

SOURCES OF NITRATE IN SNOWMELT DISCHARGE: EVIDENCE FROM WATER CHEMISTRY AND STABLE ISOTOPES OF NITRATE

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Abstract. To determine whether NO_3^- concentration pulses in surface water in early spring snowmelt discharge are due to atmospheric NO_3^- , we analyzed stream $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ values between February and June of 2001 and 2002 and compared them to those of throughfall, bulk precipitation, snow, and groundwater. Stream total Al, DOC and Si concentrations were used to indicate preferential water flow through the forest floor, mineral soil, and ground water. The study was conducted in a 135-ha subcatchment of the Arbutus Watershed in the Huntington Wildlife Forest in the Adirondack Region of New York State, U.S.A. Stream discharge in 2001 increased from 0.6 before to 32.4 mm day⁻¹ during snowmelt, and element concentrations increased from 33 to 71 $\mu\text{mol L}^{-1}$ for NO_3^- , 3 to 9 $\mu\text{mol L}^{-1}$ for total Al, and 330 to 570 $\mu\text{mol L}^{-1}$ for DOC. Discharge in 2002 was variable, with a maximum of 30 mm day⁻¹ during snowmelt. The highest NO_3^- , Al, and DOC concentrations were 52, 10, and 630 $\mu\text{mol L}^{-1}$, respectively, and dissolved Si decreased from 148 $\mu\text{mol L}^{-1}$ before to 96 $\mu\text{mol L}^{-1}$ during snowmelt. Values of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- in stream water were similar in both years. Stream water, atmospherically-derived solutions, and groundwaters had overlapping $\delta^{15}\text{N}-\text{NO}_3^-$ values. In stream and ground water, $\delta^{18}\text{O}-\text{NO}_3^-$ values ranged from +5.9 to +12.9‰ and were significantly lower than the +58.3 to +78.7‰ values in atmospheric solutions. Values of $\delta^{18}\text{O}-\text{NO}_3^-$ indicating nitrification, increase in Al and DOC, and decrease in dissolved Si concentrations indicating water flow through the soil suggested a dilution of groundwater NO_3^- by increasing contributions of forest floor and mineral soil NO_3^- during snowmelt.

Keywords: natural abundance isotopes, nitrate pulses, nitrate sources, northern hardwood forest, N-saturation, snowmelt

Introduction

Mineralization of plant organic matter and atmospheric deposition are the main sources of nitrogen (N) in forest ecosystems in the northeastern U.S. Mineralization yields ammonium (NH_4^+) which can be assimilated by biota, volatilized as ammonia, or nitrified to nitrate (NO_3^-). Volatilization of NH_4^+ is rare in forests because it requires basic conditions. Nitrification occurs when N demand by biota is smaller than the available NH_4^+ pool and results in NO_3^- leaching first to

lower soil horizons and then to surface and ground water. Nitrate is a mobile anion easily transported with water; its fate also includes uptake and denitrification. Nitrogen supply from atmospheric deposition and organic matter mineralization exceeds the biological capacity of some northeastern U.S. forests for N assimilation, resulting in a range of NO_3^- exports in surface waters, a condition known as N-saturation (Agren and Bosatta, 1988; Aber *et al.*, 1989, 1998; Stoddard, 1994). Atmospheric N deposition has been implicated in increased NO_3^- exports in streams in both, North America and Europe (Emmett *et al.*, 1998; Gundersen *et al.*, 1998; Aber *et al.*, 2003; Schleppei *et al.*, 2004; Ito *et al.*, 2005). Nitrate is a contaminant in drinking water; it is also linked to water acidification and eutrophication (Stoddard, 1994; Howarth *et al.*, 1996; Vitousek *et al.*, 1997; Mayer *et al.*, 2002; Driscoll *et al.*, 2003; Galloway *et al.*, 2003; Mitchell *et al.*, 2003). Therefore, NO_3^- is a health concern for ecosystems and humans alike.

Recent research indicates that the largest NO_3^- fluxes from forested watersheds in the U.S. occur with large runoff events, especially during early spring snowmelt when vegetation and microbial uptake of inorganic N is low (Mitchell *et al.*, 1996b; Baron and Campbell, 1997; Brooks and Williams, 1999; Inamdar *et al.*, 2004; Park *et al.*, 2003). Possible sources of NO_3^- in streamwater at snowmelt include atmospheric NO_3^- from snow, mineralization in soils under the snowpack (Zak *et al.*, 1990), groundwater during early phases of the melt (Bottomley *et al.*, 1986; McHale *et al.*, 2002), and premelt stored water and nitrification (Kendall *et al.*, 1995; Burns and Kendall, 2002; Campbell *et al.*, 2002), and a combination of these (Schleppei *et al.*, 2004). Other factors, including the presence of wetlands and a variety of vegetation types, appear to be important in regulating N generation and loss rates in regions of the northeast U.S. (Campbell *et al.*, 2002; Ito *et al.*, 2005; Mitchell *et al.*, 2003). Discerning between sources of NO_3^- will help elucidate potential storage time (short vs. long-term) in different ecosystem pools before NO_3^- export to surface water, and enhance our understanding of N-saturation mechanisms.

Atmospheric N deposition in the Adirondack region of New York averages about $3.4 \text{ kg } \text{NO}_3^- \text{-N ha}^{-1} \text{ yr}^{-1}$ of wet only inputs (Ito *et al.*, 2002). Dry deposition adds an estimated $2.6 \text{ kg } \text{NO}_3^- \text{-N ha}^{-1} \text{ yr}^{-1}$ at the Arbutus Lake Watershed located in the central Adirondacks – with the total N deposition, including $\text{NO}_3^- \text{-N}$, $\text{NH}_4^+ \text{-N}$ and dissolved organic N (DON), of $10.1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Park *et al.*, 2003). Archer Creek Catchment, the major inlet to Arbutus Lake, exports $4.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ with more than 87% during the dormant season, and with highest NO_3^- pulses observed during snowmelt (Mitchell *et al.*, 1996b, 2001). These rates and timing of NO_3^- export place Archer Creek at stage one of N-saturation (Stoddard, 1994), typical of the Adirondack region (Driscoll and Van Dreason, 1993). Nitrate dominates the N forms in export between January and June, and its concentration exceeds that of DON almost 3-fold and that of NH_4^+ almost 15-fold (Mitchell *et al.*, 2001).

Based on mass N budgets for 54 Adirondack Long Term Monitoring Lake/Watersheds there is a small, but statistically significant relationship between wet N deposition and N losses in discharge (Ito *et al.*, 2005). However, it has been clearly shown that both the temporal and spatial variation of NO_3^- in surface water is considerable and cannot be explained by atmospheric N deposition alone (Campbell *et al.*, 2002; Park *et al.*, 2003; Ito *et al.*, 2005). Additionally, an unexplained decrease in NO_3^- exports in the northeastern U.S. stream waters has been observed that was not related to changes in atmospheric N deposition (Goodale *et al.*, 2003). Therefore, understanding of N sources, and their cycling, storage, and delivery to surface waters is necessary to shed additional light on mechanisms that regulate the retention and export of N in watersheds. Specifically, we still need to understand how atmospherically-deposited N cycles, where it is stored, and how long it resides in various ecosystem pools before it is released to surface waters. Such information is important to the development of efficient and successful abatement strategies that may include ecosystem management, controls on NO_x emissions and possible linkages of N exports with climate change.

