

## Role of organic nitrogen in the nitrogen cycle of a high-elevation catchment, Colorado Front Range

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**Abstract.** Here we report on 3 years (1996–1998) of measurements of organic and inorganic nitrogen (N) fluxes to and from Green Lakes Valley, a high-elevation ecosystem in the Colorado Front Range of the Rocky Mountains. Nitrate-N ( $\text{NO}_3\text{-N}$ ) was the dominant form of N in both precipitation and stream water. Annual precipitation contained 52%  $\text{NO}_3\text{-N}$ , 32% ammonium-N ( $\text{NH}_4\text{-N}$ ), 9% dissolved organic N (DON), and 7% particulate organic N (PON). Annual export of N in streamflow was composed of 70%  $\text{NO}_3\text{-N}$ , 4%  $\text{NH}_4\text{-N}$ , 14% DON, and 12% PON. Thus the percentage of organic N increased from 16% of total N in precipitation to 26% of total N in streamflow. Subtracting inputs from outputs, Green Lakes Valley always shows net retention of inorganic N. The only form of N that showed net export was DON. DON export was low (0.18 to  $-0.13 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ), with net export recorded in 2 years and basin retention recorded in 1 year. There was a seasonal pattern in the concentrations of inorganic N ( $\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$ ) and organic N (DON + PON). Concentrations of inorganic N were  $\sim 15\text{--}25 \mu\text{mol L}^{-1}$  during base flow, increased to  $\sim 30 \mu\text{mol L}^{-1}$  on the rising limb of the hydrograph during snowmelt runoff, then decreased to  $\sim 5 \mu\text{mol L}^{-1}$  on the recession limb of late summer, with a return to base flow values in the autumn. In contrast, organic N was  $7\text{--}15 \mu\text{mol L}^{-1}$  during base flow and decreased to near or below detection limits on the rising limb of the hydrograph, with a gradual but consistent increase on the recession limb and on into the autumn. The amount of N in dissolved organic matter changed over time, with the dissolved organic carbon (DOC):DON ratio decreasing from  $\sim 45$  on the rising limb of the hydrograph to  $<20$  in the autumn. Spatially, there was a striking difference in the ratios of  $\text{NO}_3\text{-N}$  and DON between talus and tundra areas. Nitrate concentrations in surface water draining talus areas were always greater than DON. In contrast, DON concentrations in surface water draining tundra areas were always greater than  $\text{NO}_3\text{-N}$ . Concentrations of DON were not significantly correlated with DOC ( $R^2 = 0.04$ ,  $p > 0.05$ ), indicating that controls on DON export may be different than controls on DOC export. Our results suggest that the ratio of the annual mass flux of inorganic N to organic N in stream waters may provide a novel index to evaluate the N status of terrestrial ecosystems from various biomes.

### 1. Introduction

The flux of dissolved organic matter (DOM) through terrestrial ecosystems plays an important role in soil formation and nutrient dynamics [McDowell and Wood, 1984; Neff *et al.*, 2000]. Nevertheless, there is surprisingly little information on the magnitude of organic N fluxes relative to inorganic fluxes of  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$ . Twenty years ago, Sollins and McCorison [1981] emphasized that organic N must be measured if total N transfers are to be calculated because the only meaningful comparison is total N input versus output. To illustrate the potential importance of organic N, Seely and Lathja [1997] added  $^{15}\text{NO}_3^-$  to soils and reported that most of the isotopically labeled  $\text{NO}_3\text{-N}$  left the system in the form of DON. Even less is known about the role of organic N in atmospheric deposition of wetfall and dryfall [Neff *et al.*, 2001]. It has been

difficult to make quantitative evaluations of the role of atmospheric deposition of organic N in the N balances of most ecosystems because of limited data [Prospero *et al.*, 1996].

Recently, there have been a number of papers that have attempted to quantify N cycling in high-elevation ecosystems, without addressing the role of organic N. At Niwot Ridge in the Rocky Mountains, Fisk *et al.* [2001] report a missing reservoir of N after conducting an exhaustive analysis of N fluxes and pools in alpine tundra; however they did not measure organic N in the soil solution. Campbell *et al.* [2000a] measured inorganic N fluxes at the Loch Vale catchment in Rocky Mountain National Park and report that measurements of organic N are needed to better understand N fluxes and nitrogen cycling in alpine and subalpine ecosystems. Sickman and Melack [2001] conducted a regional analysis of N yield and retention in high-elevation ecosystems of the western United States but did not investigate organic N because of a lack of data.

There is particular urgency in evaluating the role of organic N in high-elevation ecosystems of the Colorado Rocky Mountains because of the recent reports of increasing amounts of inorganic N in wetfall causing a switch from N-limited to N-

saturated ecosystems [Baron *et al.*, 1994; Williams *et al.*, 1996a; Fenn *et al.*, 1998; Baron *et al.*, 2000; Williams and Tonnesson, 2000]. The dominance of organic N is common in watersheds from various biomes, including remote temperate catchments in Chile [Hedin *et al.*, 1995], neotropical basins [Lewis *et al.*, 1999], and boreal watersheds in Finland [Kortelainen *et al.*, 1997]. Similarly, at the high-elevation Emerald Lake watershed in the Sierra Nevada (United States), organic N was the major form of N export in stream water [Williams *et al.*, 1995]. What role organic N may play as high-elevation areas switch from N-limited to N-saturated ecosystems is unknown.

