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

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ARTICLE INFO

Available online 23 May 2008

Keywords:
Isotopic tracers
Sulfate
S isotopes
Vermont
Sleepers River

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 δ^{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, δ^{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 (δ^{34}S ~6–14‰); (2) contributions of pedogenic sulfate (δ^{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.

Published by Elsevier B.V.

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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0048-9697/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.scitotenv.2008.03.020

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

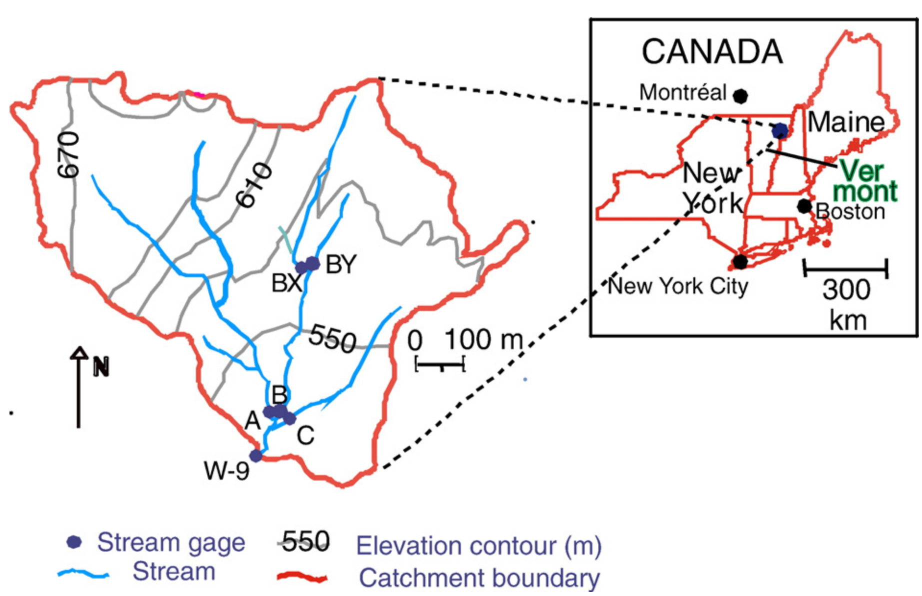

Fig. 1 – Map of Sleepers River W-9 catchment.