New diagnostic tools make it possible to distinguish between NO_3^- sources in surface waters if the original pools are isotopically distinct. Natural abundance ratios of $^{18}\text{O}/^{16}\text{O}$ in atmospheric NO_3^- are distinct from those of nitrification-derived NO_3^- , and because of that, they can be used to separate atmospheric from nitrification-derived NO_3^- in surface waters. Atmospheric NO_3^- in rain, throughfall, and snow (excluding dry deposition) for example, has isotopic values that range from +23 to +75‰ for $\delta^{18}\text{O}$ (Kendall, 1998). Recently, these values were extended to +90‰ for the northeastern U.S. (Ohte *et al.*, 2004). The isotopic value of $^{18}\text{O}/^{16}\text{O}$ for nitrification-derived NO_3^- is a function of both ^{18}O of soil water and soil O_2 , and has been calculated by adding 2/3 of the $\delta^{18}\text{O}$ value of soil water and 1/3 of the $\delta^{18}\text{O}$ value of atmospheric oxygen (Kendall, 1998). Therefore, the calculated range for nitrification-derived NO_3^- is -10 to +10‰ for normal range of ^{18}O of water (Kendall, 1998). Values of $\delta^{15}\text{N}$ range from -4 to +12‰ in atmospheric NO_3^- and from -3 to +26‰ in nitrification-derived NO_3^- . Thus, even though the $^{15}\text{N}/^{14}\text{N}$ ratios are not sufficiently distinct and the $^{18}\text{O}/^{16}\text{O}$ ratios have a wide range, together dual $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ analyses can be very useful in separating atmospheric from nitrification-derived sources of NO_3^- in surface waters (Kendall, 1998; Spoelstra *et al.*, 2001; Burns and Kendall, 2002; Mayer *et al.*, 2002; Pardo *et al.*, 2004; Ohte *et al.*, 2004; Rock and Mayer, 2004).

We used natural abundance isotopic ratios of $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ of NO_3^- , and associated hydrological and selected water chemistry data (DOC, total Al, and dissolved Si) to determine potential sources of NO_3^- during late winter and early spring NO_3^- pulses in stream water. Specifically, we wanted to evaluate the relative importance of atmospheric *versus* other NO_3^- sources in the stream before, during, and after snowmelt and to determine whether NO_3^- sources changed as a result of different snowmelt dynamics.

Methods

SITE DESCRIPTION

The study was conducted in a 135-ha Archer Creek subcatchment of the Arbutus Lake Watershed in the Huntington Wildlife Forest (HF) in the Adirondack Region of New York State (Figure 1). Bedrock at HF consists primarily of granitic gneiss (Fisher, 1957). Glacial till deposits from the continental glaciation that retreated 10,000 to 15,000 years ago dominate the parent material; they are characterized by high Si content. High sand (75%) and low clay (<10%) content provide good drainage. Boulders and stones are abundant across the soil profile. Upland soils are coarse loamy, mixed, frigid, Typic Haplorthods of the Beckett-Mundal association, less than 1 m thick. Wetlands consist of Greenwood mucky peats from 1 to 5 m thick (Somers, 1986; McHale, 1999).

The climate at the HF is continental. Mean annual temperature is 4.4 °C and mean annual precipitation is 1010 mm (Shepard *et al.*, 1989). Vegetation includes northern

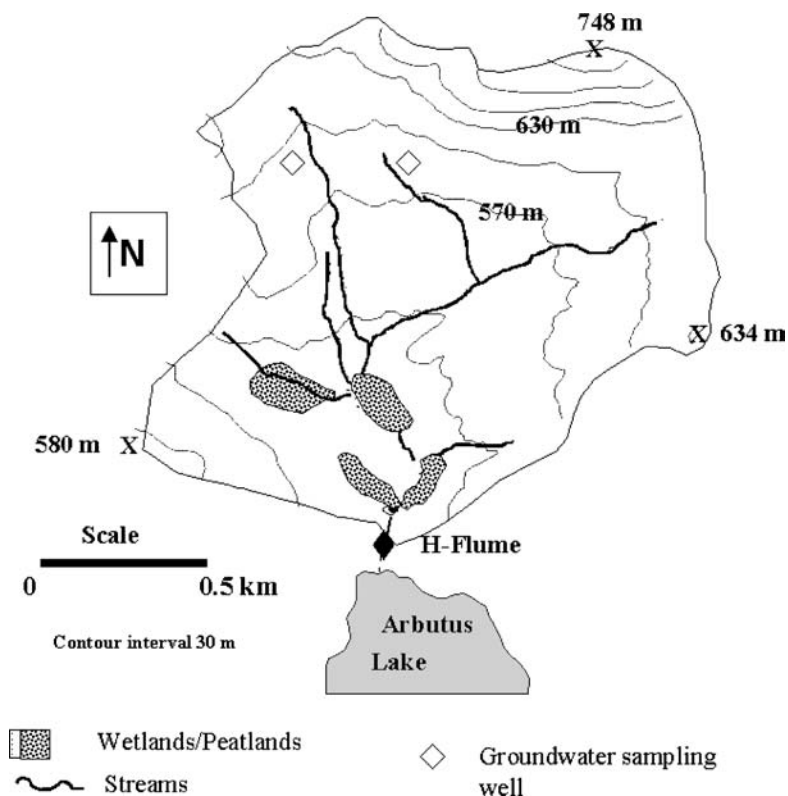


Figure 1. Map of the Arbutus Lake Watershed in Adirondack Park, N.Y.

hardwood forest, with mixed hardwood-conifer stands found mostly at lower elevations. *Fagus grandifolia* (American beech) and *Acer saccharum* (sugar maple) dominate the overstory at mid- and higher elevations. *Tsuga canadensis* (eastern hemlock) and *Picea rubens* (red spruce) replace the beech and sugar maple in the overstory at lower elevations. *Abies balsamea* (balsam fir) is scattered throughout the watershed. Some of the wetlands support *Alnus rubrum* (speckled alder), an N-fixing species (Bischoff *et al.*, 2001; Hurd *et al.*, 2001).

Archer Creek has several tributaries (Figure 1). One of the tributaries exhibits unusually high NO_3^- concentrations throughout the year (McHale *et al.*, 2002). Another tributary forms an extensive wetland before it resumes channelized flow. Because most of the vegetation of this wetland is coniferous, this is a shaded, low-lying area that remains cooler and retains snow longer in spring than most of the upper watershed. At low elevation Archer Creek flows through an open grassy field, and a small alder wetland, before it empties into Arbutus Lake.

