

Tracing sources of nitrate in snowmelt runoff using the oxygen and nitrogen isotopic compositions of nitrate

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Abstract Many upland catchments experience increased nitrate and hydrogen ion concentrations in stream water during the early snowmelt period. The dominant source of this nitrate is not well known, but likely contributors include atmospheric deposition of nitrate and ammonium in the snowpack, and soil-derived nitrate. Pilot studies initiated in three catchments during the 1994 snowmelt season show that these sources of nitrate have distinctive $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ compositions. Almost all the stream samples have nitrate $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values within the range of the premelt soil and stream waters, suggesting that atmospheric nitrate eluted from the 1994 snowpack is a minor source of nitrate in early streamflow. Therefore, the nitrate eluted from the snowpack appears to go into storage, and the nitrate pulse in stream water during early melt appears to be largely derived from precipitation from previous months or years that is flushed from storage.

INTRODUCTION

During early spring melt, episodic acidification occurs in the stream waters of many small upland catchments. This is partly due to large pulses of nitrate and hydrogen ions being flushed into the streams at the onset of melt. The immediate source of this nitrate is controversial. Two likely sources are (1) atmospherically derived nitrate in the snowpack that is eluted during early melt and transported directly to the stream, or (2) microbially produced nitrate in the soil zone that is flushed into the stream by percolating meltwater. Other potential sources of this nitrate include nitrification of snowpack ammonium (Rascher *et al.*, 1987), and atmospherically derived nitrate from earlier seasons or years that has been biologically recycled and stored in the soil zone.

Nitrogen isotope values ($\delta^{15}\text{N}$) are reported in per mil (‰) relative to atmospheric AIR, which is defined as 0‰; oxygen isotope values ($\delta^{18}\text{O}$) are reported relative to the standard VSMOW, also defined as 0‰. Nitrate produced by biologically mediated nitrification of ammonium derives 2/3 of its oxygen from ambient water and 1/3 from atmospheric O_2 , which has a $\delta^{18}\text{O}$ value of +23‰ (Bottcher *et al.*, 1990; Voerkelius, 1990). Consequently, nitrate formed in waters with $\delta^{18}\text{O}$ values in the range of -25 to -5‰ should have $\delta^{18}\text{O}$ values in the range of -9 to +4‰. The $\delta^{15}\text{N}$ of atmospheric nitrate has a moderate range of compositions centered around 0‰. It was initially expected that the $\delta^{18}\text{O}$ of nitrate in atmospheric deposition would be similar to the $\delta^{18}\text{O}$ of atmospheric O_2 . However, a recent study by Durka *et al.* (1994) found that the nitrate in precipitation in several German forests had $\delta^{18}\text{O}$ values of +55 to +75‰. Typical ranges of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of various potential sources of nitrate are listed on Table 1.

To test the applicability of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ for tracing nitrate sources to streamflow over the melt period, pilot studies were initiated in three catchments during the 1994 snowmelt season. These pilot studies included the collection and analysis of several hundred water samples at each site for major ion concentrations and water $\delta^{18}\text{O}$, and detailed hydrologic monitoring at several locations. A subset of these samples was analyzed for $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of nitrate. Only the nitrate isotope data are discussed in detail in this paper. It was hoped that the results from these pilot studies would provide needed guidelines for future full-scale investigations of nitrate sources.

Table 1 Ranges of isotopic compositions of potential sources of nitrate.

| Sources of nitrate* | $\delta^{18}\text{O}$ of nitrate (‰) | $\delta^{15}\text{N}$ of nitrate (‰) |
|---------------------------------------|--------------------------------------|--------------------------------------|
| Atmospheric NO_3^- | +23 to +75 | -10 to +9 |
| Nitrification of snow NH_4^+ | -9 to +1 | -15 to 0 |
| Nitrification of soil NH_4^+ | -5 to +7 | +4 to +9 |
| Nitrate fertilizer | +23 to +24 | -5 to +5 |
| Ammonium fertilizer | -5 to +7 | -5 to 0 |
| Animal waste | -5 to +7 | +10 to +20 |

* Data from Heaton (1986), Voerkelius (1990), Durka *et al.* (1994), and this study.

