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Mechanisms underlying export of N from high-elevation catchments during seasonal transitions

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Abstract. Mechanisms underlying catchment export of nitrogen (N) during seasonal transitions (i.e., winter to spring and summer to autumn) were investigated in high-elevation catchments of the Sierra Nevada using stable isotopes of nitrate and water, intensive monitoring of stream chemistry and detailed catchment N-budgets. We had four objectives: (1) determine the relative contribution of snowpack and soil nitrate to the spring nitrate pulse, (2) look for evidence of biotic control of N losses at the catchment scale, (3) examine dissolved organic nitrogen (DON) export patterns to gain a better understanding of the biological and hydrological controls on DON loss, and (4) examine the relationship between soil physico-chemical conditions and N export. At the Emerald Lake watershed, nitrogen budgets and isotopic analyses of the spring nitrate pulse indicate that 50 to 70% of the total nitrate exported during snowmelt (ca. April to July) is derived from catchment soils and talus; the remainder is snowpack nitrate. The spring nitrate pulse occurred several weeks after the start of snowmelt and was different from export patterns of less biologically labile compounds such as silica and DON suggesting that: (1) nitrate is produced and released from soils only after intense flushing has occurred and (2) a microbial N-sink is operating in catchment soils during the early stages of snowmelt. DON concentrations varied less than 20–30% during snowmelt, indicating that soil processes tightly controlled DON losses.

Introduction

Snowmelt- and rainfall-driven export of nitrate is a key hydrochemical feature in montane catchments and has been studied extensively over the last two decades in order to understand its underlying mechanisms and ecological consequences (Bales et al. 1990; Campbell et al. 2000, 2000; Creed and Band 1998; Sickman and Melack 1998; Stottlemyer 1992; Stottlemyer and Toczydlowski 1996). Early studies in high-elevation watersheds with sparse soils and vegetation proposed that atmospherically derived nitrate was preferentially eluted from the snowpack and trans-

ported to streams during the first fractions of snowmelt (Bales et al. 1989; Williams et al. 1993; Williams and Melack 1991a). As a further refinement, Williams et al. (1995), postulated that ammonium from the melting snowpack, rapidly nitrified in the snowpack or catchment soils, represented a significant percentage of the spring nitrate pulse. However, using isotopic tracers, Williams et al. (1996) showed that ammonium was released unaltered from the snowpack and was rapidly immobilized in underlying soils with no evidence of subsequent nitrification.

Isotopic analyses of the ^{15}N and ^{18}O of exported nitrate provide a direct method for determining nitrate sources to surface waters and have resulted in a significant change in current thinking on nitrate pulses. Investigations in montane watersheds in the eastern U.S. and at Loch Vale, Colorado, suggest that stream-water nitrate is isotopically distinct from snowpack nitrate, but similar to nitrate produced by microbial nitrification (Kendall 1998; Kendall et al. 1995; Campbell et al. 2002). Based on these studies, most of the nitrogen eluted from the snowpack appears to be taken up in catchment soils and/or vegetation and the stream nitrate pulse is derived primarily from the flushing of biologically transformed N from watershed soils.

Heterotrophic N immobilization in soils has been shown to be a sink for snowmelt dissolved inorganic nitrogen (DIN) during spring runoff (Brooks et al. 1996, 1998), although there is evidence that certain alpine plants assimilate N while snow-covered (Bilbrough et al. 2000). Nitrous oxide losses from subnivean soils at an alpine tundra site were found to exceed the annual atmospheric input of N from winter precipitation (Williams et al. 1998) and other studies have observed a rapid increase in microbial biomass in snow-covered soils at the onset of snowmelt (Brooks et al. 1999, 1996). Through a combination of factors, including carbon substrate limitation, freeze-thaw events in snow-free soils, and shifts from psychrophilic to more thermophilic microbial species, initially immobilized microbial N can be released later in the spring and summer to be used by plants and exported in streamflow (Brooks and Williams 1999; Lipson et al. 2000; Schimel and Clein 1996). Together, these studies suggest that microbial sequestration and release of snowpack N plays an important role in producing nitrate export patterns in montane catchments.

Several major questions regarding seasonal N export still remain to be answered in high-elevation ecosystems. First, what proportion of snowmelt nitrate bypasses biological systems and enters streams and lakes? More quantitative estimates of the relative contributions of snowpack and soil nitrogen to the spring nitrate pulse are needed to determine the effect of increased atmospheric N-loading on surface water chemistry and aquatic ecosystems. Second, to what extent are biological systems responsible for annual N export patterns? Although studies have shown that microbial uptake and release of DIN is an important influence on N export, the mechanisms underlying N transfers from microbial biomass to plants and surface water are still not fully understood. Rapid physico-chemical changes that take place in soils during snowmelt and other transition periods could act as triggers for N-release from microbial populations to surface waters. Finally, is dissolved organic nitrogen (DON) a major N loss during seasonal transitions? There have been few

observations of whether or not a DON ″pulse″ occurs during snowmelt or rain-events and little is known regarding the biological and hydrological controls on DON losses in high elevation catchments. Most earlier studies focused on export of DIN even though DON losses equal or exceed DIN export in many high elevation watersheds and may be a primary mechanism whereby N-limitation is maintained in terrestrial ecosystems (Sickman et al. 2001; Williams et al. 2001; Hedin et al. 1995).

Using a combination of techniques and data sources, we examine the underlying mechanisms for seasonal release of N from high elevation watersheds of the Sierra Nevada. We describe the intra-annual variability of DIN and DON export in two headwater catchments (Emerald and Topaz) and contrast this variability with the export behavior of silica, a less biologically labile compound, in order to detect the presence of biological sequestration and release of N at the watershed-scale. At the Emerald Lake watershed we examine the spring seasonal transition and estimate the relative contributions of snowpack and catchment sources to the nitrate pulse using detailed mass balances and isotopic ^{15}N and ^{18}O analyses of nitrate. Ancillary nitrate isotope data are also presented for two other high-elevation sites, Topaz Lake and the Marble Fork of the Kaweah River. These data allowed us to estimate how much snowpack nitrate escapes biological cycling in soils and enters streams during snowmelt. At Topaz Lake we examine N-dynamics during the summer-autumn transition period. Using detailed chemical time-series and records of soil temperature and moisture we investigate how changes in soil physico-chemical conditions are related to ecosystem N-losses. Overall our goal is to develop a conceptual framework for episodic N release in high-elevation ecosystems and, in doing so, help determine how these systems will respond to altered N deposition in the future.

Site descriptions

The Marble Fork of the Kaweah River basin (36°36′22″ N, 118°40′59″ W) and two of its major sub-catchments, Emerald Lake watershed and Topaz Lake watershed, are located along the western slope of the southern Sierra Nevada within Sequoia National Park. The river is a second order stream where it is gauged near the mouth of the valley (elevation 2,621 m) and drains an area of 1908 ha. The highest point in the watershed lies at an altitude of 3,493 m. The geology of the Tokopah Valley is dominated by fine and medium-grained, porphyritic granodiorite and coarse-grained granite. Most of the basin is composed of bedrock and talus, but there are significant areas of wet meadow soils in upper portions of the basin (i.e., Table Meadows and Topaz watershed) and along the margins of the river-course (see Melack et al. (1998)). Trees, mainly lodgepole and western white pine and willows, are found alongside the river as it meanders through the valley.