Moreover, the biological and hydrological processes that regulate fluxes of organic N in high-elevation catchments are unknown. The large amounts of snowfall and snow accumulation in these seasonally snow-covered catchments may affect the storage and release of organic N to catchments. Field and laboratory experiments have demonstrated that initial stages of snowmelt often have ionic concentrations many times higher than average concentrations for the whole snowpack, a phenomenon known as an ionic pulse [e.g., Johannessen and Henriksen, 1978; Colbeck, 1981]. Whether organic N is released from the snowpack in the form of an ionic pulse is unknown. High-elevation ecosystems are often composed of a mosaic of landscape types, particularly tundra, talus, and bedrock areas. Concentrations of  $\text{NO}_3\text{-N}$  are generally much higher in talus areas compared to tundra areas [Williams *et al.*, 1997; Campbell *et al.*, 2000a]. How retention and release of organic N varies with these landscape types is unknown.

We are also interested in whether information on fluxes of N species in a high-elevation catchment may provide insights into ecological controls on retention and export of N at the watershed level. There has been discussion of the potential for organic N to function as a “leak” of N from terrestrial ecosystems to aquatic ecosystems [Hedin *et al.*, 1995; Vitousek *et al.*, 1998]. Whether this “leaky faucet” hypothesis is applicable to high-elevation catchments is unknown. It is also possible that inorganic N and organic N export in streamflow respond differently to increased amounts of inorganic N in atmospheric deposition [Aber *et al.*, 1998]. Metrics such as the ratio of inorganic N to organic N in streamflow may therefore provide information on the N status of ecosystems.

Here we report on 3 years of organic and inorganic N fluxes from a high-elevation ecosystem in the Colorado Front Range of the Rocky Mountains. We also include measurements from talus and tundra subbasins in a preliminary effort to understand the interaction between N cycling and landscape type. Specific questions we evaluate include the following: (1) Are organic N fluxes in wet deposition large enough to warrant routine analysis in deposition monitoring programs in high-elevation catchments? (2) Is organic N an important component of total N export in surface waters? (3) Does including organic N in N balances affect the estimated net retention of total N in alpine catchments? (4) Is organic N preferentially eluted from the seasonal snowpack? (5) Does the quantity and character of organic N export vary seasonally? (6) Does organic N export vary between talus and tundra landscape types in the same manner as  $\text{NO}_3\text{-N}$ ? (7) Is the leaky faucet hypothesis appropriate for high-elevation catchments? (8) Does the ratio of inorganic N to organic N in stream waters provide a novel method for evaluating the N status of terrestrial ecosystems from various biomes?

## 2. Site Description

The Colorado Front Range rises directly from the Denver–Boulder–Fort Collins metropolitan area. This geographical setting results in high-elevation basins of this portion of the continental divide being located just west of large urban and agricultural activities. Green Lakes Valley ( $40^{\circ}03'\text{N}$ ,  $105^{\circ}35'\text{W}$ ) is an east facing headwater catchment, 700 ha in area, and ranging in elevation from 3250 to  $\sim 4000$  m at the continental divide (Figure 1). The catchment appears typical of the high-elevation environment of the Colorado Front Range and includes Niwot Ridge, where research has been conducted since the early 1950s [Caine and Thurman, 1990]. This site is a United Nations Educational, Scientific, and Cultural Organization (UNESCO) Biosphere Reserve and a Long-Term Ecological Research (LTER) network site. The Green Lakes Valley is a water source for the city of Boulder and is owned by the city. Public access is prohibited; hence the Green Lakes Valley does not have the grazing or recreational impacts of other high-elevation sites in the Front Range.

Climate is characterized by long, cool winters and a short growing season (1–3 months). Since 1951, mean annual temperature is  $-3.8^{\circ}\text{C}$ , and annual precipitation is 1000 mm [Williams *et al.*, 1996b]. About 80% of the annual precipitation occurs as snow. Streamflows are markedly seasonal, varying from  $<0.05\text{ m}^3\text{ s}^{-1}$  during the winter months to  $>3.0\text{ m}^3\text{ s}^{-1}$  at maximum discharge during snowmelt just below Lake Albion at the lower end of the valley. Surface waters are dilute, with acid neutralizing capacities (ANC) generally  $<200\text{ }\mu\text{eq L}^{-1}$  at all sampling sites [Caine and Thurman, 1990].

Annual balances of N species were calculated for the basin above the Green Lake 4 (GL4) outlet, which drains an area of 220 ha at an elevation of 3515 m (Figure 1). The catchment is characterized by steep rock walls and talus slopes and a valley floor of glaciated bedrock. About 20% of the basin is covered by vegetation with well-developed soil, most of which is located in the valley bottom. Soils are Cryic entisols and inceptisols on hillslopes, with histosols found on wetter sections of the valley floor.

