



## Isotopic assessment of $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ mobility during winter in two adjacent watersheds in the Adirondack Mountains, New York

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[1] Biogeochemical cycling of N and S was examined at two watersheds in the Adirondack Mountains, New York, to better understand the retention and loss of these elements during winter and spring snowmelt. We analyzed stable isotope compositions of  $\text{NO}_3^-$  ( $\delta^{15}\text{N}-\text{NO}_3^-$ ,  $\delta^{18}\text{O}-\text{NO}_3^-$ ) and  $\text{SO}_4^{2-}$  ( $\delta^{34}\text{S}-\text{SO}_4^{2-}$ ,  $\delta^{18}\text{O}-\text{SO}_4^{2-}$ ), along with concentrations and fluxes of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , in precipitation, throughfall, snowpack, snowmelt, soil water, groundwater, and stream water. Isotopic results showed no evidence of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  transformations in the forest canopy and snowpack; however, markedly decreased  $\delta^{18}\text{O}$  values of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in forest floor water suggest that microbial processing occurred in organic soil horizons. Similarly low  $\delta^{18}\text{O}$  values of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were observed in forest floor and mineral soil leachates, groundwater, and streams. Over the winter observation period, most of the  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in stream water was from a watershed-derived source, whereas atmospheric contributions were relatively minor. Despite differences in soil water  $\text{NO}_3^-$  concentrations between watersheds, the isotopic composition of  $\text{NO}_3^-$  ( $\delta^{15}\text{N}-\text{NO}_3^-$ ,  $\delta^{18}\text{O}-\text{NO}_3^-$ ) was similar, and indicated that in both watersheds most of the  $\text{NO}_3^-$  was produced by nitrification in the forest soils. Although there was likely some contribution of  $\text{SO}_4^{2-}$  from microbial oxidation of carbon-bonded sulfur, most of the stream water  $\text{SO}_4^{2-}$  appeared to be derived from weathering of S-containing bedrock or parent material. The decreased  $\delta^{18}\text{O}$  values of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in upper soil horizons indicate that atmospheric deposition of N and S was not directly linked with stream water losses, even during winter and spring snowmelt.

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### 1. Introduction

[2] Despite decades of research on the effects of N and S deposition on forest ecosystems, there are still aspects of the cycles of these elements that are not well understood. One particular gap is our lack of understanding of processes that regulate N and S retention and loss during winter. From late fall through early spring, biotic assimilation, especially vegetation uptake, is reduced and groundwater recharge is maximized. Consequently, the greatest losses of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , which are the dominant forms of N and S in stream water, occur during this period [e.g., *Likens and Bormann*, 1995]. High stream water concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  have been linked to episodic acidification during snowmelt and rain-on-snow events [*Schaefer et al.*, 1990; *MacLean et al.*, 1995], which may be toxic to aquatic biota owing to

short-term declines in pH and increases in inorganic Al [e.g., *Baker et al.*, 1996]. Although episodic acidification can occur throughout the year in seasonally snow-covered watersheds of northeastern North America, most severe acidification often occurs during spring snowmelt [*Wigington et al.*, 1996].

[3] Stable isotope compositions of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  have provided valuable information on the sources and transformations of these anions in forest ecosystems and their surface waters. Distinct stable isotopic values can be used as tracers to establish the origin of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in ecosystem compartments. A dual isotopic approach ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  and/or  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$ ) often provides more information than N or S isotope analyses alone [e.g., *Böttcher et al.*, 1990; *Durka et al.*, 1994; *Mayer et al.*, 1995; *Burns and Kendall*, 2002; *Pardo et al.*, 2004]. For  $\text{NO}_3^-$ ,  $\delta^{15}\text{N}$  has been used in urban and agricultural ecosystems to determine whether  $\text{NO}_3^-$  in drainage waters is from sources such as sewage, manure, or fertilizers [e.g., *Hübner*, 1986; *Macko and Ostrom*, 1994; *Böhlke and Denver*, 1995; *Fogg et al.*, 1998; *Kendall*, 1998; *Mayer et al.*, 2002]. However, in relatively undisturbed forested ecosystems,  $\delta^{15}\text{N}-\text{NO}_3^-$  values of various sources often are indistinct, thereby limiting the usefulness of N isotope ratios as a sole tracer for  $\text{NO}_3^-$ . The oxygen (O) isotope ratio of  $\text{NO}_3^-$  ( $\delta^{18}\text{O}$ ) often provides additional information that cannot be ascertained from  $\delta^{15}\text{N}$

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values alone. In forested watersheds, the two main sources of NO<sub>3</sub><sup>-</sup> in surface water are atmospheric deposition and microbial nitrification [Kendall, 1998]. Atmospheric δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> values in the United States range from +63 to +94‰ [Elliott et al., 2005], whereas δ<sup>18</sup>O of NO<sub>3</sub><sup>-</sup> nitrified by soil microbial communities is substantially lower (-10 to +10‰ [Kendall, 1998]). Since the O isotope ratios of these NO<sub>3</sub><sup>-</sup> sources are unique, it is possible to assess how much of the NO<sub>3</sub><sup>-</sup> in stream water is from atmospheric NO<sub>3</sub><sup>-</sup> versus how much is produced by nitrification within the watershed [Durka et al., 1994; Kendall, 1998].

[4] It is also possible to identify SO<sub>4</sub><sup>2-</sup> sources in forest ecosystems by analyzing both δ<sup>34</sup>S-SO<sub>4</sub><sup>2-</sup> and δ<sup>18</sup>O-SO<sub>4</sub><sup>2-</sup> values. In the study region there are no geological sources of NO<sub>3</sub><sup>-</sup>; however, there are geological sources of SO<sub>4</sub><sup>2-</sup>. SO<sub>4</sub><sup>2-</sup> can be derived from the following major sources: atmospheric deposition, oxidation of soil organic S, oxidation of sulfides precipitated under anoxic conditions, and weathering of S-containing minerals. The range in δ<sup>34</sup>S-SO<sub>4</sub><sup>2-</sup> values produced by the oxidation of sulfides and other S-containing minerals is large (<-10 to >+20‰ [Nielsen et al., 1991]) compared to the typical range in atmospheric deposition (+3 to +7‰ in eastern North America [Wadleigh et al., 1996; Alewell et al., 2000; Schiff et al., 2005]) and that produced by oxidation of carbon-bonded sulfur (+1 to +5‰ [Mayer et al., 1995]). If the δ<sup>34</sup>S-SO<sub>4</sub><sup>2-</sup> values of SO<sub>4</sub><sup>2-</sup> derived from S mineral weathering are different from those of precipitation and microbially produced SO<sub>4</sub><sup>2-</sup> at a given study site, they can provide clues about stream water SO<sub>4</sub><sup>2-</sup> sources [Mitchell et al., 1998; Krouse and Mayer, 2000; Bailey et al., 2004].

[5] Even though the ranges of δ<sup>34</sup>S-SO<sub>4</sub><sup>2-</sup> values in precipitation and microbially produced SO<sub>4</sub><sup>2-</sup> overlap, the ranges of δ<sup>18</sup>O-SO<sub>4</sub><sup>2-</sup> values of these two sources are typically distinct. δ<sup>18</sup>O-SO<sub>4</sub><sup>2-</sup> values in atmospheric deposition range from +7 to +17‰ in temperate regions [Krouse and Mayer, 2000]. Oxidation of carbon-bonded S within soil produces comparatively low δ<sup>18</sup>O-SO<sub>4</sub><sup>2-</sup> values (-3 to +7‰) because soil water with negative δ<sup>18</sup>O-H<sub>2</sub>O values is incorporated into the newly formed SO<sub>4</sub><sup>2-</sup> [Mayer et al., 1995]. Similarly, SO<sub>4</sub><sup>2-</sup> produced by the oxidation of sulfide minerals has δ<sup>18</sup>O-SO<sub>4</sub><sup>2-</sup> values that are low (-10 to +4‰ [Krouse and Mayer, 2000]). These differences in δ<sup>18</sup>O values make it possible to distinguish between atmospheric (i.e., direct precipitation, snowmelt) and watershed-derived (i.e., microbial oxidation of carbon-bonded S, re-oxidation of soil sulfides, weathering of S-containing minerals) sources of SO<sub>4</sub><sup>2-</sup>.

[6] There have been relatively few studies that have used the natural abundance of N, S and O isotopes in NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> to examine N and S cycling during winter. Much of our knowledge of winter S cycling in forest ecosystems is based on tracer experiments, whereby enriched <sup>34</sup>S-SO<sub>4</sub><sup>2-</sup> or the radioactive isotope <sup>35</sup>S-SO<sub>4</sub><sup>2-</sup> is applied to the snowpack [Houle et al., 2004; Campbell, 2006]. These studies have shown that much of the SO<sub>4</sub><sup>2-</sup> deposited in snow during winter is retained in organic soil horizons. However, the retention mechanism is unclear. On the basis of reported δ<sup>18</sup>O-SO<sub>4</sub><sup>2-</sup> values in stream water, only a small fraction of atmospheric SO<sub>4</sub><sup>2-</sup> enters streams unaltered, and the large remainder has undergone at least one immobilization and remineralization cycle in the biosphere or pedosphere [e.g.,

Shanley et al., 2005]. Even during peak snowmelt, watershed-derived SO<sub>4</sub><sup>2-</sup> is typically dominant in stream water [Shanley et al., 2005]. Analysis of cosmogenic <sup>35</sup>S has shown that much of the S in stream water SO<sub>4</sub><sup>2-</sup> during snowmelt is several months to years old, suggesting that SO<sub>4</sub><sup>2-</sup> is stored in soil and/or groundwater before it is transported to streams by snowmelt water [Shanley et al., 2005].