The Emerald Lake subbasin (36°35′49″ N, 118°40′29″ W) has an outlet elevation of 2800 m. The 120 ha watershed is granitic with steep slopes (mean slope

31°) and 616 meters of vertical relief. Bedrock is mainly granodiorite with mafic inclusions, aplite dikes and pegamite veins. Poorly developed soils cover about 20% of the watershed and these are acidic and weakly buffered (Melack et al. 1998). The primary clay minerals are vermiculite, kaolinite and gibbsite. Vegetation in the Emerald Lake basin is sparse, consisting of scattered conifers (lodgepole and western white pine), low woody shrubs, grasses and sedges. Most areas of developed soil contain vegetation.

The Topaz Lake watershed (36°37′30″ N, 118°38′11″ W) is 165 ha in area and located at the head of the Marble Fork watershed, about 6 km north–northwest of Emerald Lake. Vertical relief in the basin is 275 meters and the watershed has a southern exposure; outlet elevation is 3218 m. Parts of the upper basin have extensive meadows (grasses and sedges) and short-lived ponds during snowmelt. There is a small stand of foxtail pines in the upper eastern portion of the watershed ($\sim$ 25 trees). Alpine brown soils are found throughout the watershed, often forming complexes with rocks and bedrock outcrops. The geology of the basin is dominated by fine-grained, porphyritic granodiorite containing abundant mafic inclusions. The phenocrysts include potassium feldspar, hornblende, biotite and plagioclase.

Detailed measurements of N pools and transformation have been made in the Emerald Lake catchment. At Emerald, about 90% of the basin's N storage is contained in soils, litter and soil solution with the balance held in vegetation (Williams et al. 1995). Internal cycling within the soil N pool is dominated by mineralization of soil organic matter and biological uptake. Measurements of atmospheric N deposition and N yield suggest that annual catchment N turnover is less than 5%. Nitrogen fixation and denitrification have not been extensively measured.

Precipitation in the catchments falls predominately as snow during the winter and accumulates with little melt or evaporative losses until spring snowmelt. Rainfall is sparse, comprising $\sim$ 10% of annual precipitation and occurs predominantly in the autumn. Snowmelt typically begins in April with peak discharge usually occurring in June.

Methods

Snowpack

Snowpack DIN was measured in the Emerald Lake watershed at maximum accumulation on or near April 1 during 1996, 1997 and 1998. Basin-wide, snow-depth surveys and measurements of snow density collected from snowpits were combined to estimate catchment snow water equivalent (SWE). Chemical samples were obtained in snowpits by collecting duplicate, continuous, vertical sections of the accumulated snowpack. Mean chemical concentrations from the snowpits were multiplied by SWE to compute the total DIN and nitrate content of the snowpack. Nitrate and DIN release from the snowpack were estimated as the product of snowmelt volume and corrected snowpack N concentrations. We assumed that snowmelt

volume equaled outflow discharge during the snowmelt period since losses to evaporation and groundwater are negligible during the early snowmelt season (Leydecker and Melack 1999). To account for ionic enrichment of snowmelt (i.e., preferential elution), enrichment factors were used to correct the snowpack DIN and nitrate concentrations. These factors were based on measured ionic losses determined from sequential snowpits sampled in late April and May; enrichment factors ranged from 1.06 to 2 for nitrate and from 1.19 to 2 for DIN, relative to the bulk snow.

Stream, soil and climate measurements

Catchment outflows were sampled for ammonium, nitrate, silica and DON at 1 to 4-day intervals using automated samplers (ISCO) from 1996 to 1999. Samples used for DON analyses were kept frozen at −20 °C until analyzed. All other samples were kept at 5 °C.

Discharge was measured with v-notch weirs at Emerald and Topaz outflows using a continuous record of stage recorded with a solid-state datalogger. At Marble Fork outflow, a stage-discharge relationship, established using dye or salt-dilution discharge determinations (60 slug and constant injection measurements) (Melack et al. 1998), was used with continuous stage records to compute discharge.

Soil moisture was measured at Topaz with a time domain reflectometry (TDR) sensor and recorded hourly on the datalogger. Air temperature was measured with shielded thermistors at three weather stations within the Marble Fork catchment.

Chemical analyses of stream and snowpack samples

Ammonium was determined from filtered water samples by the indophenol blue method (detection limit, 0.5 μmoles L^{-1}, i.e., μM) (Strickland and Parsons 1972). Nitrate was measured on a DIONEX ion chromatograph, employing an AS4A or AS14 separation column and conductivity detection (detection limit, 0.05 μM). Silica was determined by the silico-molybdate method (Strickland and Parsons 1972) either manually or on a Latchat autoanalyzer (detection limit, 0.5 μM). Total dissolved nitrogen (TDN) was determined by persulfate digestion (Valderrama 1981), and DON was computed as the difference between TDN and DIN (detection limit for DON was 1.0 μM).

Isotopic measurements of nitrate and water

Nitrate isotope samples (i.e., $\delta^{18}O_{(NO3)}$ and $\delta^{15}N_{(NO3)}$) were collected from the Emerald, Topaz and Marble Fork outflows in 1998 (n = 9, n = 3 and n = 3, respectively), and from the Emerald and Topaz outflows in 1999 (n = 7 and n = 4, respectively). Snowpack samples were collected from pits dug during spring snow surveys in 1996 (n = 3), 1998 (n = 2) and 1999 (n = 2). All samples were collected using the field and laboratory procedures of Chang et al. (1999). Owing to the low concentration of nitrate in these samples (< 10 μM) and the analytical requirement for ca. 70 μmoles of nitrate for the dual isotopic procedure, sample volumes ranged

from 10 to 70 liters. Snow samples were melted in 100-liter polyethylene tanks at a cabin near the study sites before processing.

Water samples for $\delta^{18}O_{(H20)}$ were collected (unfiltered, in 60 mL, zero headspace, polyethylene bottles) from all samples used for nitrate isotopes and at additional times during snowmelt runoff from the Emerald, Topaz and Marble Fork outflows. The samples were stored at 5 °C until processed and analyzed on the mass spectrometer (Sofer and Gat 1972).

Nitrate isotope analyses were performed on either a Finnigan Mat 251 or Europa Scientific Tracermass/Roboprep stable isotope mass spectrometer. $\delta^{18}O_{(H20)}$ analyses were run on a Finnigan model Delta-S stable isotope mass spectrometer. Nitrogen isotope values ($\delta^{15}N$) are reported in per mil (‰) relative to atmospheric air; oxygen isotope values ($\delta^{18}O$) are reported relative to the standard VSNOW. Precision of laboratory standards for $\delta^{15}N$ ranged from +/– 0.1 to 0.5 ‰ (SD) and for $\delta^{18}O$ were 0.2 ‰ (SD).

Results

Watershed N budgets

Solute balances for the initial 20–25% of snowmelt runoff were computed for 1996–1998 at Emerald (Table 1). In all three years the amount of nitrate exported from the catchment during this period was approximately equal to the entire snowpack nitrate pool and about 75% of snowpack DIN content (Table 1). No major rain or snow storms occurred during these snowmelt seasons, thus the only N-input to the catchment was snowmelt. Assuming complete assimilation of ammonium in snowmelt (Williams et al. 1996), then from 70 to 80% of the nitrate exported during the first 20–25% of snowmelt came from catchment soils. Assuming rapid and complete nitrification of ammonium in snowmelt, then 40–60% of total DIN export must have originated from soils and talus.