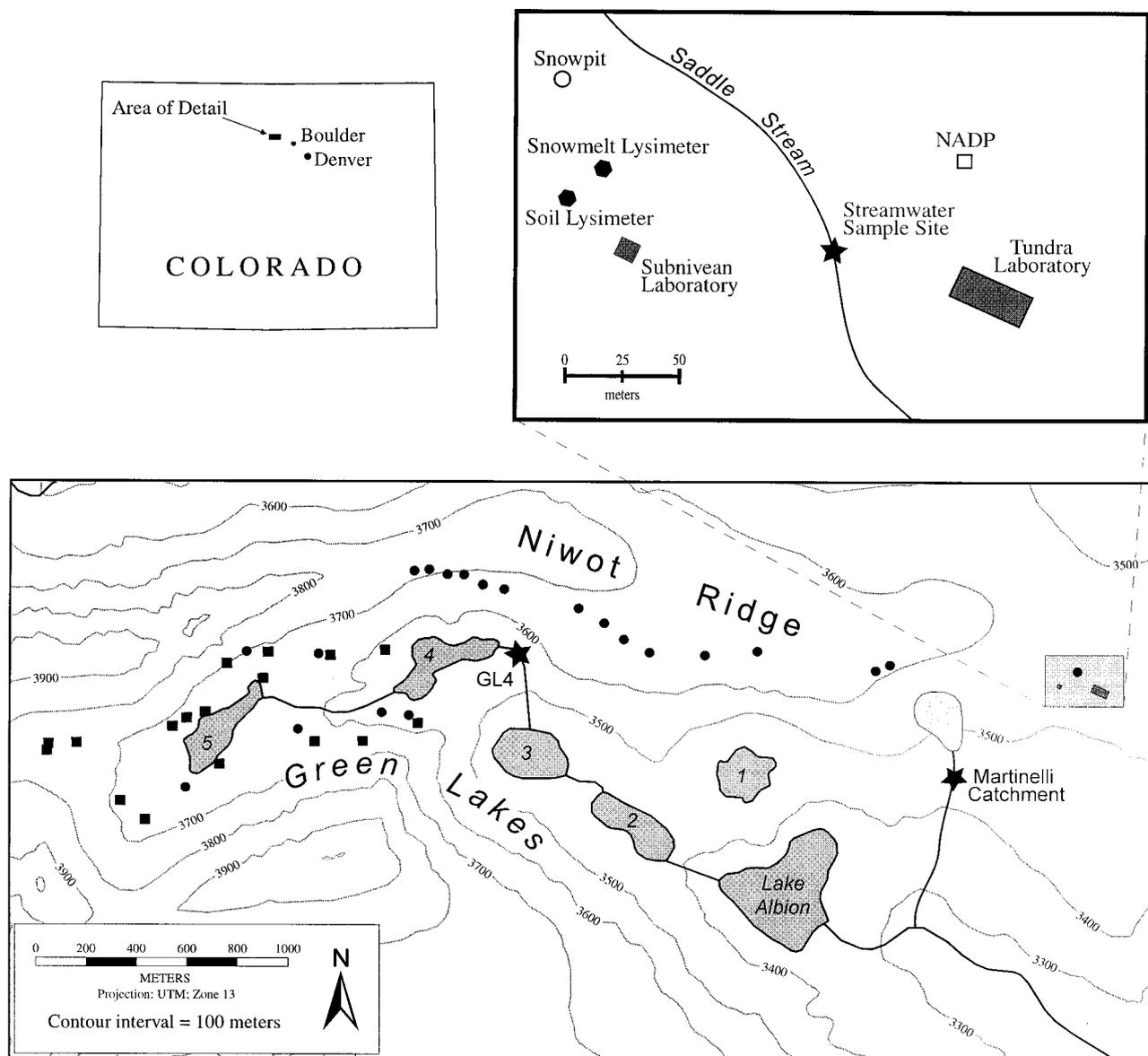
Niwot Ridge forms the northern boundary of the Green Lakes Valley, with several experimental areas including snow lysimeters and a subnivean laboratory in the Saddle area (Figure 1). The Niwot Ridge LTER program maintains an Aerometrics wet-chemistry collector at the Saddle site (Figure 1) as part of the National Atmospheric Deposition Program. The Saddle stream is an ephemeral stream that drains the experimental area on Niwot Ridge (Figure 1); this catchment area is  $\sim 8$  ha. Vegetation is alpine tundra; soils are Cryochrepts developed in a 2 m thick diamicton of granitic parent material.

Paired with the Saddle catchment is the 8 ha Martinelli catchment, located  $\sim 400$  m from the Saddle stream on Niwot Ridge (Figure 1). Surface water samples were also collected from a seasonal stream draining this catchment. In contrast to the Saddle area, the Martinelli catchment is similar to talus areas, with a poorly developed soil structure, little vegetation, and large amounts of snow deposition with a late melting snow patch [Caine, 1989].

## 3. Methods

### 3.1. Sample Collection

**3.1.1. Snow.** Physical and chemical properties of snow are routinely measured on a weekly basis at the Saddle site on



**Figure 1.** Topographic map of the Green Lakes Valley and Niwot Ridge and enlargement of the experimental study area on the Niwot Ridge saddle. Nitrogen mass balances were calculated for the area above the outflow of Green Lake 4 (GL4). The National Acid Deposition Program (NADP) wet-chemistry collector, snow pits, and snow and soil lysimeters were located on the Saddle area of Niwot Ridge. Streams draining the Saddle catchment (8 ha, tundra area) and Martinelli catchment (8 ha, talus area) were also sampled on a weekly basis for nitrogen species. Stream sampling sites are marked by stars. Synoptic sampling sites are identified by circles (tundra) and squares (talus).

Niwot Ridge; detailed sampling protocols have been presented by Williams *et al.* [1996c, 1999]. In the same area, release of  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$ , particulate organic nitrogen (PON), and dissolved organic nitrogen (DON) from the snowpack were investigated by collecting snowpack meltwater in  $1\text{ m}^2$  snow lysimeters before contact with the ground following the protocol of Williams *et al.* [1996c]. Meltwater flowed by gravity from the snow lysimeters  $\sim 5\text{ m}$  into a subnivean laboratory, where grab samples were collected about daily. Additionally, an annual snow survey is conducted in Green Lakes Valley at maximum snow accumulation to measure the spatial distribution of snow quantity and quality.

