Sources, transformations, and hydrological processes that control stream nitrate and dissolved organic matter concentrations during snowmelt in an upland forest

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[1] We explored catchment processes that control stream nutrient concentrations at an upland forest in northeastern Vermont, USA, where inputs of nitrogen via atmospheric deposition are among the highest in the nation and affect ecosystem functioning. We traced sources of water, nitrate, and dissolved organic matter (DOM) using stream water samples collected at high frequency during spring snowmelt. Hydrochemistry, isotopic tracers, and end-member mixing analyses suggested the timing, sources, and source areas from which water and nutrients entered the stream. Although stream-dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) both originated from leaching of soluble organic matter, flushing responses between these two DOM components varied because of dynamic shifts of hydrological flow paths and sources that supply the highest concentrations of DOC and DON. High concentrations of stream water nitrate originated from atmospheric sources as well as nitrified sources from catchment soils. We detected nitrification in surficial soils during late snowmelt which affected the nitrate supply that was available to be transported to streams. However, isotopic tracers showed that the majority of nitrate in upslope surficial soil waters after the onset of snowmelt originated from atmospheric sources. A fraction of the atmospheric nitrogen was directly delivered to the stream, and this finding highlights the importance of quick flow pathways during snowmelt events. These findings indicate that interactions among sources, transformations, and hydrologic transport processes must be deciphered to understand why concentrations vary over time and over space as well as to elucidate the direct effects of human activities on nutrient dynamics in upland forest streams.

1. Introduction

[2] The complex ecosystem processes that directly affect stream nitrate and dissolved organic matter (DOM) concentrations in upland forests are of great ecological importance. However, quantifying how human activities such as nitrogen enrichment and climate change affect soil nutrient status, ecosystem functioning, and stream nutrient loading remains a challenge [*National Research Council*, 2001; *Aber et al.*, 2003; *Driscoll et al.*, 2003; *Gundersen et al.*, 2006]. Nitrogen and DOM are abundant and biogeochemi-cally active in forested landscapes and streams. Studies of temperate, upland forested catchments have identified that nitrate and DOM may be hydrologically flushed to forest streams from chemically distinct source areas in the landscape as water flows laterally via shallow subsurface and overland pathways during storm events [*Schiff et al.*, 1990; *Creed et al.*, 1996; *Boyer et al.*, 2000]. Although stream nitrate and DOM may originate from similar surficial flow paths during storm events [*McHale et al.*, 2000; *Inamdar et al.*, 2004; *Hood et al.*, 2005; *Mitchell et al.*, 2006], the reasons why flushing responses differ among nitrate, dissolved organic nitrogen (DON), and dissolved organic carbon (DOC) are not always clear.

[3] Isotopic and hydrochemical tracers are validated approaches to elucidate the sources and processes that affect the variation of stream nitrate [*Kendall et al.*, 2007]. Recently, high-resolution temporal sampling has shown that atmospheric sources of nitrate may have more pronounced effects on stream nitrate concentrations than previously known [*Ohte et al.*, 2004]. This finding highlights a need to better understand how atmospherically deposited nitrate cascades through biogeochemical cycles or is directly transported to streams. In forested catchments, nitrate isotopic

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signatures differentiate nitrate contributed directly from rain or snow because the +60 to +100‰ range in $\delta^{18}O$ of atmospheric nitrate is distinct from the -10 to $+15‰$ range of nitrified sources (i.e., the nitrate produced via coupled mineralization and nitrification) [*Kendall*, 1998; *Kendall et al.*, 2007]. Furthermore, the recent development of the microbial denitrifier method for $\delta^{15}N$ [*Sigman et al.*, 2001] and $\delta^{18}O$ [*Casciotti et al.*, 2002] makes the precise, rapid analysis of large numbers of samples feasible.

[4] Tracers of DOM are also useful when deciphering sources and flow paths that affect streamflow. For example, increased humic acid fractions of DOC during stormflow reflect contributions from source areas in surficial soils [*Cronan and Aiken*, 1985; *Hood et al.*, 2005]. Furthermore, the $\delta^{13}C$ values of DOC ($\delta^{13}C$-DOC), which is now more easily measured using a high-throughput technique [*St.-Jean*, 2003], may distinguish between DOC that originates from freshly leached organic matter in surficial soils and microbially degraded DOC from groundwater flow paths [*Schiff et al.*, 1990].

[5] In our study, we use a hydrological approach in which stream water samples are collected at high frequency at an upland forest in the northeastern United States during snowmelt events when nitrate, DON, and DOC concentrations increase, often to the annual highest levels. We use tracer data and end-member mixing analysis to quantify hydrological flushing processes that link terrestrial source areas to stream nutrient dynamics in upland forested catchments. The findings from our study emphasize that source quantification is important for understanding the reasons why nitrogen species and DOM composition vary in upland catchments during large magnitude, extended duration snowmelt runoff events that have an overriding influence on annual stream nutrient loadings. In contrast to some past studies that suggest minimal inputs of atmospheric nitrate to streams, we found that atmospheric nitrate was a source of stream and soil water nitrate especially during the early phases of snowmelt. Because we quantify the amount of nitrate that directly originates from an atmospheric source, our findings provide information that is relevant to assess natural and anthropogenic stream nitrate loadings.

2. Site Description

[6] We studied catchment processes at watershed 9 (W-9), a 40.5 ha forested subbasin of the Sleepers River Research Watershed and a site in the Water Energy and Biogeochemical Budgets program of the U.S. Geological Survey [*Shanley*, 2000]. Pope Brook drains W-9 and is a headwater tributary of the Sleepers River drainage which in turn flows to the Passumpsic River, the Connecticut River, and the Atlantic Ocean. The mountainous W-9 is near Saint Johnsbury, Vermont.

[7] Total nitrogen inputs to the catchment from wet atmospheric deposition are chronically elevated like most forested regions of the northeastern United States; the average total nitrogen input from 1978 to 1998 was 13.2 kg ha^{-1} a^{-1} [*Campbell et al.*, 2004]. A seasonal snowpack starts accumulating during November and typically melts between mid-March and late April. The mean annual precipitation is 1323 mm, 20 to 30% of the precipitation falls as snow, and peak annual streamflow often occurs during snowmelt [*Shanley et al.*, 2002a, 2002b].

[8] The northern hardwood forest at W-9 is predominantly sugar maple (*Acer saccharum*) with some yellow birch (*Betula alleghaniensis*), white ash (*Fraxinus americana*), red spruce (*Picea rubens*), and balsam fir (*Abies balsamea*). The forest was partially logged during 1929, selectively cut during 1960, and currently continues to accrue biomass. Watershed 9, with elevations between 519 and 686 m, is a south facing catchment on the eastern flanks of the Kittredge Hills. The terraced glacial topography is characterized by steep slopes with relatively flat midelevation benches. The bedrock is calcareous granulite interbedded with quartz mica phyllite [*Hall*, 1959]. A base layer of dense glacial till that is overlain by up to three meters of moderately to excessively well-drained Inceptisols and Spodosols. Poorly drained Histosols have formed in wetlands (about 5% of the catchment area) and riparian areas [*Shanley et al.*, 2003]. Soil patches in W-9 may freeze to shallow depths (tens of centimeters) but widespread impermeable frost layers have not been observed [*Shanley and Chalmers*, 1999].

[9] Hydrological processes have been intensively studied at the Sleepers River Watershed. During the late 1960s, *Dunne and Black* [1970, 1971] first quantified dynamic subsurface and surface flow processes in variable source areas that control the movement of water from the landscape to a stream. Subsequent studies have found that stormflow chemistry is influenced by preferential flow paths that route storm runoff through surficial soils that have high hydraulic conductivities [*Kendall et al.*, 1999; *McGlynn et al.*, 1999; *Shanley et al.*, 2003]. Water levels in upland soils may vary over depths of several meters depending upon wetness conditions [*Hjerdt*, 2002; *Shanley et al.*, 2003] and hydraulic conductivities exponentially decrease with depth in hillslope soils [*Kendall et al.*, 1999]. The preferential flow of water through surficial soils delivers event new water to streams and new water contributions up to 40% have been measured at W-9 [*Shanley et al.*, 2002a]. At W-9, stream nitrate concentrations often peak early in snowmelt events and stream DOM concentrations peak at the maximum streamflow of an event [*Shanley*, 2000; *Shanley et al.*, 2002b; *Ohte et al.*, 2004].

