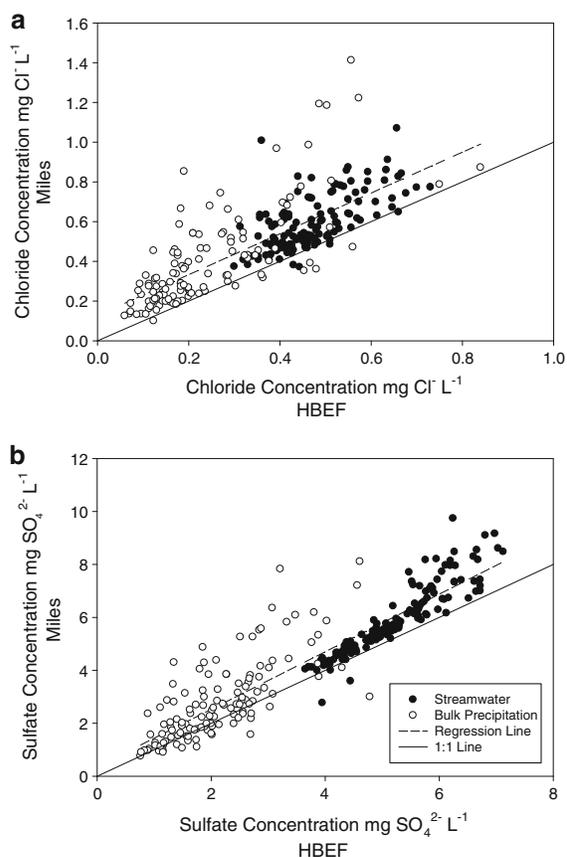
The Seasonal Kendall test was used to investigate trends overtime in W6 precipitation inputs, and streamwater outputs. This test accounts for the natural variability caused by seasonality (Helsel et al. 2006) and is robust in that it can handle missing values. The code for this program has been provided and packaged by the U.S. Geological Survey (USGS) (Helsel et al. 2006). Trends of sulfate concentrations and stable O isotopic differences in bulk deposition and streamwater sulfate in W6, and differences between watersheds and seasonality were evaluated in our study.

The values of W6 streamwater and precipitation sulfate and chloride concentration from our study were compared to the original HBEF values through a regression analysis. HBEF monthly volume-weighted streamwater and bulk precipitation chemistry data (available at <http://hubbardbrook.org>), were combined into seasonal averages in the sampling time scheme shown in Table 1.

Results and discussion

HBEF bulk precipitation and streamwater concentration

Sulfate and chloride concentrations from this study were compared to the HBEF original values (Fig. 1).

**Fig. 1** Bulk precipitation (RG11) and streamwater from W6 for the years 1968–1994 as measured for this study (Miles), and past studies (HBEF). **a** Chloride concentrations ($\text{mg Cl}^{-1} \text{L}^{-1}$) and **b** sulfate concentrations ($\text{mg SO}_4^{2-} \text{L}^{-1}$)

The seasonal averages of the original HBEF concentration data and the seasonal concentration values for this study (linear regression lines are displayed) are compared in Figs. 1a, b. The slopes and y-intercepts for each regression line are very close to 1 and 0, respectively; for the chloride and sulfate data the regression line slopes are 1.03 and 1.09, respectively. The r^2 values for chloride and sulfate regressions are 0.59, and 0.84, respectively. The consistency in these results supports that the storage of the samples had little effect on solute concentrations of Cl^{-} and SO_4^{2-} with a small increase in concentration likely due to evaporation and hence slow water vapor loss from the plastic storage containers. Our composite seasonal samples were not created from equal portions of subsamples (due to subsampling policy), therefore it was expected that our chemical measurements may

