Tracing sources of nitrate in snowmelt runoff using a high-resolution isotopic technique

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[1] The denitrifier method to determine the dual isotopic composition ($\delta^{15}N$ and $\delta^{18}O$) of nitrate is well suited for studies of nitrogen contributions to streams during runoff events. This method requires only 70 nmol of NO_3^- and enables high throughput of samples. We studied nitrate sources to a headwater stream during snowmelt by generating a high-temporal resolution dataset at the Sleepers River Research Watershed in Vermont, USA. In the earliest phase of runoff, stream NO_3^- concentrations were highest and stream discharge, NO_3^- concentrations, and $\delta^{18}O$ of NO_3^- generally tracked one another during diurnal melting. The isotopic composition of stream NO_3^- varied in-between atmospheric and groundwater NO_3^- end members indicating a direct contribution of atmospherically-derived NO_3^- from the snow pack to the stream. During the middle to late phases of snowmelt, the source shifted toward soil NO_3^- entering the stream via shallow subsurface flow paths. *INDEX TERMS:* 1615 Global Change: Biogeochemical processes (4805); 1719 History of Geophysics: Hydrology; 1860 Hydrology: Runoff and streamflow; 4870 Oceanography: Biological and Chemical: Stable isotopes. **Citation:** Ohte, N., S. D. Sebestyen, J. B. Shanley, D. H. Doctor, C. Kendall, S. D. Wankel, and E. W. Boyer (2004), Tracing sources of nitrate in snowmelt runoff using a high-resolution isotopic technique, *Geophys. Res. Lett.*, *31*, L21506, doi:10.1029/2004GL020908.

1. Introduction

[2] Nitrogen export from terrestrial to aquatic ecosystems is linked to various environmental problems such as nitrogen saturation [*Stoddard*, 1994] and freshwater acidification where atmospheric deposition of nitrogen is high [*Murdoch and Stoddard*, 1992]. Although water chemistry is routinely measured in regional to national scale monitoring programs (e.g., http://waterdata.usgs.gov/nwis and http://themes.eea.eu.int/Specific_media/water/data), our understanding of the mechanisms that regulate the temporal and spatial variability of NO_3^- fluxes from the landscape to streams is limited.

[3] Recent detailed studies of forested catchments offer considerable insight to sources of river water [e.g., *Burns et al.*, 1998; *McGlynn et al.*, 1999; *Sickman et al.*, 2001] and link atmospheric deposition to the transport of nitrogen to streams [*Williams et al.*, 1995; *Campbell et al.*, 2000; *Boyer and Howarth*, 2002]. However, the influence of atmospheric deposition on nitrogen export in seasonally snow-covered catchments has not been well documented for short-term discharge events.

[4] NO_3^- isotopic measurements have recently been used to determine stream NO_3^- sources [*Williard et al.*, 2001; *Campbell et al.*, 2002; *Burns and Kendall*, 2002]. *Kendall* [1998] documented that $\delta^{18}O$ and $\delta^{15}N$ values of NO_3^- from various sources have distinct isotopic signatures and that $\delta^{18}O$ of NO_3^- is significantly more variable than $\delta^{15}N$ of NO_3^- of various source end members. The NO_3^- isotopes can be used as a tracer of atmospherically derived NO_3^- because atmospheric nitrate has distinctly higher $\delta^{18}O$ than NO_3^- originating from microbial processing (i.e., nitrification) in forest soils [*Kendall*, 1998].

[5] To determine NO_3^- sources during snowmelt, we simultaneously measured $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- using the denitrifier method on samples collected at a seasonally snow-covered catchment in the northeastern United States. The denitrifier method is a novel procedure developed by *Sigman et al.* [2001] and *Casciotti et al.* [2002] that enables high throughput of samples because it requires less water and laboratory preparation than previous methods [*Silva et al.*, 2000]. This paper describes the utility and advantages of using the denitrifier method to generate high-resolution isotopic data to identify sources of stream water NO_3^- during snowmelt.