3. Methods

[10] During the 2003 and 2004 snowmelt events, hydrology and chemistry were intensively measured. The collection, processing, and analysis of samples are described herein with additional information included as Text S1 in the auxiliary material.[1] Streamflow was calculated from a stage-discharge relationship according to U.S. Geological Survey protocols. Since 1991, stream stage has been measured every five minutes at a 120° V notch weir instrumented with a float-driven potentiometer. Logged stream stages were verified with manual stage readings.

[11] Precipitation amount was measured with a weighing bucket gauge at a meteorological station (R29) in a forest clearing near the W-9 stream gauge. Precipitation samples for chemistry were collected weekly or more frequently from a polyethylene bucket.
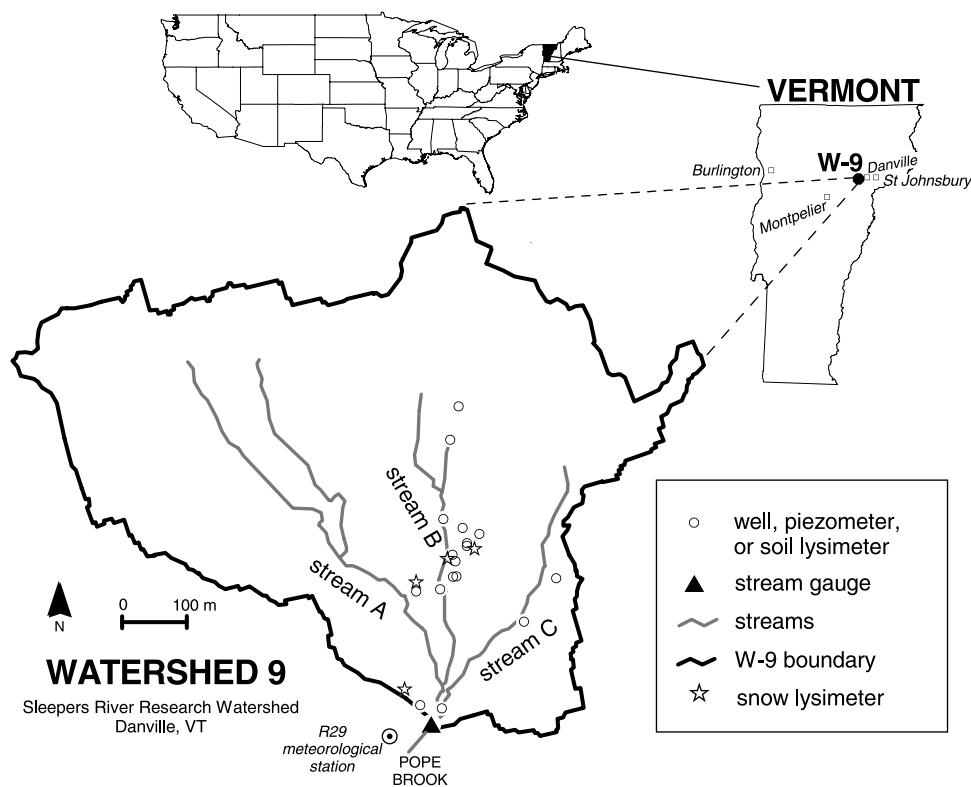
Figure 1. Map of the 41 ha forested Watershed 9 at the Sleepers River Research Watershed (44°29′28″N, 72°9′43″W) shows streams, the stream gauge, subsurface water sampling points, and snowmelt collectors.

[12] Snow water equivalent was measured with an Adirondack snow sampling tube (Text S1). During 2004, snowmelt amount, chemistry, and isotopic composition were measured on meltwater that drained from the base of the snowpack into buried PVC reservoirs (Text S1). Snowmelt water samples were collected at least daily after substantial melt (greater than 1 mm).

[13] Samples of W-9 stream water were collected weekly and additional grab samples were collected daily or more frequently, especially after the onset of snowmelt. To augment grab sampling, an ISCO automatic sampler collected stream water when threshold changes in streamflow triggered sample collection (intervals ranging from minutes to hours).

[14] Groundwater and soil water chemistry were measured at sites located throughout the catchment (Figure 1). At least one casing volume of groundwater was evacuated prior to sampling. A nested pair of shallow (0.3 m) and deep (2.1 m) piezometers in the riparian zone near the W-9 stream gauge was sampled on 22 days between 25 March and 5 May 2004. Other wells were sampled monthly from January through March or several times during April to characterize the spatial variation of groundwater chemistry during 2004. During 2003, to measure when shallow soils saturated, groundwater levels were logged every 10 to 30 min at riparian (T-3 piezometer), midslope (MI recording well), and upslope (UP recording well) positions on a planar hillslope. Shallow soil water samples were collected from soil lysimeters at the MI (0.10 m depth) and UP (0.13 m depth) sites. After melt pulses or rain-on-snow events, zero-tension soil lysimeters were checked to determine when the

samplers filled with vadose zone soil water and samples were collected on three dates during 2003 and 2004.

[15] Water samples for analysis of major ion concentration, total nitrogen concentration, and nitrate isotopes were filtered through 0.45 μm membrane filters. Aliquots for ion and total nitrogen analyses were refrigerated until analyzed and nitrate isotope samples were frozen. Nitrate concentrations were measured using a Dionex DX-500 ion chromatograph. For a subset of the samples, aliquots for total nitrogen analysis were prepared by the alkaline persulfate oxidation technique [*Solorzano and Sharp*, 1980] and concentrations were measured by flow injection analysis on a Lachat AutoAnalyzer. Dissolved organic nitrogen concentrations were calculated as the difference between total nitrogen and nitrate concentrations. Nitrite was not quantifiable in any sample. Ammonium was not measured in our study because ammonium is usually below detection limits so ignoring ammonium has a minimal effect on calculated DON concentrations for W-9 stream waters. Calcium, magnesium, strontium, and silica concentrations were measured by inductively coupled plasma optical emission spectrometry (Perkin-Elmer Optima 330 DV).

3.1. Chemical and Isotopic Analyses

[16] To trace sources of stream water, nitrate, and DOM, natural abundance isotope ratios were measured on a subset of the water samples. Nitrate isotope samples were processed using the bacterial denitrifier method [*Sigman et al.*, 2001; *Casciotti et al.*, 2002]. The oxygen (δ^{18}O-nitrate) and nitrogen (δ^{15}N-nitrate) isotopic compositions were measured on a Micromass IsoPrime mass spectrometer. Isotopic

composition was corrected and adjusted for exchange and fractionation against blanks and international nitrate isotopic standards USGS 34 and 35 [*Böhlke et al.*, 2003].

[17] During 2006, the oxygen isotopic composition of some water samples (δ^{18}O-water) was prepared by the carbon dioxide equilibration method [*Epstein and Mayeda*, 1953] and analyzed on a Finnigan MAT 251 mass spectrometer. Additional samples were analyzed during 2007 by laser absorption spectrometry using a Los Gatos Research 908 Liquid-Water Isotope Analyzer after cross calibration of the two techniques.

[18] Stream, soil, and groundwater DOC samples were filtered through 0.7 μm binder-free glass fiber filters into amber glass bottles and refrigerated. Because sample collection spanned the duration of different DOC studies, concentrations were measured by catalyzed persulfate wet oxidation on total organic C analyzers at several laboratories (Text S1). Indices of DOC composition were measured for some samples. The carbon isotopic composition of DOC (δ^{13}C-DOC) was measured for 20 of the 2004 stream samples and three groundwater samples on a Micromass IsoPrime continuous flow mass spectrometer that was interfaced with a total organic carbon analyzer. Our implementation of the method described by *St.-Jean* [2003] is presented by *Doctor et al.* [2008]. The δ^{13}C of ten leaf litter samples collected during autumn 2003 was measured on a Carlo Erba elemental analyzer interfaced with a Micromass Optima mass spectrometer to quantify the δ^{13}C of a source of leached DOC. During 2004, the hydrophobic organic acid (HPOA) fraction of DOC from eleven stream samples was determined by analytical absorption chromatography [*Aiken et al.*, 1992]. The HPOA fraction was isolated using Amberlite XAD8 resin. The first fractionation sample was collected after snowmelt started. The remaining samples were collected at times of high flow and distributed throughout snowmelt.