SITE DESCRIPTIONS

The pilot studies were conducted at three watersheds in the USA: Biscuit Brook and Dry Creek tributaries of the West Branch of the Neversink River, Catskill Mountains, New York; Andrews Creek and Icy Brook, Loch Vale watershed, Rocky Mountain National Park, Colorado; and four tributaries of Sleepers River, Danville, Vermont.

The Catskill Mountains consist of nearly flat-lying sandstone, shale, and conglomerate covered by glacial till and thin soils. The two sub-basins studied are largely forested. About 75% of the drinking water in New York City is derived from reservoirs in the region. NO_3^- concentrations in streams have been increasing since the 1970s, and have a significant and increasing role in surface water acidification (Murdoch & Stoddard, 1992).

The Loch Vale watershed is 660 ha in area and ranges in elevation from 3050 to 4026 m; the Andrews Creek and Icy Brook sub-basins occupy about 75% of the watershed and are nearly entirely alpine. Less than 1% of these sub-basins are forested

and only 5 to 15% is covered by well-developed soils formed on granitic bedrock. Total storage of soil water and groundwater was estimated to be less than 5% of the mean annual outflow (Baron & Denning, 1992).

The Sleepers River watershed is a 111-km² basin with several sub-basins of various sizes and land uses developed on carbonate schist. Elevations range from 195-790 m. Most of the samples were collected at W-9, a 47-ha forested catchment. Soil is developed on silty till which covers the bedrock to thicknesses of 1-3 m. Three nested basins show increasing percentages of new water during rain storms and snowmelt with increasing basin size (Shanley *et al.*, in review).

METHODS

Atmospheric deposition was sampled by collecting snow profiles and cores at several locations prior to melt and by collecting snowmelt in lysimeters throughout the melt period. A few rain samples were also collected. Nitrate in soil was sampled by collecting shallow soil-water samples. There was insufficient nitrate for analysis in Loch Vale soils, perhaps because it had already been leached away. Stream samples were collected before, during, and after the melt period.

We recently developed methods to concentrate nitrate in the field and to prepare the nitrate for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ analyses (Wilkison *et al.*, in review; Silva *et al.*, in review; and Silva *et al.*, in preparation). The new methods (1) concentrate nitrate from dilute waters that previously could not be easily analyzed; (2) simplify transport, storage, and archiving of samples; and (3) eliminate the need for using hazardous chemicals for preserving or preparing samples for $\delta^{18}\text{O}$ analysis.

Approximate nitrate concentrations were measured in the field to determine how much water to collect for isotopic analysis. The waters were filtered to remove particulates and then dripped through commercially available, prefilled, disposable anion-exchange columns. The columns were capped, chilled, and shipped to the laboratory for preparation or archiving. At the laboratory, the nitrate was stripped from the columns, neutralized, and filtered. The solution was then split into two aliquots for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ preparations. The aliquot for $\delta^{15}\text{N}$ was freeze-dried and then converted to pure N_2 gas by sealed tube combustion with Cu, CuO, and CaO (Kendall & Grim, 1990); the analytical precision of the entire procedure using laboratory reagents is 0.05‰.

For $\delta^{18}\text{O}$ preparation, oxygen-bearing anions other than nitrate were removed by precipitation (Amberger & Schmidt, 1988), and the sample was filtered and passed through a cation-exchange column. To eliminate the use of hazardous chemicals like mercuric cyanide, we developed a new method for $\delta^{18}\text{O}$ preparation (Silva *et al.*, in preparation) whereby the samples were neutralized with Ag_2O , the AgCl removed by filtration, and any residual DOC removed by agitation with activated carbon and subsequent filtration. The sample was then freeze-dried in a quartz tube and combusted to CO_2 using an excess of graphite. Yields of CO_2 were consistently better than 95% and analytical precision was about 0.5‰ (Silva *et al.*, in preparation) in tests with reagent AgNO_3 .