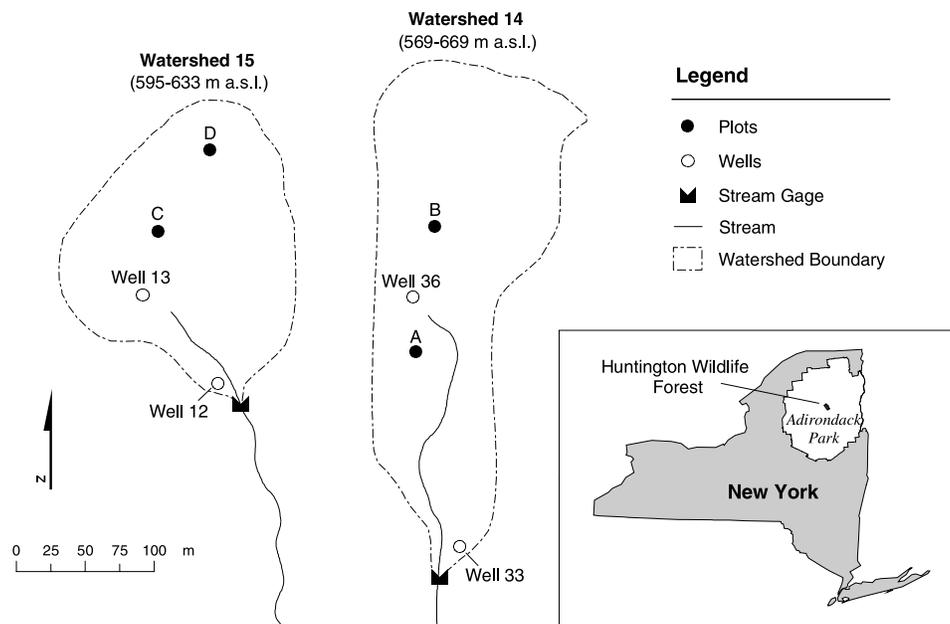
[7] Most of the NO<sub>3</sub><sup>-</sup> in stream water of forested catchments is from nitrification [Kendall et al., 1996; Spoelstra et al., 2001; Williard et al., 2001; Burns and Kendall, 2002; Campbell et al., 2002; Sickman et al., 2003; Ohte et al., 2004; Pardo et al., 2004; Piatek et al., 2005], although the proportion of stream water NO<sub>3</sub><sup>-</sup> derived from the atmosphere (i.e., snow) can exceed microbial contributions during some snowmelt events [Burns and Kendall, 2002; Ohte et al., 2004]. Since nitrification rates are relatively low throughout the winter, a significant portion of the NO<sub>3</sub><sup>-</sup> in stream water during snowmelt may be generated during the previous summer or fall. There is also evidence that sub-nival nitrification may be an important source of NO<sub>3</sub><sup>-</sup> during winter [Rascher et al., 1987]. The lack of water movement through soils when precipitation falls as snow may allow NO<sub>3</sub><sup>-</sup> to accumulate and then be released during spring snowmelt.

[8] We examined two small watersheds in the Adirondack Mountains of New York that receive rates of acidic deposition that are considered high for North America (total N deposition = 10.1 kg N ha<sup>-1</sup> yr<sup>-1</sup>, total S deposition = 6.3 kg S ha<sup>-1</sup> yr<sup>-1</sup> [Park et al., 2003]). The watersheds are in close proximity and have similar physiographical characteristics, yet both have significantly different concentrations of stream water NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. The principle objectives of this study were to: (1) use natural abundances of stable isotopes of S, N, and O to better understand the retention and cycling of N and S in forest ecosystems during winter; (2) determine if differences in soil chemistry between watersheds contributed to differences in the concentrations, fluxes and isotopic composition of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in stream water; and (3) identify sources of stream water NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> during winter and spring snowmelt.

## 2. Methods

### 2.1. Study Site and Sampling Design

[9] The study was conducted at the Huntington Forest (44°0'14"N, 74°14'48"W) near the town of Newcomb in the Adirondack Park, New York (Figure 1). We monitored two small subwatersheds (WS14 is 3.5 ha and WS15 is 2.5 ha) within the 135 ha Archer Creek watershed. The Archer Creek watershed drains into Arbutus Lake and has been the site of several studies that have examined N and S biogeochemical cycling during winter [Mitchell et al., 1996a; Park et al., 2003, 2005; Piatek et al., 2005]. The regional climate is cool, humid and continental. Average maximum daily air temperatures from 1941–2004 ranged from -4°C in January to 25°C in July at the Huntington Forest (Adirondack Ecological Center - SUNY-ESF, unpublished data, 2005). Total precipitation averages 1035 mm annually with a mean monthly range of 76 mm in January to 96 mm in November. Continuous snowcover is present throughout the winter and lasts 131 days, on average. Maximum depth of snow on the



**Figure 1.** Site map showing the location of stream gages, plots, and wells in WS14 and WS15 in the Archer Creek Watershed, Huntington Wildlife Forest, New York.

ground averaged 779 mm over the long-term record and typically occurs during February. The forest vegetation is northern hardwood, predominantly comprised of sugar maple (*Acer saccharum*), American beech (*Fagus grandifolia*), and white ash (*Fraxinus americana*). Eastern white pine (*Pinus strobus*), American basswood (*Tilia americana*), eastern hophornbeam (*Ostrya virginiana*), and yellow birch (*Betula alleghaniensis*) are associated in varying mixtures. Soils are spodosols, primarily of the Becket-Mundal series (coarse-loamy, mixed, frigid, Typic Haplorthods). The bedrock at the Huntington Forest is broadly classified as paragneiss and schist; however, the regional geology is complex, consisting of a number of structurally deformed metasedimentary and igneous rocks [de Waard and Walton, 1967].

[10] The two watersheds (WS14 and WS15) were selected for this research because they have markedly different biogeochemical characteristics despite similar physiographical features, such as area, elevation, slope, and aspect (Table 1). Factors that contribute to differences in nutrient cycling between watersheds have been evaluated by Christopher *et al.* [2006]. WS14 has significantly higher elemental and extractable soil calcium (Ca<sup>2+</sup>), extractable NO<sub>3</sub><sup>-</sup>, and pH than WS15. WS14 also has a greater basal area of base-rich indicator tree species (i.e., sugar maple, American basswood, eastern hophornbeam) and fewer base-poor species (i.e., American beech, eastern white pine). These differences in soil and vegetation are manifested in stream water chemistry, most notably, significantly higher pH and higher concentrations of NO<sub>3</sub><sup>-</sup> and Ca<sup>2+</sup> in WS14.

## 2.2. Instrumentation and Sample Collection

[11] Two study plots were established in each of the two watersheds (Figure 1). Each plot was divided into a grid of 16, 4-m × 4-m cells. Equipment for sampling throughfall, snowpack, snowmelt, and soil water for chemistry and

isotopic analyses was allocated randomly to individual cells in each watershed. Bulk precipitation was collected at two locations in a clearing at the Adirondack Ecological Center (AEC), 3.8 km from the study watersheds. All samples,

**Table 1.** Characteristics of WS14 and WS15<sup>a</sup>

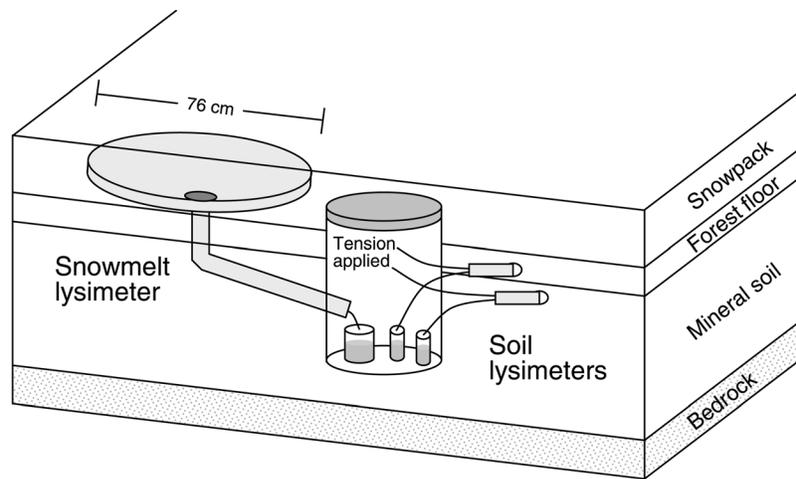
Characteristics	WS14 (More Base-Rich)	WS15 (Less Base-Rich)
Physiographical features		
Area, ha	3.5	2.5
Elevation range, m	570–670	590–630
Mean Slope, deg	16	10
Mean Aspect, <sup>b</sup> deg	200	168
Tree species, m <sup>2</sup> ha <sup>-1</sup> basal area		
<i>Acer saccharum</i> <sup>c</sup>	18.5	11.1
<i>Fagus grandifolia</i>	3.5	6.4
<i>Fraxinus americana</i>	5.3	8.8
<i>Tilia americana</i> <sup>c</sup>	6.5	0.1
<i>Pinus strobus</i>	1.2	7.9
<i>Ostrya virginiana</i> <sup>c</sup>	1.3	0.0
Forest floor		
pH (in CaCl <sub>2</sub> )	5.4	4.1
Elemental Ca, g kg <sup>-1</sup>	15.2	3.4
Extractable NO <sub>3</sub> <sup>-</sup> -N, μg g <sup>-1</sup>	2.0	0.2
Mineral soil		
pH (in CaCl <sub>2</sub> )	4.6	3.6
Elemental Ca, g kg <sup>-1</sup>	54.5	23.1
Extractable Ca <sup>2+</sup> , g kg <sup>-1</sup>	2.6	0.3
Extractable NO <sub>3</sub> <sup>-</sup> -N, μg g <sup>-1</sup>	2.4	1.0
Stream water chemistry		
pH	7.3	6.7
SO <sub>4</sub> <sup>2-</sup> -S, <sup>d</sup> mg L <sup>-1</sup>	3.2	3.3
NO <sub>3</sub> <sup>-</sup> -N, <sup>d</sup> mg L <sup>-1</sup>	1.0	0.4
Ca <sup>2+</sup> , <sup>d</sup> mg L <sup>-1</sup>	17.1	8.6

<sup>a</sup>Christopher *et al.* [2006].

<sup>b</sup>Expressed in positive degrees from 0 to 360, measured clockwise from the north.

<sup>c</sup>Base-rich indicator tree species.

<sup>d</sup>Annual volume-weighted mean.



**Figure 2.** Schematic diagram of snowmelt lysimeter and soil water lysimeters.

except soil water and groundwater samples were collected biweekly during two winters (2002–2003 and 2003–2004); soil water and well samples were collected only during the second winter. Chemical analyses were conducted on all samples, and isotopic analyses were conducted on samples collected at 2- to 4-week intervals during the second winter.

[12] Bulk precipitation was sampled as both rain and snowfall. Rain was collected with polyethylene funnels that drained into covered sample bottles. The 15-cm-diameter funnels were mounted 1.5 m above the ground surface and contained acid-washed, polyester fiber to prevent airborne particulates from contaminating the samples. Snowfall was collected with 15-cm-diameter polyvinyl chloride (PVC) tubes lined with polyethylene bags. Since isotopic analyses required a large sample volume, 75-L open-top containers were collocated with the precipitation collectors for chemical analyses. Throughfall collectors were identical to bulk precipitation collectors, but were placed underneath the forest canopy at three randomly selected locations in each of the plots in WS14 and WS15. Throughfall fluxes were computed by multiplying the measured sample volume by the concentration for each collection period.