3.2. Flux Calculation and Mixing Analysis

[19] To calculate stream solute fluxes, a concentration was multiplied by the corresponding total runoff in a time period to calculate the flux per interval spanning the midpoint between samples. With hydrochemical data from past studies at W-9 [*Kendall et al.*, 1999; *Hjerdt*, 2002; *Shanley et al.*, 2002a], we calculated fluxes of water and nutrients from W-9 for the years 1992, 1993, 1994, 1996, 1999, and 2000 as well as 2003 and 2004. The center of mass for the period from 1 January to 31 May was computed as the date when the cumulative stream export of water, nitrate, DON, or DOC mass from W-9 exceeded fifty percent, similar to *Hodgkins et al.* [2003].

[20] During 2004 when snowmelt and groundwater end-members of stream water were characterized with frequent samples, end-member mixing analysis (EMMA) was used to calculate the amount of stream water that originated from groundwater, shallow soil water, and precipitation [*Christophersen et al.*, 1990]. A principle components analysis of standardized conservative chemical (calcium, magnesium, strontium, and silica concentrations) and isotopic (δ^{18}O-water) tracers was used to develop the EMMA model [*Burns et al.*, 2001; *Hooper*, 2003]. The fractions (f) of groundwater (GW), surficial soil water (SW), and pre-

cipitation (PPT) were calculated by solving the following equations:

$$f_{GW} + f_{SW} + f_{PPT} = 1 \qquad (1)$$

$$U_{1_{stream}} = f_{GW} \times U_{1_{GW}} + f_{SW} \times U_{1_{SW}} + f_{PPT} \times U_{1_{PPT}} \qquad (2)$$

$$U_{2_{stream}} = f_{GW} \times U_{2_{GW}} + f_{SW} \times U_{2_{SW}} + f_{PPT} \times U_{2_{PPT}} \qquad (3)$$

where U_1 and U_2 are the first and second principle components from the principle components analysis. The U space of end-members [see *Hooper*, 2003] was varied by date according to input data from precipitation (chemistry of rain and meltwaters) and soil water. Groundwater concentrations varied more over space than time and the groundwater end-member was defined by averaging data from synoptically sampled well locations (eight sites). Because surficial soil waters and precipitation interact along shallow subsurface flow paths as these waters flow to streams, these two components were summed to calculate an index of water that is contributed in response to stormflow, the quick flow fraction [*Hornberger et al.*, 1998].

$$f_{quick\ flow} = f_{SW} + f_{PPT} \qquad (4)$$

At W-9, quick flow suggests preferential flow along shallow subsurface and overland flow paths in response to precipitation or snowmelt inputs. The uncertainty ($W_{3\text{-comp}}$) was calculated for each EMMA component (GW, SW, or PPT) according to the approach of *Genereux* [1998] as adapted by *Burns et al.* [2001] (Text S1).

[21] Nitrate sources during the 2003 and 2004 snowmelt runoff events were separated into two fractions (f), atmospheric (ATM) and nitrified (NIT), using a two-component mixing model in which snowmelt or rainwater (c_{ATM}) and groundwater from hillslope wells (c_{NIT}) were used as mixing end-members to solve the equations,

$$f_{ATM} + f_{NIT} = 1 \qquad (5)$$

$$c_{stream} = f_{ATM} \times c_{ATM} + f_{NIT} \times c_{NIT} \qquad (6)$$

where c is the δ^{18}O-nitrate of each component contributing nitrate to stream water as identified by the subscripts ATM or NIT. The flux of stream water nitrate originating from atmospheric sources was calculated by multiplying the total nitrate flux by the atmospheric fraction (f_{ATM}). Uncertainty ($W_{2\text{-comp}}$) of the two-component mixing analysis was calculated according to the approach of *Genereux* [1998] (Text S1).

4. Results

[22] In all years when high-frequency samples were collected, the nitrate centers of mass occurred on average 6.3 ± 1.8 (standard error) days before the water centers of mass (Figure 2). The DOC centers of mass occurred an average of 0.5 ± 0.5 day after the water centers of mass. In the 2 years when high-frequency samples were analyzed for
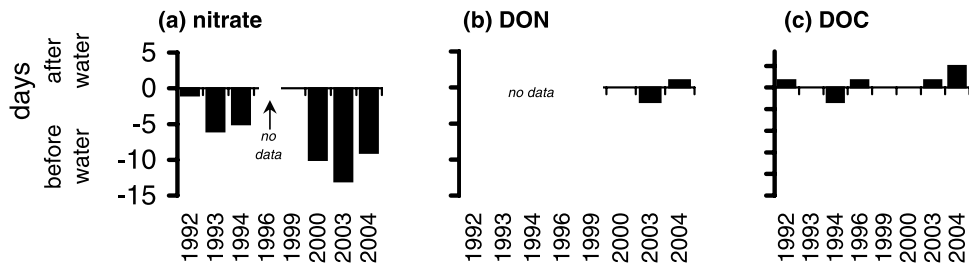
Figure 2. Among years, the (a) early nitrate center of mass (up to 6 days) and the late (b) DON and (c) DOC centers of mass (relative to water) documented how nutrient fluxes varied among solutes.

DON, the DON center of mass occurred 2 days before the water center of mass in 2004 and 1 day after in 2003.

[23] To examine differences among solute concentration and flux patterns during snowmelt, we highlight results from 2004 when multiple tracers of stream water and solute sources were simultaneously measured at high frequency along with snowmelt input, groundwater, and soil water chemistry. Snow started to accumulate during December 2003 and snowmelt occurred during March and April 2004 (Figure 3). Immediately before snowmelt, the maximum snow water equivalent (SWE) was 222 mm and streamflow was 0.02 mm h^{-1}. During the first week of March 2004, 10% of the SWE (28 mm) was lost from the snowpack in response to warm air temperatures and rainfall causing streamflow to increase to a high of 0.11 mm h^{-1}. During this first snowmelt pulse, snow that covered the stream channel melted into the stream, areas of saturation overland flow were observed near the stream, and hillslopes remained snow covered. Streamflow recession occurred from 7 to 24 March when temperatures were below freezing. During these two weeks, SWE increased to 216 mm and the stream channel was again covered with snow.

[24] A second period of snowmelt started 25 March 2004. The stream was snow covered until the end of the first week

of April. During the second week of April, snow melted from near-stream areas and exposed these variable source areas to rain that fell later during April. During a rain-on-snowmelt event on 13 to 14 April, the peak streamflow of 0.58 mm h^{-1} and quick flow of 0.23 ± 0.02 mm h^{-1} were measured (Figure 4). After 20 April, SWE was no longer measurable (Figure 3).

4.1. Stream Hydrochemistry

[25] We describe the differences among stream nitrate, DON, and DOC concentration patterns prior to presenting results that show how sources and source areas varied during snowmelt 2004. Under winter base flow conditions, stream nitrate concentrations increased steadily from 8.5 to 13.9 μmol L^{-1} while streamflow decreased from January to the beginning of snowmelt (Figure 4). On the basis of hydrochemical patterns, snowmelt was divided into three distinct phases (pulse 1 of early melt, pulse 2 of early melt, and late melt; Figure 5). Stream nitrate concentration responses were complex. During pulse 1 of early melt, stream nitrate concentrations rapidly increased to a high of 33.3 μmol L^{-1} on 3 March when streamflow was 0.08 mm h^{-1}. After this first early nitrate peak, concentrations declined to premelt base flow levels during stream-
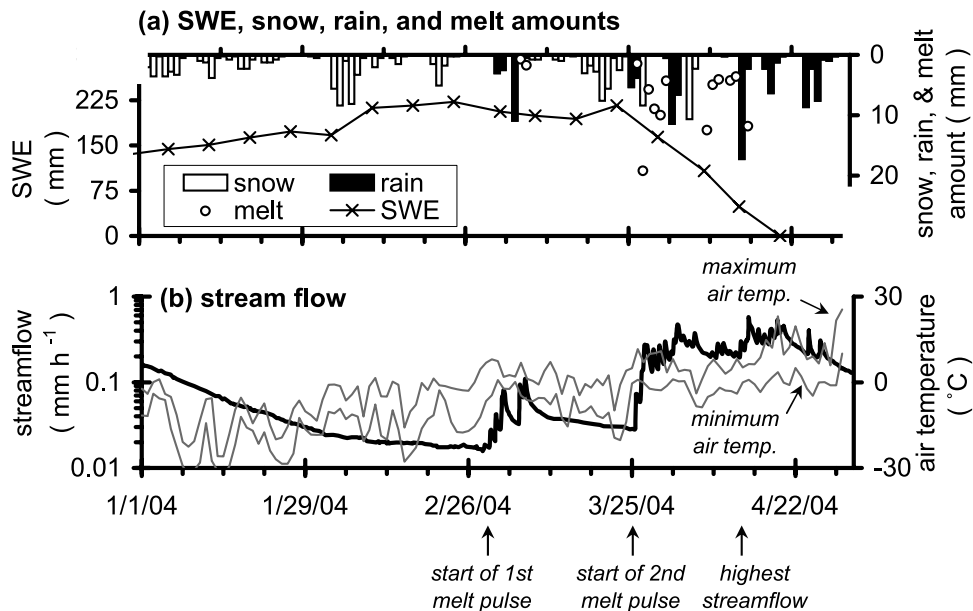