Various logistical problems caused some samples to be left unfiltered, filtered, or on the columns for up to 2 weeks unchilled and possibly subject to biological reaction. For some samples, there was less nitrate recovered from the columns than expected on

the basis of the measured nitrate contents of the original water. In addition, about 30% of the samples had such low CO₂ yields (< 10 μmol) that the δ¹⁸O values are somewhat questionable. Consequently, our best estimates of the reproducibility of nitrate δ¹⁸O values for this pilot study are ±2‰ for samples > 50 μmol and ±5‰ for samples < 10 μmol; the reproducibility for δ¹⁵N is probably better than ±0.5‰. Data for samples < 5 μmol are not plotted on the figures because of the poor precision of the analyses; these samples were almost all snow and melt samples with nitrate δ¹⁸O values in the range of +20 to +30‰. Our methods have been improved to eliminate these problems.

RESULTS AND DISCUSSION

Characterization of nitrate sources

Atmospheric deposition Snow at the three sites has nitrate and ammonium concentrations in the ranges of 10–20 μeq l⁻¹ and 1–10 μeq l⁻¹, respectively; the solutes are eluted from the snowpack early in the melt period. The nitrate and ammonium concentrations of snowmelt change rapidly during the early melt period; for example, preferential elution caused the nitrate and ammonium concentrations at Loch Vale to drop from 50 to 15 μeq l⁻¹ and 20 to 5 μeq l⁻¹, respectively, in less than 1 week.

Too few snow and snowmelt samples were analyzed for nitrate isotopic compositions to allow many generalizations, but a few patterns can be noted. There appears to be considerable spatial and temporal variability in the δ¹⁸O and δ¹⁵N values. In general, the ranges in melt are the same as in the snow. The nitrate in snow has a wide range of isotopic compositions, with δ¹⁸O values of +20 to +60‰ and δ¹⁵N values of -1 to +9‰. Almost all the samples that have δ¹⁸O values < +30‰ are very small samples; hence, these compositions are somewhat questionable. All three sites have nitrate δ¹⁸O values heavier than the +23‰ of atmospheric O₂. These heavy values make the atmospheric nitrate very distinctive. Samples from the Catskills (Fig. 1(a)) have the lightest and least variable δ¹⁸O values, with a range of +25 to +40‰, and the widest range of δ¹⁵N values (10‰). The δ¹⁸O value of the snowpack and snowmelt appear to change during the melt period; hence, careful sampling with snowmelt lysimeters will be required to assess the changes in isotopic compositions with time.

Four rain samples were collected at Loch Vale (Fig. 1(b)) from May to October. They have nitrate and ammonium concentrations equal to or greater than snow samples. The nitrate in summer rain appears to have heavier δ¹⁸O values than in snow, possibly related to the heavier water δ¹⁸O values of precipitation in the summer. More sampling is required to detect any seasonal change in the δ¹⁸O and δ¹⁵N of rain caused by seasonal changes in water δ¹⁸O or nitrate source.

Little is known about why the δ¹⁸O of atmospheric nitrate is much heavier than atmospheric O₂, or about possible temporal and spatial variability in the δ¹⁸O content. The only other data on the δ¹⁸O of nitrate in precipitation are from German forests (Voerkelius, 1990; Durka *et al.*, 1994). Possible explanations include fractionations associated with nitrate formation in thunderstorms, incomplete combustion of fossil fuels in power plants and vehicle exhaust, and photochemical reactions in the atmosphere. Some of these processes have been shown to fractionate nitrogen (Heaton, 1990). The