STREAM DISCHARGE AND WATER CHEMISTRY

Snow depth and snowfall were measured with a snow stake every morning of each winter day by the Adirondack Ecological Center staff at the NADP/NTN site ~1.3 km from Arbutus Lake. Precipitation data were obtained from the NADP site located at HF (<http://nadp.sws.uiuc.edu>); daily precipitation for spring 2002 was not available after early May (Figure 2). Melted precipitation was measured by a Belfort weighing-type rain gage, and maximum and minimum temperatures were read from a hygrothermograph chart. Stream discharge has been monitored on Archer Creek, the main inlet to Arbutus Lake, continuously since 1994. An H-flume located 10 m away from the lake and equipped with automated stage-height reading recorded at 15-min intervals. Fifteen-minute data were averaged daily. The H-flume was enclosed, and a heater was used to keep the water inside ice-free.

Duplicate weekly samples were taken at the H-flume for determining water chemistry with more frequent sampling during storm and snowmelt events. Chemistry for those days without actual measurements was estimated by linear extrapolation. Fluxes were determined by multiplying daily discharge values by nitrate concentrations.

Samples for chemical analyses were shipped on ice to the Biogeochemistry Laboratory at SUNY-ESF in Syracuse, NY, where they were analyzed as follows: NO_3^- on a Dionex IC, DOC on a Tekmar-Dohrmann Phoenix 8000 TOC analyzer, and total Al and dissolved Si on a Perkin-Elmer ICP-AEC Div 3300 instrument. All DOC samples were filtered with 0.5 μm glass fiber filter prior to analysis. The laboratory is a participant in the U.S. Geological Survey performance evaluation program to ensure data quality. A system of calibration QC, detection QC, analytical blanks and replicates is used with every set of samples (Mitchell *et al.*, 2001).

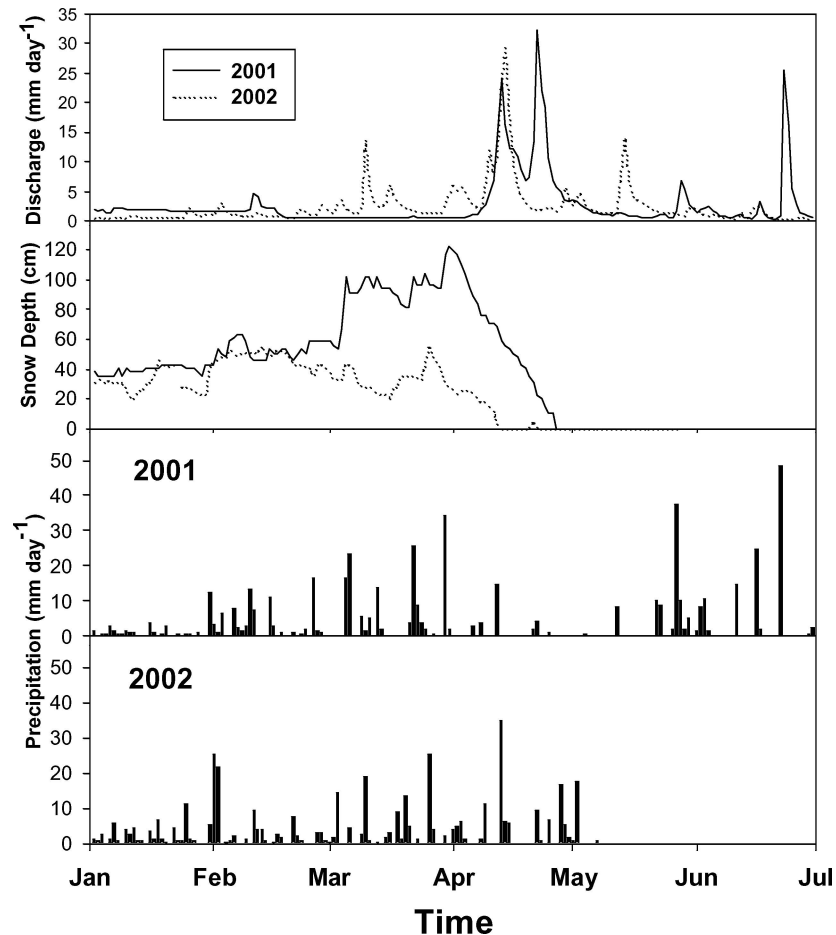


Figure 2. Daily discharge, snow depth, and precipitation from January to June of 2001 and 2002 in Arbutus Lake Watershed in the Adirondack Park, N.Y.

SAMPLE COLLECTION FOR NATURAL ABUNDANCE ISOTOPES

For the 2001 snowmelt, only stream water was sampled to test the procedures and establish the range of isotopic values. Samples were obtained directly at the H-flume in the beginning and in the middle of each month starting on February 25 until June 18. Throughfall and bulk precipitation values were determined in September and October 2001. Two specially-made collectors were placed under each: deciduous canopy, coniferous canopy, and in the open (total of 6 collectors). Each collector consisted of three 1-m long sections of plastic gutters delivering precipitation through a piece of window screen (to filter coarse particulates) into a common capped bucket. Collection periods for each sample ranged from 2 days to 1 week, depending on precipitation amounts and NO_3^- concentrations. During

longer collection periods (more than 1 day and less than 1 week), samples were removed periodically from buckets and refrigerated unfiltered in the dark until sufficient amount ($>100 \text{ mol NO}_3^-$) was collected for isotopic analysis of NO_3^- . “Grab” snow samples were collected in February 2002 from two locations in the watershed, at the flume, and about 300 m north of the flume; snow was melted and the resulting water was treated as above. Reported isotopic values for $\delta^{18}\text{O}$ of NO_3^- of throughfall, bulk precipitation, and snow in this region (northeastern U.S.) have a seasonal variation of only 2–4‰ (Pardo *et al.*, 2003); therefore, we believe that fall throughfall and bulk precipitation and a one-time snow sampling gave us a sufficient representation of isotopic values of atmospheric NO_3^- at our site.

Groundwater sampling was often hindered by inaccessibility of wells in deep snow. Isotopic analysis of groundwater NO_3^- was not possible in most wells in the growing season due to very low NO_3^- concentrations. Groundwater was obtained in June 2002 from two wells installed in the spring of 2000 and located in the upper reaches of Archer Creek (Figure 1). One of these wells exhibits consistently high NO_3^- concentrations throughout the year. Results of previous hydrogeochemical studies suggested that this well was influenced by deep groundwater (well depth of 144 cm with 55 cm of screening from the bottom) with high NO_3^- concentrations (McHale *et al.*, 2002). Water in the wells was pumped out prior to sampling. About 1 hour was needed to recharge the deep groundwater well, and overnight for the other well. We collected from 3 to 20 L of water per sample, depending on NO_3^- concentrations, to obtain $>100 \text{ mol}$ of NO_3^- for isotopic analyses.

Isotopic preparation followed the procedures of Chang *et al.* (1999), which adapted the method of Silva *et al.* (2000) for low NO_3^- concentrations. Briefly, pre-filtered water sample was passed through two resins on columns, cation (hydrogen form, Biorad Co.) and anion (chloride form, Biorad Co.). Aliquots were taken before and after passing through the resins to check for NO_3^- recovery. Anion columns with concentrated NO_3^- were shipped on ice from the HF to the Biogeochemistry Laboratory at SUNY-ESF for processing.