Figure 3. (a) Weekly snow water equivalent (SWE) measurements show the accumulation and melt of the 2004 snowpack. (b) Streamflow varied with snowmelt when air temperatures were above freezing and when several small rainfall events occurred.
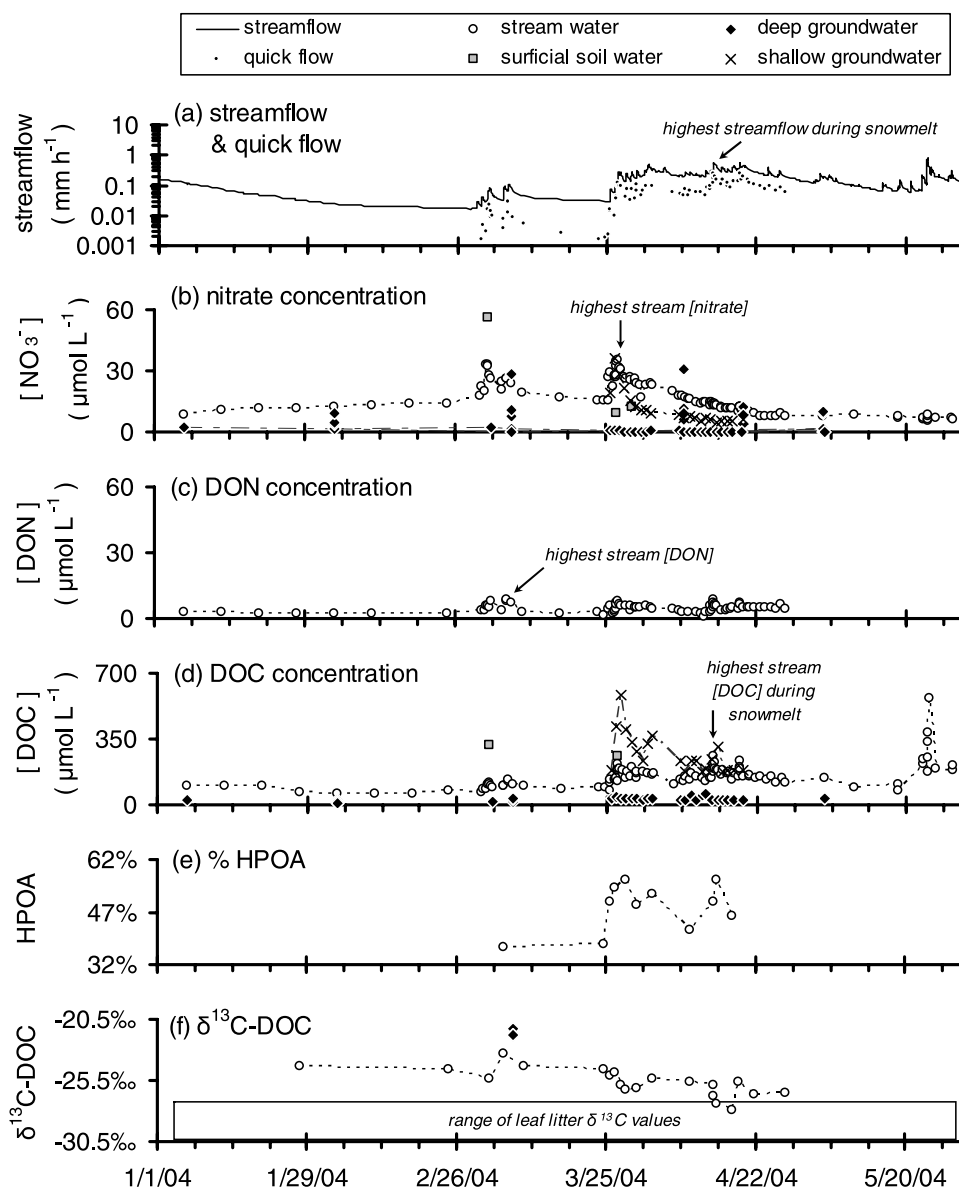
Figure 4. (a) Quick flow during the 2004 snowmelt tracked streamflow. (b) The highest stream nitrate concentration occurred early during snowmelt. In contrast, (c) stream DON concentration, (d) DOC concentration, and (e) hydrophobic acid fraction (HPOA) were highest at the time of highest streamflow. (f) Stream δ^{13}C-DOC was most negative at peak streamflow.

flow recession. Pulse 2 of early melt occurred when snowmelt resumed and the highest stream nitrate concentration of 35.2 μmol L^{-1} was measured on 27 March when streamflow was 0.27 mm h^{-1}. After 27 March during late melt, nitrate concentrations varied in parallel with diurnal streamflow fluctuations, however the magnitudes of nitrate concentration increases were small and increasingly damped as snowmelt progressed (i.e., the response of nitrate concentrations to stormflow attenuated with time). For example, when the highest streamflow of snowmelt 2004 occurred around midnight on 13 April, the high nitrate concentration of 14.9 μmol L^{-1} was nearly identical to the premelt nitrate concentration and was considerably less than the early peak concentration of 35.2 μmol L^{-1}. After 20 April as streamflow receded, stream nitrate concentrations were less than 10 μmol L^{-1}, a value that was about half the presnowmelt concentration. Stream nitrate concen-

tration and log transformed quick flow amount were positively correlated (p $\leq$ 0.00003 and R$^2 \geq$ 0.75) during the two early pulses of snowmelt and were negatively correlated (p = 0.001, R^2 = 0.20) during late melt (Figure 5).

[26] During winter base flow, stream DOC concentration decreased (Figure 4). During snowmelt, the highest DOC concentration (258 μmol L^{-1}) during snowmelt occurred at peak streamflow (0.58 mm h^{-1}) of 13 to 14 April 2004. Stream DOC concentrations consistently increased as streamflow increased and were positively correlated with log transformed streamflow (p = 2 $\times$ 10^{-17}, R^2 = 0.55) and log transformed quick flow amount (p = 3 $\times$ 10^{-23}, R^2 = 0.71, Figure 5). During streamflow recession after snowmelt, streamflow was about four times higher than premelt base flow and stream DOC concentrations were more than double the premelt base flow concentrations.
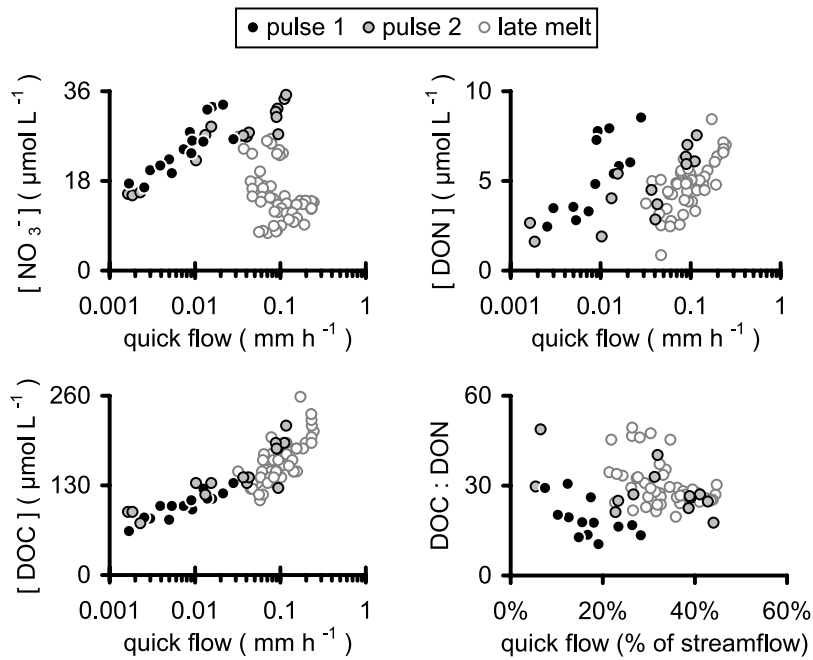
Figure 5. During 2004, nitrate, DOC, and DON concentrations increased with quick flow amount. During each snowmelt phase, the stream DOC:DON was positively correlated with quick flow (as a percent of streamflow). Pulse 1 samples were collected from 1 to 16 March, pulse 2 samples were collected from 23 to 27 March, and late melt samples were collected from 27 March to 27 April.