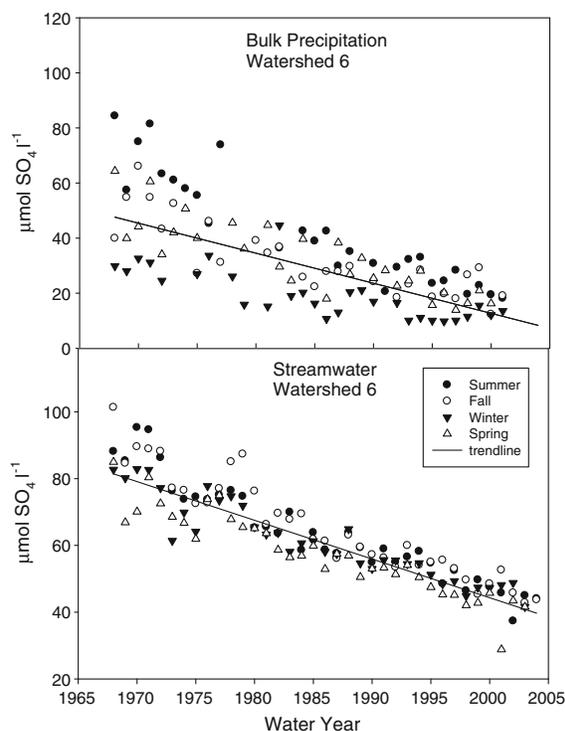


Fig. 2 Seasonal sulfate concentrations in the HBEF W6 bulk precipitation and streamwater in $\mu\text{mol SO}_4^{2-} \text{l}^{-1}$ (1968–2004). The *trend lines* were calculated using Seasonal Kendall Tests. See Table 3 for equations

not be completely comparable to earlier chemistry measurements on the original precipitation samples. Previous studies that have analyzed the $\delta^{34}\text{S}_{\text{SO}_4}$ values of the archived samples have also suggested that there were no discernable changes in concentrations associated with sample storage (Alewell et al. 1999, 2000).

The two sample paired t-test determined that W6 precipitation sulfate concentration, $[\text{SO}_4^{2-}]$, was significantly lower than streamwater sulfate concentrations ($P < 0.0001$). There also was more temporal variation in precipitation samples than streamwater samples, as is illustrated in Fig. 2. The ANOVA analysis comparing $[\text{SO}_4^{2-}]$ of W6 streamwater and precipitation found that the mean winter precipitation sulfate concentrations were the lowest ($19.5 \mu\text{mol SO}_4^{2-} \text{l}^{-1}$), and summer precipitation sulfate concentration was higher ($42.2 \mu\text{mol SO}_4^{2-} \text{l}^{-1}$) than in the other seasons (Table 1). Greater concentrations of sulfate in precipitation during summer have been reported previously for HBEF and in North America in general (Likens and Bormann 1995). In the Northeastern U.S. the demand for electricity is greater

during the warm summer season when air conditioning is widely used. About 50% of the electricity is generated from coal combustion (Energy Information Administration 2007). Therefore greater use of fossil fuels and accelerated emission and conversion of $\text{SO}_2(\text{g})$ to SO_4^{2-} during the warm summer period is the cause of the observed seasonality in sulfate concentrations in atmospheric deposition (Likens et al. 2002; Mitchell et al. 1992). There is less temporal variation in streamwater sulfate concentration compared to precipitation due to the internal cycling of S including cycling through biota and soil buffering adsorption/desorption processes, as indicated in previous studies (Alewell et al. 1999; Likens et al. 2002).

As expected, sulfate concentrations showed significant decreasing trends for both precipitation and streamwater (Fig. 2) due to decreasing S emissions during the 36 year observation period. Seasonal Kendall Trend tests of both precipitation and W6 stream sulfate concentrations support overall decreasing trends (accounting for seasonality). Precipitation values ranged from ~ 48 to $8 \mu\text{mol SO}_4^{2-} \text{l}^{-1}$, and displayed a highly significant ($P < 0.0001$) decrease of $-1.09 \mu\text{mol SO}_4^{2-} \text{l}^{-1} \text{yr}^{-1}$. Concentrations in the W6 stream ranged from ~ 81 to $40 \mu\text{mol SO}_4^{2-} \text{l}^{-1}$ with a highly significant ($P < 0.0001$) decrease of $-1.16 \mu\text{mol SO}_4^{2-} \text{l}^{-1} \text{yr}^{-1}$ (Table 2).