Samples on anion resin in columns were stored at 2°C until further processing. Nitrate was extracted with 30 ml of 3M HCl, and solution neutralized and purified with silver oxide; in this step, we ground the silver oxide powder with a glass mortar rather than simply mixed it into the solution. After a series of purifications and filtration, the sample was frozen and freeze-dried to solid silver nitrate. This solid was later weighed into silver capsules (Elemental Microanalysis Limited). Samples were shipped to the USGS Isotopic Laboratory in Menlo Park, CA for isotopic ratio determination of N and O by pyrolysis (Eurovector EA at 1300°C) on a Micromass IsoPrime stable isotope mass spectrometer.

The reported values are defined as:

$$\delta^{15}\text{N} = \left(\frac{{}^{15}\text{N}/{}^{14}\text{N}_{\text{sample}}}{{}^{15}\text{N}/{}^{14}\text{N}_{\text{standard}}} - 1 \right) \times 1000[\text{‰}]$$

$$\delta^{18}\text{O} = \left(\frac{{}^{18}\text{O}/{}^{16}\text{O}_{\text{sample}}}{{}^{18}\text{O}/{}^{16}\text{O}_{\text{standard}}} - 1 \right) \times 1000[\text{‰}]$$

Procedural quality was controlled with every step of the procedure. First, most of the samples were collected, processed, and analyzed in duplicate. Duplicate isotopic determinations on each sample were averaged; however, due to low nitrate levels in one of the sampled wells, only one isotopic determination was possible. Second, a potassium nitrate solution at concentrations matching those of field samples was passed through resin columns, processed, and analyzed with each batch of field samples in 2002. Third, USGS Isotopic Laboratory uses AgNO_3 internal standard with $\delta^{15}\text{N}$ of 15.95‰ relative to air nitrogen and $\delta^{18}\text{O}$ of 19.6‰ relative to SMOW; the oxygen of the AgNO_3 was prepared for calibration using the older, closed tube method before there were internationally accepted standards for $\delta^{18}\text{O}-\text{NO}_3^-$. Analytical precision for our samples was $\pm 0.6\%$ for $\delta^{15}\text{N}$ and $\pm 0.7\%$ for $\delta^{18}\text{O}$.

High concentrations of DOC in surface waters are thought to obscure true values of $\delta^{18}\text{O}-\text{NO}_3^-$ in the sample by possibly contaminating the sample with DOC-derived oxygens. This could occur if the resins failed to remove all DOC from water sample. During sample preparation in our study, DOC, when present, was readily visible on both columns as a dark line that moved downward with increasing water volume on the resins. We changed to a fresh column each time the line reached the bottom of the cation or anion resin. While not specifically tested, our resin eluent was free of DOC when it was colorless rather than having a faint yellowish tint. Surface water NO_3^- collected in 2001 had high $\delta^{18}\text{O}$ -values due to a contamination that could not be attributed to DOC. A close linear relationship between the amount of silver oxide remaining in the sample after filtration and oxygen isotopic values of these samples permitted a mass balance adjustment for the oxygen isotopic contribution of the silver oxide. For all subsequently collected samples, we used 0.2 m glass fiber filters (Millipore) rather than 0.5 m, as was done originally, to remove all remaining silver oxide as the final step before freeze-drying; with that we also eliminated the need for this adjustment.

Results

SNOW COVER AND DISCHARGE

The 2001 and 2002 late winter/early spring discharge dynamics differed from each other because of mid-winter thaws that were common in 2002, but did not occur in 2001. Mid-winter thaws are characterized as short-duration (one to a few days) thaws that produce considerably lower peaks in discharge than the main melt that ends the snowpack duration. “Main” snowmelt then occurs at the end of the snowpack season and results in a distinct, major peak in discharge. Thus, snow cover in 2001 was continuous, and winter ended with a dramatic melt and a decrease in snow cover from a maximum of 122 cm on March 31st to 0 cm on April 25th (Figure 2). In contrast, the 2002 snow cover increased and decreased several times and the

maximum never reached 60 cm (Figure 2). Stream discharge in 2001 was very low at about 1 mm day^{-1} in mid-March and then sharply increased to 24 mm day^{-1} on April 12 with a maximum of 32 mm day^{-1} on April 21 (Figure 2). Discharge in 2002 increased and then decreased three times between mid-March and mid-April with two substantial peaks (14 mm day^{-1} on March 10 and 30 mm day^{-1} on April 12). Except for Feb. 21, 2001, and Jan. 14, 2002 when it rained, precipitation between January and March was as snow; rain increased in importance starting in April in both years (Figure 2 and <http://nadp.sws.uiuc.edu>).

NITRATE CONCENTRATIONS AND FLUXES, AND WATER CHEMISTRY

During the 2001 study period, NO_3^- concentration peaked twice at $47 \mu\text{mol L}^{-1}$ in February and $69 \mu\text{mol L}^{-1}$ shortly after snowmelt in mid-April (Figure 3). In 2002, NO_3^- concentrations peaked three times between the end of January and early May at 40 to $52 \mu\text{mol L}^{-1}$ (Figure 4). Starting in late April in both years, NO_3^- concentrations in surface water progressively decreased.

Nitrate-N flux from January 1 to June 30 totaled 2.9 kg ha^{-1} in 2001 and 1.9 kg ha^{-1} in 2002. Total annual (January 1–December 31) NO_3^- -N flux for 2001 was 3.1 kg ha^{-1} and 2.2 kg ha^{-1} for 2002. Thus, our study period included 95 and 90% of the annual NO_3^- drainage loss in 2001 and 2002, respectively. These high loss rates during these periods are comparable to those observed for an entire year from 1995 to 1998 with average annual fluxes of $2.5 \text{ kg ha}^{-1} \text{ NO}_3^-$ -N (Mitchell *et al.*, 2001).

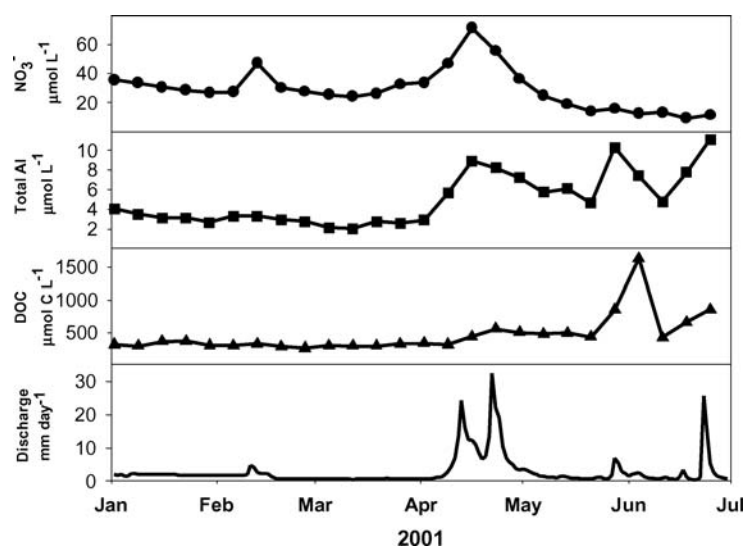


Figure 3. Nitrate, total Al, and dissolved organic carbon (DOC) concentrations, and discharge from January to June of 2001 in Arbutus Lake Watershed in the Adirondack Park, N.Y.