[27] Under winter base flow, stream DON concentration decreased (Figure 4). During snowmelt, stream DON concentration increased as streamflow increased and was positively correlated with log transformed streamflow (p = 6.75 × 10^{-19}, R^2 = 0.64, Figure 4). Stream DON concentration peaked at 8.53 μmol L^{-1} during early March and a second time on 14 April 2004 (8.44 μmol L^{-1}) at peak streamflow. In stream water, DON concentrations attenuated somewhat during the snowmelt event. Stream DON concentration was positively correlated with log transformed quick flow amount during the first melt pulse (p = 0.002, R^2 = 0.59), during the second pulse prior to the highest streamflow (p = 0.0004, R^2 = 0.66), and after the highest streamflow (p = 0.00000003, R^2 = 0.49, Figure 5). Like DOC, stream DON concentrations during streamflow recession after snowmelt were about double the presnowmelt base flow concentrations.

[28] Stream DOM composition changed during snowmelt. The stream DOC to DON ratio (DOC:DON) was lowest during pulse 1 and shifted to higher values during pulse 2 and late snowmelt (Figure 5). The DOC:DON was negatively correlated with the percent contribution from quick flow during pulse 1 (p = 0.044, R^2 = 0.32), pulse 2 (p = 0.038, R^2 = 0.31), and late melt (p = 0.012, R^2 = 0.14). From the first sample to the peak streamflow of snowmelt, the HPOA fraction of stream DOC increased from 37% to 50% (Figure 4). A negative linear relationship between log-transformed streamflow and δ^{13}C-DOC was significant (p = 0.00004, R^2 = 0.62) and showed that lower δ^{13}C-DOC values occurred at times of higher discharge.

[29] High-frequency data from snowmelt 2003 provide additional information on streamflow and nutrient responses to snowmelt. Snowmelt 2003 was four weeks shorter than in 2004 and the maximum streamflow of 1.5 mm h^{-1} during snowmelt 2003 was 2.5 times greater than that of 2004 (0.6 mm h^{-1}). Stream nitrate concentrations during 2003 peaked early and nitrate responses to stormflow subsequently attenuated [*Ohte et al.*, 2004]. During 2003, stream DOC and DON concentrations peaked when streamflow was highest (Figure 6). Relative to 2003, peak stream nitrate concentration was 44% higher, DOC was 19% lower, and DON was 103% higher during 2004 (Figures 4 and 6). During both years, stream nitrate concentrations were always greater than DON concentration.

[30] The 2003 data also show how groundwater levels at different landscape positions varied with streamflow and chemistry. Riparian areas were hydrologically connected to the stream at all times as shown by near-surface water levels and water table fluctuations that were synchronous with streamflow (Figure 6). Surficial soils on hillslopes were not connected to the stream via shallow subsurface flow paths during early snowmelt when nitrate concentrations peaked. Later during melt, when stream flow, DOC concentrations, and DON concentrations peaked, hillslope groundwater levels had risen into the upper meter of the soil where saturated hydraulic conductivities were exponentially higher than deeper soils [*Kendall et al.*, 1999].

4.2. Stream Water and Nutrient Sources

[31] Among individual rain-on-snow and rainfall events during 2004, the amounts (6 to 23 mm, Figure 3) and nitrate concentrations (5 to 92 μmol L^{-1}, Figure 7) of rainfall were highly variable. Although meltwater nitrate concentrations from the snow collectors were as high as 59 μmol L^{-1} during the first early melt pulse and 98 μmol L^{-1} during the second early melt pulse, concentrations rapidly diminished and decreased to a low of 3 μmol L^{-1} during mid-April (Figure 7). Nitrate concentrations of meltwater were higher
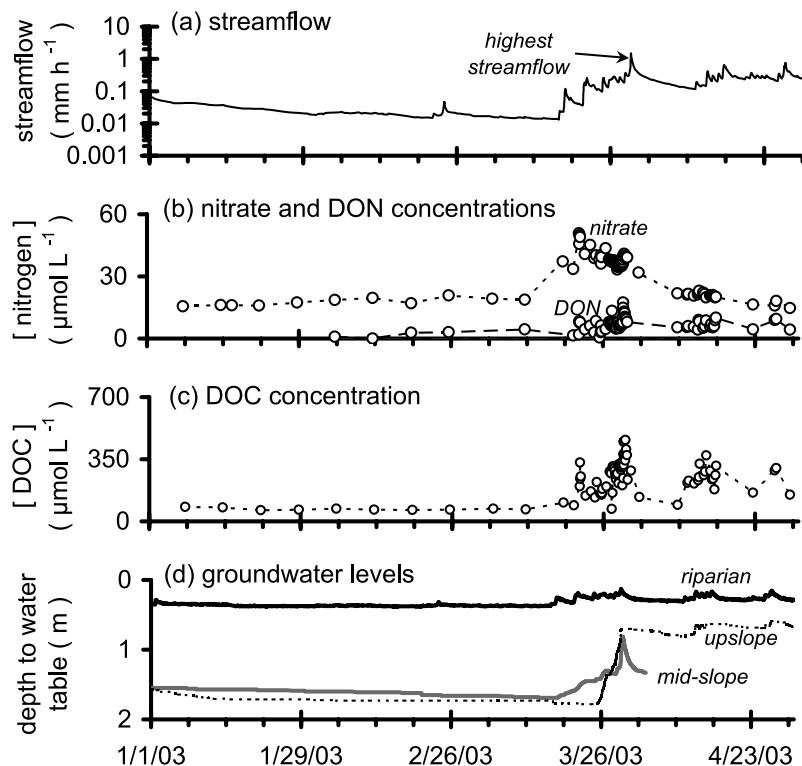
Figure 6. (a) In 2003, the highest streamflow during snowmelt occurred 8 days after the highest nitrate concentration. (b and c) The highest nitrate concentration occurred early during the 2003 snowmelt, while DON and DOC concentrations were highest with the highest streamflow. (d) Water levels show the depth to saturation in the soil profile at riparian, midslope, and upslope wells.

than shallow soil water and shallow groundwater concentrations until 1 April 2004. The peak nitrate concentration of meltwater occurred the same day as the peak stream concentration.

[32] During 2004, δ^{18}O-nitrate of premelt stream water (-5.0 to -0.8‰) and groundwater (-2.3 to $+2.2$‰, Table 1) were in the theoretical range for a nitrified source in this environment (-10 to $+15$‰ [*Kendall*, 1998]). The atmospheric nitrate end-member of snow, snowmelt, and rain ranged from $+76$ to $+101$‰ (Table 1 and Figure 7). The maximum stream δ^{18}O-nitrate of $+42.6$‰ occurred when the nitrate concentration of stream and snowmelt water was highest on 2 March (Figure 7). Mixing analysis of nitrate sources revealed a 48% peak contribution of atmospheric and 52% contribution of nitrified nitrate to the W-9 stream. In contrast to δ^{18}O-nitrate, δ^{15}N-nitrate values of end-member waters overlapped within a range of -3 to $+7$‰ which was too narrow to further distinguish among nitrate sources and transformations in the forested W-9 (Table 1).

[33] During 2003, nitrate inputs from atmospheric sources were highest (up to 26.1 ± 7.3%) early during melt and 0.5 to 15.5% after an early high-concentration pulse of nitrate [*Ohte et al.*, 2004]. Again during 2004, atmospheric contributions were highest (up to 48.1 ± 1.0%) early during melt and 0.4 to 9.8% during late melt. The uncertainty of nitrate source estimates was 7.3 to 8.1% during 2003 and 1.0 to 1.3% during 2004. Between 1 January and 30 April, the yield of atmospheric nitrate in stream water was 6.5 ± 0.5 mg m^{-2} during 2003 and 4.7 ± 0.07 mg m^{-2} during 2004. In both 2003 and 2004, the atmospheric nitrate was 7% of the total nitrate yield.

[34] On 27 March 2004, the shallow soil water δ^{18}O-nitrate value was $+69.7$‰. Mixing analysis of nitrate sources revealed 80% atmospheric and 20% nitrified nitrate in soil waters. During 2003, δ^{18}O-nitrate of shallow soil water decreased from $+71$‰ (83% from an atmospheric source) on 1 April to $+14$‰ (19% from an atmospheric source) on 15 April 2003. During 2004, soil water nitrate from a direct atmospheric source was 80% or more on the two March dates when zero-tension lysimeters yielded shallow soil water (Figure 7).