HBEF bulk precipitation and streamwater $\delta^{18}\text{O}$ of sulfate

The $\delta^{18}\text{O}$ values of precipitation sulfate were about 4.6‰ higher (STD = 1.8, $P < 0.0001$) than those of streamwater sulfate (Table 3). Seasonal differences in $\delta^{18}\text{O}_{\text{SO}_4}$ values (Fig. 3) using ANOVA analysis and Tukey pairwise comparisons showed that winter precipitation $\delta^{18}\text{O}_{\text{SO}_4}$ values (6.3‰) were significantly lower than all other seasons which were all greater than 8.0‰ (STD = 1.8, $P < 0.0001$). There were no seasonal differences for streamwater $\delta^{18}\text{O}_{\text{SO}_4}$ values (STD = 0.9).

Over the period from 1968 through 2004 the $\delta^{18}\text{O}_{\text{SO}_4}$ values of precipitation increased from ~ 6.5 to 9.5‰ ($P < 0.0001$) displaying less seasonal variation in the more recent years (Fig. 3; Table 2). This pattern suggests that the reduced S emissions since the 1970s resulted in changes in SO_4^{2-} sources or SO_2 oxidation mechanisms in the atmosphere. There was,

Table 2 Results from Seasonal Kendall trend tests of sulfate in HBEF precipitation (P) and streamwater (W6) seasonal samples (1968–2004)

Parameter	Type	Equation of line	τ	P -value
$[\text{SO}_4^{2-}]$ ($\mu\text{mol l}^{-1}$)	P	$y = 47.6 - 1.09 * \text{year}$	-0.740	$P < 0.0001$
$[\text{SO}_4^{2-}]$ ($\mu\text{mol l}^{-1}$)	W6	$y = 81.5 - 1.16 * \text{year}$	-0.861	$P < 0.0001$
$\delta^{18}\text{O}$ (‰)	P	$y = 6.51 + 0.08 * \text{year}$	0.570	$P < 0.0001$
$\delta^{18}\text{O}$ (‰)	W6	Not significant	-0.133	$P = 0.1421$

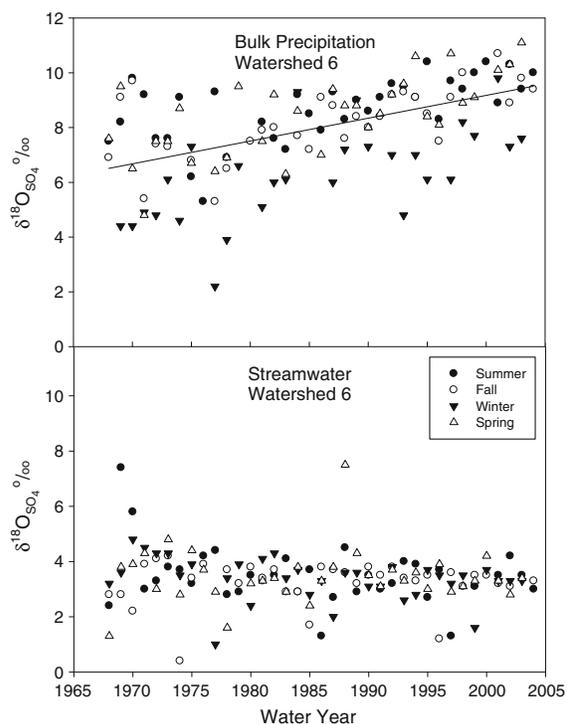
Table 3 Descriptive statistics [number of samples (n), mean, standard deviation (STD) and range of values] of $\delta^{18}\text{O}$ sulfate (%) of HBEF precipitation (RG-11) and streamwater from 1968–2004

	n	Mean	STD	Minimum–maximum (range)
Precipitation				
Summer	35	8.7	1.2	5.3–10.4 (5.1)
Fall	31	8.2	1.3	5.3–10.7 (5.4)
Winter	28	6.3	1.7	2.2–9.8 (7.6)
Spring	32	8.4	1.4	4.8–11.1 (6.3)
All	126	8.0	1.8	2.2–11.1(8.9)
Streamwater				
Summer	34	3.5	1.1	1.3–7.4 (6.1)
Fall	35	3.2	0.8	0.4–4.2 (3.8)
Winter	35	3.4	0.8	1.0–4.8 (3.8)
Spring	35	3.5	1.0	1.3–7.5 (6.2)
All	139	3.4	0.9	0.4–7.5 (7.1)