Annual and seasonal variations in outflow nitrogen concentrations

Detailed time series of dissolved N fluxes and silica are presented for two dissimilar years (1998, above-normal runoff; 1999, below-normal runoff) in Figures 1 and 2. At Emerald, during both years, nitrate concentrations had two peaks: one at the earliest evidence of increased runoff and another, larger peak 1 to 4 weeks before maximum outflow (Figure 1a & 1b). After the second peak, nitrate levels fell slightly, until mid-June when concentrations declined exponentially. During earlier periods of the winter, nitrate concentrations were below 2 μM (data not presented).

There was evidence of pulses in both DON and silica at Emerald in late April or early May of both years. Peak DON levels occurred a few days (1999) to weeks (1998) prior to peak nitrate concentration (Figure 1a & 1b). Following these pulses, both DON and silica declined as runoff increased, reaching near-minimum concen-

Table 1. Solute balance of inorganic N-species during the first 20–25% of snowmelt runoff at the Emerald Lake watershed. Catchment export is the amount of nitrate or DIN in basin outflow. Snowpack storage is the amount of solute contained in the basin snowpack at maximum accumulation plus any additional snow which fell after the spring snow-survey. Nitrogen release from the snowpack was computed as the product of snowmelt volume (estimated from outflow discharge) and corrected snowpack nitrate and DIN concentrations (see Methods). The estimated soil contribution reflects the amount of catchment flux not accounted for by snowpack release and is expressed as a percentage of actual flux; separate estimates are given for nitrate (assuming total assimilation of snowpack ammonium) and DIN.

Year	Dates	Solute	Fraction of Snow-melt Runoff	Total Snowpack Storage kilomoles	Release From Snowpack kilomoles	Catchment Export kilomoles	Estimated Soil Contribution
1996	1-April to	Nitrate	21%	2.2	0.4	2.1	81%
	May 15	DIN		6.2	1.2	2.1	41%
1997	1-April to	Nitrate	24%	2.2	0.6	2.0	70%
	May 15	DIN		3.2	0.7	2.1	64%
1998	1-April to	Nitrate	20%	2.9	1.0	3.3	70%
	15-June	DIN		4.4	1.5	3.4	55%

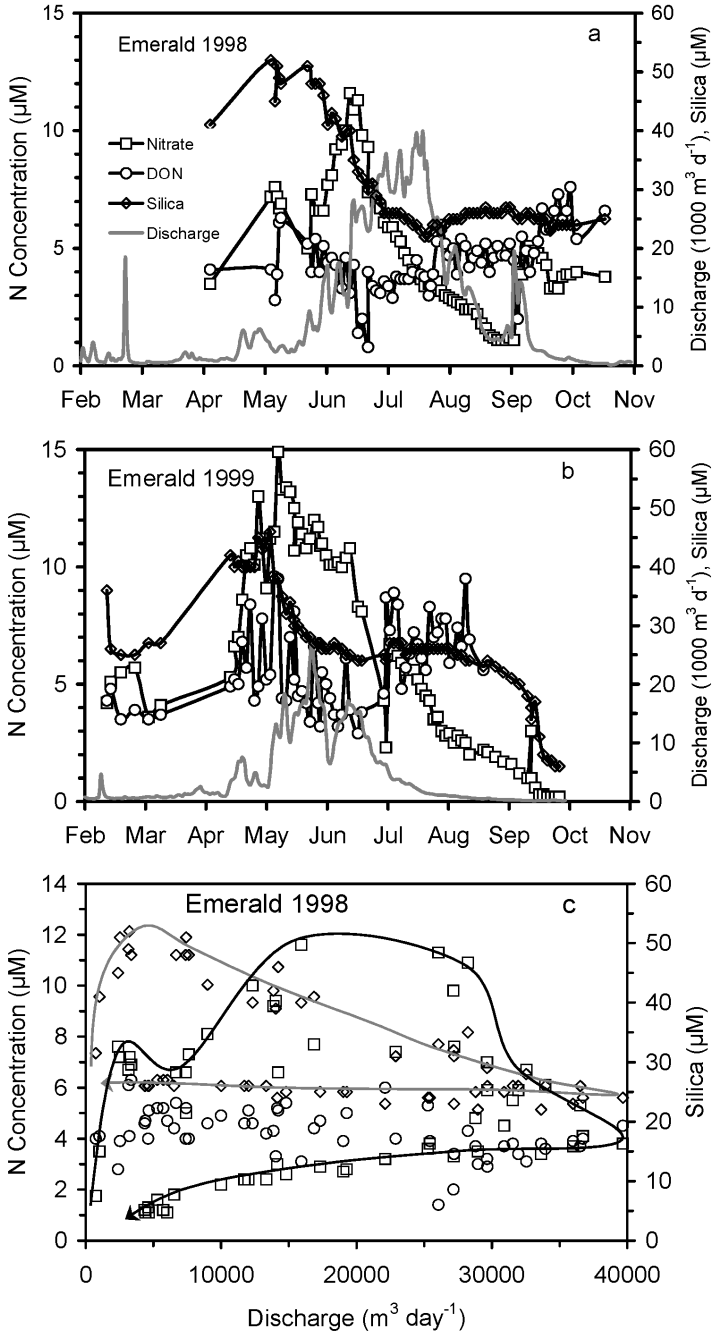

Figure 1. Outflow nitrogen and silica concentrations and daily discharge for Emerald Lake during the snowmelt period of 1998 (a) and 1999 (b) and concentration-discharge relationship for nitrate, DON and silica during snowmelt 1998 (c). Tic marks denote the beginning of the month.