**3.1.2. Rain.** The Niwot Ridge/Green Lakes Valley LTER site participates in the National Acid Deposition Program (NADP), which operates  $\sim 200$  wet precipitation collectors throughout the continental United States. Samples are collected and analyzed using the same protocols, so that precipitation chemistry may be compared among sites, with data available from the Illinois State Water Survey, Urbana, at <http://nadp.sws.uiuc.edu>. The NADP program analyzes most major solutes, including  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$ . However, DON and PON are not measured as part of the NADP sampling protocol. We analyzed splits of the NADP samples for  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$ , DON, and PON. Our analysis of  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$

were used only as a quality control check with NADP results. A paired-difference *t* test between results from our laboratory and the NADP laboratory showed no significant difference for either  $\text{NH}_4\text{-N}$  or  $\text{NO}_3\text{-N}$  ( $n = 67$ ;  $p > 0.05$  for both N species).

**3.1.3. Surface waters.** Surface waters were collected as grab samples at daily to weekly sampling frequency at the outflow of GL4, Saddle stream, and Martinelli stream. Additionally, synoptic stream samples were collected from talus and tundra areas in the Green Lakes Valley during snowmelt runoff in 1998 (Figure 1). Water samples were collected in polyethylene bottles (following the protocol of *Campbell et al.* [2000b]), soaked with deionized water overnight, and then rinsed copiously five times; bottles were further rinsed three times with sample water at the time of collection. Samples were collected ~10 cm below the water surface in turbulent areas where the water column was well mixed. All water samples were transported the same day as collection to our wet-chemistry laboratory and treated the same as melted snow samples. Samples for dissolved organic carbon (DOC) were collected from the outflow of GL4 and during the synoptic survey in 1998, using precombusted, amber-colored glass bottles with Teflon-lined caps.

### 3.2. Laboratory Analyses

All water and snow samples were analyzed for pH, ANC, conductance, major ions, and reactive silicate (Si), following the protocols presented by *Williams et al.* [1996c]. Subsets of all samples were immediately filtered through prerinsed (300 mL), 47 mm Gelman A/E glass fiber filters with a nominal pore size of 1.0  $\mu\text{m}$ . Nitrate was analyzed using a Dionex DX 500 ion chromatograph with an IonPac AS4A-SC analytical column. The detection limit was 0.03  $\mu\text{mol L}^{-1}$ , and precision was 1.1%. Ammonium was measured on a Lachat QuikChem 4000 Flow Injection Analyzer using a method based on the Berthelot reaction. The detection limit was 0.33  $\mu\text{mol L}^{-1}$  and precision was 0.91% [Seibold, 1995]. Total N (TN) concentrations were determined by using potassium persulfate digestion to oxidize all forms of N into  $\text{NO}_3\text{-N}$  on both unfiltered and filtered samples. Nitrate was then measured on Lachat QuikChem 4000 flow injection analyzer. Detection limits for TN were 0.17  $\mu\text{mol L}^{-1}$ , and precision was 1.62% [Seibold, 1995]. The difference between PON and DON is operational and defined by the size of particle that will pass through the 1.0  $\mu\text{m}$  filter. DON was calculated by subtracting measured inorganic N from total N on filtered samples, and PON was calculated by subtracting total dissolved N from total N on unfiltered samples.

Samples for DOC were filtered through precombusted glass fiber filters and stored in precombusted amber glass bottles. Dissolved organic carbon was analyzed by combustion to  $\text{CO}_2$  on a Dohrman carbon analyzer. Detection limits were 8  $\mu\text{mol L}^{-1}$ , and precision was 2%.

### 3.3. Mass Balance Calculations

Annual input-output balances were determined for  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$ , DON, and PON for water years beginning November 1 and ending October 31 from November 1995 through October 1998. Precipitation chemistry and quantity have been measured continuously since 1984 at the Saddle site on Niwot Ridge as part of the NADP program. However, these types of precipitation gauges are prone to large measurement errors in sampling snowfall amounts in windy alpine environments [Wil-

iams *et al.*, 1998; *Campbell et al.*, 2000a]. Furthermore, the spatial variability of snow accumulation confounds extrapolation of point measurements to the basin scale. Therefore November to April precipitation amounts and quality were calculated from snow surveys conducted in the first week of May. The density and chemical content of snow was sampled in six snowpits spatially distributed over Green Lakes Valley following the protocol of *Williams and Melack* [1991]. Snow depth was measured at several hundred points (e.g., 403 in 1998) using a stratified sampling scheme. Average snow water equivalence (SWE) for the basin was then calculated by multiplying mean snow depth by mean snow density. Chemical loading for snow was calculated as average SWE times the volume-weighted mean concentrations in the snowpack, multiplied by basin area. The NADP precipitation amounts were used from May through October because summer rains are less subject to redistribution by wind [Williams *et al.*, 1998]. Outputs in stream water were obtained by multiplying the weekly concentrations ( $\mu\text{mol L}^{-1}$ ) by measured daily water fluxes ( $\text{m}^3 \text{day}^{-1}$ ) surrounding each chemical sample and dividing by basin area. Daily mass inputs and outputs were summed over the water year and reported as  $\text{kg ha}^{-1} \text{yr}^{-1}$ . To insure comparison with other investigations [e.g., *Campbell et al.*, 2000b] and in keeping with past conventions [Likens and Bormann, 1995], inputs in precipitation minus stream water outputs are used to express net gains or losses from the catchment.