however, no significant relationship between sulfate concentrations and $\delta^{18}\text{O}_{\text{SO}_4}$ values in precipitation suggesting that the relationship between the precipitation sulfate concentrations and $\delta^{18}\text{O}_{\text{SO}_4}$ values are due to multiple factors as discussed below. Streamwater $\delta^{18}\text{O}_{\text{SO}_4}$ values exhibited little seasonal variation or overall change during the study indicating that the internal processes responsible for ecosystem sulfate cycling and the resultant $\delta^{18}\text{O}_{\text{SO}_4}$ dampened any seasonal effects associated with atmospheric deposition. The importance of internal sulfur cycling in affecting $\delta^{18}\text{O}$ values of soil and streamwater sulfate has been found in previous studies (Mayer et al. 1995; Mitchell et al. 1998) with further details provided below within the section on “Stable Oxygen Isotopes in Streamwater Sulfate”.

Precipitation sulfate formation

Precipitation sulfate consists of primary and secondary sulfates. Each of these forms of sulfate has different

**Fig. 3** Seasonal $\delta^{18}\text{O}$ (‰) of sulfate in the HBEF W6 precipitation and streamwater (1968–2004). The trend line was calculated using Seasonal Kendall Tests

modes of formation and ranges of isotopic values (Holt and Kumar 1991). Primary sulfates are formed during fossil fuel combustion in smoke stacks at very high temperatures ($\sim 450^\circ\text{C}$), and have a narrow range of $\delta^{18}\text{O}_{\text{SO}_4}$ values around $+40\text{‰}$ (Holt et al. 1982; Jamieson and Wadleigh 1999), much higher than those of secondary sulfates. Secondary sulfates are formed in the atmosphere at lower temperatures via heterogeneous and homogenous oxidation of SO_2 . The SO_2 oxidation reactions are complex and are influenced by temperature, solar radiation, and the appropriate concentrations and equilibrium constants of $\text{SO}_2(\text{g})$ and oxidants including precipitation water and air (Feichter et al. 1996). Secondary sulfates have a wide

range of $\delta^{18}\text{O}_{\text{SO}_4}$ values of about -15 to $+20\%$ (Jamieson and Wadleigh 1999).

Stable oxygen isotopes in precipitation water

Our results indicate that $\delta^{18}\text{O}_{\text{SO}_4}$ values in precipitation are lower, seasonally, in the winter and show a general trend of increasing values during the 36-year study. These seasonal and long-term annual trends are likely a function of the relative contribution of heterogeneously formed secondary sulfates versus primary sulfates (in response to decreased SO_2 emissions), as well as other factors. The stable isotopic composition of precipitation water ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$) is influenced by a number of factors including temperature, and geographic parameters that affect the rain out intensity of precipitation events including latitude, distance from the marine water source and altitude (Dansgaard 1964; Yurtsever and Gat 1981; Gat 1997). Temperature is the dominant control on $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of precipitation water. Therefore air temperature and the average $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of precipitation will be closely related and predictable (Rozanski et al. 1992; Vachon et al. 2010; Welker 2000); this temperature dependence explains seasonal variability in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of precipitation which may ultimately be reflected in $\delta^{18}\text{O}_{\text{SO}_4}$ values of precipitation sulfate.

Seasonality in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$

The stable isotopic composition of atmospheric water vapor and precipitation are quite varied, and show seasonality, typically depleted in winter and enriched in summer (Dutton et al. 2005; Welker 2000). Most researchers have examined monthly averages of long-term data (Gat and Airey 2006; Yurtsever and Gat 1981). Monthly average O isotope ratios of precipitation have been modeled and interpolated by the International Atomic Energy Agency (IAEA) Global Network “Isotopes in Precipitation” (GNIP) Program globally (using available data from 1961–1999). Month-to-month variation of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values at any location are correlated to temperature (Vachon et al. 2010). The IAEA estimate of the annual average $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ value of precipitation for the Northeast region of the U.S. ranges from -10 to -14% . The monthly average $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values for precipitation in the months

of June (summer), and December (winter) $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ are distinctly different and range from -6 to -10% , and -14 to -18% , respectively. Hence, winter and summer precipitation $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ may differ by at least 4% (IAEA 2001). It should be noted that these estimates are for the entire Northeastern region of the U.S., including coastal areas. Therefore these estimates are not directly related to our study. The predicted values of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ were calculated from the IAEA-GNIP global data set according to an algorithm developed by Bowen and Wilkinson (2002) and refined by Bowen and Revenaugh (2003) and Bowen et al. (2005) (http://wateriso.eas.purdue.edu/waterisotopes/pages/data_access/da_main.html).