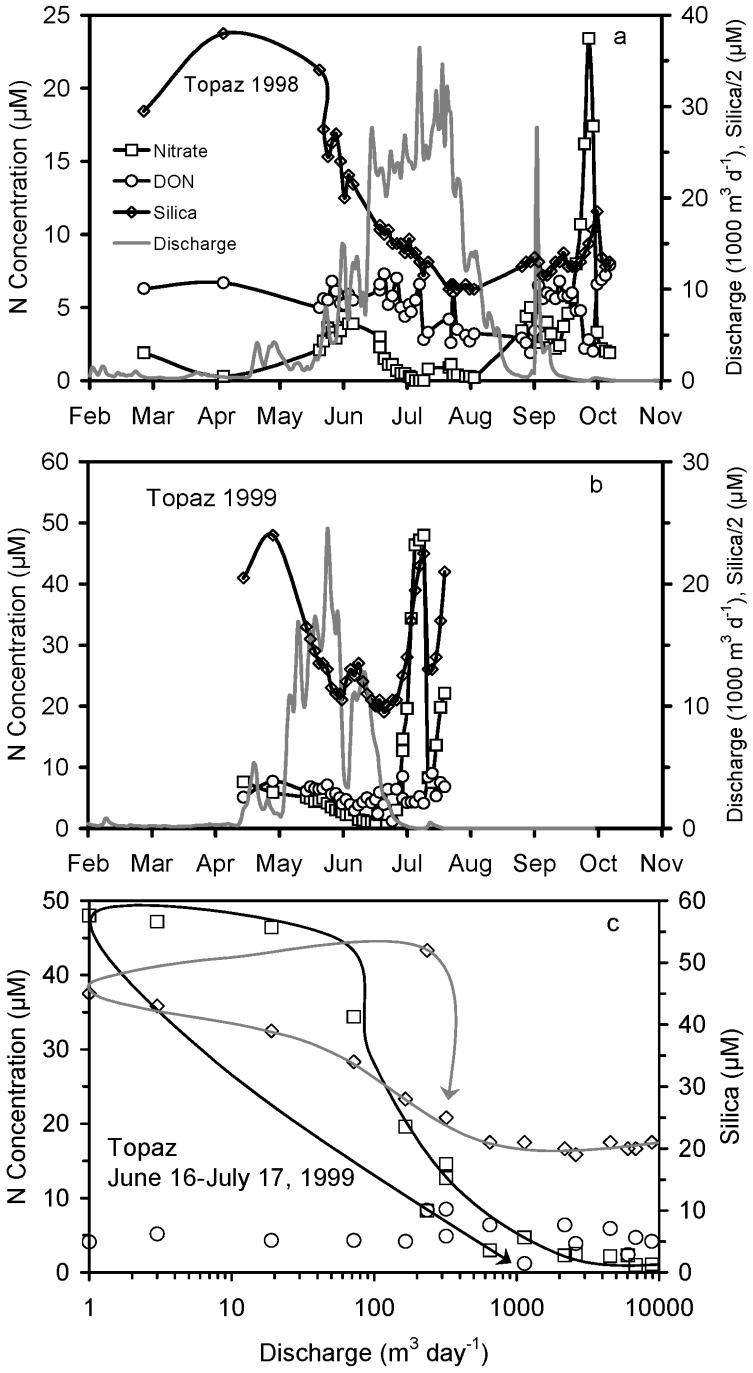

Figure 2. Outflow nitrogen and silica concentrations (divided by 2 for display purposes) and daily discharge for Topaz Lake during the snowmelt period of 1998 (a) and 1999 (b) and concentration-discharge relationship for nitrate, DON and silica from June 16 to July 17 during 1999 (c).

trations at maximum outflow. As runoff declined on the falling hydrograph limb, silica concentrations remained constant or decreased while DON gradually increased. The concentration discharge relationships for nitrate and silica exhibited clockwise hysteresis, although the actual shape of the trajectories are quite different on the rising hydrograph limb between discharges of 10,000 and 30,000 $m^3\ d^{-1}$ (Figure 1c; 1998 shown, but all years are similar). Nitrate concentrations returned to pre-melt levels near the end of snowmelt runoff, while silica concentrations did not fully recover until late in the subsequent winter (Leydecker et al. 1999). No significant relationship was observed between discharge and DON concentration at Emerald.

The N export pattern found at Topaz was in most respects the opposite of the pattern described above and is unique among the high-elevation catchment we have studied (Sickman and Melack 1998). There was a small snowmelt nitrate pulse and exponential decline at Topaz prior to peak runoff in 1998, but no pulse was evident in 1999 (Figure 2a & 2b). During the late spring and early summer, nitrate levels were near the detection limit. On average nitrate concentrations typically reach a maximum at Topaz during the months of October and November (data not presented).

Silica had similar patterns during both years at Topaz: a concentration pulse at the onset of snowmelt prior to the nitrate pulse (if evident) followed by a gradual decline of 60–75% as runoff increased (Figure 2a& 2b). DON concentrations fell slightly during snowmelt with little indication of a pulse and reached a minimum value along the falling hydrograph limb.

At Topaz, the following concentration-discharge relationships were noted: (1) during snowmelt, nitrate and silica exhibited clockwise hysteresis while no DON-discharge relationship was evident (not shown); and (2) on the falling hydrograph in late summer and autumn of 1998 and 1999, nitrate exhibited a counter-clockwise pattern while the silica pattern was clockwise, and again DON showed no relationship with discharge (Figure 2c). As runoff declined at Topaz, a complex pattern of solute concentrations was observed (Figures 2 and 3). Pulses in nitrate and silica occurred in both years at the end of snowmelt while DON levels were more stable. The nitrate and silica pulses were more or less concurrent although the nitrate peak occurred first in 1998. Silica and nitrate levels then declined abruptly following small rain events in late September 1998 and mid July 1999.

Isotopic analyses of nitrate and water

For snow and stream samples collected at Emerald, Topaz and Marble Fork, $\delta^{15}N_{(NO3)}$ values ranged from ca. −7 to +3.5 ‰, and $\delta^{18}O_{(NO3)}$ varied from about +7 to +35 ‰ (Figure 4). Three clusters were identified based on dual-isotopic signatures: (1) isotopically enriched snow samples ($\delta^{15}N \sim -3$ to +3.5 ‰ and $\delta^{18}O \sim +25$ to +35 ‰); (2) isotopically depleted stream samples collected at the onset of snowmelt runoff ($\delta^{15}N \sim -7$ to −5.5 ‰ and $\delta^{18}O \sim +7$ to +13 ‰); and (3) stream samples with intermediate isotopic values collected during the later stages of snowmelt. There was generally less overlap in the ^{18}O signatures of the clusters

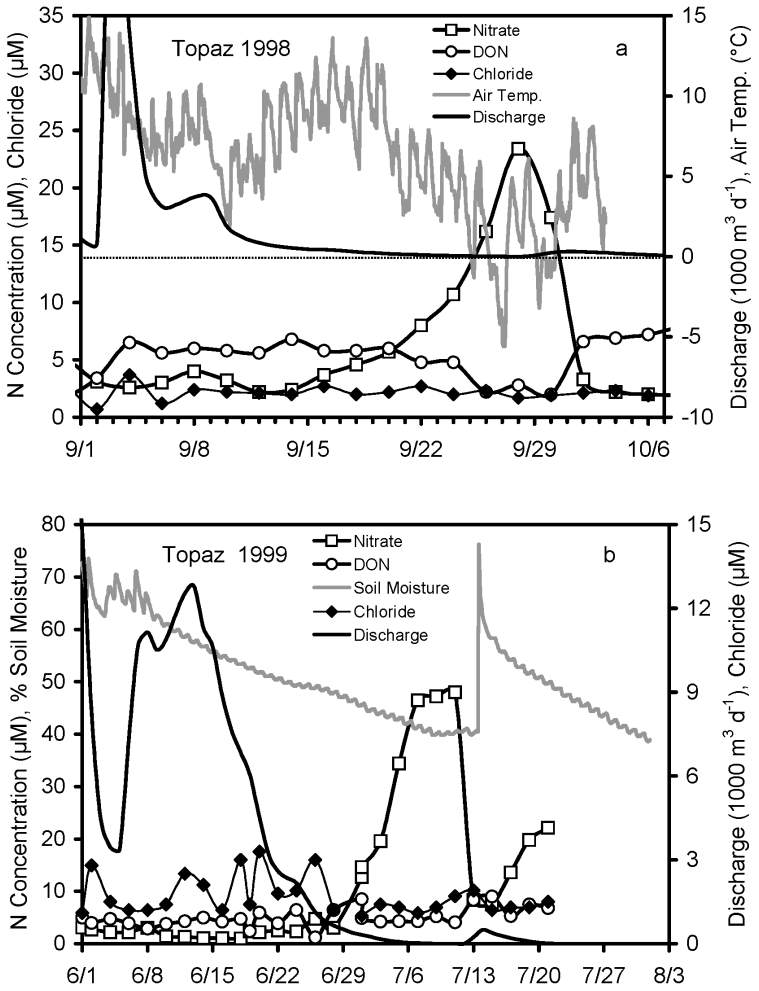

Figure 3. Time series of nitrogen and chloride concentrations in the outflow, outflow discharge, air temperature and soil moisture at the Topaz Lake watershed during 1998 (a) and 1999 (b).

compared with ^{15}N. Overall, $\delta^{18}O_{(NO3)}$ was similar at all three sites during the later stages of snowmelt, but $\delta^{15}N_{(NO3)}$ tended to be higher at Topaz (Figure 4).