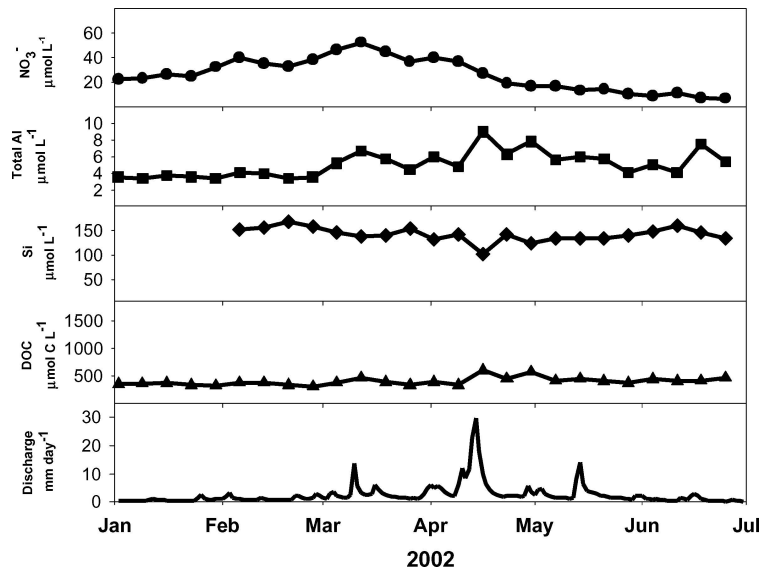


Figure 4. Nitrate, total Al, dissolved Si, and dissolved organic carbon (DOC) concentrations, and discharge from January to June of 2002 in Arbutus Lake Watershed in the Adirondack Park, N.Y.

Nitrate concentrations ranged from 6 to $18 \mu\text{mol L}^{-1}$ in throughfall under coniferous canopy, 24 to $27 \mu\text{mol L}^{-1}$ in throughfall under hardwood canopy, and were $30 \mu\text{mol L}^{-1}$ in bulk precipitation. Snow collected in February contained $29 \mu\text{mol L}^{-1}$ NO_3^- at the H-flume and $37 \mu\text{mol L}^{-1}$ in the upper reaches of the watershed.

Groundwater collected in June 2002 from the well with elevated NO_3^- concentrations had $137 \mu\text{mol NO}_3^- \text{ L}^{-1}$, while the other well had only $5.4 \mu\text{mol L}^{-1}$. The average mean well NO_3^- concentration of ~ 25 wells located within the entire Archer Creek catchment was $\sim 30 \mu\text{mol L}^{-1}$ from 2000 to 2002 (Christopher, unpublished data).

In 2001, total Al in surface water at the H-flume increased from about $3 \mu\text{mol L}^{-1}$ before snowmelt, to between 7 and $12 \mu\text{mol L}^{-1}$ in three pulses during and after snowmelt (Figure 3). In 2002, total Al concentrations increased with increasing discharge in early March to a maximum of $10 \mu\text{mol L}^{-1}$ on April 15 (Figure 4). Dissolved organic C concentrations increased markedly during the 2001 snowmelt from a relatively constant $\sim 300 \mu\text{mol C L}^{-1}$ before snowmelt, to $\sim 1500 \mu\text{mol C L}^{-1}$ by the end of May (Figure 3). In 2002, DOC exhibited more variation in concentration, with four small peaks of ~ 400 – $600 \mu\text{mol C L}^{-1}$ (Figure 4). Dissolved Si concentrations, measured in 2002 only, decreased from $148 \mu\text{mol L}^{-1}$ before snowmelt to $96 \mu\text{mol L}^{-1}$ at the peak of discharge. Total Al and DOC concentrations were positively correlated in both years, with $r = 0.72$ in 2001 and $r = 0.81$ in 2002 ($p < 0.0001$). Dissolved Si and DOC concentrations were negatively correlated, with $r = -0.71$ and $p < 0.0001$.

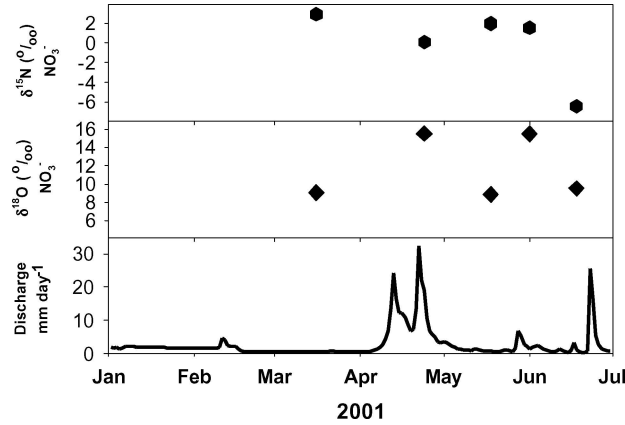


Figure 5. $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values, and discharge from January to June 2001 in the Arbutus Lake Watershed in the Adirondack Park, N.Y.

NATURAL ABUNDANCE ISOTOPIC VALUES OF NO_3^-

Stream water $\delta^{15}\text{N-NO}_3^-$ values at the H-flume ranged from -6.4‰ in mid-June of 2001 to $+3.4\text{‰}$ at the end of February of 2002. The mean for both years was $+1.2\text{‰}$ (Figures 5 and 6). Values of $\delta^{18}\text{O-NO}_3^-$ in the stream ranged from $+5.9$ to $+15.5\text{‰}$ at the end of February, 2002 and in April/June, 2001, respectively. The mean for both years was $+10.4\text{‰}$ (Figures 5 and 6). Values of $\delta^{15}\text{N-NO}_3^-$ in throughfall, bulk precipitation, and snow spanned the same range as for stream water, with a mean of

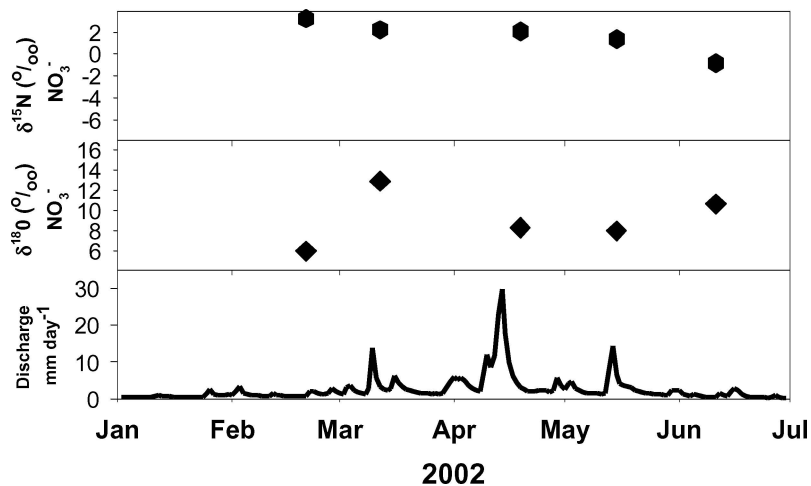


Figure 6. $\delta^{15}\text{N-NO}_3^-$, $\delta^{18}\text{O-NO}_3^-$ values, and discharge from January to June 2002 in the Arbutus Lake Watershed in the Adirondack Park, N.Y.