The Online Isotopes in Precipitation Calculator (OIPC) was used to estimate annual and monthly values for $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ in precipitation at HBEF (latitude 43.93° , longitude -71.75° , altitude 350 m). Seasonal values estimated specifically for the HBEF, based on monthly values of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ from the online calculator and monthly average precipitation for the study period, are shown in Table 4. The overall range of mean $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ bulk precipitation values is from -5.4% in winter to -2.4% in summer, resulting in a difference of 3.0% . The mean winter $\delta^{18}\text{O}_{\text{SO}_4}$ bulk precipitation value was $+6.3\%$, and mean summer value was $+8.7\%$, resulting in a difference of 2.4% , in our study. Both $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values show similar seasonal patterns, being lowest in winter and hence suggesting that precipitation water $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ composition is affecting $\delta^{18}\text{O}_{\text{SO}_4}$ values.

Table 4 Study mean $\delta^{18}\text{O}$ values for sulfate HBEF precipitation (RG-11) during seasonal sampling for specified time periods, and estimated volume-weighted mean $\delta^{18}\text{O}$ values for precipitation based on Bowen and Wilkinson (2002), Bowen and Revenaugh (2003), and Bowen et al. (2005) (%)

Precipitation	Period	$\delta^{18}\text{O}$ mean for precipitation sulfate	$\delta^{18}\text{O}$ mean for precipitation water
Overall	1968–2004	8	−3.7
Summer		8.7	−2.4
Fall		8.2	−3.5
Winter		6.3	−5.4
Spring		8.4	−3.4

Trends in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ in precipitation as a function of temperature

Isotopic data are available online in the GNIP Water Isotope System for Data Analysis Visualization and Electronic Retrieval (WISER) as part of The IAEA Isotope Hydrology Information System (ISOHIS) Database (IAEA 2006). The closest GNIP program site to the HBEF that has a long-term record of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values in precipitation is the Ottawa, Ontario, Canada site managed by the Canadian Network for Isotopes in Precipitation (CNIP). Annual mean $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and temperature for 1970–2007 are displayed in Fig. 4a, b. As expected, there is a significant ($P = 0.004$) relationship between $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values in precipitation and temperature ($y = 0.58 \times -14.60$, $r^2 = 0.31$) (Fig. 4a). The data from the Ottawa site also show a general increasing trend in the average annual $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ average values although this relationship is not statistically significant. The relative importance of the $\delta^{18}\text{O}$ values of precipitation water in the formation of precipitation sulfates is detailed below.

Stable oxygen isotopes in precipitation sulfate

Different forms of sulfate have distinct $\delta^{18}\text{O}_{\text{SO}_4}$ ranges. Seawater-derived sulfate has a very narrow range of $\delta^{18}\text{O}_{\text{SO}_4}$ values near +9‰, and makes a small contribution at the HBEF (Alewell et al. 2000). Using chemical data and $\delta^{34}\text{S}_{\text{SO}_4}$ values, Alewell et al. (2000) found that average marine sulfate contribution to precipitation at HBEF was 3% in the summer and 6% in the winter. Therefore, marine derived sulfates influence a very small portion of precipitation sulfate and its $\delta^{18}\text{O}_{\text{SO}_4}$ value in this study.

There are few other studies that have measured the $\delta^{18}\text{O}_{\text{SO}_4}$ value of precipitation in our study region. In a study that included isotopic analysis of the snowpack at Sleepers River, Vermont it was found that the average $\delta^{18}\text{O}_{\text{SO}_4}$ value for the snowpack was ~12.0‰ in 2000 (Shanley et al. 2005). This value is similar to the higher $\delta^{18}\text{O}_{\text{SO}_4}$ values (~11‰) found at the HBEF during the latter period of our study (2000–2004).