[35] Groundwater nitrate concentrations were heterogeneous among the synoptically sampled wells on 8 and 19 April 2004 (Figure 4). Groundwater wells sampled the entire screened interval that extended from the soil surface to bedrock. In contrast, the shallow (T-6) and deep (T-4) piezometers in the riparian zone sampled specific-depth groundwaters and characterized depth-stratified flow path chemistry. Groundwater from the deep piezometer consistently had low nitrate concentrations (<1.0 μmol L^{-1}). Nitrate δ^{18}O of shallow riparian groundwater peaked at 57.7‰ (67% from an atmospheric source) coincident with the peak nitrate concentration of 36.4 μmol L^{-1}, the highest concentrations of stream nitrate, and the peak atmospheric nitrate contribution to the stream (Figure 7). After 27 March, nitrate concentrations of soil water and shallow riparian groundwater were less than stream nitrate concentrations.

[36] Soil water DOC concentrations from zero-tension lysimeters were higher than stream concentrations (Figure 4). Groundwater DOC concentrations (25 to 58 μmol L^{-1}) from the deep piezometer were always less than stream DOC concentrations. Concentrations of DON were not measured
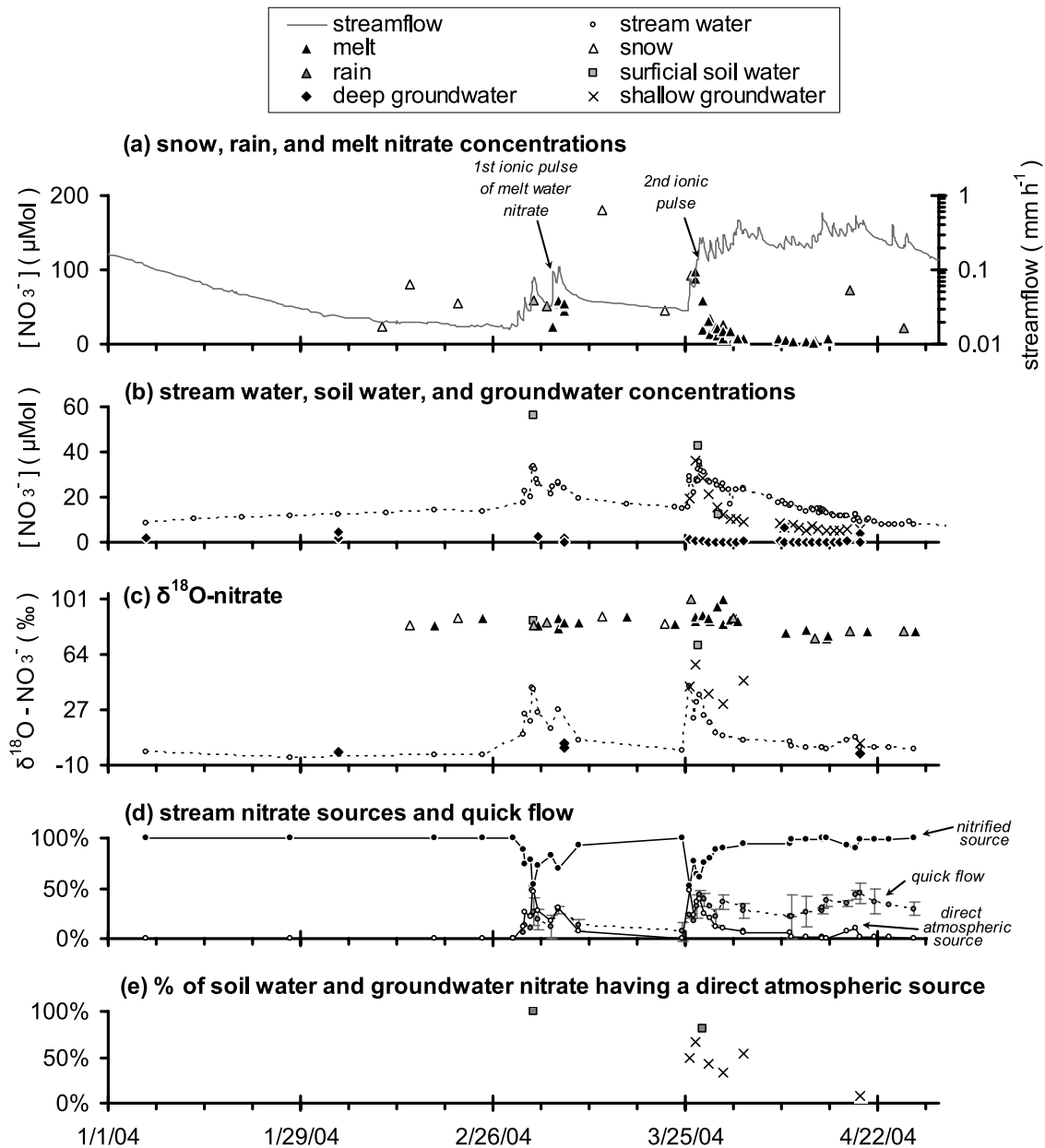
Figure 7. The highest nitrate concentrations of (a) meltwater and (b) stream water and shallow riparian groundwater occurred during two pulses early during the 2004 snowmelt. (c) During stormflow, stream and groundwater δ^{18}O-nitrate shifted toward an atmospheric end-member. Maximum atmospheric contributions to (d) stream and (e) soil and shallow groundwater coincided with the ionic pulses. The uncertainty estimates of quick flow magnitude are shown with the error bars. For nitrate sources, the uncertainties (less than 1.3%) are not shown.

for piezometer samples and soil waters. Shallow groundwater DOC was more variable than deep groundwater and ranged from 174 to 583 μmol L^{-1}. Shallow groundwater DOC concentrations were more than double the stream DOC concentration during early snowmelt. At and after the peak streamflow of the snowmelt event, stream, soil water, and shallow groundwater DOC concentrations were similar.

[37] The δ^{13}C-DOC of stream water was similar to groundwater during early snowmelt and shifted toward the δ^{13}C composition of leaf litter as snowmelt progressed. On 7 March 2004, groundwater δ^{13}C-DOC from three samples

was -21.6 ± 0.3‰. The mean δ^{13}C of leaf litter collected during autumn 2003 was -29.5‰ (-27.0 to -30.5‰).

5. Discussion

[38] To establish a framework to understand controls on stream chemistry at W-9 during snowmelt and other temperate upland forested catchments, we first present a conceptual model (Figure 8) that updates and unifies well-established concepts of catchment response that have previously been presented for water, nitrate, and DOM. Temporal changes in stream chemistry reflect the sequence in which hydrological flow paths link source areas to streams. As catchment

Table 1. Ranges of δ^{15}N-Nitrate and δ^{18}O-Nitrate for Stream, Soil, and Groundwaters

	Number of Samples	δ^{15}N-Nitrate (‰)	δ^{18}O-Nitrate (‰)
2003 [Ohte et al., 2004]			
Premelt W-9 stream	1	+3.0	−7.7
Snowmelt W-9 stream	75	−0.3 to +7.4	−2.5 to +19.8
Shallow soil water	5	−11.7 to +7.2	+5.1 to +71.1
Groundwater (wells)	6	+1.7 to +5.9	−10.6 to +21.1
Rainfall	3	−1.8 to −3.8	+77.6 to +88.4
Snow	0	−	−
Meltwater	0	−	−
2004			
Premelt W-9 stream	4	+1.2 to +1.9	−5.0 to −0.8
Snowmelt W-9 stream	32	−0.1 to +1.8	−0.4 to +42.6
Shallow soil water	1	−0.3	+69.7
Groundwater (wells)	3	+1.9 to +4.7	−2.3 to +2.2
Shallow riparian groundwater (piezometer)	6	−0.1 to +7.1	+4.5 to +57.7
Rainfall	7	−2.6 to +2.3	+75.7 to +100.8
Snow	4	−0.8 to +1.1	+83.9 to +89.2
Meltwater	4	−1.0 to +1.4	+82.0 to +86.8