[13] Snowpack samples were obtained by vertically coring through the entire snowpack using a 10-cm-diameter, beveled PVC tube. Multiple cores (a minimum of three) were composited from both plots into a single sample for each watershed. Snow depth and snow water equivalent (SWE) also were measured biweekly at one snow course established in one plot (A and D) of each watershed. Ten snow cores were taken at 1-m intervals along a transect using an Adirondack Snow Tube. At each point, snow depth was recorded and the core was weighed to measure SWE. As part of long-term, routine monitoring, snow depth was also measured by staff at the AEC every morning with a stationary snow stake. Soil frost depth was measured biweekly in each plot in WS14 and WS15 with soil frost gages [Ricard *et al.*, 1976]. Soil temperature was measured at two depths (10 and 40 cm) at 15-min intervals in each plot.

[14] Snowmelt samples were collected with three snowmelt lysimeters in each plot in both watersheds. Polyethyl-

ene pans (76 cm diameter  $\times$  7.6 cm height) placed on the surface of the forest floor (Figure 2) collected melt water, which drained by gravity through a PVC pipe into sample jugs housed in containers buried in the ground. These containers were insulated to prevent sample freezing. An additional snowmelt lysimeter was installed in each plot to measure snowmelt volume to calculate chemical fluxes. Snowmelt volume lysimeters were identical to the lysimeters used to collect samples for chemical and isotopic analyses, but they drained into tipping buckets that were connected to data loggers to record snowmelt volume at 15-min intervals.

[15] Soil water was collected with porous cup, tension lysimeters (5 cm diameter) installed horizontally in pairs at 10-cm (forest floor) and 40-cm depths (mineral soil). Soil lysimeters were connected by tubing to sample bottles housed in the containers used for snowmelt lysimeter sampling (Figure 2). Soil water lysimeters were installed during fall 2002. Sample collection began 1 year later, to ensure that there was adequate time for the lysimeters to equilibrate following installation disturbance. Soil water samples were collected at 2-week intervals and tension was applied (30 kPa) the day before the samples were collected. For isotopic analyses, all the soil water samples from each watershed were composited into a single sample.

[16] To calculate fluxes of ions through soil, vertical soil water movement was modeled using the BROOK90 hydrologic model [Federer *et al.*, 2003]. Model parameters were modified for this site, in keeping with Mitchell *et al.* [1996b]. The model was run on a daily time-step using the following meteorological input data: air temperature (measured at plots A and D), relative humidity (measured at D only), wind speed, solar radiation, and precipitation (measured at the AEC). Soil water fluxes of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were obtained by multiplying the biweekly concentration data by the modeled daily water flux.

[17] Groundwater samples were collected from wells constructed of 5-cm diameter PVC piping coupled to sections from 30 to 38 cm long with screened inlet ports [Mitchell *et al.*, 2006]. Two wells were installed in each watershed (wells 12 and 13 in WS15; wells 33 and 36 in

WS14; Figure 1) to obtain groundwater for chemical analyses. Groundwater samples for isotopic analyses were collected only from wells 13 and 36. Samples were hand-pumped into collection bottles.

[18] Stream water samples for chemical and isotopic analyses were collected at the outlets of WS14 and WS15 (Figure 1), just upstream of the gaging station. Stream stage height also was measured at the watershed outlets at 4-hr intervals using capacitance rods housed in stilling wells. Stage height was related to discharge with a rating curve based on data collected over a range of stream stages [see *Christopher*, 2004]. Daily streamflow (millimeters) was computed by summing the 4-hour streamflow measurements. Nutrient outputs were obtained by multiplying the biweekly concentrations (mg L<sup>-1</sup>) by the measured daily water fluxes (L ha<sup>-1</sup> d<sup>-1</sup>) surrounding each chemical sample.

### 2.3. Chemical and Isotopic Analyses

[19] Samples were transported on ice to the laboratory at the USDA Forest Service, Durham, New Hampshire, within 2 days of collection. Upon returning to the laboratory, snow samples were melted at room temperature. All samples were stored in the dark at 2°C until analysis. Within 4 days of collection, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> concentrations were measured using ion chromatography (Metrohm 761) with an in-line 0.15- $\mu$ m cellulose membrane filter. Samples for isotopic analyses were filtered through 0.45- $\mu$ m high-capacity filter capsules. Samples were acidified with dilute HCl to pH 3 to remove HCO<sub>3</sub><sup>-</sup>, which competes with NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> on anion exchange resins. On the basis of concentration data, the appropriate amount of sample water was passed through chromatography columns (Bio-Rad, AG 1X-8 resin) to retain the amount of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> necessary for isotopic analyses (1 mg NO<sub>3</sub><sup>-</sup>-N and 1 mg SO<sub>4</sub><sup>2-</sup>-S). Resin columns were sent by courier to the Isotope Science Laboratory at the University of Calgary, Alberta, Canada.

[20] The procedures for isotopic determination of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> are based on methods described by *Silva et al.* [2000], *Giesemann et al.* [1994], and *Kornexl et al.* [1999]. SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> were eluted from each column using 15 mL 3 M HCl. For SO<sub>4</sub><sup>2-</sup> isotopic analyses, 1 mL of 0.2 M BaCl<sub>2</sub> solution was added to the eluant to precipitate SO<sub>4</sub><sup>2-</sup> as BaSO<sub>4</sub>. The precipitate was recovered by filtration through a 0.45- $\mu$ m membrane filter and air-dried. BaSO<sub>4</sub>-S was converted to SO<sub>2</sub> by high temperature reaction in an elemental analyzer and <sup>34</sup>S/<sup>32</sup>S ratios were determined using an isotope ratio mass spectrometer in continuous flow mode (CF-IRMS). For O isotopic analyses of SO<sub>4</sub><sup>2-</sup>, BaSO<sub>4</sub>-O was converted to CO at 1450°C in a pyrolysis reactor, and <sup>18</sup>O/<sup>16</sup>O ratios of the gas were measured by CF-IRMS.

[21] To isolate NO<sub>3</sub><sup>-</sup>, excess Ba<sup>2+</sup> was removed from the remaining eluant using a cation exchange column. The eluant then was neutralized with Ag<sub>2</sub>O, creating an AgCl precipitate that was removed by filtration. The solution, which contained dissolved Ag<sup>+</sup> and NO<sub>3</sub><sup>-</sup>, was freeze-dried to form pure AgNO<sub>3</sub>. The AgNO<sub>3</sub> was converted to N<sub>2</sub> in an elemental analyzer and <sup>15</sup>N/<sup>14</sup>N ratios were determined using CF-IRMS. For O isotopic analyses of NO<sub>3</sub><sup>-</sup>, AgNO<sub>3</sub>-O was converted to CO at 1350°C in a pyrolysis reactor, and <sup>18</sup>O/<sup>16</sup>O ratios of the gas were measured by CF-IRMS.

[22] N, S and O isotope ratios are expressed in the internationally accepted delta notation in per mil (‰),

$$\delta(\text{‰}) = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 10^3, \quad (1)$$

where  $R$  is the <sup>34</sup>S/<sup>32</sup>S or <sup>18</sup>O/<sup>16</sup>O ratio of SO<sub>4</sub><sup>2-</sup>, or <sup>15</sup>N/<sup>14</sup>N or <sup>18</sup>O/<sup>16</sup>O ratio of NO<sub>3</sub><sup>-</sup> of a sample or standard. The internationally accepted standards are: Vienna-Canyon Diablo Troilite (V-CDT) for S isotopes, AIR for N isotopes, and Vienna Standard Mean Ocean Water (V-SMOW) for O isotopes. For calibrating N and O isotope analyses on NO<sub>3</sub><sup>-</sup>, reference materials IAEA N1 ( $\delta^{15}\text{N} = 0.43\text{‰}$ ), N2 ( $\delta^{15}\text{N} = 20.3\text{‰}$ ), NO3 ( $\delta^{15}\text{N} = 4.7\text{‰}$ ,  $\delta^{18}\text{O} = 25.6\text{‰}$ ), USGS 23 ( $\delta^{15}\text{N} = 180\text{‰}$ ), USGS 34 ( $\delta^{18}\text{O} = -27.9\text{‰}$ ) and USGS 35 ( $\delta^{18}\text{O} = 57.5\text{‰}$ ) were used. Reference materials utilized for S and O isotope analyses on SO<sub>4</sub><sup>2-</sup> were NBS 127 ( $\delta^{34}\text{S} = 20.3\text{‰}$ ,  $\delta^{18}\text{O} = 9.3\text{‰}$ ), IAEA S05 ( $\delta^{34}\text{S} = 0.5\text{‰}$ ) and IAEA SO6 ( $\delta^{34}\text{S} = -34.1\text{‰}$ ). The overall analytical precision including sample pretreatment, gas preparation, and mass spectrometric analyses was  $\pm 0.5\text{‰}$  for  $\delta^{34}\text{S}$ ,  $\delta^{15}\text{N}$ , and  $\delta^{18}\text{O}$  measurements.

[23] Statistical analyses were performed using a one-way analysis of variance (ANOVA). Where significant variations existed, pairwise comparisons for post-hoc determination of significant differences between means were made using a Tukey's Honestly Significant Difference (HSD) test. Since the watersheds were unreplicated, statistical comparisons of chemical concentrations in stream water between watersheds were made using a paired t-test. Within our study, all statistical comparisons were assessed at  $\alpha = 0.05$ .