2. Study Site and Analytical Methods

[6] Stream water, soil water, groundwater, and precipitation samples were collected in the 40.5 ha headwater catchment (W-9) of the Sleepers River Research Watershed in Vermont (Figure 1). Snowmelt is typically the dominant annual hydrological event at this site. Snow cover at W-9 is present from mid-November to late April and comprises 25–30% of the 1320 mm of annual precipitation [*Shanley et al.*, 2004]. Peak discharge usually occurs during snowmelt in April, and minimum flow occurs between July and October [*Shanley et al.*, 1995]. The bedrock of W-9 is a calcareous granulite interbedded with quartz mica phyllite [*Newell*, 1970]. The catchment is entirely forested with mixed northern hardwoods.

[7] Stream flow was measured at a V-notch weir, and precipitation was measured in an adjacent clearing. Snow water equivalent (SWE) was measured at the snow survey station 1.5 km south of the W-9 weir.

[8] From the onset of snowmelt, stream samples were collected at the W-9 weir at least daily. During the most

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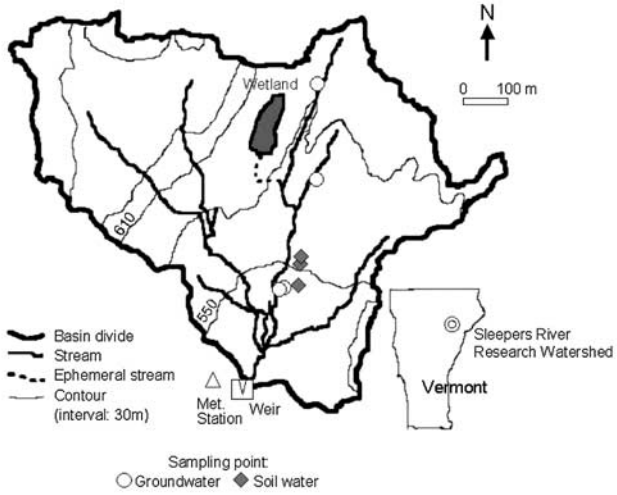

Figure 1. Location of the study catchment, field instrumentation and sampling points.

active snowmelt periods and rain-on-snow events, samples were collected at least every three to six hours. Fewer samples were collected during periods of hydrograph recession such as 1 to 10 April. Bulk precipitation samples were collected in a polyethylene bucket at the W-9 meteorology station. Soil waters were sampled with zero-tension lysimeters at two locations on a mid-catchment hillslope where water infiltrates vertically through the unsaturated zone. The soil water samples were collected from three depths (13, 43, and 104 cm) at a midslope site and two depths (10 and 46 cm) at an upslope site on 1 April. Groundwater was sampled from wells in the riparian zones throughout the catchment. The instruments and sampling locations are mapped in Figure 1.

[9] Filtered (0.45 μm) aliquots were analyzed for NO_3^- concentration by ion chromatography at the College of Environmental Science and Forestry, State University of New York in Syracuse. Dissolved inorganic carbon (DIC) concentrations were measured on filtered (0.7 μm) samples with a TIC/TOC analyzer at the U.S. Geological Survey stable isotope laboratory in Menlo Park. Frozen aliquots were analyzed for $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- using the denitrifier method at the stable isotope laboratory in Menlo Park. In this method, cultured denitrifying bacteria (*Pseudomonas chlororaphis*) that lack N_2O reductase convert the nitrogen and oxygen from NO_3^- to nitrous oxide (N_2O). The isotopic composition of the generated N_2O was then measured by mass spectrometry. Details of the procedures used for preparation of denitrifier cultures, conversion of the NO_3^- to N_2O, extraction and isotopic analysis of N_2O, and correction for nitrogen and oxygen isotopic measurements are given by *Sigman et al.* [2001] and *Casciotti et al.* [2002]. A minimum of 70 nmol NO_3^- was needed to analyze samples on a Micromass Isoprime stable isotope mass spectrometer. The standard error of an internal KNO_3 laboratory standard was ±0.05‰ for $\delta^{15}N$ and ±0.2‰ for $\delta^{18}O$ of NO_3^-.