wetness increases during stormflow events, the solutes in the stream reflect the sources that are available and the amount of water that flows through the source areas of those solutes [*Hornberger et al.*, 1994; *Bishop et al.*, 2004]. Under low antecedent moisture conditions prior to events, surface saturation and lateral flow through soils is limited to near-stream areas. During the initial wetting period of large events, overland flow across saturated surfaces in a small portion of a catchment may rapidly route direct runoff to streams [*Dunne and Black*, 1971; *McGlynn et al.*, 1999]. As infiltration progresses, the water table rises to saturate the land surface across an increasing area of the landscape as controlled by topographic gradients [*Beven and Kirkby*, 1979; *Hornberger et al.*, 1994]. Downslope areas that are closer to the stream connect first and upslope areas connect later via lateral flow paths as zones of surface and subsurface saturation expand [*Hjerdt*, 2002; *Bishop et al.*, 2004]. Preferential subsurface flow paths in highly transmissive shallow soils may rapidly transmit water and solutes when saturation expands into surficial hillslope source areas, as shown by previous studies at W-9 [*Kendall et al.*, 1999; *McGlynn et al.*, 1999; *Shanley et al.*, 2003]. When catchment wetness during a stormflow event is highest, lateral flow along surficial pathways is most spatially extensive and more water flows through the landscape to streams. At sites that have different lithologies than the glacial tills and impermeable bedrock of W-9, analogous hydrological responses along different preferential flow paths (e.g., deep macropores, distinct layers and lenses in soils, bedrock features) contribute quick flow and solutes to streams [*Mulholland*, 1993; *Sidle et al.*, 2001; *Katsuyama et al.*, 2005].

[39] Solute sources reflect organic matter and atmospheric inputs as well as biogeochemical processes that cycle nutrients through mobile organic and inorganic forms. In headwater catchments that are forested, stream DOM largely originates from terrestrial (allochthonous) sources [*Aiken and Cotsaris*, 1995]. Biological exudates and soluble organic matter are leached when water laterally flows through surficial soils or as overland flow interacts with the forest floor [*Schiff et al.*, 1990; *Kaplan and Newbold*, 1993;

McHale et al., 2000]. When flow path contact times are long, concentrations decrease as DOM degrades and the relative amount of DON increases such that long, slow flow paths may have groundwaters with a lower DOC to DON ratio (DOC:DON) [*Hood et al.*, 2005]. Temporal changes in the stream DOC:DON and other compositional measures reflect depth-stratified inputs as DOM moves to streams along particular flow paths during storm events. In surficial soils, DOM that is freshly leached is less biologically degraded, the DOC:DON is higher, and DOM chemistry and isotopic ratios are more similar to the leached source (litter, soil organic matter, or biological exudates). Terrestrially derived DOM may be contributed to streams with little or no alteration of chemical properties when preferentially transported along surficial flow paths and contact times are short. As variable source areas expand farther from streams, larger amounts of less degraded, more humic DOC are transported along surficial flow paths as more of a catchment hydrologically connects to a stream [*Cronan and Aiken*, 1985; *McDowell and Likens*, 1988]. Similarly, freshly derived DOM having δ^{13}C-DOC similar to the δ^{13}C composition of surficial organic matter sources derived from plant tissue or exudates is flushed to a stream when streamflow is high.

[40] Whether deposited as ammonia, ammonium, nitric acid, nitrogen dioxide, or nitrate, most nitrogen from atmospheric sources is assimilated into terrestrial organic pools where the nitrogen remains sequestered for weeks to years or longer. After organically bound nitrogen is mineralized and nitrified, the mobilized nitrate may be leached and transported to streams [*Rascher et al.*, 1987; *Kendall et al.*, 1995]. This circuitous pathway through the biological pool is an indirect way that elevated atmospheric deposition and the saturation of biological nitrogen uptake may affect groundwater and stream chemistry [*Stoddard*, 1994; *Fernandez and Adams*, 2000; *Aber et al.*, 2003].

[41] Some studies that evaluate sources of stream nitrate using natural abundance isotopic tracers report that most stream nitrate during snowmelt originates from nitrification in soils [*Kendall et al.*, 1995; *Campbell et al.*, 2002; *Piatek et al.*, 2005; *Campbell et al.*, 2006] or from nitrogen saturation of biological uptake [*Durka et al.*, 1994]. Although the balance of the stream nitrate at W-9 (Figure 7) was nitrified in the catchment prior to snowmelt and was transported along deep subsurface flow paths or quick flow pathways through surficial soils, our results show that a high-stream nitrate concentration may originate from precipitation that is directly routed to streams as water flows through the environment. The important practical implications are that some nitrate may not be altered by terrestrial biogeochemical processes, a fraction of atmospherically deposited nitrate only remains in a catchment as long as the snowpack persists (weeks to months), and some atmospheric nitrate in rainfall may rapidly reach the stream.

[42] During winter at W-9, riparian areas were hydrologically connected to the stream at all times as shown by near-surface water levels and water table fluctuations that were synchronous with streamflow (Figure 6). During early snowmelt, nitrate contributions to the stream from both atmospheric and nitrified sources must have originated from near-stream areas because hillslope groundwater levels remained deep in the soil profile. Near channel meltwaters
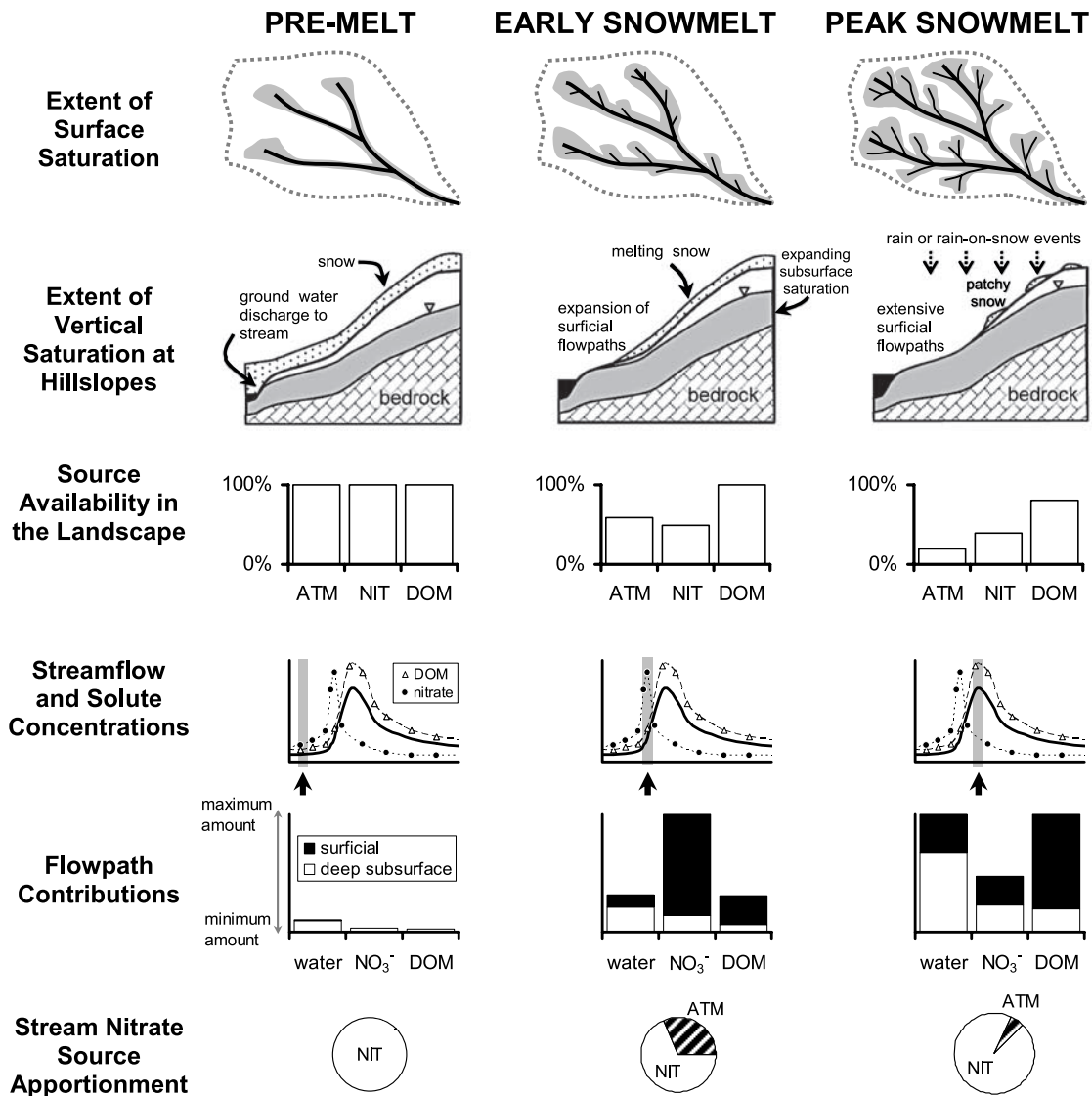
Figure 8. Simplified conceptual model of catchment-scale processes that control stream nitrate and DOM concentrations during snowmelt in an upland temperate forest. With snowmelt, high-concentration sources become hydrologically linked to streams via lateral and preferential flow through shallow subsurface and overland pathways after the water table rises into surficial soils. Stream nitrate concentrations peak early when near-stream source areas hydrologically connect and high-concentration nitrate from atmospheric (ATM) and nitrified (NIT) sources are available but decrease later in melt as the supply becomes depleted. Stream DOM concentrations peak when surficial contributing areas are most extensive and high-concentration DOM is leached from an abundant source pool that is concentrated in surficial soils.