We chose not to estimate atmospheric deposition of N in dryfall. The amount of organic N in dryfall has rarely been measured [Neff *et al.*, 2001]. Inorganic N in dryfall has been estimated for Niwot Ridge and ranges from 25 to 50% of inorganic N in wetfall [Sievering *et al.*, 1992, 1996]. *Campbell et al.* [2000a] estimated similar values for the nearby Loch Vale watershed in Rocky Mountain National Park. *Campbell et al.* [2000b] recently conducted an input-output mass balance for organic and inorganic N in northeastern United States and reported only N in wetfall because of the inherent difficulties in estimating N in dryfall at the basin scale. For this manuscript we followed the approach of *Campbell et al.* [2000b].

## 4. Results

### 4.1. Nitrogen Balances

Nitrate was the dominant form of N in both precipitation and stream water (Table 1). For the period 1996 to 1998, N in precipitation was composed of 52%  $\text{NO}_3\text{-N}$  ( $\pm 5\%$ ), 32%  $\text{NH}_4\text{-N}$  ( $\pm 2\%$ ), 9% DON ( $\pm 4\%$ ), and 7% PON ( $\pm 1\%$ ). Inorganic N composed 84% of N in precipitation, and organic N composed 16% of N. Nitrate composed an even greater percentage of N exported in streamflow. For the 3 years 1996–1998, streamflow N averaged 70%  $\text{NO}_3\text{-N}$  ( $\pm 5\%$ ), 4%  $\text{NH}_4\text{-N}$  ( $\pm 0.6\%$ ), 14% DON ( $\pm 5\%$ ), and 12% PON ( $\pm 1\%$ ). The percentage of organic N increased from 16% of total N in precipitation to 26% of total N in streamflow, a difference of 60%.

Inputs of  $\text{NO}_3\text{-N}$  ranged from 2.17 to 2.78  $\text{kg ha}^{-1} \text{yr}^{-1}$ ,  $\text{NH}_4\text{-N}$  ranged from 1.20 to 1.93  $\text{kg ha}^{-1} \text{yr}^{-1}$ , DON ranged from 0.15 to 0.54  $\text{kg ha}^{-1} \text{yr}^{-1}$ , and PON ranged from 0.27 to 0.35  $\text{kg ha}^{-1} \text{yr}^{-1}$  (Table 1). The N outputs were lowest for  $\text{NH}_4\text{-N}$  (~0.13  $\text{kg ha}^{-1} \text{yr}^{-1}$ ) and much higher and more variable for  $\text{NO}_3\text{-N}$  at 1.62 to 2.13  $\text{kg ha}^{-1} \text{yr}^{-1}$ . Output of DON was always less than  $\text{NO}_3\text{-N}$ , ranging from 0.18 to 0.61  $\text{kg ha}^{-1} \text{yr}^{-1}$ . For all years, export of inorganic N in streamflow (1.73–2.26  $\text{kg ha}^{-1} \text{yr}^{-1}$ ) was always larger than the export of

**Table 1.** Annual Deposition, Export, and Retention of N Species at Green Lake 4, 1996–1998<sup>a</sup>

	1996	1997	1998
<i>Inputs</i>			
NH <sub>4</sub> <sup>+</sup>	1.93 (34)	1.36 (31)	1.20 (30)
NO <sub>3</sub> <sup>-</sup>	2.78 (50)	2.17 (50)	2.31 (59)
DON	0.54 (10)	0.48 (11)	0.15 (4)
PON	0.35 (6)	0.33 (8)	0.27 (7)
Total	5.60	4.34	3.93
<i>Outputs</i>			
NH <sub>4</sub> <sup>+</sup>	0.14 (5)	0.13 (4)	0.11 (5)
NO <sub>3</sub> <sup>-</sup>	1.87 (72)	2.13 (69)	1.62 (78)
DON	0.36 (14)	0.61 (20)	0.18 (9)
PON	0.21 (8)	0.20 (7)	0.17 (8)
Total	2.58	3.07	2.08
<i>Net Retention</i>			
NH <sub>4</sub> <sup>+</sup>	1.79	1.23	1.09
NO <sub>3</sub> <sup>-</sup>	0.91	0.04	0.69
DON	0.18	-0.13	-0.03
PON	0.14	0.13	0.10

<sup>a</sup>Values are given in kg ha<sup>-1</sup>. Numbers in parentheses show the percentage of a particular species in that year's makeup.

organic N (0.35–0.81 kg ha<sup>-1</sup> yr<sup>-1</sup>). Outputs of PON were always low, ranging from 0.17 to 0.21 kg ha<sup>-1</sup> yr<sup>-1</sup>.