3. Results and Discussion

[10] Discharge started to increase on 16 March 2003 with the onset of snowmelt (Figure 2a). As is typical at W-9 [*Shanley et al.*, 2002], the highest NO_3^- concentration occurred at the beginning of snowmelt well before the peak of stream flow. With the exception of several storm events,

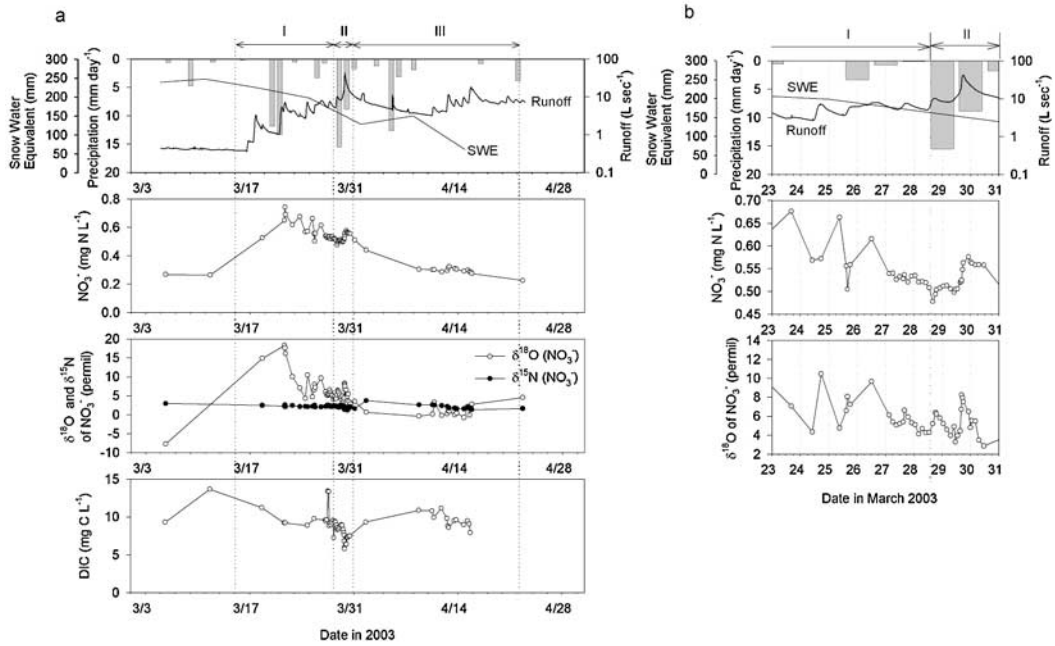

Figure 2. (a) Precipitation, runoff, snow water equivalent (SWE), NO_3^- concentration, $\delta^{18}O$ and $\delta^{15}N$ of NO_3^-, and DIC concentration during snowmelt 2003. Phase I was 16 to 29 March, Phase II was 29 to 31 March, and Phase III was 1 to 22 April. Precipitation includes rain and snow that fell in this period. (b) Detailed precipitation, runoff, SWE, NO_3^- concentration and $\delta^{18}O$ of NO_3^- data from 23 to 30 March.