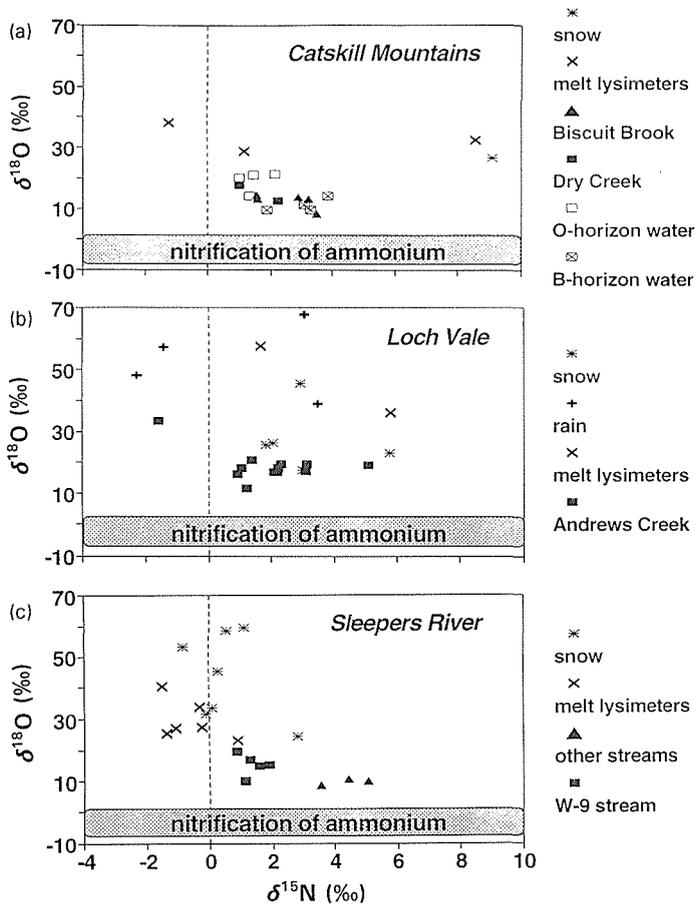


Fig. 1 $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values of nitrate samples from the Catskill Mountains, New York (a); Loch Vale watershed, Colorado (b); and Sleepers River watershed, Vermont (c).

impact of these processes on watershed nitrate budgets may be traceable if the $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ compositions are distinctive. Because the $\delta^{18}\text{O}$ of the snow reflects changes in air-mass sources, there is likely to be a correlation between water $\delta^{18}\text{O}$ and nitrate $\delta^{18}\text{O}$ values.

The molar ratio of ammonium to nitrate in precipitation in these catchments ranges from 1:2 to 1:10. Little ammonium is found in streamflow, suggesting that it is either nitrified within the snowpack or in the soil zone during the melt period, or it is adsorbed onto the soil. Although the $\delta^{18}\text{O}$ of nitrate in precipitation is heavier than other potential sources of nitrate and isotopically distinctive, nitrification of atmospheric ammonium to nitrate would cause the atmospheric source to be less distinguishable. Furthermore, the new nitrate would have $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values that are probably within 5‰ of the corresponding values for nitrification of soil ammonium. If ammonium is nitrified in the snowpack, or if there is temporal variability in the $\delta^{18}\text{O}$ of nitrate in snow, sequential snow lysimeter samples, instead of snow cores, must be used for the composition of the atmospheric end-member. Tracer tests with ^{15}N -labeled ammonium added to the

snowpack may help resolve the question of whether snow ammonium is a significant source of nitrate to streamflow (Williams *et al.*, 1994).

Soil Microbially produced nitrate in the soil is the other main potential source of nitrate in stream water. Mineralization of N in leaf litter and in the organic layer of the soil followed by nitrification while the soils are covered with an insulating layer of snow may be an important source of nitrate to surface waters during snowmelt (Rascher *et al.*, 1987); this nitrate is then flushed into the stream during snowmelt.

At the Catskills (Fig. 1(a)), lysimeters installed in the O and B soil horizons were monitored during the melt period. Nitrate concentrations ranged from 10 to 40 $\mu\text{mol l}^{-1}$, with the maximum concentrations near the time of maximum discharge. Water- $\delta^{18}\text{O}$ values showed that the soil water contained temporally variable mixtures of snowmelt and pre-melt water, with more snowmelt in the O horizon soils than in deeper soils. Nitrate in the O horizon samples had heavier $\delta^{18}\text{O}$ values and slightly lighter $\delta^{15}\text{N}$ values than in the B horizon samples, and the water in the O horizon had a lighter $\delta^{18}\text{O}$ value than water in the B horizon; this is consistent with marginal influence of atmospheric nitrate and snowmelt water in the shallow soils diminishing to almost none in the B horizon.