Subtracting inputs from outputs, the mass balance estimates suggest there was always net retention of inorganic N in the basin (Table 1). More than 90% of NH<sub>4</sub>-N in wet fall was retained. In contrast, only 2–33% of the NO<sub>3</sub>-N in annual precipitation was retained. The only form of N that showed net export in any year was DON. The net DON balance was almost

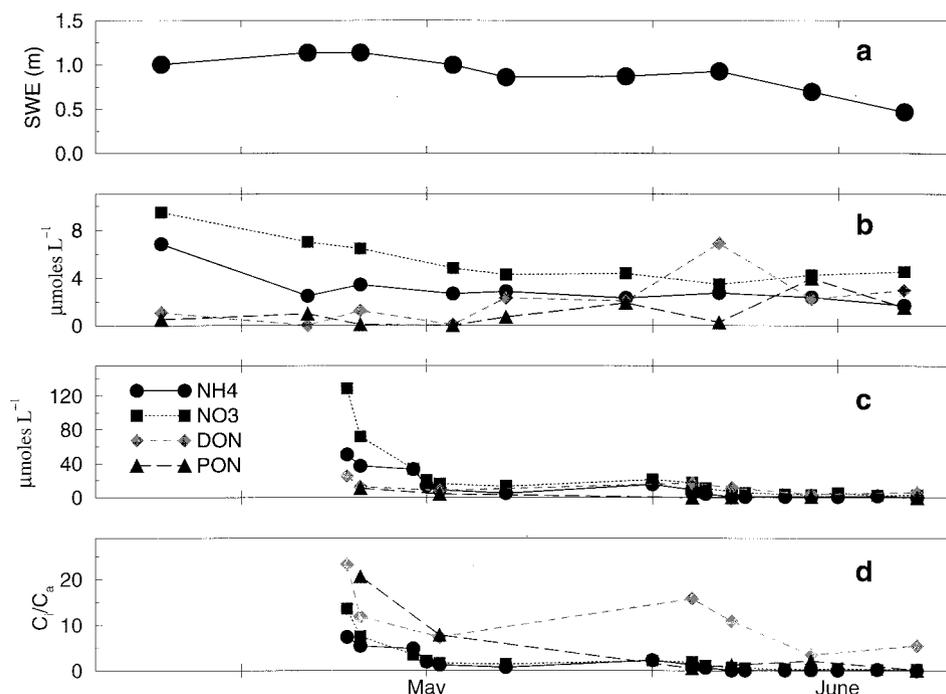
zero each year (0.18 to -0.13 kg ha<sup>-1</sup> yr<sup>-1</sup>), with a small net loss in 2 years and net retention in 1 year. Surprisingly, our results show a net retention of PON.

## 4.2. Concentrations

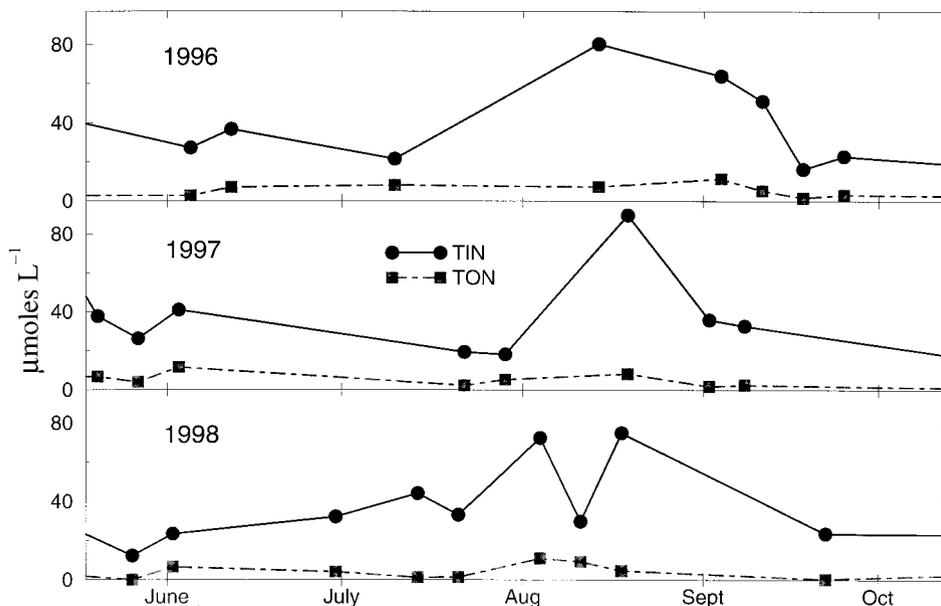
**4.2.1. Snow.** Snow water equivalence at the Saddle site on Niwot Ridge decreased from a maximum of 1.1 m on May 6, 1996, to 0.4 m on June 20, 1996 (Figure 2a). Concentrations of NO<sub>3</sub>-N and NH<sub>4</sub>-N in the snowpack generally declined with time after snowmelt started in early May, from ~9 μmol L<sup>-1</sup> at the initiation of snow melt to 3.5 μmol L<sup>-1</sup> on June 20 for NO<sub>3</sub>-N and from 7 to 2 μmol L<sup>-1</sup> for NH<sub>4</sub>-N (Figure 2b). In contrast, both DON and PON were more variable over time. For example, DON increased from ~1 μmol L<sup>-1</sup> at the initiation of snowmelt to 7 μmol L<sup>-1</sup> on June 6.

Concentrations of all forms of N were higher in snowpack meltwater (collected in snow lysimeters before contact with the ground) compared to bulk snowpack concentrations at the initiation of snowmelt runoff (Figure 2c). The ratio of the forms of N in meltwater  $C_i$  to bulk concentrations of the snowpack at the initiation of snowmelt  $C_a$  shows that all forms of N were concentrated in the first fraction of snowmelt runoff, a process generally termed an “ionic pulse” (Figure 2d). Concentrations of inorganic N then decreased in an exponential fashion with time until they were less than bulk snowpack concentrations at the initiation of snowmelt. Interestingly, both DON and PON had higher values of the  $C_i/C_a$  ratio (~20) compared to inorganic N (5–15). The high  $C_i/C_a$  values for DON in early June are consistent with additional sources of DON added to the snowpack after the initiation of snowmelt.