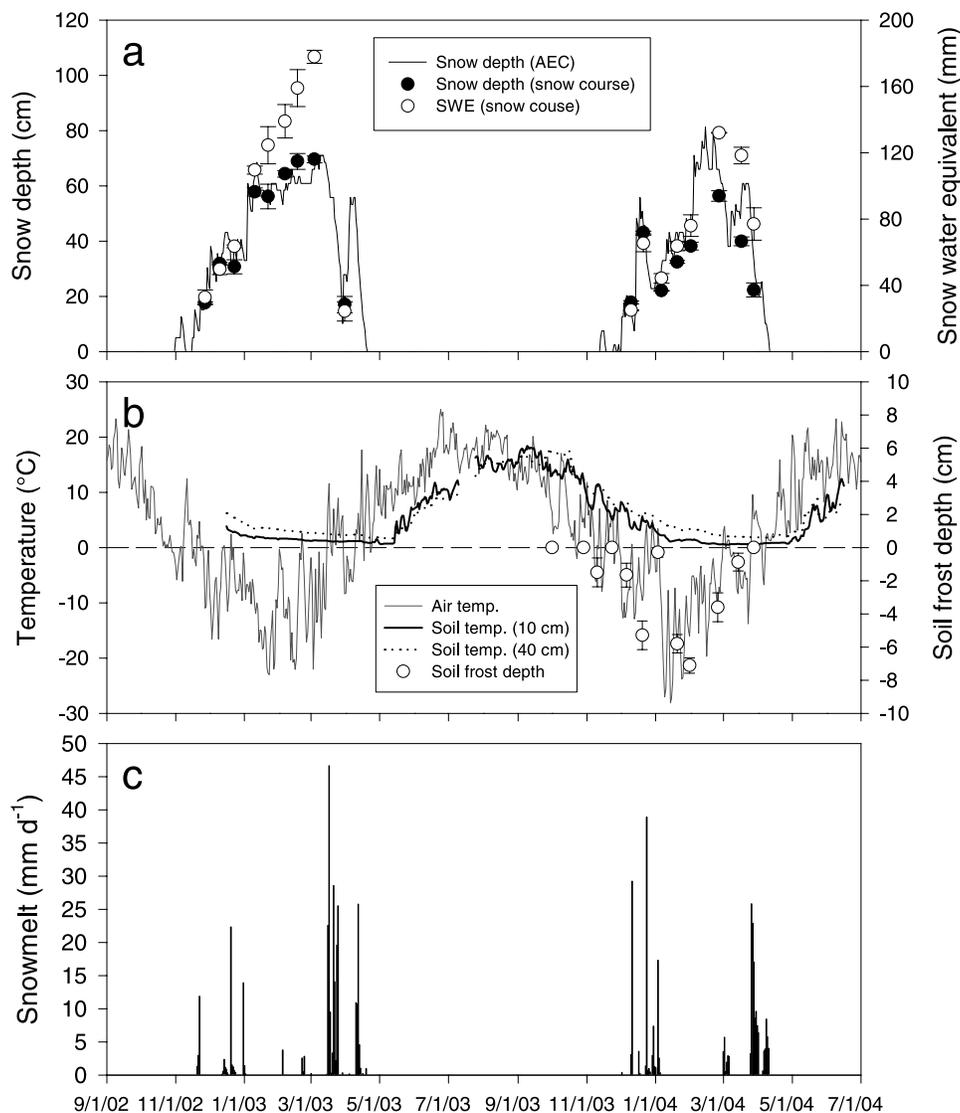
## 3. Results

### 3.1. Winter Hydrology and Meteorology

[24] The climate during the two study winters (2002–2003 and 2003–2004) was typical for the site, based on 64 years of meteorological data. There was approximately 250 mm of precipitation during the first winter (December through March) and 290 mm during the second winter, which was slightly less than the long-term mean of 313 mm ( $\pm 72$  SD). Maximum snow depths were 71 cm and 81 cm during the first and second study winters, respectively, which was similar to the long-term mean of 78 cm ( $\pm 22$  SD; Figure 3a). The period of snow cover was similar to the long-term mean dates of 2 December through 12 April. Snow cover lasted from 16 November 2002 to 19 April 2003 during the first winter and from 2 December 2003 to 10 April 2004 during the second winter.

[25] Soil frost measurements conducted during winter 2003–2004 indicated that a portion of the organic soil horizon was frozen beneath the snowpack throughout much of the winter (Figure 3b). Maximum soil frost depth was 7 cm at the end of January 2004. Soil temperatures, measured at the same depth as the soil lysimeters (10 and 40 cm), remained above freezing throughout both winters. Temperatures at the 10-cm depth were consistently lower than the 40-cm depth during the snow-covered period. Minimum daily soil temperatures during winter were 0.6°C and 1.8°C at 10- and 40-cm depths, respectively.

[26] Maximum air temperatures were below freezing for 99 and 90 nonconsecutive days during the first and second winters, respectively. Midwinter thaws were fairly common



**Figure 3.** (a) Snow depth and snow water equivalent; (b) air temperature, soil temperature and soil frost depth; and (c) snowmelt data collected from September 2002 to July 2004. Error bars show standard error of the mean.

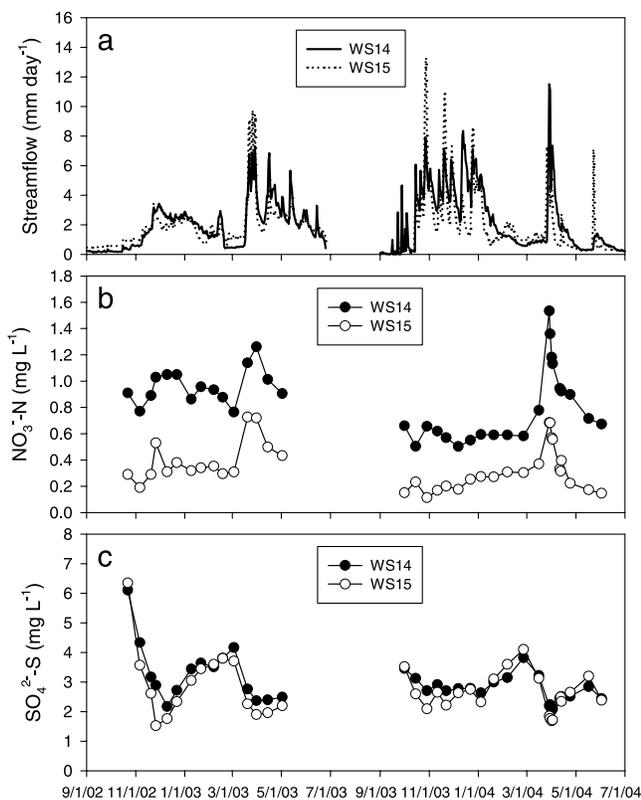
(Figure 3c). During the first winter, the major spring snowmelt began on 16 March 2003 and ended on 19 April 2003. During the second winter, spring snowmelt lasted from 25 March 2004 to 10 April 2004. These major snowmelt events that occurred at the end of the snow-covered season resulted in a distinct major peak in streamflow (Figure 4a). In general, streamflow was higher in the fall and spring compared to midwinter because precipitation accumulates in the snowpack during cold weather rather than infiltrating the soil.

### 3.2. Concentrations and Fluxes of $\text{NO}_3^-$ and $\text{SO}_4^{2-}$

[27] Among atmospheric samples (i.e., precipitation, throughfall, snowpack, snowmelt),  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations in snowmelt were the most variable and were significantly higher than concentrations in the snowpack, throughfall and precipitation ( $P < 0.001$  for both  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ; Figure 5). Mean concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were lowest in the snowpack; however, snowpack concen-

trations were not significantly lower than concentrations in throughfall and precipitation, with the exception of throughfall  $\text{SO}_4^{2-}$  in WS14. Belowground concentrations of  $\text{SO}_4^{2-}$  increased monotonically as water moved through the soil into the groundwater and toward the watershed outlet. By contrast, belowground concentrations of  $\text{NO}_3^-$  were highest in forest floor water, and decreased as water moved deeper through the mineral soil and into the groundwater.

[28] As reported previously [Christopher *et al.*, 2006], concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in stream water differed between WS14 and WS15, despite the close proximity of the watersheds and similar physiographical characteristics. Inter-watershed differences in  $\text{NO}_3^-$  concentrations were most notable in soil water, groundwater and stream water (Figures 4b, 5a, and 6). Mean  $\text{NO}_3^-$  concentrations in soil and stream water in WS14 exceeded those in WS15 by a factor of 2 during the snow-covered period. Throughout the study, stream water concentrations of  $\text{NO}_3^-$ -N in WS14 were consistently 0.3 to 0.8 mg L<sup>-1</sup> higher than in WS15



**Figure 4.** (a) Streamflow and stream water concentrations of (b) NO<sub>3</sub><sup>-</sup>-N and (c) SO<sub>4</sub><sup>2-</sup>-S at WS14 and WS15 from September 2002 to July 2004.

(Figure 4b). Average groundwater NO<sub>3</sub><sup>-</sup>-N concentrations in WS14 were more than 5 times greater than in WS15. Mean stream water concentrations of SO<sub>4</sub><sup>2-</sup>-S also were slightly, but significantly higher (paired *t*-test, *P* < 0.001, *n* = 36) in WS14 (3.0 mg L<sup>-1</sup>) than in WS15 (2.7 mg L<sup>-1</sup>). Ground-

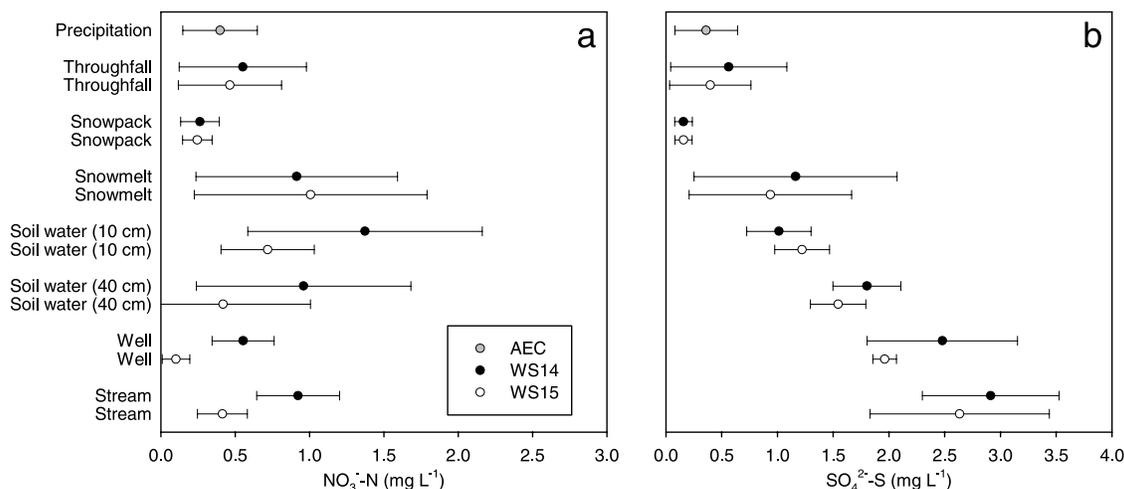
water from well 36 in WS14 had SO<sub>4</sub><sup>2-</sup>-S concentrations that were 0.8 to 1.9 mg L<sup>-1</sup> higher than concentrations measured in the other three wells.

[29] Fluxes of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> during the snow-covered period also differed between watersheds (Table 2). NO<sub>3</sub><sup>-</sup>-N fluxes in soil water and stream water in WS14 were more than double those in WS15. In WS14, NO<sub>3</sub><sup>-</sup> fluxes in stream water and forest floor leachates were greater than fluxes in throughfall and snowmelt. By contrast, WS15 had lower fluxes in soil water and stream water compared to throughfall and snowmelt. Fluxes of SO<sub>4</sub><sup>2-</sup> in both watersheds increased as water passed through soil to the stream. The SO<sub>4</sub><sup>2-</sup>-S fluxes in stream water were nearly 7 kg ha<sup>-1</sup> greater than fluxes in mineral soil leachates (Table 2).