At Emerald, we examined the isotopic variation of nitrate in relation to the spring nitrate pulse and oxygen isotopes of water. In both 1998 and 1999, $\delta^{18}O_{(NO3)}$ declined by 6 to 8 ‰ with the beginning of snowmelt in early April (Figure 5a & 5b). A similar decline of 2 to 3 ‰ was observed for $\delta^{15}N_{(NO3)}$. Thereafter, $\delta^{18}O_{(NO3)}$ increased, reaching a maximum ca. 3 weeks after the peak in nitrate concentrations (mid-June in 1998 and late-May in 1999). $\delta^{15}N_{(NO3)}$ values during both years returned to pre-melt values by late April. Minimum $\delta^{18}O_{(H2O)}$ occurred midway between the $\delta^{18}O_{(NO3)}$ minimum and maximum, coinciding with the larger peak in

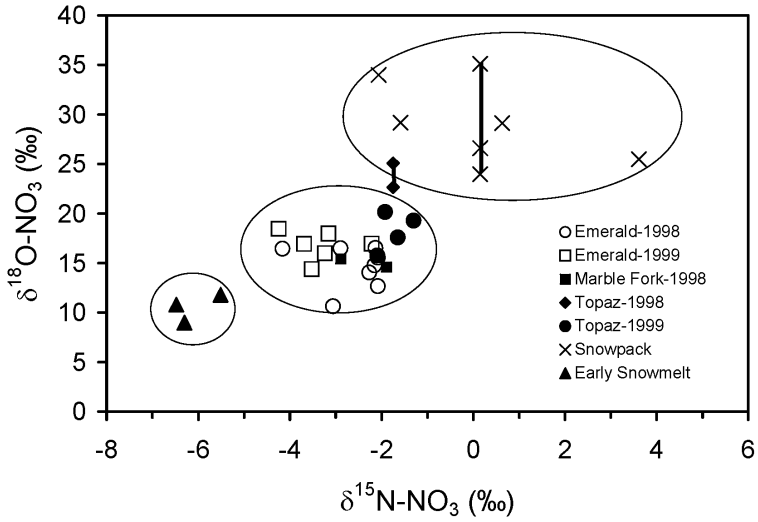

Figure 4. Nitrate isotopes for surface water and snow samples collected in the Tokopah Valley, Sequoia National Park, from 1996 through 1999. For snow samples collected in 1996 and Topaz outflow samples in 1998, only oxygen isotopes were determined owing to insufficient nitrate collection (i.e., less than 50 μmoles). To display these samples in the figure they were assigned the mean $\delta^{15}N_{(NO3)}$ value of snow and Topaz outflow, respectively, and connected by a line to distinguish them from other samples.

nitrate concentration. Overall, there was little isotopic difference between the two nitrate pulses observed during both years. The nitrate maxima for both years at Emerald were similar (ca. 12 to 14 μM) as was the overall variation in oxygen and nitrogen isotopes of nitrate (10–12 ‰ and 3–4 ‰, respectively). In contrast, the oxygen signature of water varied more in 1998 (the higher runoff year) than in 1999 (i.e., 11 ‰ vs. 6 ‰).

Discussion

Relative contributions of snowpack and soil N to the spring nitrate pulse

Two causal mechanisms have been suggested for the snowmelt nitrate pulse in montane streams: (1) preferential elution of nitrate from the snowpack; and (2) flushing of nitrate, produced by microbial nitrification, from catchment soils. Early occurrence of the stream nitrate pulse (prior to peak snowmelt) led earlier researchers at Emerald Lake to conclude that the pulse was primarily caused by elution from the melting snowpack and was not biologically mediated (Williams and Melack 1991b). Preferential elution from the snowpack is the result of solute enrichment of the outer coating of snow crystals due to snow metamorphism (Bales et al. (1989, 1993)). These coatings are then ″washed″ from the snowpack during the first release of melt-water. The soil-nitrate mechanism assumes that atmospheric

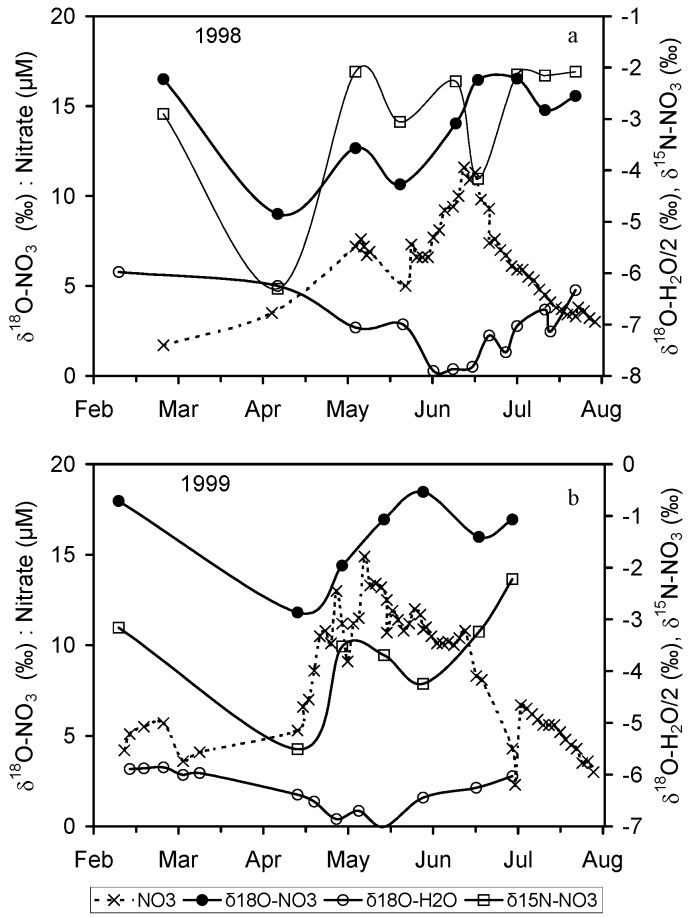

Figure 5. Time series of $\delta^{15}N_{(NO3)}$, $\delta^{18}O_{(NO3)}$, $\delta^{18}O_{(H2O)}$ and nitrate concentrations in Emerald Lake outflow during the snowmelt period of 1998 (a) and 1999 (b).

nitrate released from the melting snowpack goes into temporary storage, presumably in microbial biomass (Brooks et al. 1998), and that the nitrate pulse is composed primarily of microbially-produced nitrate with some prior-year atmospheric deposition (Kendall et al. 1995).