**4.2.2. Rain.** Here we present results from precipitation as rain from 1996 to 1998, from about the start of the snowmelt



**Figure 2.** Concentrations of N species in snow and snowpack meltwater at an index site on Niwot Ridge during the period of snowmelt runoff in 1996. (a) Change in snow water equivalence with time. (b) Concentrations of N species in snow. (c) Concentrations of N species in snowpack meltwater before contact with the ground. (d) The ratio of N species in snowpack meltwater ( $C_i$ ) to bulk snowpack concentrations at the initiation of snowmelt ( $C_a$ ), the magnitude of the “ionic pulse.”

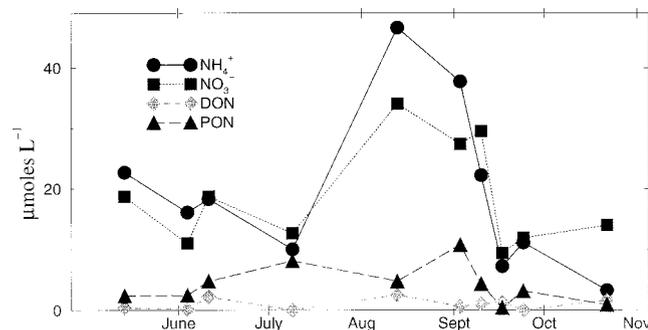


**Figure 3.** Concentrations of total inorganic nitrogen (TIN = NH<sub>4</sub>-N + NO<sub>3</sub>-N) and total organic nitrogen (TON) in rainfall (May–October 1996–1998) at the NADP collector on Niwot Ridge located at an elevation of 3500 m.

season in May, through the summer months, and on through the end of October (Figure 3). Inorganic N was always greater than organic N ( $p < 0.001$ ,  $n = 45$ ) in every measurement of rainfall chemistry. The values of inorganic N ranged from 4 to 90  $\mu\text{mol L}^{-1}$  with a mean of 32  $\mu\text{mol L}^{-1}$ , compared to a range from 0 to 12  $\mu\text{mol L}^{-1}$  and mean of 4  $\mu\text{mol L}^{-1}$  for organic N. The inorganic and organic N values were weakly correlated, with an  $R^2$  of 0.21 ( $p = 0.001$ ,  $n = 45$ ). The highest concentrations for both inorganic and organic N in all three years occurred in August and September.

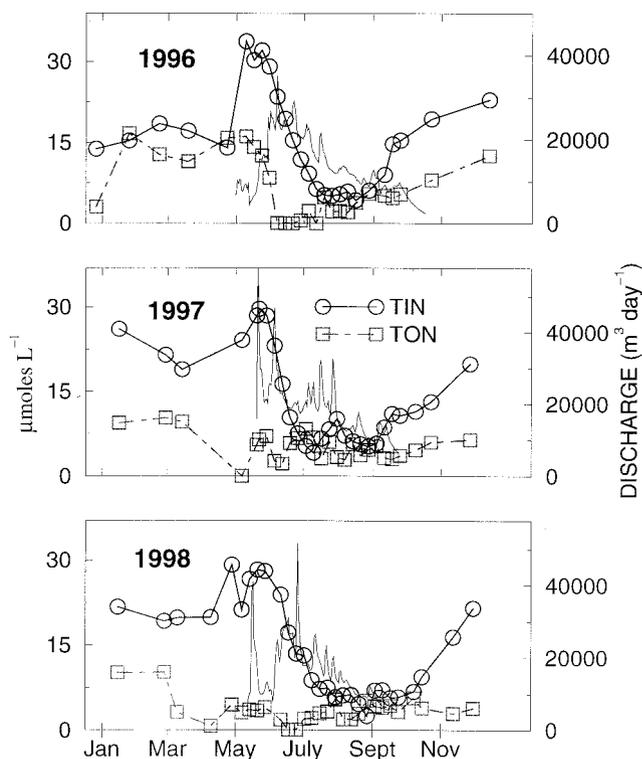
For the 1996 rainfall season, we present more detailed information on NH<sub>4</sub>-N, NO<sub>3</sub>-N, DON, and PON (Figure 4). Patterns were similar for the other years. For all rain events, concentrations of NH<sub>4</sub>-N and NO<sub>3</sub>-N were greater than either DON or PON. Ammonium values were highly correlated with NO<sub>3</sub>-N values ( $R^2 = 0.77$ ,  $p < 0.001$ ,  $n = 10$ ), while DON values showed no correlation with PON values ( $R^2 = 0.03$ ,  $p = 0.61$ ,  $n = 10$ ).