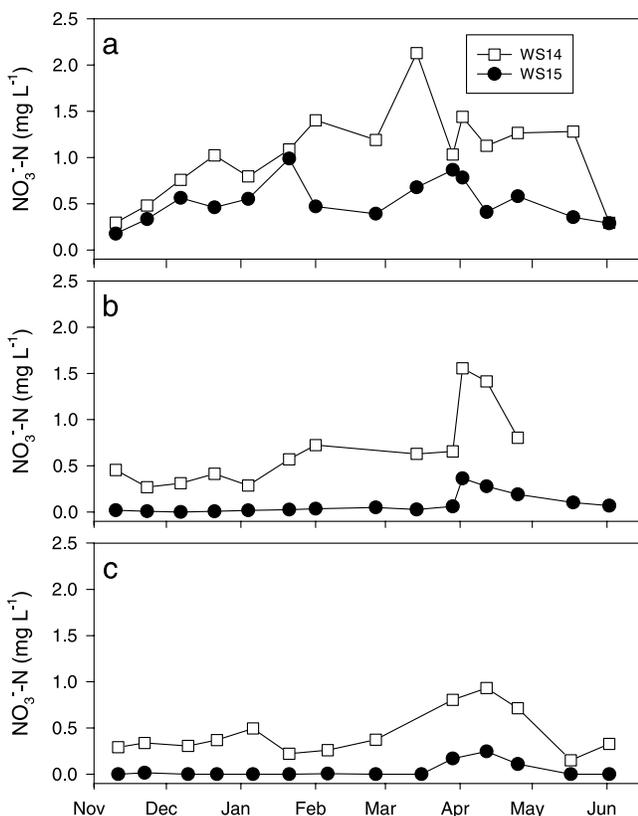
[30] Although the study period did not include data for the entire year, some seasonal trends were apparent. During spring snowmelt, there was a marked increase in stream water NO<sub>3</sub><sup>-</sup> concentrations, whereas concentrations of SO<sub>4</sub><sup>2-</sup> declined during this period (Figure 4). Concentrations of NO<sub>3</sub><sup>-</sup> in forest floor water were higher during winter compared to late fall and spring (Figure 6a). Soil water NO<sub>3</sub><sup>-</sup> at the 40-cm depth sharply increased during spring snowmelt, which coincided with increases in well water and stream water NO<sub>3</sub><sup>-</sup>. By contrast, there were no obvious seasonal trends in concentrations of SO<sub>4</sub><sup>2-</sup> in forest floor water, mineral soil water and groundwater (Figure 7). Similar seasonal trends for NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> have been reported previously for soil solutions at the Huntington Forest [Mitchell *et al.*, 1992a].

### 3.3. Isotopic Compositions of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>

[31] The range of mean δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> values in all ecosystem compartments was -0.7 to +1.9‰ (total range = -7.0 to +5.9‰) with much overlap among all types of samples (Figure 8a). A one-way ANOVA revealed no significant differences in δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> values (*P* > 0.05) among sample types. By contrast, there were significant differences in the δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> values among samples types (*P* < 0.001;



**Figure 5.** Mean concentrations of NO<sub>3</sub><sup>-</sup>-N and SO<sub>4</sub><sup>2-</sup>-S (±1 SD) in WS14 and WS15 and at the Adirondack Ecological Center (precipitation only). Values in precipitation, throughfall, snowpack, snowmelt, and stream water are for the snow-covered period of the first (16 November 2002 through 19 April 2003) and second (2 December 2003 to 10 April 2004) study winters. Well and soil water data were collected during the second winter only.



**Figure 6.** (a) Temporal trends in  $\text{NO}_3^-$ -N concentrations in forest floor water at 10-cm depth, (b) mineral soil water at 40-cm depth, and (c) groundwater during 2003–2004.

Figure 8b). A post-hoc Tukey HSD test revealed that  $\text{NO}_3^-$  from terrestrial sources (i.e., soil water, well water, stream water) was significantly more depleted in  $^{18}\text{O}$  than  $\text{NO}_3^-$  from atmospheric sources (i.e., precipitation, throughfall, snowpack, snowmelt). The range of mean atmospheric  $\delta^{18}\text{O}-\text{NO}_3^-$  values was +54.0 to +81.6‰ (total range = +25.7 to +89.8‰), whereas the range of mean O isotope ratios for  $\text{NO}_3^-$  from terrestrial sources was +1.2 to +11.0‰ (total range = -2.2 to +18.6‰).

[32] Like the isotopic composition of atmospheric  $\text{NO}_3^-$ , both  $\delta^{34}\text{S}-\text{SO}_4^{2-}$  and  $\delta^{18}\text{O}-\text{SO}_4^{2-}$  values showed considerable overlap among atmospheric samples (precipitation, throughfall, snowpack, snowmelt). Mean  $\delta^{34}\text{S}$  values of atmospheric  $\text{SO}_4^{2-}$  ranged from +4.6 to +5.3‰ (total range = +3.6 to +6.7‰) and mean  $\delta^{18}\text{O}-\text{SO}_4^{2-}$  values ranged from +10.0 to +14.4‰ (total range = +8.0 to +18.4‰) during the observation period. Similar to the O isotope ratios of  $\text{NO}_3^-$ ,

$\delta^{18}\text{O}-\text{SO}_4^{2-}$  values were significantly higher in atmospheric samples compared to samples from terrestrial sources ( $P < 0.001$ ), but there were no significant differences within these sources (soil water, groundwater, stream water). The  $\delta^{34}\text{S}-\text{SO}_4^{2-}$  values were significantly different between watersheds for soil water, well water and stream water ( $P < 0.001$ ). Within WS15 there were no significant differences in  $\delta^{34}\text{S}-\text{SO}_4^{2-}$  values among soil water, well water and stream water, whereas in WS14 well water and stream water  $\delta^{34}\text{S}-\text{SO}_4^{2-}$  values were significantly lower than soil water values. Atmospheric samples had higher variability in all isotopic parameters (i.e.,  $\delta^{15}\text{N}-\text{NO}_3^-$ ,  $\delta^{18}\text{O}-\text{NO}_3^-$ ,  $\delta^{34}\text{S}-\text{SO}_4^{2-}$ ,  $\delta^{18}\text{O}-\text{SO}_4^{2-}$ ) than terrestrial samples (Figure 8).

[33] The range of  $\delta^{18}\text{O}-\text{NO}_3^-$  values of stream water in our study (Figure 9a) was within the range of microbially derived  $\text{NO}_3^-$  reported in the literature (-5 to +16‰ [Kendall, 1998; Mayer et al., 2001]). The highest stream water  $\delta^{18}\text{O}-\text{NO}_3^-$  value was recorded in WS14 (+14.0‰) during a major snowmelt event that occurred on 29 March 2004. Well water  $\delta^{18}\text{O}-\text{NO}_3^-$  values were also within the range of microbially derived  $\delta^{18}\text{O}-\text{NO}_3^-$  during the observation period, except on 29 March 2004 when the  $\delta^{18}\text{O}-\text{NO}_3^-$  value for well water in WS15 was +18.6‰. There was no  $\delta^{18}\text{O}-\text{NO}_3^-$  value determined for the well in WS14 on that date because an insufficient amount of  $\text{NO}_3^-$  was collected for isotopic analysis.

[34] Stream water  $\delta^{18}\text{O}-\text{SO}_4^{2-}$  values ranged from -0.7 to +4.0‰ (Figure 9b) and were within the range of  $\delta^{18}\text{O}-\text{SO}_4^{2-}$  from a watershed-derived source (<+0.6‰ [Mayer et al., 1995]). The highest stream water  $\delta^{18}\text{O}-\text{SO}_4^{2-}$  values were observed during the snowmelt event on 29 March 2004 in both watersheds. Well water  $\delta^{18}\text{O}-\text{SO}_4^{2-}$  ranged from -0.7 to +3.4‰, also consistent with a watershed-derived source of  $\text{SO}_4^{2-}$ , and showed no indication of an increase on 29 March 2004 in either watershed.

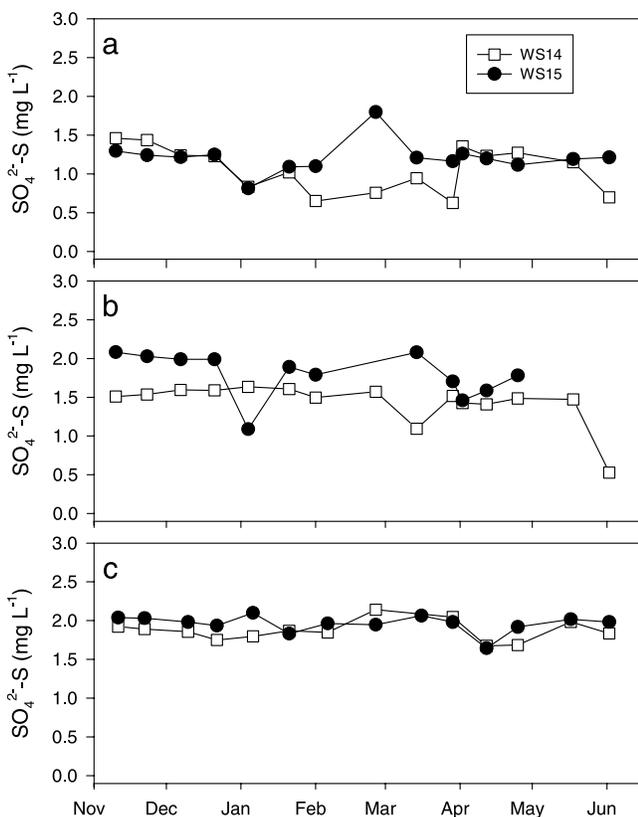
## 4. Discussion

### 4.1. Atmospheric Sources of $\text{NO}_3^-$ and $\text{SO}_4^{2-}$

[35] The lowest atmospheric  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations were found in the snowpack, which is consistent with other studies that have demonstrated that rapid ion elution through melting snow during periodic winter thaws results in a more dilute standing snowpack [Bales et al., 1989; Williams and Melack, 1991]. The highest atmospheric concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were measured in snowmelt, which was likely a result of both sublimation and dry deposition to the snowpack. The snowmelt water flux was 77 and 82% of the throughfall water flux in WS14 and WS15, respectively, indicating that  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were

**Table 2.** Fluxes of Water,  $\text{NO}_3^-$ -N, and  $\text{SO}_4^{2-}$ -S in WS14 and WS15 During the Snow-Covered Period of the Second Winter, 2 December 2003 to 10 April 2004

Flux	WS14			WS15		
	Water, mm	$\text{NO}_3^-$ -N, kg ha <sup>-1</sup>	$\text{SO}_4^{2-}$ -S, kg ha <sup>-1</sup>	Water, mm	$\text{NO}_3^-$ -N, kg ha <sup>-1</sup>	$\text{SO}_4^{2-}$ -S, kg ha <sup>-1</sup>
Throughfall	250	1.4	1.6	228	1.3	1.1
Snowmelt	192	1.7	1.9	188	1.4	1.3
Soil water (10 cm)	185	2.3	1.8	186	1.1	2.3
Soil water (40 cm)	182	1.6	3.4	182	0.7	2.8
Stream water	370	2.7	10.1	350	1.1	9.5



**Figure 7.** (a) Temporal trends in  $\text{SO}_4^{2-}\text{-S}$  concentrations in forest floor water at 10-cm depth, (b) mineral soil water at 40-cm depth, and (c) groundwater during 2003–2004.

more concentrated in snowmelt water (Table 2). The higher fluxes of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in snowmelt water compared to throughfall may be attributable to direct dry deposition to the snowpack that likely exceeded dry deposition captured in throughfall collectors [Valdez et al., 1987; Conklin et al., 1993].