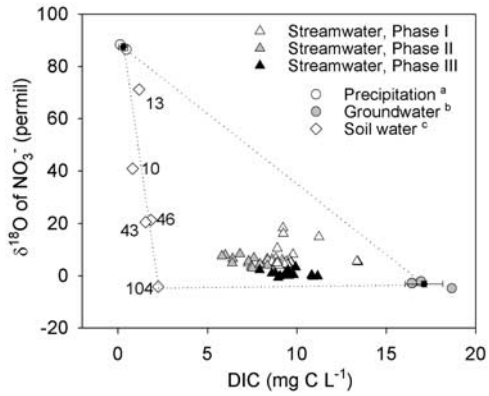

Figure 3. Mixing diagram using DIC concentration and $\delta^{18}O$ of NO_3^-. The mean and standard deviation are shown for precipitation and groundwater. The dotted triangle connects the mean values of precipitation and groundwater, and soil water from the deep (104 cm) lysimeter. (a) Precipitation was sampled 21 and 30 March. (b) Groundwaters were sampled 24 March from four wells that were greater than 150 cm deep. (c) Soil waters were sampled 1 April with zero-tension lysimeters at two different locations on a hillslope. The numbers next to the soil water samples indicate the depth in cm of the lysimeter.

NO_3^- concentration generally decreased as snowmelt flow recession continued through May.

[11] Based on the temporal patterns of runoff and SWE, the snowmelt period can be divided into three phases. In the earliest period of snowmelt (Phase I, 16 to 29 March), discharge increased gradually in response to several small rain-on-snow events. Diurnal variation of NO_3^- concentrations tracked diurnal variation in discharge from 23 to 30 March (Figure 2b). Rainfall from 29 to 31 March (Phase II) induced the period of highest runoff. A cold spell occurred from 1 to 12 April (Phase III) and discharge decreased until 12 April when diurnal melt cycles resumed. Snowmelt essentially ended 16 April.

[12] Throughout the study, $\delta^{18}O$ of stream NO_3^- ranged from −7.7 to +18.3‰ and generally tracked the pattern of NO_3^- concentration variation. In particular, discharge, NO_3^- concentration, and $\delta^{18}O$ had remarkably similar diurnal fluctuation patterns from 23 to 30 March (Figure 2b). In contrast to $\delta^{18}O$, $\delta^{15}N$ of NO_3^- varied little (+1.2 to +3.8‰). In latter Phase III, $\delta^{18}O$ of NO_3^- slightly increased in response to further snowmelt and increased runoff.

[13] *Kendall* [1998] compiled data to establish characteristic values for various sources including NO_3^- from atmospheric (snow and rain) and microbially produced (soil and ground water) sources. The range of $\delta^{18}O$ of atmospheric NO_3^- is +23 to +75‰ and $\delta^{18}O$ of NO_3^- nitrified from ammonium (NH_4^+) by soil microbial communities is −5 to +7‰. Our data, along with recent unpublished data from the northeast United States by C. Kendall, E. M. Elliott, and S. D. Wankel, USGS (unpublished data, 2004), extend the $\delta^{18}O$ of atmospheric NO_3^- range to +90‰. During snowmelt, $\delta^{18}O$ of stream NO_3^- ranged from −0.7 to +18.3‰. These values fell between the isotopic composition of atmospheric and nitrified NO_3^-, suggesting a mix of snowmelt, soil water, and groundwater. For example, the early, high concentration nitrate pulse having a $\delta^{18}O$ of NO_3^- of +18.3‰ suggested that melt water was a substantial source of atmospheric NO_3^- to the stream at the start of snowmelt.

[14] DIC was a useful tracer because groundwater was in contact with the carbonate-rich bedrock and had distinctly higher DIC concentrations than soil water [*McGlynn et al.*, 1999] (Figure 3). In Figure 2a, the DIC concentration was highest (9–14 $mgCL^{-1}$) before snowmelt when baseflow groundwater contributed all NO_3^- and DIC (17–19 $mgCL^{-1}$) to the stream. Stream DIC concentration decreased during Phase I suggesting dilution of groundwater with snowmelt water (0.1–0.5 $mgCL^{-1}$) and soil water (0.8–2.2 $mgCL^{-1}$) (Figure 3). Stream DIC concentration was lowest in Phase II at the peak of snowmelt. Although stream DIC concentration increased in Phase III associated with the gradual decrease of stream discharge, the highest concentration in Phase III was still lower than the pre-melt period. Relative to pre-melt, this low DIC concentration suggested that shallow subsurface water discharged into the stream, including melt water that infiltrated through the soil.