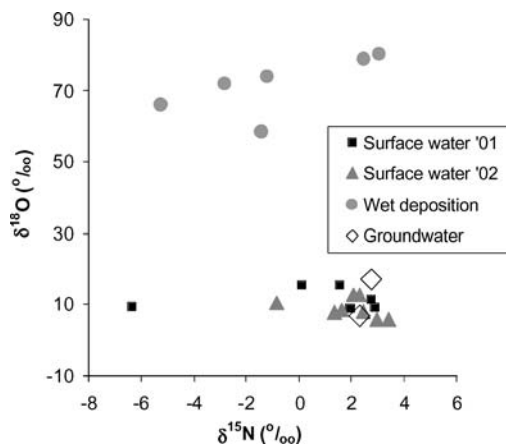


Figure 7. Values of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate in surface water (squares and triangles for 2001 and 2002, respectively) collected from February to June of 2001 and 2002, wet deposition (circles) collected from August 2001 to February 2002, and groundwater (empty diamonds) collected in spring of 2002 at the Arbutus Lake Watershed, Adirondack Park, N.Y.

-0.9‰ . Values of $\delta^{18}\text{O}$ for atmospheric NO_3^- ranged from $+58.3\text{‰}$ in throughfall under deciduous canopy to $+77.3\text{‰}$ under coniferous canopy to $+80.0\text{‰}$ in the snowpack from the upper watershed, with an overall mean of $+72.0\text{‰}$ (Figure 7). Groundwater values ranged from $+2.3$ to $+2.7\text{‰}$ for $\delta^{15}\text{N}\text{-NO}_3^-$, and from $+6.8$ to $+17.0\text{‰}$ for $\delta^{18}\text{O}\text{-NO}_3^-$.

Values of $\delta^{15}\text{N}\text{-NO}_3^-$ in stream water at the inlet increased for NO_3^- concentrations between 10 to $30\ \mu\text{mol L}^{-1}$, and leveled off at NO_3^- concentrations $>30\ \mu\text{mol L}^{-1}$ (Figure 8). The positive correlation between $\delta^{15}\text{N}\text{-NO}_3^-$ values and NO_3^- concentrations was significant only for 2002 ($r = 0.54$, $p < 0.1$ in 2001 and $r = 0.70$, $p < 0.02$ in 2002).

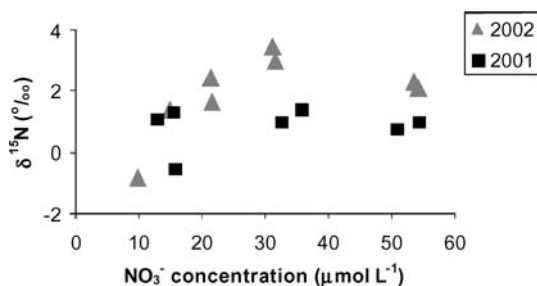


Figure 8. The relationship between nitrogen concentrations and $\delta^{15}\text{N}$ values in duplicate surface water samples collected from mid-February and mid-June of 2001 ($r = 0.54$) and 2002 ($r = 0.70$) at the Arbutus Lake watershed, Adirondack Park, N.Y.

Discussion

APPROACH

The premise of the natural abundance isotopic tracing technique in identifying sources of mixed NO_3^- solutions is that the original sources are isotopically distinct from one another. The primary isotopically-distinct sources of NO_3^- are atmospheric, with a range of +23 to +90‰ for $\delta^{18}\text{O}$ (Kendall, 1998; Ohte *et al.*, 2004), and nitrification-derived, with a theoretical range of -10 to +10‰ (Kendall, 1998). The $\delta^{18}\text{O}$ values for atmospheric NO_3^- at our site showed a clear (41–73‰) separation from our groundwater $\delta^{18}\text{O}$ - NO_3^- values of +6.8 to +17.0‰. Based on this separation, we can conclude that these two sources of NO_3^- , atmospheric and groundwater, are isotopically distinct on our site, and the technique can be used to determine the presence of these NO_3^- sources in surface water.

Our atmospheric $\delta^{18}\text{O}$ - NO_3^- values of +58 to +80‰ were within the range and somewhat higher than previously reported for rain, throughfall, snow, and snowmelt NO_3^- worldwide (Kendall, 1998), and snow at the Hubbard Brook Experimental Forest, New Hampshire (Pardo *et al.*, 2004). Our values also fitted well with those recently reported for another northeastern U.S. site, 270 km to the east, at Sleepers River, Vermont (Ohte *et al.*, 2004), and were comparable to mean $\delta^{18}\text{O}$ value of +50.5‰ in precipitation in the Catskill Mountains (Burns and Kendall, 2002), 200–300 km south southwest, which receive some of the highest rates of N deposition in the northeastern U.S. (Ollinger *et al.*, 1993).

Our groundwater $\delta^{18}\text{O}$ - NO_3^- values were higher than theoretical for nitrification-derived NO_3^- , although values as high as +16‰ may be “normal” (Kendall, 1998). Some of the highest values of $\delta^{18}\text{O}$ - NO_3^- (+14‰) have been reported for nitrification occurring in acid forest floors (Mayer *et al.*, 2001). Variability in the $\delta^{18}\text{O}$ - NO_3^- values is expected based on differences in water sources; enrichment in ^{18}O - NO_3^- may be due to the evaporation and enrichment in ^{18}O of water, alteration of the theoretical proportion of oxygen from water versus from air, enrichment in isolated soil pores, and infiltration of precipitation or snow NH_4^+ during melting (Kendall, 1998 and sources therein). We can rule out evaporation with certainty, due to climatic conditions during the study period (moist and cool). All other possibilities would be addressed best with $\delta^{18}\text{O}$ values of water, which were not available. So, while the atmospheric and groundwater NO_3^- are clearly isotopically distinct, we cannot completely rule out a potential minor contribution of atmospheric sources, in addition to nitrification, to our groundwater NO_3^- .