[36] Despite significant differences in the concentrations and fluxes of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  among atmospheric sources, there was no significant difference in their isotopic composition (Figure 8). Kinetic isotope effects during any biological process that removes  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  have the potential to cause isotopic enrichment of heavy isotopes in the residual pool. Significant  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  transformations occur in the forest canopy during the growing season [Lindberg and Garten, 1988; Lovett, 1992]; however, we found no indication of isotopic fractionation in throughfall  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  during winter. This result was anticipated because isotopic discrimination by vegetation is typically minor [Krouse and Grinenko, 1991; Kendall, 1998] and leaf uptake is insignificant during winter, particularly for senescent deciduous vegetation. Furthermore, when precipitation falls as snow, it has less interaction with the forest canopy, thereby limiting the potential for isotopic discrimination.

[37] Isotopic data from our study also show that there were no detectable transformations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  within the snowpack. Mineralization of snowpack litter N and nitrification of snowpack  $\text{NH}_4^+$  [Schaefer and Driscoll, 1993] has the potential to affect the isotopic composition of

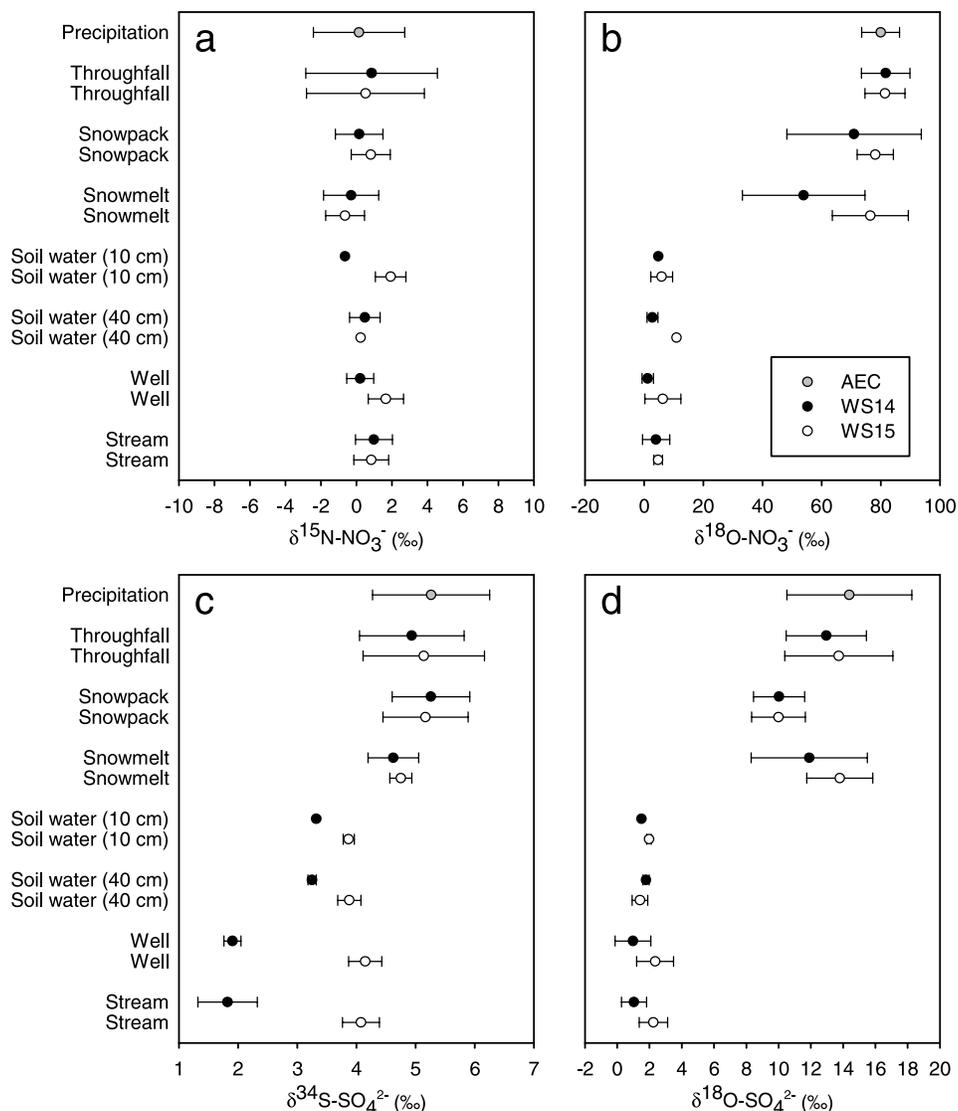
$\text{NO}_3^-$ . Similarly, oxidation of carbon-bonded S in litterfall within the snowpack could cause variations in  $\delta^{34}\text{S}\text{-SO}_4^{2-}$  and/or  $\delta^{18}\text{O}\text{-SO}_4^{2-}$  values. Studies in polar regions have shown that  $\text{NO}_3^-$  within the snowpack can be depleted by photolysis, resulting in a shift in its isotopic composition [Hastings et al., 2004; Blunier et al., 2005]. Our finding of no significant isotopic fractionation in the snowpack is similar to that of a study by Campbell et al. [2002] in an alpine watershed in Colorado. Additionally, experiments in which isotopically-labeled tracers (e.g.,  $^{15}\text{N}\text{-NO}_3^-$ ,  $^{15}\text{N}\text{-NH}_4^+$ ,  $^{34}\text{S}\text{-SO}_4^{2-}$ ) were applied to the snowpack, have shown no indication of N and S cycling within the snowpack [Williams et al., 1996; Campbell, 2006].

[38] The variability of isotopic compositions of atmospheric  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  was greater than the variability of watershed-derived  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  (Figure 8). Sources that influence the isotopic composition of atmospheric  $\text{SO}_4^{2-}$  include emissions from fossil fuel combustion, biogenic gases released from soils, wetlands, and sediments (e.g.,  $\text{H}_2\text{S}$  and dimethyl sulfide), and sea salt aerosols in coastal areas [Newman et al., 1991; Alewell et al., 2000]. The isotopic composition of  $\text{NO}_3^-$  also is affected by fossil fuel combustion, as well as factors such as  $\text{NO}_3^-$  formation by lightning and N volatilization in soils [Kendall, 1998; Elliott et al., 2005]. These influences, along with shifting seasonal weather patterns and storm tracks, all contribute to the variability in the isotopic composition of atmospheric  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . Oxygen isotope data indicate that  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in soil water, groundwater and stream water is largely produced in the forest floor, rather than from direct atmospheric deposition. Substantial homogenization occurs within the watershed as  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  is assimilated and remineralized. The lower variability in the isotopic composition of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in soil water, groundwater and stream water indicates that belowground processes buffer the isotopic composition, and thus, reduce variability.

[39] Atmospheric  $\delta^{34}\text{S}\text{-SO}_4^{2-}$  and  $\delta^{15}\text{N}\text{-NO}_3^-$  values mainly reflect various S and N sources, whereas  $\delta^{18}\text{O}$  values of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in precipitation are primarily dependent on the oxidation pathways of  $\text{SO}_2$  and  $\text{NO}_x$  in the atmosphere. Even though precipitation samples in our study were not collected throughout the entire year, some seasonal patterns in the  $\delta^{18}\text{O}$  values of atmospheric  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were evident (Figure 9). The  $\delta^{18}\text{O}\text{-SO}_4^{2-}$  values in precipitation were lower during winter compared to spring and early summer, which largely reflects seasonal trends in  $\delta^{18}\text{O}$  values of atmospheric water vapor involved in oxidation reactions [see Holt and Kumar, 1991]. In contrast,  $\delta^{18}\text{O}\text{-NO}_3^-$  values were highest during the winter, which may be attributed to several factors [see Pardo et al., 2004] including seasonal differences in chemical reaction pathways in the atmosphere. During summer, the photochemically reactive hydroxyl radical with a low  $\delta^{18}\text{O}$  value is more likely to react with  $\text{NO}_x$  to form  $\text{NO}_3^-$ , whereas during winter, ozone with a higher  $\delta^{18}\text{O}$  value is more likely to be a reactant.