At our study catchments, the total amount of nitrate held in the snowpack at the onset of melt equaled or exceeded annual nitrate export. This finding is consistent with preferential-elution since annual nitrate losses can be accommodated by snowpack nitrate inputs. However, when N input-output budgets are computed for earlier portions of the snowmelt period, there is insufficient snowpack nitrate to explain the observed catchment export (Table 1). It is unlikely that lake-processes significantly affect catchment nitrate export during the early part of snowmelt since phytoplankton productivity is low and temperature stratification in the lake isolates sediments from colder inflowing waters running through the lake. Therefore, the

input-output budgets indicate that a large proportion of the nitrate found in streams during early snowmelt is derived from terrestrial portions of the watershed.

The Emerald, Topaz and Marble Fork catchments lack a well-developed groundwater system (Kattelmann and Elder 1991). About 80 to 90% of the streamflow during snowmelt is new water from the snowpack, but almost all of this water passes through catchment components such as soil and talus (A. Kramer-Huth, personal communication). Thus, in our study sites there are only two major sources of nitrate to streams during snowmelt: (1) inputs from melting snow and (2) nitrate produced or stored in catchment soils and talus. Since the dual isotopic analysis of nitrate for the three study sites showed that snowpack nitrate was isotopically distinct from stream nitrate during snowmelt, then soil nitrate must be a substantial contributor to nitrate export (Figure 4). At Emerald, both $\delta^{18}O_{(NO3)}$ and $\delta^{15}N_{(NO3)}$ declined as snowmelt began (Figure 5), and we hypothesize that the nitrate in these samples (mean $\delta^{18}O_{(NO3)}$ = +10.5 ‰, mean $\delta^{15}N_{(NO3)}$ = −6.1 ‰) was characteristic of nitrate derived from microbial mineralization and nitrification in catchment soils and talus; these isotopic values fall within the range reported for soil nitrate in other studies where direct measurements were made (Kendall 1998).

Using bulk snow $\delta^{18}O_{(NO3)}$ and stream $\delta^{18}O_{(NO3)}$ from the onset of snowmelt (as a proxy for soil $\delta^{18}O_{(NO3)}$) as end members in a two-component separation of stream nitrate sources, we estimate the soil-nitrate contribution during snowmelt to be about 70 to 75% at Emerald and the Marble Fork, and 40 to 60% at Topaz (Table 2). These percentages are consistent with estimates of soil contributions derived from the input-output budgets presented earlier. The isotopic separation ignores temporal variation in the isotopic composition of both end members. However at Loch Vale, Campbell et al. (2002) reported no consistent evidence for isotopic fractionation of nitrate from melting snow; thus our assumption of a constant snowpack end-member appears reasonable. However, if soil nitrate was more depleted than we have assumed (likely, since some atmospheric nitrate probably contributed to stream nitrate during early snowmelt), then our 2-component separation underestimates the contribution of snowpack nitrate. More precise estimates of the relative contributions of snowpack and soil N to lakes and streams will require a complete isotopic characterization of these sources and additional study on the fate of snowpack ammonium. Snowmelt in the Sierra Nevada occurs over a period of up to 5 months, ample time for snowpack DIN to be repeatedly cycled through biological systems. For example, measurements of snowpack $\delta^{15}N_{(NH4)}$ made at Emerald (−1.6 ‰), combined with an expected fractionation of −12 to −29 ‰ ($\delta^{15}N_{(NO3)} < \delta^{15}N_{(NH4)}$) for nitrification of ammonium, would produce nitrate with a $\delta^{15}N_{(NO3)}$ ca. −10 to −27. Nitrified ammonium, combined with snowpack nitrate, (average $\delta^{15}N_{(NO3)}$ of +0.5 ‰) could produce nitrate with isotopic values similar to those found in Sierran streams during snowmelt, i.e., −3 to −5 ‰. Thus, our isotopic evidence cannot rule out the possibility that some proportion of outflow nitrate originates from nitrified snowpack ammonium.

Table 2. Isotopic analysis of nitrate sources to surface waters during the snowmelt periods of 1998 and 1999. Estimates of $^{18}O\text{-}NO_3$ values for soil water and snowpack used in mixing analyses, along with the volume-weighted mean $\delta^{18}O\text{-}NO_3$ in Emerald Lake (ELW), Topaz Lake (TLW) and Marble Fork (MFK) outflows, are included. Nitrate-source percentages were computed using a two-compartment mixing model.

	$\delta^{18}O\text{-}NO_3$ Value	% Soil NO_3	% Snow NO_3
Soil-water-1998	+9.0	–	–
Snowpack-1998	+35.1	–	–
ELW-1998	+15.5	75	25
MFK-1998	+17.2	69	31
TLW-1998	+23.5	44	56
Soil-water-1999	+11.6	–	–
Snowpack-1999	+31.6	–	–
ELW-1999	+17.0	73	27
TLW-1999	+18.9	63	37

Catchment-scale evidence for biotic regulation of N flushing from soils

At all study sites, export of ammonium was negligible during snowmelt, even though snowpack ammonium concentrations equaled or exceeded nitrate. While some ammonium could have been rapidly nitrified or sequestered in aquatic algae, we believe most was assimilated or adsorbed in terrestrial portions of the watersheds since ammonium was rarely detectable in inflowing lake waters. Current evidence suggests that microbial uptake is the dominant ammonium sink during the first half of snowmelt when the catchments are snow-covered and soil temperatures are just above freezing. However, recent studies have shown that plants may also play a role in early sequestration of snowmelt N (Bilbrough et al. 2000; Sickman et al. 2001).

At the catchment-scale, biotic control of the nitrate pulse at Emerald is indicated by differences in export patterns between nitrate and silica (Figures 1 and 2) since silica concentration patterns in spring result from non-biological processes such as weathering, chemical equilibrium and hydrology. Silica concentrations at Emerald are more tightly linked to discharge than nitrate which exhibited larger day-to-day fluctuations. These differences indicate biological control of catchment nitrate release, and also suggest that silica sources to streams are relatively diffuse whereas nitrate source areas may be more limited, i.e., spatially confined to areas of soils or talus (Sickman et al. 2002).

Concentration discharge patterns for nitrate and silica at Emerald differ the most during the middle portion of the rising snowmelt hydrograph when the main nitrate pulse was observed (Figure 1c). Abiotic processes such as snowpack elution and flushing of an over-winter buildup of soil nitrate, cannot fully explain the nitrate trajectory. If the main nitrate pulse was the result of over-winter accumulation of labile N in soil solutions and subsequent piston flushing (Campbell et al. 1995), then we would observe a single large peak at the onset of snowmelt similar to that

observed for silica. Instead, the Emerald data suggest that most of the soil nitrate was produced during active snowmelt and that snowpack DIN released during the winter and early snowmelt was consumed within terrestrial portions of the catchment. The silica and smaller nitrate pulse at the onset of snowmelt may be indicative of flushing of over-winter products of weathering and mineralization-nitrification, respectively, from small near-lake meadows. However, since discharge is low, the actual amount of nitrate lost from these soils is small. Since average snow depth in the Emerald Lake watershed can reach 5–6 meters, it seems unlikely that plants are active this early in the melt season. Thus, microbial dynamics are the most likely explanation for the observed N uptake and release pattern in the watershed.