Nitrification-derived NO_3^- occurs in the soil-forest floor complex, where it is produced from mineralization and nitrification of organic matter, and in groundwater, where it resides after leaching from the plant-rooting zone. In addition to distinguishing between atmospheric and nitrification sources, it is important to try to distinguish between the soil *versus* groundwater sources of NO_3^- in surface waters because that will determine possible methods of controlling NO_3^- export from

watersheds. Therefore, to substantiate NO_3^- source data, we used total Al, dissolved Si, and DOC concentrations in stream water to indicate prevalent water flow paths that were likely to have contributed to the total stream flux during NO_3^- pulses. An increase in stream Al during snowmelt on a site with Spodosol soils indicates Al mobilization from the mineral soil (Driscoll *et al.*, 1984), especially without a simultaneous increase in DOC; increased DOC concentrations suggest forest floor contributions (Cronan and Aiken, 1985; Mulholland *et al.*, 1990; Hornberger *et al.*, 1994; Boyer *et al.*, 1997; Michalzik *et al.*, 2001; Inamdar *et al.*, 2004). Wetlands are a possible contributor of DOC in addition to the forest floor. However, because wetlands are not expected to produce NO_3^- pulses, the potential contribution of wetlands to the DOC flux does not change our conclusions regarding sources of NO_3^- . High dissolved Si concentrations can be used in post-glacial catchments such as ours to indicate till groundwater contributions (Hinton *et al.*, 1994; Hazlett *et al.*, 2001). Positive correlations between Al and DOC, and a negative correlation between dissolved Si and DOC at our site during snowmelt supported our choices for indicators of the pathways of water movement.

WINTER SOURCES OF NITRATE

Before the onset of the main snowmelt in 2001, values of natural abundance isotopes of N and O in NO_3^- indicated nitrification as a source of NO_3^- . Elevated dissolved Si and low NO_3^- , total Al, and DOC concentrations suggested that groundwater generated most of the water flux. Therefore, groundwater appeared to be the main contributor to NO_3^- flux in Archer Creek during that time. These data support the conclusions of previous hydrogeochemical studies of base flow chemistry and the importance of groundwater in this catchment (McHale *et al.*, 2002).

Fluctuating discharge before the main snowmelt in 2002 was due to brief mid-winter thaws caused by above-freezing air temperatures (data not shown); concomitant peaks in NO_3^- and total Al concentrations indicated that NO_3^- was flushed from soil storage. Dissolved organic carbon concentrations during mid-winter thaws fluctuated about the low for the season suggesting that the increase in water flux did not originate in high DOC-generating compartments such as wetlands or the forest floor. The largest wetland in our watershed supports mostly coniferous trees which create a shaded cool environment that loses snow cover later than other areas in the watershed (personal observations), and, probably does not undergo mid-winter thaws due to a cooler microclimate.

NITRATE SOURCES DURING THE MAIN SNOWMELT

Dramatic decreases in snow cover and concomitant increases in discharge, and in NO_3^- , total Al, and DOC concentrations marked the changes associated with main snowmelt in both years. Also, a prominent decrease in dissolved Si concentration was observed in 2002, the only year for which Si data were available. Snowpack had

relatively high NO_3^- concentrations, suggesting that snowmelt could raise surface water NO_3^- concentrations rather than dilute them as suggested for other sites (Rascher *et al.*, 1987; Williams *et al.*, 1996; Brooks and Williams, 1999). However, a direct comparison of $\delta^{15}\text{N}-\text{NO}_3^-$ and, in particular, $\delta^{18}\text{O}-\text{NO}_3^-$ values of surface water and wet deposition effectively eliminated snow-stored atmospheric NO_3^- as a major source of the observed NO_3^- pulse in surface water. The isotopic composition of NO_3^- in surface water was distinctly different from that of atmospheric NO_3^- , almost identical to that of our groundwater NO_3^- , and within the expanded range of nitrification NO_3^- of -10 to $+16\text{‰}$ for $\delta^{18}\text{O}$ (Kendall, 1998; Mayer *et al.*, 2001). The upper range of these values may be due to a heavier $\delta^{18}\text{O}$ of the water source of oxygen, or a minor atmospheric NO_3^- inclusion, and more work is needed to elucidate these possibilities (Kendall, 1998).

The groundwater well sampled in this study yielded very high NO_3^- concentrations which may result from high rates of NO_3^- production in the soil in the immediate vicinity of this well, and subsequent leaching. This well is within a sub-catchment this is characterized by higher concentrations of NO_3^- in the soil and surface waters than elsewhere in the watershed (Christopher *et al.*, 2005). High NO_3^- levels in this groundwater well were reported previously and appear to persist throughout the year (McHale *et al.*, 2002).

The increase in DOC concentrations occurring slightly after the peak in discharge as snowmelt progresses suggests an increasing contribution of flow from the forest floor (Hornberger *et al.*, 1994; Boyer *et al.*, 1997, 2000). The concentrations of total Al and DOC in stream water closely matched both discharge and increase in NO_3^- concentration during snowmelt, indicating that as discharge increased, the proportion of soil water and, with it, soil NO_3^- , also increased. By contrast, dissolved Si concentrations decreased as discharge increased, substantiating the likelihood of an addition of a water source with low Si concentrations from upper mineral soil or the forest floor. Thus, based on the high Al and an increase in DOC concentrations, a decrease in dissolved Si concentration, and on nitrification as the source of NO_3^- , we conclude that NO_3^- in surface water during the main snowmelt originated in soil, and became mixed with groundwater NO_3^- present in the creek before snowmelt. As snowmelt proceeded, the relative proportions of groundwater to mineral soil and then to forest floor water decreased. The function of melt water appears to have been to flush the soil solution to surface waters and replace it in the soil profile.

Based on results from TOPMODEL simulations, Inamdar *et al.* (2004) also suggested that displacement of stored soil water and ground water during storms were important to flow generation in the Archer Creek catchment. A displacement of pre-melt water has been described also for Sleepers River in Vermont (McGlynn *et al.*, 1999) and other catchments across the U.S. (Burns and Kendall, 2002; Campbell *et al.*, 2002).

How can NO_3^- from soil and forest floor be flushed to the stream while NO_3^- from the snowpack retained in the soil? The answer lies probably in the sequence of

these events and in water storage capacity in the soil profile in this catchment. When air temperatures are at or below freezing, and snow does not melt, we can reasonably assume that water does not flow through the system. Soil temperatures under the snow, though not measured in this study, can remain above freezing despite below freezing air temperatures (Fitzhugh *et al.*, 2001, 2003; Mitchell *et al.*, 1996a), and hence organic matter mineralization can take place. Absence of plant N-uptake during the dormant season renders ammonium available for nitrification. Lack of water movement allows for a build up of NO_3^- in the soil horizons. When water flow resumes in response to a thaw, NO_3^- is flushed from storage to lower soil profile, or to groundwater and stream. The amount of melt water and available flow paths probably determine the destination of NO_3^- movement. The fact that mid-winter thaws at our site in 2001 produced several small NO_3^- peaks is consistent with NO_3^- accumulation in the soil profile and the release of accumulated NO_3^- to stream with increase in discharge; the lack of a large NO_3^- peak in main snowmelt seems to be due to the exhaustion of the soil NO_3^- pool available for flushing. The effects of aboveground temperature and snowmelt dynamics on nitrate losses from the entire Arbutus Watershed were shown by Park *et al.* (2003). As the water equivalent in snow undergoes year-to-year variations, and flow paths can change as well, the presence and relative proportion of atmospheric NO_3^- in stream waters within a site can be expected to change from year-to-year. Among-site variation in relative proportions of NO_3^- sources to stream water may also be due to differences in the soil storage capacity of watersheds.