The $\delta^{18}\text{O}$ of nitrate in pre-melt soil and stream waters is 10 to 20‰ heavier than expected. Given the range of $\delta^{18}\text{O}$ values of soil waters (about -20 to -10‰), the $\delta^{18}\text{O}$ of nitrate should be in the range of -6 to +1‰ if the nitrate was produced by microbial nitrification. The more positive values may in part reflect isotopic fractionations resulting from the extensive recycling of nitrate; processes such as uptake and denitrification cause enrichment of the residual nitrate. However, there is no specific evidence of any kinetic enrichment. A more likely possibility for temperate catchments such as Sleepers River and the Catskills is that the soil and shallow groundwater storages were recharged by percolating snowmelt during mid-winter thaws in 1994, and that the heavy nitrate $\delta^{18}\text{O}$ values reflect the partial atmospheric source of this soil nitrate. The inverse correlations of nitrate and water $\delta^{18}\text{O}$ values in the soil horizons provide some support for this theory. If the behavior of sulfate is analogous to that of nitrate, the ^{35}S content of pre-melt soil waters can be used to test whether the soil solutes are derived from the current snowpack; with a half-life of 87 days, there is negligible ^{35}S in sulfate deposited a year ago.

An alternate explanation for the enriched $\delta^{18}\text{O}$ values, and the most likely explanation for the Loch Vale data, is that the premelt nitrate in the catchment is a combination of nitrate derived from precipitation recharged from previous years and nitrate formed locally, and hence has intermediate $\delta^{18}\text{O}$ compositions ranging from about +5 to +20‰. In other words, the rate of atmospheric deposition of nitrate is large relative to the rates of microbial nitrification on biological consumption. Hence, atmospheric nitrate has a sufficiently long residence time in the soil that it retains its atmospheric "signature" on a year-long basis. It is unclear where this nitrate reservoir might be located at Loch Vale; the few soil samples collected had insignificant nitrate concentrations. This hypothesis can be tested by examining the $\delta^{18}\text{O}$ values of rain and soil nitrate during other seasons, and by incubating soils to determine the composition of microbially produced nitrate.

Sources of nitrate in stream water

Nitrate concentrations in the streams in the three catchments ranged from low values of about $10 \mu\text{mol l}^{-1}$ to greater than $50 \mu\text{mol l}^{-1}$ during the nitrate "pulses." Ammonium concentrations were negligible.

Hydrograph separations using $\delta^{18}\text{O}$ show that during the time of maximum nitrate concentrations, the stream water contains significant amounts of pre-melt waters. The nitrate isotopic compositions of stream water during the high-nitrate pulses are, however, not distinctive and they plot approximately in the middle of the range $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values of streamflow.

Nitrate samples from seven different tributaries in the three catchments were analyzed for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. All samples except one from Loch Vale (Fig. 1(b)) plot within a narrow 15‰ range of $\delta^{18}\text{O}$ values, with only a 4‰ range in $\delta^{15}\text{N}$ values. This range is identical to the range of values for soil waters at the Catskills, and is outside the $\delta^{18}\text{O}$ range of almost all the snow and melt samples. Only snow samples with CO_2 yields $< 10 \mu\text{mol}$ and, consequently, somewhat questionable $\delta^{18}\text{O}$ values, overlap with the stream samples.

Stream W-9, which drains a pristine forested catchment at Sleepers River, shows only a 10‰ range in $\delta^{18}\text{O}$ and a 1‰ range in $\delta^{15}\text{N}$ (Fig. 1(c)); there is no obvious correlation with water $\delta^{18}\text{O}$ or chemistry. The three samples from other streams have distinctively heavier $\delta^{15}\text{N}$ values and slightly lighter $\delta^{18}\text{O}$ values. These three streams derive a larger percentage of their flow from shallow flowpaths than at the W-9 catchment (Shanley *et al.*, in review), and their drainages contain significant amounts of pasture land and agricultural land. The lighter $\delta^{18}\text{O}$ values and heavier $\delta^{15}\text{N}$ values of the mixed-use catchments may reflect significant contributions of nitrate from animal waste.