Other data collected at Emerald support our supposition for microbial uptake and release of N during snowmelt. Soil water collected prior to the onset of snowmelt from five sites in the Emerald basin during 1987 had concentrations of nitrate and ammonium near the detection limit (Williams et al. 1995). However, nitrate levels in shallow soil solutions increased later in the spring and at one location exceeded 70 μM for two consecutive weeks prior to peak runoff. These high nitrate levels are unlikely to be a result of preferential nitrate elution since the highest DIN concentrations measured in snow lysimeters at Emerald during 1987 were 28 μM.

Similar N uptake and release has been observed in soils at the plot-scale in the Rocky Mountains of Colorado. At Niwot Ridge, investigations of microbial dynamics in alpine tundra and dry meadows revealed a seasonal pattern wherein plant uptake dominates the summer growing season and maximal microbial assimilation takes place in autumn and winter (Brooks et al. 1998; Lipson et al. 1999). These studies found that microbial biomass gradually increased through the autumn and winter, peaking at the initiation of snowmelt and declining as snowmelt progressed. Nitrogen transfers between pools occurs in the late autumn and winter, via decomposition of plant litter by microbes, and in the spring by unknown microbial processes. In the Sierra Nevada, soil lysimeter and outflow data from Emerald are consistent with this seasonal pattern of microbial sequestration and release of DIN.

Controls on DON export patterns

We observed no increase in DON concentrations at the end of snowmelt corresponding to the plot-scale increases in soil amino acids observed at Niwot Ridge (Lipson and Monson 1998). However, if most of DON consisted of recalcitrant compounds, then the dynamics of more biologically active DON (e.g., amino acids) could have been masked. Other studies in seasonally snow-covered regions have also shown no DON peak, e.g., two boreal rivers in Sweden (Stepanauskas et al. 2000), and in high elevation streams in the Colorado Front Range (Williams et al. 2001). The lack of large DON peaks and muted intra-annual variability suggests that, at the catchment scale, a hydrologically-mediated mechanism is needed to maintain steady stream DON concentrations as runoff varies by several orders of magnitude, i.e., more DON must be released from soils as runoff increases to counteract dilution effects.

At Emerald, concentrations of most inorganic solutes decrease by 40 to 50% during snowmelt, with the exception of sulfate (declines of < 25%), where concentrations are believed to be mediated by a soil pH absorption-desorption mechanism (Clow et al. 1996; Melack et al. 1998). Sulfate is adsorbed when pH is low and released as soil solution pH rises. In the Sierra Nevada, snowmelt has an alkalizing effect on soil pH since winter soil solutions are more acidic than infiltrating melt water, owing to high levels of soil pCO_2 and organic acids. On average (1985–1998), H^+ concentrations in outflow at Emerald declined from 0.92 μEq L^{-1} (pH 6.0) to 0.52 μEq L^{-1} (pH 6.3) during the course of snowmelt. Since DON (as a component of dissolved organic matter from soils) has a weak negative charge (Oliver et al. 1983), small intra-annual changes in stream DON levels could also result from pH-regulated, abiotic processes such as adsorption-desorption on soil exchange sites or changes in the solubility of humic substances controlled by flushing rates and pH.

How do seasonal transitions trigger microbial N release?

In some studies, decreases in microbial biomass, associated with freeze-thaw events after snow ablation have been used to explain N release during the transition from winter to spring (Brooks et al. 1998; Jaeger et al. 1999; Schimel and Clein 1996). However, recent data suggest that winter microbial populations are adapted to fairly rapid temperature fluctuations (Brooks et al. 1996) and can survive to temperatures as low as −5 °C (Clein and Schimel 1995). Owing to a milder maritime climate, and deep snow cover, soils seldom freeze in the Sierra Nevada during the winter and spring (Sickman et al. (2001), J Sickman unpublished data), suggesting that freeze-thaw events are not required to induce N losses.

In 1998 and 1999, we observed large increases in outflow nitrate concentrations at Topaz at the end of snowmelt (Figure 3). In both years, nitrate concentrations increased as discharge declined, but chloride levels stayed constant (demonstrating little evapo-concentration of soil solutions or stream water). Nitrate levels began to increase on September 16, 1998. On September 25, when night-time air temperatures fell below freezing, outflow nitrate increased markedly, and remained high until rain on September 30 wetted soils and raised air temperatures above 0 °C (Figure 3a). During this episode of maximum nitrate and below freezing temperatures DON levels in the stream fell by half.

Prior to the September 30 storm, catchment soils were generally dry, excepting riparian and meadow soils surrounding the lake. When air temperature fell below 0 °C a surface crust of ice formed on these wetter soils. Higher outflow nitrate levels could be explained by lysis of soil microbes in frozen meadow soils, however, decreasing DON levels would argue against this mechanism. Lyzed microbes would presumably release DON, increasing stream concentrations. The lack of a DON pulse suggests that either: (1) surviving microbes were able to metabolize the released DON; (2) excess DON was adsorbed by some abiotic soil process; or (3) observed soil nitrate losses were caused by a mechanism other than microbial mortality.

A similar post-snowmelt nitrate peak was measured during warmer temperatures in July 1999 (Figure 5b), which indicates that freeze-thaw microbial mortality was unlikely to be the main cause of N-release. Soil moisture at Topaz during 1999 gradually decreased as snowmelt declined and nitrate levels rose. Rain on July 14 caused soil moisture levels to rise and nitrate levels to drop, but DON and chloride levels held steady, indicating that neither stream water nor soil solutions were appreciably diluted by precipitation volume nor influenced by precipitation chemistry. We hypothesize that increasing nitrate concentrations during these episodes at Topaz were caused by vegetation senescence, brought on by low water potential, which altered the balance between microbial mineralization/nitrification and plant nitrogen-uptake. This process could have been reinforced in 1998 by freeze-induced vegetative mortality. However, we have no explanation for why silica (Figure 2) increased along with nitrate. Similar increases in nitrate and silica have been observed in the Catskill Mountains when groundwater became progressively more important to stream flow as discharge declined in the late summer and autumn (Burns et al. 1998). The Topaz watershed lacks perennial streams, but it is possible that stream water originates from progressively deeper soils as runoff declines. Further plot-scale study is needed to fully understand the geochemical, biological and hydrological processes occurring in alpine soils as they dry out in late autumn.

Laboratory investigations suggest that winter microbial populations are sensitive to prolonged temperatures above 0 °C, e.g., a decline in microbial biomass after a two week exposure to above freezing temperatures (Lipson et al. 2000). One explanation for this temperature-sensitivity is that cellular enzymes in psychrophilic bacteria may not be stable above 0 °C (Feller et al. 1996). Another is that warmer temperatures may starve microbial populations due to increased use of carbon substrates (e.g., respiration or other metabolic pathways) (Lipson et al. 2000) or a switch in substrate use patterns (e.g., microbial biomass and products vs. detritus) (C Mikan and J Schimel, unpublished data). During the spring transitional period, Lipson et al. (2000) hypothesize that winter psychrophilic bacteria are replaced by other, more mesophilic, taxa. We observed small peaks in outflow DON in early snowmelt at Emerald that could indicate a species transition, but not at Topaz, suggesting no large-scale die-off of microbial populations during spring runoff. Furthermore, since our data demonstrate a fundamental difference in the export behavior of DON and nitrate, no single biological cause, thus far proposed, can account for both nitrate pulses and regulation of DON concentrations in stream water.