[15] The source of NO_3^- in each runoff phase was examined with a simple end member mixing analysis [*Christophersen et al.*, 1990] using DIC and $\delta^{18}O$ of NO_3^- with precipitation, soil water and groundwater as the three end members (Figure 3). Rain samples from 21 and 30 March were used as proxies of precipitation inputs because snowmelt water samples were not collected. The groundwater end member data came from four wells that were more than 150 cm deep. Soil water DIC concentrations from all five depths were low and different from groundwater. DIC and $\delta^{18}O$ of NO_3^- of soil waters plotted along a line between precipitation and deep soil water. The $\delta^{18}O$ values of soil water NO_3^- varied with depth (−4.2 to +71‰) and was highest near the soil surface. The $\delta^{18}O$ of soil water NO_3^- in deep soil (−4.2‰) and ground waters (−2.2 to −4.9‰) were similar and within the range of NO_3^- nitrified from NH_4^+ [*Kendall*, 1998]. The decrease of $\delta^{18}O$ of soil water NO_3^- with depth indicates an atmospheric NO_3^- signature in shallow soil water that evolves into a nitrified NO_3^- signature with depth along the vertical flow path through biogeochemical transformations or as snow melt water mixes with soil water.

[16] Stream NO_3^- concentrations were highest at the beginning of Phase I (20 March). In this period, the DIC concentrations and $\delta^{18}O$ of NO_3^- of stream water fell along a precipitation and groundwater mixing line, indicating that stream water was a mix of snowmelt water and groundwater with a minimal soil water contribution (Figure 3). The temporal sequence of concentration and isotope data indicated that elevated stream NO_3^- concentrations were contributed from a dominant source of atmospheric NO_3^- that then shifted to a mixture of atmospheric and nitrified NO_3^- as snowmelt proceeded (Phase II). In early Phase I, melt water from the snow pack covering the channel and near stream areas likely melted directly into the stream and contributed to the high stream NO_3^- concentrations. As snow melted from above the channel, variable source areas [*Dunne and Black*, 1971] began to expand as surface saturation connected melt waters from near-stream areas to the stream. In late Phase I, the diurnal variation in $\delta^{18}O$ of NO_3^- tracked the diurnal stream discharge (Figure 2b) even after snow above the channel had melted away. However,

the variation of concentration and $\delta^{18}O$ of NO_3^- became dampened relative to the stream discharge variation as time and melt progressed suggesting that snow melt plus rain on 29 and 30 March generated shallow subsurface flow paths that contributed water and nitrate to stream flow. As the melt progressed, the direct input of atmospheric nitrate quickly diminished as soil water contributions increased until peak melt. As melt water and precipitation recharged groundwater throughout snowmelt, groundwater inputs gradually increased during Phase I but stabilized at an elevated level in Phase III when groundwater contributions were once again the dominant water and NO_3^- source.

[17] A previous study at Sleepers River concluded that microbially produced NO_3^- from shallow subsurface flow paths was the dominant source of stream NO_3^- during snowmelt [*Kendall et al.*, 1995] although the source contributions were less certain because of the coarse resolution of the data sets (<10 total samples over the snowmelt period). In contrast, our new, high-resolution data indicate an early contribution of atmospheric NO_3^- from snow covering the channel and near-stream zone. The high concentration pulse of NO_3^- consisting largely of atmospheric NO_3^- from the snow pack was made easier by our high-resolution sampling and isotopic approach. Moreover, our approach demonstrated a shift in NO_3^- source from meltwater to soil water as snowmelt progressed.

[18] The small sample volume and the reduced laboratory procedures of the denitrifier method enable high throughput of samples and permit the collection of high-resolution data sets. This method offers many opportunities to study how water and NO_3^- sources to streams vary over time and respond to human influences on nitrogen cycles in watersheds (e.g., elevated atmospheric deposition and nitrogen saturation).

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