At Loch Vale, all but one of the samples from Andrews Creek have nitrate $\delta^{18}\text{O}$ values within a narrow range of +10 to +20‰. These samples show no correlation of nitrate $\delta^{18}\text{O}$ and water $\delta^{18}\text{O}$; stream samples with water $\delta^{18}\text{O}$ values indicating a range of 0 to 100% pre-event water in the stream have indistinguishable nitrate $\delta^{18}\text{O}$ values. The most obvious explanation for the almost constant $\delta^{18}\text{O}$ composition of nitrate and the lack of correlation of nitrate $\delta^{18}\text{O}$ and water $\delta^{18}\text{O}$ is that little of the nitrate in Andrews Creek is derived from melting of the 1994 snowpack.

One stream sample from Andrews Creek (Fig. 1(b)) has a nitrate $\delta^{18}\text{O}$ value almost 15‰ heavier and a $\delta^{15}\text{N}$ value 2‰ lighter than any of the other stream samples. This sample was collected on 20 April prior to any significant melting of the pack when a sunny day caused surficial melting of snow and surface runoff of this melt to the weir. The water $\delta^{18}\text{O}$ value and chemical composition of this sample suggest that melting snow is the source of the water, and the nitrate $\delta^{18}\text{O}$ is consistent with a snow source for much or all the nitrate. This sample demonstrates that when the nitrate and water are known to be derived from the snowpack, the isotopic data agree; hence, this sample provides convincing support of the validity of the dual-isotope approach for distinguishing nitrate sources.

At the Catskills, stream samples from Biscuit Brook and Dry Creek (Fig. 1(a)) show the same range of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values as the soil waters collected over the same time interval. The $\delta^{18}\text{O}$ of water in the two streams is virtually identical, too. There is a rough correlation of the temporal changes in the $\delta^{18}\text{O}$ of water, $\delta^{18}\text{O}$ of nitrate, and the

$\delta^{15}\text{N}$ of nitrate at Biscuit Brook, consistent with small additions of melt nitrate to stream water at the start of the high-flow period.

CONCLUSIONS

We conclude that analysis of both the $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of nitrate provides excellent separation of nitrate sources. Almost all the stream samples have nitrate $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values within the range of the pre-melt waters, indicating that atmospheric nitrate from the 1994 snowpack is a minor source of nitrate in early runoff. Therefore, the nitrate eluted from the snowpack appeared to go into storage, and most of the nitrate in streamflow during the period of potential acidification was derived from the soil. The main sources of uncertainty in calculating the relative contributions from the two nitrate sources are the ranges in the end-member compositions and uncertainty about whether snow ammonium is retained in the soil or is nitrified to nitrate and flushed into surface waters.

The $\delta^{18}\text{O}$ of nitrate in pre-melt waters is heavier than expected. The more positive values may indicate: (1) recharge of shallow storage by percolating snowmelt from mid-winter thaws, or (2) that atmospheric nitrate is actually a dominant source of nitrate to the catchment on a yearly basis.

Recent work in several German forests (Durka *et al.*, 1994) that also concluded that atmospheric deposition is a major source of nitrate to these catchments. They found that the lowest fraction of atmospheric nitrate was found in limed or relatively healthy forests, where nitrate consumption by plants and soil micro-organisms was sufficient to recycle a large portion of the deposited nitrate, and that sites with declining forests showed higher proportions of nitrate derived from the atmosphere and little recycling of nitrate by the ecosystem. All our forests are apparently healthy, and there are insufficient data to make any conclusions about the relationships between $\delta^{18}\text{O}$ of nitrate in storage and the relative rates of nitrate deposition, advection through the soil, and biological consumption. Nevertheless, our data indicate that these forests are leaking nitrate that is derived, in large part, from atmospheric deposition; this may be an early warning sign that these forest ecosystems are being damaged by air pollution and acid rain.