#### 4.2. Microbial Sources of $\text{NO}_3^-$ and $\text{SO}_4^{2-}$

[40] Microbial cycling of N and S appears to be important in the study watersheds during winter and imparts control on the retention and release of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in watershed soils. The striking shift in the O isotope ratios of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  toward lower  $\delta^{18}\text{O}$  values in soil water collected at

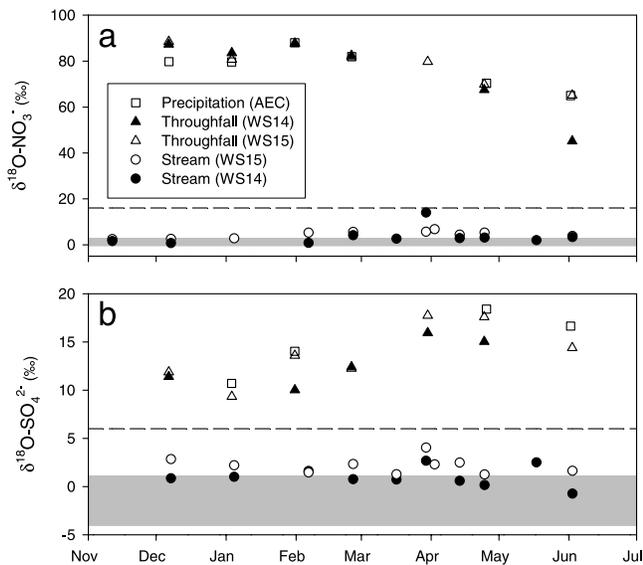


**Figure 8.** Mean isotopic values of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  ( $\pm 1$  SD) in WS14 and WS15 and at the Adirondack Ecological Center (precipitation only). Samples were collected during the snow-covered period (2 December to 10 April) of 2003–2004.

the 10-cm depth indicates that  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in soil waters were not derived from direct leaching of atmospheric deposition. Instead,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in organic soil horizons appeared to be largely derived from oxidation of organic N and S, and therefore, likely cycled through the biomass. For  $\text{SO}_4^{2-}$ , possible alternative reasons for the comparatively low  $\delta^{18}\text{O}$  values in shallow soil water are: (1) reoxidation of sulfides formed in anoxic microsites; (2) weathering of S-containing minerals; and possibly (3) hydrolysis of organic (ester) sulfates. It is unlikely that the reoxidation of sulfides or mineral S weathering contributes much to the low  $\delta^{18}\text{O}-\text{SO}_4^{2-}$  values, since the forest floor contains mostly organic matter. Hydrolysis of ester sulfates is believed to cause only a minor decrease in  $\delta^{18}\text{O}-\text{SO}_4^{2-}$  by only 2 to 3‰ with respect to precipitation  $\text{SO}_4^{2-}$  [Mayer *et al.*, 1995], and cannot entirely explain the 10 to 12‰ difference between snowmelt and soilwater  $\delta^{18}\text{O}-\text{SO}_4^{2-}$  in our study. Hence, oxidation of carbon-bonded S appears to be the most likely

explanation for the low  $\delta^{18}\text{O}$  values of  $\text{SO}_4^{2-}$  in soil seepage water at the 10-cm depth.

[41] Since  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are not thought to exchange O with  $\text{H}_2\text{O}$  [Chiba and Sakai, 1985; Kendall, 1998], and isotopic fractionation by soil sorption/desorption is negligible [Hübner, 1986; Van Stempvoort *et al.*, 1990; Kendall, 1998; Mitchell *et al.*, 1998], the most likely explanation for the depletion of  $^{18}\text{O}$  in soil water  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  is oxidation of organic N and S. During this process, O from soil water with negative  $\delta^{18}\text{O}$  values becomes incorporated into the newly formed  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , thus explaining the marked difference between  $\delta^{18}\text{O}$  values of atmospheric and soil  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . Once the  $\delta^{18}\text{O}$  values of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were “reset” in upper soil horizons, they did not change significantly as water moved into the mineral soil, groundwater and stream water pools. Since microbial production is the major source of  $\text{NO}_3^-$  throughout the soil profile,  $\delta^{18}\text{O}-\text{NO}_3^-$  values do not change with depth. The constancy in  $\delta^{18}\text{O}-\text{SO}_4^{2-}$  values indicate that some  $\text{SO}_4^{2-}$



**Figure 9.** Atmospheric and stream water  $\delta^{18}\text{O}-\text{NO}_3^-$  and  $\delta^{18}\text{O}-\text{SO}_4^{2-}$  values at WS14 and WS15 from December 2003 through June 2004. Precipitation samples were collected at the Adirondack Ecological Center. The dashed line indicates the upper limit of (a)  $\delta^{18}\text{O}-\text{NO}_3^-$  produced by microbial nitrification and (b)  $\delta^{18}\text{O}-\text{SO}_4^{2-}$  produced by organic S mineralization and/or weathering of sulfide minerals based on values reported in the literature. The shaded area shows the calculated range in (Figure 9a)  $\delta^{18}\text{O}-\text{NO}_3^-$  produced by microbial nitrification and (Figure 9b) the  $\delta^{18}\text{O}-\text{SO}_4^{2-}$  produced by biological oxidation of carbon-bonded sulfur.

produced in deeper soil horizons may also be from a mineralization of carbon-bonded S, or alternatively from sulfide oxidation, a process that would produce similar  $\delta^{18}\text{O}-\text{SO}_4^{2-}$  values. It was possible to collect only a limited number of soil water samples with tension lysimeters owing to the lack of soil water movement during the snow-covered period and large water volume requirement for isotopic analyses. Consequently, most of the soil water samples for isotopic analyses were collected during snowmelt events. Our isotopic data indicate that, even at times of substantial infiltration and recharge, the majority of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in forest floor water was derived from mineralization of soil organic matter, and was not directly derived from atmospheric deposition.

[42] A simple two-end member mixing analysis can be used to estimate the percentages of stream water  $\text{NO}_3^-$  derived from nitrification and from atmospheric deposition. Since microbially produced  $\text{NO}_3^-$  is thought to derive two O atoms from ambient soil water and one from atmospheric  $\text{O}_2$  [Hollocher *et al.*, 1981; Andersson and Hooper, 1983; Kumar *et al.*, 1983; Hollocher, 1984],  $\delta^{18}\text{O}-\text{NO}_3^-$  values from nitrification can be calculated if the  $\delta^{18}\text{O}$  values of soil water and atmospheric  $\text{O}_2$  are known. The  $\delta^{18}\text{O}-\text{O}_2$  of the atmosphere is +23.5‰ [Kroopnick and Craig, 1972] and soil water  $\delta^{18}\text{O}-\text{H}_2\text{O}$  in the Arbutus watershed typically ranges from -12 to -8‰ [McHale *et al.*, 2002]. On the basis of these values,  $\delta^{18}\text{O}-\text{NO}_3^-$  produced by nitrification would be approximately -0.2 to +2.5‰ (Figure 9a). These

calculated theoretical  $\delta^{18}\text{O}-\text{NO}_3^-$  values are similar to or slightly lower than values of microbially produced  $\text{NO}_3^-$  measured in the field or laboratory, which range from +0.2 to +16.1‰ [Amberger and Schmidt, 1987; Mayer *et al.*, 2001; Williard *et al.*, 2001; Burns and Kendall, 2002]. Higher  $\delta^{18}\text{O}-\text{NO}_3^-$  values of measured, microbially produced  $\text{NO}_3^-$  have been attributed to factors such as the influence of denitrification, nitrification by different types of soil microbes (fungi), alternate reaction pathways, and sampling disturbance [Kendall, 1998; Mayer *et al.*, 2001; Williard *et al.*, 2001; Burns and Kendall, 2002].

[43] The calculated  $\delta^{18}\text{O}-\text{NO}_3^-$  value from nitrification and the average measured  $\delta^{18}\text{O}-\text{NO}_3^-$  in precipitation can be used as end members to estimate the proportion of nitrification-derived  $\text{NO}_3^-$  in streams. Using these calculations we estimate that >90% of the  $\text{NO}_3^-$  in both streams was from microbial sources, with the exception of peak snowmelt in WS14 when 82% of the  $\text{NO}_3^-$  was derived from nitrification. These estimates are similar to estimates from other studies in northeastern North America [e.g., Spoelstra *et al.*, 2001; Burns and Kendall, 2002; Pardo *et al.*, 2004; Piatek *et al.*, 2005], indicating that even during snowmelt little atmospheric  $\text{NO}_3^-$  is conservatively transported to streams.

[44] Much like  $\text{NO}_3^-$ , the O in microbially produced soil  $\text{SO}_4^{2-}$  comes from either water or atmospheric  $\text{O}_2$ . Following the convention of Mayer *et al.* [1995], the  $\delta^{18}\text{O}-\text{SO}_4^{2-}$  of microbially produced S can be estimated. Assuming that 60 to 70% of the O in  $\text{SO}_4^{2-}$  is from soil water ( $\delta^{18}\text{O}-\text{H}_2\text{O} = -12$  to  $-8$ ‰) and that the enrichment factors for water and O incorporation are 0‰ and  $-8.7$ ‰, respectively [Lloyd, 1967], the  $\delta^{18}\text{O}$  values of  $\text{SO}_4^{2-}$  produced by biological oxidation of carbon-bonded S would be expected to range from  $-4.0$  to  $+1.1$ ‰ (Figure 9b). Similar  $\delta^{18}\text{O}-\text{SO}_4^{2-}$  values could be produced by the reoxidation of sulfides precipitated under anoxic conditions, since 60 to 90% of the O in  $\text{SO}_4^{2-}$  comes from soil water during these reactions [Toran and Harris, 1989]. However, it is unlikely that reoxidation of sulfides was significant in the upper soil horizon since almost all of the S occurs in organic form. Regardless of what caused the depletion of  $^{18}\text{O}$  in soil water  $\text{SO}_4^{2-}$ , it is clear that most of the  $\text{SO}_4^{2-}$  in streams during the winter is derived from sources within the watershed rather than from direct atmospheric deposition.

[45] Cold temperatures are not optimal for microbial activity in seasonally snow-covered soils, and microbial processes, such as N and S mineralization, generally progress more slowly at low temperatures [e.g., MacDonald *et al.*, 1995; Groffman *et al.*, 2001]. Surficial frost was present beneath the snowpack throughout much of the winter to a maximum depth of 7 cm. However, the relatively deep snow insulated soil from prolonged subfreezing air temperatures (Figures 3a and 3b). Consequently, portions of the organic horizon remained unfrozen, and soil temperatures at the 10-cm depth were consistently above freezing throughout the winter and were well above the limits for microbial activity which can proceed at temperatures near and below 0°C [Dorland and Beauchamp, 1991; Clein and Schimel, 1995].