may also have been routed to the stream via saturation overland flow across variable source areas. Hillslope groundwater levels rose near the soil surface by the time of peak streamflow during snowmelt. During 2003, these time-lagged connections of surficial source areas in uplands coincided with peak inputs of water and the highest concentrations of DON and DOC (Figure 6) but occurred well after peak nitrate concentrations of meltwater, shallow soil water, shallow riparian groundwater, and stream waters.

[43] Our study highlights the need to collect samples early in snowmelt, at high frequency, and over the entire range of streamflow conditions to capture nitrate dynamics. Weekly sampling typical of many studies may not provide sufficient resolution to unambiguously apportion nitrate

sources and sampling that does not include the early stages of snowmelt may not detect the highest stream nitrate concentrations. Furthermore, isotopic tracers may be needed to quantify the direct connections between anthropogenic sources, atmospheric deposition, ecosystem nitrogen enrichment, and stream chemistry [*Ohte et al.*, 2004; *Elliott et al.*, 2007]. For DOC and DON, less frequent, flow proportional sampling in addition to weekly sampling is usually sufficient to decipher when water flows along the surficial flow paths that are the sources of high concentrations of stream DOM during events.

[44] Although atmospheric deposition is not a major DOM source, infiltration of melt and rainwater contributed to stream DOC variation by leaching DOM from surficial

soils. As shown by shallow soil water and riparian groundwater concentrations at W-9, DOC concentration was high in surficial soil layers while concentrations of deeper groundwater DOC remained low (Figure 6). In early snowmelt, stream water DOM originated from near-stream areas. The initially high DOC concentrations at the shallow piezometer suggest an initially high concentration riparian source that was diluted by hillslope water when upslope surficial flow paths were active (Figure 4). During 2004, the relationship between quick flow and DOM concentrations, increased inputs of hydrophobic acids, and low δ^{13}C-DOC that was similar to leaf litter δ^{13}C (Figure 4) were all indicative of DOM that was leached when surficial upland soils were hydrologically connected to the stream and water inputs from surficial flow paths (i.e., quick flow) were the largest (Figure 5).

[45] The variation of stream DON reflected the balance between flow path interaction and source areas. Early during snowmelt, stream DON concentrations were highest when variable source areas initially expanded around streams into riparian source areas (Figure 4). Stream DOM composition changed during snowmelt as shown by decreased δ^{13}C-DOC, increased percent HPOA, and increased DOC:DON (Figures 4 and 5). As snowmelt progressed and the relative contribution of quick flow increased, stream DOM had relatively less DON (i.e., higher DOC:DON). Nonetheless, the total inflow of DOM increased causing high DON concentrations to occur at the time of peak streamflow.

[46] The literature on hydrological flushing of solutes from catchments documents instances of source and transport limitation [Creed and Band, 1998; Boyer et al., 2000] and differences among solutes at various times and places [Burns, 2005]. When a solute is contributed from a source that originates along a transient preferential flow path during stormflow, stream solute concentrations will be high until the source is exhausted or flow subsides. At W-9, stream DOC concentration increased with increased flow and peaked during highest stormflow (Figures 4 and 6) suggesting that the amount of water flowing through source areas was insufficient to leach all of the DOC. Elsewhere in the humid northeast United States, similar transport-dominated DOC flushing is observed [McDowell and Likens, 1988; Inamdar and Mitchell, 2006; Mitchell et al., 2006], a response that differs from upland catchments in the Rocky Mountains of Colorado (USA) where melting snow leaches and exhausts the available supply [Boyer et al., 1997; Hood et al., 2005].

[47] At W-9, the late centers of mass for DON and DOC relative (Figure 2) to nitrate are attributable to the different supplies of these solutes. Nitrate flushing to streams at W-9 was source limited after the early, high-concentration pulses. Stream nitrate concentrations peaked early during melt when direct input of high-concentration meltwater from snow that covered the channel contributed nitrate having an atmospheric isotopic signature (Figures 7 and 8). Stream nitrate concentrations decreased later during melt because the snowpack nitrate supply and shallow soil water pools that were the source of initially high stream concentrations became depleted. By the end of snowmelt, base flow nitrate concentrations were reset from winter highs to low concentrations (Figure 4) that persist through summer [Sebestyen, 2008] when high biological demand for nitrogen limits nitrate availability [Stoddard, 1994].

[48] In surficial hillslope soil, the variation of nitrate concentrations in soil water may be attributed to precipitation inputs, leaching, and transformations. At W-9, nitrate from snowmelt having an atmospheric δ^{18}O-nitrate signature infiltrated shallow soils early in the melt and was a larger contributor to unsaturated zone waters than nitrate from nitrified sources (Figure 7). As shown for the depth stratified samples from piezometers, the atmospheric source affected nitrate concentrations along shallow groundwater flow paths but did not affect deep groundwater nitrate concentrations. The change in isotopic composition of soil water nitrate from a predominantly atmospheric source (83%) to a predominantly nitrified source (81%) later during the 2003 snowmelt (Figure 7) indicated nitrification in shallow soils like that at Adirondack mountain catchments in New York [Campbell et al., 2006] and the nearby Hubbard Brook Experimental Forest in New Hampshire [Campbell et al., 2007]. In-stream nitrification may also explain W-9 stream nitrate concentrations that increased during winter when base flow concentration was higher than most groundwater samples (Figure 4).

6. Conclusions

[49] Differences among solute sources, biogeochemical controls on nutrient availability, and catchment transport processes explained dynamic stream nitrate and DOM responses during snowmelt at an upland, forested catchment. Because atmospheric deposition contributes nitrate to catchments and surficial flow paths link source areas in the landscape to streams, atmospherically deposited nitrate may be rapidly transported during snowmelt. This hydrological flushing of atmospheric nitrate indicates that high stream nitrate concentrations during storm events do not necessarily reflect nitrogen saturation of biological uptake as shown for W-9 at the Sleepers River Research Watershed.

[50] Multiple drivers of ecosystem change such as land cover change, climate change, and pollution highlight an ongoing need to quantify effects on forests and streams. Excess nitrogen from anthropogenic sources continues to rain down across landscapes, cascades through terrestrial biogeochemical cycles [Stoddard, 1994; Galloway et al., 2003], and affects stream nitrate concentrations in upland forests where atmospheric deposition is the only source of anthropogenic nitrogen. Understanding how catchment processes affect DOM transport may help to elucidate whether reported increases of stream DOC concentrations are a response to interannual hydrological variability as well as nitrogen enrichment of ecosystems [Goodale et al., 2005], climate change [Evans et al., 2006], or reduced acidic deposition [deWit et al., 2007].

[51] Inputs to streams from atmospheric sources are ecologically important and quantifying the catchment export of direct atmospheric nitrate inputs bridges a gap in our knowledge of ecosystem responses to nitrogen pollution. Our study is an example of how a hydrological approach can be used to detect and quantify the direct effects of atmospheric nitrogen pollution on forest streams. Although the direct yield of nitrate from atmospheric sources (7% of the stream nitrate outflow from the catchment) between January and April may be small, the amounts are quantifi-

able with high-frequency measurements and isotopic source apportionment. Likewise, our findings show that nitrified nitrate was diluted or displaced from surficial soils and flow paths by atmospheric nitrate during early snowmelt. Although nitrification did occur later during snowmelt, more than 50% of the nitrate in soil and shallow groundwaters after the onset of snowmelt directly originated from atmospheric sources. These findings suggest a need to monitor the nitrate sources and transformations that affect stream nitrate concentrations during stormflow events as an approach to elucidate the direct effects of atmospheric nitrogen pollution on forested ecosystems.

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