A conceptual hypothesis: redox-regulation of microbial N sources and sinks

The combination of microbial respiration and deep snow cover results in elevated pCO_2, and low pH and oxygen levels in soils (Solomon and Cerling 1987). At Emerald, evidence for this assertion includes stream pH patterns during snowmelt and early snowmelt surface-water samples that are supersaturated with carbon dioxide (J Sickman, unpublished data). Low nitrate levels in soils prior to snowmelt may be indicative of low redox potentials and microbial N-demand; both conditions are likely since microbial activity continues under relatively mild winter soil tempera-

Table 3. Nitrogen isotopic composition of various biological samples collected in the Tokopah Valley during October 2000. Standard errors of replicates (n = 2) are shown in parentheses.

Material	$\delta^{15}N$ (‰)
Lichens	−10.8 (0.2)
Mosses	−5.4 (0.3)
Succulents	−4.2 (0.7)
Woody Vegetation	−3.3 (0.5)
Grass and Sedge	1.6 (0.2)
Marmot Scat	0.0 (0.6)
Meadow Soil:	
0–5 cm	−0.1 (0.5)
10 cm	+1.7 (0.5)
20 cm	+6.0 (0.5)
45 cm	+6.7 (0.6)

tures in the Sierra Nevada. We have not made measurements of pCO_2 or soil redox conditions to support these suppositions, but several studies have measured high rates of gaseous N losses during the winter in other seasonally snow-covered regions with colder winter soil temperatures (Brooks et al. 1997; Williams et al. 1998). In addition, Meixner and Bales (2003) found that their carbon and nitrogen simulation-model could not accurately depict nitrate export patterns in the Emerald Lake watershed until denitrification was properly modeled using the results of Del Grosso et al. (2000).

Evidence for denitrification includes observation of H_2S odors in meadow and riparian areas in the Emerald and Topaz catchments and isotopically enriched ^{15}N values in meadow soil profiles. Table 3 shows $\delta^{15}N$ values of various biological materials collected in the Marble Fork watershed. Values ranged from ca. −11 ‰ for non-N fixing rock lichens (*Lecidea atrobrunnea* and *Candelariella sp.*) receiving N inputs only from atmospheric sources, to −6 to +2 ‰ for various plants. Deep soil layers in meadows surrounding Emerald and Topaz lakes contained isotopically enriched N (> +6 ‰), indicative of denitrification.

We hypothesize that redox and pH conditions in catchment soils can account for the DIN sink during early snowmelt at Emerald, and at Topaz during much of the snowmelt season, and for regulation of DON concentrations in streams of both catchments. During early snowmelt, wet, low-redox and low pH soils (e.g., riparian and meadow soils near streams and lakes) act as sinks for snowmelt DIN and sequester DON, while well drained upland soils, with higher redox potentials and higher infiltration rates serve as sources of microbial nitrate. Later, as flushing increases, soil redox potentials and pH rise in N-consuming soils, owing to the high oxygen content and higher pH of infiltrating snowmelt waters. Oxygenation favors nitrification and soil-nitrate flushing, contributing to the spring nitrate pulse. Higher pH and flushing rates result in DON release from soils (via ion exchange and solubility processes) counteracting the dilutional effect of snowmelt on stream DON

levels. Nitrate flushing continues until appreciable areas of the catchment become snow-free and increased vegetation uptake reduces nitrate availability, and/or the available supply of labile organic N and ammonium is exhausted. As soil flushing subsides, microbial respiration decreases soil pH, causing adsorption of DON to exchange sites and decreasing the solubility of humic substances, thereby reducing losses of DON while snowmelt runoff declines.

At Emerald, pH and redox-regulation of N-export can explain: (1) the absence of DIN in soil water prior to snowmelt, (2) the lack of a large nitrate pulse at the onset of runoff, (3) the apparently simultaneous uptake of snowpack DIN by soils and release of soil nitrate at the catchment-scale, and (4) moderated DON levels in streams. At Topaz, more extensive meadows soils provide a larger redox-driven DIN sink during snowmelt explaining: (1) the lack of a large nitrate pulse during snowmelt, (2) high stream nitrate concentrations in the late summer and autumn as soils dry out, (3) declines in stream nitrate levels following autumn rain storms, and (4), as at Emerald, consistent DON levels in streams.

Summary and conclusions

In this study we had four objectives: (1) determine the relative contribution of snowpack and soil N-sources to the spring nitrate pulse, (2) look for evidence of biotic control of N losses at the catchment scale, (3) examine DON export patterns to gain a better understanding of the biological and hydrological controls on DON loss and (4) examine the relationship between soil physico-chemical conditions and N export. Using multiple lines of evidence (isotopic, lysimeters and catchment mass balances) we draw the following conclusions regarding nitrate-sources to streams: (1) 50 to 70% of the total nitrate export during snowmelt runoff was derived from catchment soils, (2) the soil nitrate contribution was greatest at the onset of snowmelt, (3) comparisons between stream nitrate concentrations and nitrate isotopic composition suggest that both snowpack and soil nitrate are found in streams during the nitrate peak and, (4) the nitrate-concentration maximum occurs when snowmelt nitrate contributions to streamflow are near maximum. Silica and DON exhibited concentration maxima at the onset of snowmelt followed by rapid dilution as melt increased; this pattern is consistent with an over-winter buildup of these constituents in soils followed by flushing and dilution by snowmelt. The relative constancy of DON concentrations in stream-water indicates a strong regulation mechanism is needed to maintain steady DON concentrations as rates of soil flushing and runoff rapidly change. In contrast, nitrate concentrations gradually rise to a maximum a few weeks before peak runoff, suggesting the nitrate pulse is not simply the flushing of accumulated nitrate from soils or snowpack, but one of sequestration and release of nitrate from microbial pools in soils and talus. The trigger responsible for releases from these terrestrial N pools is not completely understood, but we hypothesize that pH and redox condition acts as master controls on microbial N transformations, determining whether soils serve as a net source or sink.

Release of soil nitrate was also observed during the transition from moist to dry soil conditions at Topaz in the summer and autumn. We hypothesize that the release of nitrate was a transfer of N from microbial pools to surface waters due to vegetation senescence brought on by low water potential in soils (possibly aided by freezing) which altered the balance between microbial mineralization/nitrification and plant uptake. Owing to a lack of DON pulses during these transition periods, we do not believe N export resulted primarily from microbial mortality caused by freeze-thaw events or by shifts from psychrophilic to more mesophilic microbial species in soils.

Given the widespread occurrence of N-fixing symbioses, current theory suggests that terrestrial plant communities are N limited because of N losses not under the control of the plant community (Vitousek and Field 1999). Commonly proposed mechanisms for these losses are leaching of DON (Hedin et al. 1995) and denitrification (Vitousek et al. 1998). However, high-elevation ecosystems, experiencing strong seasonal transitions, may behave differently. The persistence of N limitation in these systems, and the inability of plant communities to prevent episodic nitrate losses, may be related to microbial and hydrologic processes which conspire to induce temporal and spatial disconnections between inorganic N availability and demand; these disconnections primarily involve DIN and are confined to transitions between plant growing and non-growing seasons. Terrestrial ecology has traditionally focused on growing season dynamics, but a consensus is emerging that biogeochemical processes occurring during dormant seasons are just as significant to ecosystem biogeochemistry. Our research suggests that DIN losses during seasonal transitions may be another mechanism maintaining N-limitation of alpine and subalpine communities.

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