[46] Depending on redox conditions, microbial denitrification and bacterial dissimilatory  $\text{SO}_4^{2-}$  reduction may affect the respective isotopic composition of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in drainage waters. Microbes sequentially use  $\text{O}_2$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  as electron acceptors under decreasing

redox potential. Therefore, denitrification and bacterial dissimilatory SO<sub>4</sub><sup>2-</sup> reduction may occur during winter if soil microsites become water-saturated or if a soil frost layer limits O<sub>2</sub> exchange with the atmosphere. Several studies have found that denitrification is an important pathway for N loss in water-saturated forest soils during early spring [Groffman *et al.*, 1993; Nyborg *et al.*, 1997]. Denitrification causes progressive enrichment of <sup>15</sup>N with decreasing NO<sub>3</sub><sup>-</sup> concentrations, as microbes preferentially reduce <sup>14</sup>NO<sub>3</sub><sup>-</sup> compared to <sup>15</sup>NO<sub>3</sub><sup>-</sup> [e.g., Mariotti *et al.*, 1988]. Another indicator of denitrification is a progressive increase in δ<sup>15</sup>N and δ<sup>18</sup>O values at a ratio of 2:1 in the residual NO<sub>3</sub><sup>-</sup> [Amberger and Schmidt, 1987; Böttcher *et al.*, 1990]. We found no significant inverse relationship between δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> values and NO<sub>3</sub><sup>-</sup> concentrations in well water (WS14, δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> = 2.88 - 3.73 NO<sub>3</sub><sup>-</sup>-N, R<sup>2</sup> = 0.14, P = 0.54; WS15, δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> = 5.93 - 19.58 NO<sub>3</sub><sup>-</sup>-N, R<sup>2</sup> = 0.09, P = 0.62) or stream water (WS14, δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> = 2.16 - 1.41 NO<sub>3</sub><sup>-</sup>-N, R<sup>2</sup> = 0.19, P = 0.33; WS15, δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> = 1.71 - 2.36 NO<sub>3</sub><sup>-</sup>-N, R<sup>2</sup> = 0.17, P = 0.36). There was also no concurrent increase in δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> and δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> values in well water (WS14, δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> = 1.19 - 0.38 NO<sub>3</sub><sup>-</sup>-N, R<sup>2</sup> = 0.03, P = 0.83; WS15, δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> = 13.24 - 3.64 NO<sub>3</sub><sup>-</sup>-N, R<sup>2</sup> = 0.34, P = 0.30) or stream water (WS14, δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> = 8.01 - 3.48 NO<sub>3</sub><sup>-</sup>-N, R<sup>2</sup> = 0.18, P = 0.48; WS15, δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> = 4.85 - 0.21 NO<sub>3</sub><sup>-</sup>-N, R<sup>2</sup> = 0.03, P = 0.74). These data indicate that there was no isotopic evidence for denitrification during the observation period of this study. However, these isotopic results should be interpreted with caution because if denitrification completely removes NO<sub>3</sub><sup>-</sup> in water-saturated microsites, no isotopically enriched NO<sub>3</sub><sup>-</sup> will remain. The remaining water can then mix with water sources that contain NO<sub>3</sub><sup>-</sup> that is unaffected by denitrification, causing a decrease in NO<sub>3</sub><sup>-</sup> concentrations without any detectable isotope effect.

[47] Dissimilatory SO<sub>4</sub><sup>2-</sup> reduction causes enrichment of <sup>34</sup>S in soil water SO<sub>4</sub><sup>2-</sup> [Alewell and Novak, 2001]. The sulfide produced is largely incorporated into organic matter and iron-containing minerals [Giblin and Wieder, 1992], and has characteristically low δ<sup>34</sup>S values due to kinetic isotope fractionation favoring the conversion of the light <sup>32</sup>S isotope. Sulfide products possibly could be reoxidized and leached from soil as SO<sub>4</sub><sup>2-</sup> during snowmelt when watershed soils are rewetted. These redox reactions are often important during cycles of wetting and drying in wetlands, hyporheic zones and riparian areas [Dillon *et al.*, 1997; Schiff *et al.*, 2005; Mitchell *et al.*, 2006]; however, their importance during winter and spring snowmelt is unknown. We found no evidence of an inverse relationship between δ<sup>34</sup>S-SO<sub>4</sub><sup>2-</sup> values and SO<sub>4</sub><sup>2-</sup> concentrations in groundwater (WS14, δ<sup>34</sup>S-SO<sub>4</sub><sup>2-</sup> = 1.84 - 0.03 SO<sub>4</sub><sup>2-</sup>-S, R<sup>2</sup> = 0.06, P = 0.75; WS15, δ<sup>34</sup>S-SO<sub>4</sub><sup>2-</sup> = 4.77 - 0.37 SO<sub>4</sub><sup>2-</sup>-S, R<sup>2</sup> = 0.70, P = 0.08) or stream water (WS14, δ<sup>34</sup>S-SO<sub>4</sub><sup>2-</sup> = 0.27 + 0.74 SO<sub>4</sub><sup>2-</sup>-S, R<sup>2</sup> = 0.70, P = 0.18; WS15, δ<sup>34</sup>S-SO<sub>4</sub><sup>2-</sup> = 3.74 + 0.11 SO<sub>4</sub><sup>2-</sup>-S, R<sup>2</sup> = 0.64, P = 0.06). Additionally, NO<sub>3</sub><sup>-</sup> concentrations in surface soil solution were fairly high throughout the winter (Figure 6a), suggesting that bacterial (dissimilatory) SO<sub>4</sub><sup>2-</sup> reduction did not occur in the soil zone.

[48] The concentrations of NO<sub>3</sub><sup>-</sup> in stream water were markedly different between the two watersheds. In a previous study, Christopher *et al.* [2006] showed that overall

higher microbial NO<sub>3</sub><sup>-</sup> production in WS14 resulted from higher nitrification rates associated with vegetation type and soil base status. Our study indicates that there was no major difference in the isotopic composition of NO<sub>3</sub><sup>-</sup> between watersheds because even though different amounts of NO<sub>3</sub><sup>-</sup> were produced in each watershed, nitrification was still the major source of NO<sub>3</sub><sup>-</sup>. Concentrations of NO<sub>3</sub><sup>-</sup> increased during winter in soil water at the 10-cm depth, suggesting that NO<sub>3</sub><sup>-</sup> accumulated in surface soils beneath the snowpack (Figure 6a). Concentrations of NO<sub>3</sub><sup>-</sup> in deeper soils (40-cm depth) and wells remained relatively constant throughout the winter, followed by a sharp peak during snowmelt runoff. This peak occurred when the NO<sub>3</sub><sup>-</sup> that accumulated in surface soil was transported through deeper soil horizons to streams. While some of the NO<sub>3</sub><sup>-</sup> in stream water during spring snowmelt may have been produced during the previous summer and fall and subsequently stored in groundwater, nitrification beneath the snowpack also appeared to contribute to the stream water NO<sub>3</sub><sup>-</sup> peak.

[49] On the basis of the forest floor concentration data, there was no obvious indication of increases in SO<sub>4</sub><sup>2-</sup> in soil water during winter (Figure 7a). The isotopic data indicate that most of the forest floor SO<sub>4</sub><sup>2-</sup> was microbially produced; however, in contrast to NO<sub>3</sub><sup>-</sup>, no SO<sub>4</sub><sup>2-</sup> peak was evident during snowmelt in soil solution, groundwater, and stream water. It is possible that soil adsorption/desorption processes buffered SO<sub>4</sub><sup>2-</sup> concentrations, thereby minimizing short-term variations. As the hydrologic transport time lengthened, the concentration of SO<sub>4</sub><sup>2-</sup> in the groundwater increased as demonstrated by the comparatively high fluxes of SO<sub>4</sub><sup>2-</sup> in stream water during base flow (Table 2).

### 4.3. Geologic Sources of SO<sub>4</sub><sup>2-</sup>

[50] Concentrations and fluxes of SO<sub>4</sub><sup>2-</sup> increased as the contact time between water and mineralogical substrates lengthened (Table 2 and Figure 5b), indicating that oxidation of labile sulfides [Mitchell *et al.*, 2006] and/or the weathering of S-containing bedrock minerals are an important source of SO<sub>4</sub><sup>2-</sup> in these watersheds. There is also a possibility that desorption of nongeological SO<sub>4</sub><sup>2-</sup> (i.e., atmospheric, organic soil) from exchange sites in the mineral soil may have contributed to these increases [Mitchell *et al.*, 1992b]. Stream water had the highest concentrations of SO<sub>4</sub><sup>2-</sup>, possibly indicating that SO<sub>4</sub><sup>2-</sup> additions mainly occurred as the length of the flow path increased from source areas to the watershed outlet. The dilution of stream water SO<sub>4</sub><sup>2-</sup> during snowmelt events also suggests that S derived from weathering of S in parent material and bedrock was an important source of stream water SO<sub>4</sub><sup>2-</sup> (Figure 4). It is likely that during snowmelt, water with comparatively low SO<sub>4</sub><sup>2-</sup> concentrations was rapidly transported to streams, lowering the relative proportion of weathering-derived SO<sub>4</sub><sup>2-</sup> reaching the stream. In contrast, NO<sub>3</sub><sup>-</sup>, for which there is no known geological source in this region, increased in stream water during snowmelt events presumably as NO<sub>3</sub><sup>-</sup> produced in organic soil horizons was transported to streams.

[51] Mean concentrations of SO<sub>4</sub><sup>2-</sup>-S in stream water were slightly higher in WS14 compared to WS15 (3.0 and 2.7 mg L<sup>-1</sup>, respectively). Groundwater SO<sub>4</sub><sup>2-</sup>-S concentrations at well 36 in WS14 were substantially and consistently higher (by 0.5 to 2.2 mg L<sup>-1</sup>) than

concentrations measured in the other three wells, indicating that the extent of SO<sub>4</sub><sup>2-</sup> formation via sulfide oxidation in the groundwater may vary locally within these watersheds. Interwatershed differences in stream water and groundwater δ<sup>34</sup>S-SO<sub>4</sub><sup>2-</sup> values likely reflect spatial heterogeneity in the sulfur isotope ratios of various mineralogical sources (Figure 8c). Oxidation of sulfide minerals, such as pyrite and pyrrhotite, often with negative δ<sup>34</sup>S values, appears to contribute to stream water SO<sub>4</sub><sup>2-</sup>, particularly in WS14. Pyrite has been found in hydrothermal calcite veins at several locations within Hamilton County, New York, where our study site was located [Richards and Robinson, 2000]. Bedrock weathering is a feasible explanation for the comparatively low δ<sup>34</sup>S-SO<sub>4</sub><sup>2-</sup> values and high SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> concentrations in well and stream water in WS14 (Table 1).

## 5. Conclusions

[52] Biological cycling of N and S during winter historically has been considered of little importance since assimilation by soil microbes and forest vegetation is limited by cold temperatures. Our data indicate that despite near-freezing soil temperatures and considerable infiltration during snowmelt events, most of the atmospheric NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> that infiltrated the forest floor was cycled through the organic N and S pools in the pedosphere and/or biosphere. Low δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> values in forest floor water during winter shows that almost all the NO<sub>3</sub><sup>-</sup> was produced by nitrification. Similarly low δ<sup>18</sup>O-SO<sub>4</sub><sup>2-</sup> values indicate that forest floor SO<sub>4</sub><sup>2-</sup> was produced by oxidation of carbon-bonded S. Throughout the snow-covered season, nearly all the NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in stream water was derived from terrestrial, rather than atmospheric sources. Differences in soil base-status between watersheds likely influenced nitrification rates, which resulted in markedly different stream water concentrations of NO<sub>3</sub><sup>-</sup> between watersheds. By contrast, differences in stream water concentrations of SO<sub>4</sub><sup>2-</sup> were relatively minor, presumably because internal S sources, including the weathering from S-containing minerals, dominated stream water SO<sub>4</sub><sup>2-</sup> export.

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