NITRATE SOURCES AFTER THE MAIN SNOWMELT

In the Archer Creek catchment, atmospheric NO_3^- that was deposited in snow was not detected in surface waters by mid-June when this study ended. Because our sampling was biweekly rather than event-based, there is a possibility that a small pulse of melt water was not detected. Overall, the decrease in NO_3^- concentrations indicated that NO_3^- sources operating during the melt, that is, nitrification, decreased in their importance, and the rapid rise in Si concentration indicated an once-again increasing contribution of groundwater. Also, the process of nitrification itself may have slowed in spring due to increased uptake by plants of ammonium. Alternatively, and possibly concomitantly, water volumes moving through the soil profile may have been insufficient to deliver accumulated NO_3^- to the creek. The late spring increase in DOC, without the concomitant increase in Al or NO_3^- may be due to the flushing of the conifer wetland as it loses snow and probably resumes biological activity later than the upland areas. In fact, the single low $\delta^{15}\text{N}$ value detected during the 2002 spring peak in discharge may be indicative of a different source of organic matter turnover than otherwise observed.

Snowpack NO_3^- , along with melt water, apparently replaced soil and perhaps even groundwater NO_3^- in the storage. The fate of snowpack NO_3^- that came to reside in the soil profile may include biological uptake, denitrification, and storage in

soil and/or groundwater. Long-term soil storage is unlikely because it would indicate that atmospheric NO_3^- bearing its distinct isotopic values would be eventually flushed to the stream during storms that follow snowmelt and that did not seem to be the case until June 30 in 2001 and 2002. In fact, the more time that passes between snowmelt and subsequent storm events, the less likely it is that the snow-deposited NO_3^- would be detected in surface waters because NO_3^- concentrations in surface waters decrease markedly with the onset of the growing season in this watershed, suggesting high rates of N uptake by biota (Mitchell *et al.*, 2001; Park *et al.*, 2003).

The fate of snow-deposited NH_4^+ was not evaluated. However, it is not likely that any NH_4^+ in snow that was nitrified (Schaefer and Driscoll, 1993) was a substantial source of surface water NO_3^- since this NO_3^- would have the same fate as the snow source that we evaluated.

COMPARISON WITH OTHER STUDIES

Many studies have attempted to determine NO_3^- sources in runoff from spring snowmelt, and many of them employed natural abundance isotopes of ^{15}N and ^{18}O in NO_3^- as tracers. Burns and Kendall (2002) showed the presence of nitrification-derived and lack of atmospheric NO_3^- in spring runoff in the Catskill Mountains of New York; they concluded that snowmelt NO_3^- went into storage. Pardo and others (2004) detected no atmospheric NO_3^- signal during spring snowmelt despite a 6‰ higher values of $\delta^{18}\text{O}$ in winter than in summer. Similar to our study, their sampling frequency may have been insufficient to detect a short-duration snowmelt pulse. Ohte and others (2004) observed an early pulse of snowmelt and a fast shift to soil NO_3^- as snowmelt progressed indicating a direct flow of melt water to the stream channel. Spoelstra and others (2001) determined that nitrification-derived NO_3^- constituted almost 70% of NO_3^- in snowmelt runoff at the Turkey Lakes Watershed in Ontario, Canada, while 30% was atmospherically-derived. At the Turkey Lakes Watershed, discharge at snowmelt seems to be controlled by water flow through shallow soil horizons without entering basal till (Hazlett *et al.*, 2001). In our study, water flow paths include basal till, as evidenced by increases in Si concentrations in this study and by hydrogeochemical data from previous studies (McHale *et al.*, 2002); thus, storage in our soil profile is presumably greater. This suggests that, for the same amount of snow, a smaller volume of melt water can be stored in the soil before entering the stream at the Turkey Lakes Watershed than at our site, and available soil storage may explain the differences in these two studies. Hydrological storage appeared to control the differences in NO_3^- exports between two watersheds at the Hubbard Brook Experimental Forest in New Hampshire (Pardo *et al.*, 2004).

Using a two-tracer three-component hydrograph separation with H_2^{18}O and Cl^- as tracers, McHale *et al.* (2002) determined for our site that snowmelt contributed 5%, soil water 15%, and till groundwater 75% to total streamflow during

the snowmelt of 1996. Again, these percentages, especially of snowmelt, will vary depending on how much melt water is available to enter and flush storage in the soil profile or groundwater, and on the physical characteristics of soil storage itself, i.e. whether there is a frozen layer that limits soil storage. In Sleepers River Watershed, Vermont, for example, melt water inputs to stream were 10–40% higher when the ground was frozen than when it was not (Shanley *et al.*, 2002).

FREQUENCY OF SAMPLING

Discharge in our catchment is very responsive to water movement through the system, regardless of whether water moves due to mid-winter thaws, the main snowmelt, or rain events. Solute concentrations and fluxes, in decreasing order those of NO_3^- , total Al, and DOC, were also responsive to water movement. The apparent differences in sensitivity of these solutes to water flux are probably due to water flow paths and biological activity generating NO_3^- and DOC. In the event of frozen soil, direct runoff of meltwater over the soil surface might cause altogether different dynamics (Shanley *et al.*, 2002). Because of this responsiveness, more frequent sampling for natural abundance isotopes may have been more appropriate to fully eliminate the possibility of mixing in the stream of ground and soil water NO_3^- with atmospheric NO_3^- .

Conclusions

Based on isotopic analysis indicating nitrification, and water chemistry indicating water flow through mineral soil/forest floor, we conclude that the main source of NO_3^- in the stream during late winter/early spring NO_3^- pulses of 2001 and 2002 was nitrification in the forest floor – mineral soil complex. Atmospheric NO_3^- in the snowpack, regardless of snowpack size or melt dynamics, did not seem to play a major role in stream NO_3^- during spring NO_3^- pulses, except perhaps for the minor component that may have been present in groundwater. These findings add to the growing body of work which shows that N from atmospheric deposition is retained and cycled in forests, which may be related to forest health (Durka *et al.*, 1994), and that nitrification-derived NO_3^- is the primary source of NO_3^- for export. Therefore, a successful strategy for lowering of NO_3^- exports in surface waters will require a greater understanding of those factors that regulate generation and retention of NO_3^- in soils. Ours supports previous studies which showed that especially during periods of low discharge, groundwater may be an important source of NO_3^- to surface water. Therefore, the processes that contribute to NO_3^- transfer to groundwater also need to be quantified (Mitchell, 2001). To reconcile the presence in stream water of atmospheric NO_3^- on other sites and contribution of melt water to snowmelt runoff at our site in 1996 (McHale *et al.*, 2002), we propose that soil storage capacity of the catchment is responsible for inter-site variability, while flow

paths and amount of snow available for melting affects within-site year-to-year variation. It is also possible that with more frequent sampling for isotopic analysis, we could have detected small atmospheric NO_3^- pulse during the main snowmelt, as observed elsewhere.

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