The significant positive trend in $\delta^{18}\text{O}_{\text{SO}_4}$ over time shows that precipitation sulfates have become progressively enriched in ^{18}O during the 36 year period

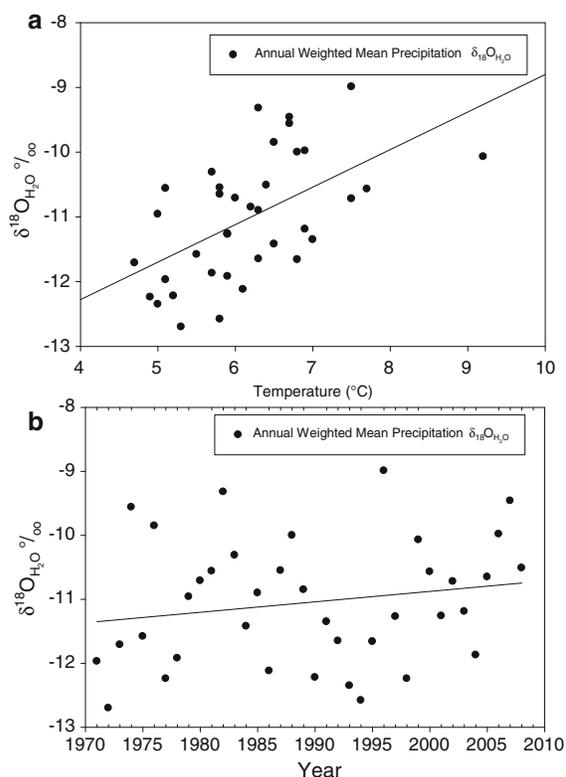


Fig. 4 Annual weighted mean $\delta^{18}\text{O}$ (‰) of precipitation water at Ottawa, Ontario, Canada GNIP site (1970–2007). **a** Annual $\delta^{18}\text{O}$ versus average annual temperature. **b** Annual $\delta^{18}\text{O}$ over time. Standard regression *trend lines* shown

(Fig. 3). The importance of temperature with respect to the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of precipitation has been described above and may explain at least a portion of the long-term trend of enrichment of ^{18}O in precipitation sulfates. This increase in $\delta^{18}\text{O}_{\text{SO}_4}$ values of precipitation is partially consistent with increases in the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ due to increased temperature (Rozanski et al. 1992) in the Northeast United States (Mitchell and Jones 2005) and more specifically at the HBEF (Likens 2011; Vadeboncoeur et al. 2006). The incorporation of O from precipitation water during the heterogeneous formation of secondary sulfates partially contributes to precipitation sulfate $\delta^{18}\text{O}_{\text{SO}_4}$ values. Precipitation $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ is depleted in ^{18}O compared to atmospheric oxygen $\delta^{18}\text{O}$ (+23.5‰) resulting in lower $\delta^{18}\text{O}_{\text{SO}_4}$ values compared to sulfate formed using atmospheric O_2 . The long-term trend in precipitation sulfate $\delta^{18}\text{O}_{\text{SO}_4}$ values may be in part a

reflection of changes in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values in precipitation water, as discussed in further detail below.

Precipitation sulfate at the HBEF is a mixture of sulfates; the exact proportions of primary sulfates, and types of secondary sulfates in bulk precipitation sulfate are currently unknown. A contributing factor for the observed increasing trend of $\delta^{18}\text{O}_{\text{SO}_4}$ in precipitation in our study is linked, in part, to temperature effects. Heterogeneous SO_2 oxidation reactions dominate at lower temperatures while homogeneous oxidation reactions are more important at higher temperatures. During the cold winter season when heterogeneous oxidation is more prevalent, $\delta^{18}\text{O}_{\text{SO}_4}$ values of precipitation sulfate are lower ($\sim 2.4\text{‰}$) than during summer when temperatures are higher and homogeneous reactions are more important.