These pilot studies have clearly indicated that careful sampling of potential sources will be required for accurate estimates of their relative contributions to streamflow. In particular, the observed variability in the $\delta^{18}\text{O}$ of atmospherically derived nitrate makes it vital that snow lysimeters be positioned at several elevations, and that adequate samples be collected to assess temporal and spatial variability in the $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of newly eluted nitrate from the snowpack. Soil and shallow groundwater must be sampled several times in early winter, prior to any thaws; it is unclear how much variability might be found in these waters. The effect of nitrification of snow and soil ammonium on N budgets is unknown, and will require careful sampling combined with field experiments with ^{15}N -labeled ammonium to decipher.

REFERENCES

- Amberger, A. & Schmidt, H.-L. (1988) Naturliche Isotopengehalte von Nitrat als Indikatoren für dessen Herkunft. *Geochim. Cosmochim. Acta*, **51**, 2699-2705.
- Baron, J. & Denning, A. S. (1992) Chapter 3. Hydrologic budget estimates. In: *Biogeochemistry of a Subalpine Ecosystem: Loch Vale Watershed* (ed. by J. Baron), 12-27. Springer-Verlag, New York.

- Bottcher, J., Strelbel, O., Voerkelius, S. & Schmidt, H.-L. (1990) Using isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy aquifer. *J. Hydrol.* **114**, 413-424.
- Durka, W., Schulze, E.-D., Gebauer, G. & Voerkelius, S. (1994) Effects of forest decline on uptake and leaching of deposited nitrate determined from ^{15}N and ^{18}O measurements. *Nature* **372**, 765-767.
- Heaton, T. H. E. (1986) Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review. *Chem. Geol. (Isot. Geosci. Sec.)* **59**, 87-102.
- Heaton, T. H. E. (1990) $^{15}\text{N}/^{14}\text{N}$ ratios of NO_x from vehicle engines and coal-fired power stations. *Tellus* **42B**, 304-307.
- Kendall, C. & Grim, E. (1990) Combustion tube method for measurement of nitrogen isotope ratios using calcium oxide for total removal of carbon dioxide and water. *Anal. Chem.* **62**, 526-529.
- Murdoch, P. S. & Stoddard, J. L. (1992) The role of nitrate in the acidification of streams in the Catskill Mountains of New York. *Wat. Resour. Res.* **28**, 2707-2720.
- Rascher, C. M., Driscoll, C. T. & Peters, N. E. (1987) Concentration and flux of solutes from snow and forest floor during snow-melt in the West-Central Adirondack Region of New York. *Biogeochemistry* **3**, 209-224.
- Shanley, J. B., Kendall, C., Smith, T. E. & Wolock, D. M. The effect of catchment size and land cover on the contributions of meltwater to stream discharge during snowmelt in a Vermont watershed (in review).
- Silva, S. R., Kendall, C. & Chang, C. C. Y. A new method of preparing dissolved nitrate for oxygen isotopic analysis (in preparation).
- Silva, S. R., Kendall, C., Wilkison, D. H. & Avanzino, R. J. Preparation of nitrate, collected onto anion exchange resin columns for nitrogen isotope analysis. (in review).
- Voerkelius, S. (1990) Isotopendiskriminierungen bei der Nitrifikation und Denitrifikation: Grundlagen und Anwendungen der Herkunfts-Zuordnung von Nitrat und Distickstoffmonoxid. Ph.D. Dissertation, Tech. Univ. München.
- Williams, M. W., Brooks, P. D., Schmidt, S. K. & Mosier, A. (1994) Evaluation of isotopically-labelled nitrogen (N) and salt tracers to understand the origin of nitrate in surface waters of high-elevation catchments. *EOS (Trans. AGU) Supplement* **75**, 279.
- Wilkison, D. H., Kendall, C., Ziegler, A. C. & Silva, S. R. Procedure for concentration of dissolved nitrate plus nitrite for $\delta^{15}\text{N}$ analyses using anion exchange resins (in review).