During heterogeneous SO_2 oxidation, precipitation water contributes 75% of the O in the newly formed sulfate (Jamieson and Wadleigh 1999). The 4‰ seasonal difference in precipitation $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of IAEA-GNIP values, and the 3‰ seasonal difference from OIPC site-specific calculated values, between winter and summer are likely reflected in the 2.4‰ seasonal difference in precipitation sulfate ($\delta^{18}\text{O}_{\text{SO}_4}$) at the HBEF. Temperature dependent heterogeneous oxidation reactions are largely responsible for observed patterns of precipitation sulfate ($\delta^{18}\text{O}_{\text{SO}_4}$) at the HBEF. These seasonal differences in $\delta^{18}\text{O}_{\text{SO}_4}$ values may also be magnified by greater S emissions during the summer.

Stable oxygen isotopes in streamwater sulfate

The distinct difference between the $\delta^{18}\text{O}$ values of precipitation and streamwater sulfate strongly support previous work that has suggested that atmospheric inputs of S to watersheds undergo substantial cycling and transformations within the soil before exiting into drainage waters. The small temporal variation in the $\delta^{18}\text{O}_{\text{SO}_4}$ values of streamwater sulfate indicates that those processes affecting the oxygen isotope ratios of stream water sulfate are relatively consistent over time. At the HBEF, and other sites there is a large organic S pool (i.e., carbon-bonded S and ester sulfate) and a smaller inorganic sulfate pool (i.e., adsorbed sulfate) associated with soil S transformations. The importance of the biologic cycling of S within the

large organic S pool is consistent with other studies that have suggested a 9-year residence time of S in HBEF soils (Likens et al. 2002) that would dampen any temporal trends in the $\delta^{18}\text{O}_{\text{SO}_4}$ values of streamwater. During the mineralization of ester sulfates little O isotope fractionation and exchange occurs because this is a hydrolysis reaction. In contrast, during C-bonded S mineralization, water and gaseous O_2 in the soil can both contribute O during the formation of sulfate. This typically results in low $\delta^{18}\text{O}$ values of soil sulfates (Bailey et al. 2004; Mayer et al. 1995; Shanley et al. 2005) since it has been estimated that $\sim 66\%$ of the O in mineralized soil sulfate is derived from soil water (Krouse and Mayer 2000; Novák et al. 2000). The weathering and oxidation of sulfide minerals might also affect soil $\delta^{18}\text{O}_{\text{SO}_4}$ values but this source of sulfate at the HBEF is relatively small compared to atmospheric S inputs and mineralization of organic S compounds in the soils (Bailey et al. 2004; Likens et al. 2002).

Conclusions

There has been a significant increase in the $\delta^{18}\text{O}_{\text{SO}_4}$ values of precipitation sulfate at HBEF from 1968 to 2004. This increase suggests that there has been a change in secondary sulfate formation, either in the proportion of heterogeneous to homogeneous oxidation or in the $\delta^{18}\text{O}$ values of oxidants (i.e., precipitation water), or both. A relationship between temperature and the heterogeneous formation of sulfate and $\delta^{18}\text{O}_{\text{SO}_4}$ values is apparent. This relationship is consistent with long-term changes in air temperature and precipitation $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values over mid- and high-latitude regions from 1960 to 1990, though it explains only a portion of the positive trend over time. The seasonal variation in precipitation $\delta^{18}\text{O}_{\text{SO}_4}$ values is consistent with a strong temperature relationship as affected by the contribution of the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of precipitation water, and the higher proportion of heterogeneous $\text{SO}_2(\text{g})$ oxidation during the cold winter period.

The lower $\delta^{18}\text{O}_{\text{SO}_4}$ in streamwater compared to precipitation suggests the importance of internal cycling of S especially through the large organic S pool in the HBEF ecosystem. The very low variation

in $\delta^{18}\text{O}_{\text{SO}_4}$ values in streamwater is consistent with other studies that have suggested the importance of this large organic soil S pool combined with the smaller inorganic sulfate pool and adsorption and desorption processes in affecting both the chemical release and long-term isotopic composition of sulfate in streamwater.

Acknowledgments This research was funded by grants from the National Science Foundation (NSF) as part of the Hubbard Brook Ecosystem Study, including the LTER and LTREB programs. It would not have been possible without the long-term, archived samples, and the time and effort put forth by many researchers within the Hubbard Brook Ecosystem Study. The study and dedication of the SUNY-ESF Biogeochemistry Laboratory and the University of Calgary Isotope Science Laboratory is gratefully acknowledged.

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