**4.2.3. Stream water.** Despite year-to-year variations, there was a clear seasonal pattern in the concentrations of

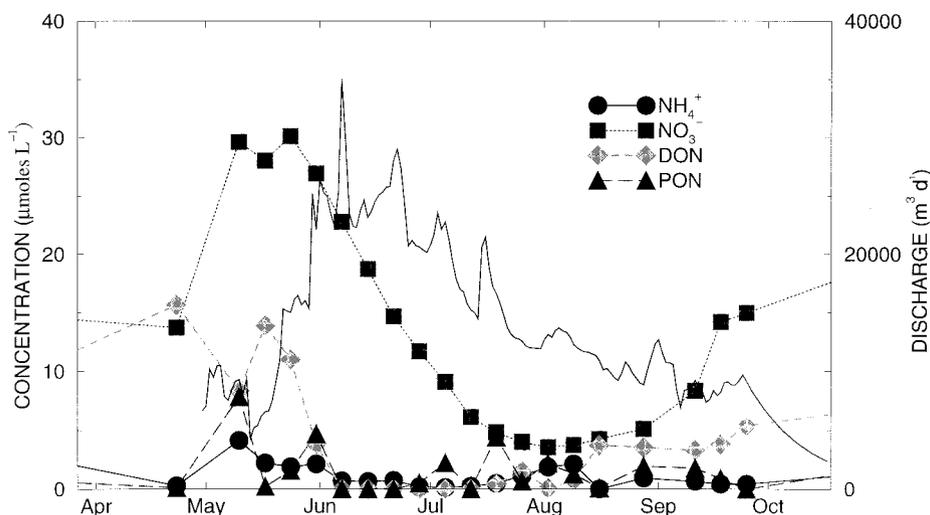


**Figure 4.** More detailed information on NH<sub>4</sub>-N, NO<sub>3</sub>-N, DON, and PON for the 1996 rainfall season. Concentration patterns were similar for the other years.

inorganic and organic N at the outflow of GL4 (Figure 5). Concentrations of inorganic N were  $\sim 15\text{--}25 \mu\text{mol L}^{-1}$  during winter, increased to  $\sim 30 \mu\text{mol L}^{-1}$  on the rising limb of the hydrograph before falling to  $\sim 5 \mu\text{mol L}^{-1}$  on the recession



**Figure 5.** Concentrations of total inorganic nitrogen (TIN = NH<sub>4</sub>-N + NO<sub>3</sub>-N) and total organic nitrogen (TON) in stream water outflow from Green Lake 4, 1996–1998. Discharge was measured from about May 1 to September 30 each year.



**Figure 6.** More detailed information on  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$ , DON, and PON for 1996. Patterns in concentration were similar for the other years.

limb, and then returned to base flow values in the autumn. In contrast, organic N was  $7\text{--}15 \mu\text{mol L}^{-1}$  during winter, decreased to near or below detection limits on the rising limb of the hydrograph, with a gradual and consistent increase on the recession limb of the hydrograph and on into the autumn. These results suggest that the pulse of organic N released from the snowpack did not contribute to organic N concentrations in streamflow.

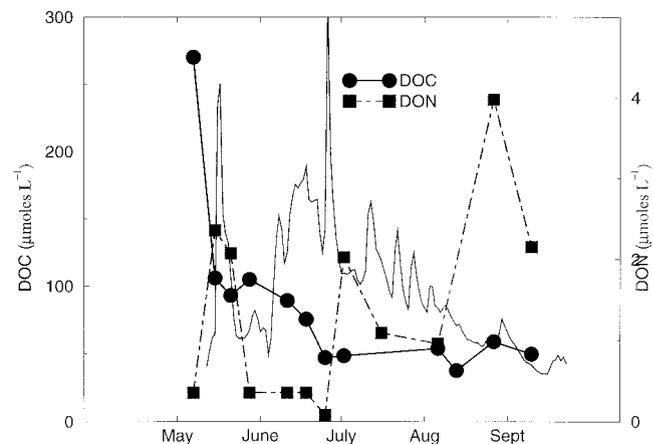
The seasonal patterns in inorganic and organic N were driven primarily by changes in  $\text{NO}_3^-$  and DON concentrations and not by  $\text{NH}_4^+$  and PON concentrations (Figure 6). In 1996, for example,  $\text{NH}_4\text{-N}$  concentrations were always at or near detection limits and varied little with discharge. Concentrations of PON were more episodic, ranging from detection limits to  $8 \mu\text{mol L}^{-1}$ , also with no relationship to discharge. There was a strong hysteresis in the relationship of  $\text{NO}_3\text{-N}$  to discharge, with  $\text{NO}_3\text{-N}$  concentrations elevated on the rising limb of the hydrograph and inversely related to discharge (mean of  $27 \mu\text{mol L}^{-1}$ ,  $R = -0.86$ ) and much lower concentrations on the recession limb of the hydrograph and directly related to discharge (mean of  $8.8 \mu\text{mol L}^{-1}$ ,  $R = 0.41$ ). In contrast, DON was inversely related to discharge (mean of  $3.13$ ,  $R = -0.53$ ) with little hysteresis when compared to  $\text{NO}_3\text{-N}$ . Note that we use the correlation coefficient  $R$  instead of the coefficient of determination  $R^2$  to emphasize the arithmetic sign associated with the inverse relationship.

**4.2.4. Dissolved organic carbon.** Measurements of DOC at the outflow of GL4 in 1998 may provide qualitative information on the controls on DON export and whether there is a change in the character of DON over time. The concentrations of DOC were high at the initiation of snowmelt and then decreased with time, from  $270 \mu\text{mol L}^{-1}$  at the initiation of melt to  $\sim 50 \mu\text{mol L}^{-1}$  in the fall (Figure 7). In contrast, concentrations of DON were generally at or below detection limits of  $0.17 \mu\text{mol L}^{-1}$  then increased to  $\sim 4 \mu\text{mol L}^{-1}$  in the fall. Concentrations of DON were not significantly correlated with DOC ( $R^2 = 0.04$ ,  $p > 0.05$ ), indicating that controls on DON export may be different than controls on DOC export. The DOC:DON ratio decreased by more than a factor of 2, from  $\sim 45$  in late May and early June on the rising limb of the hydrograph to  $< 20$  in September. The decrease in the DOC:

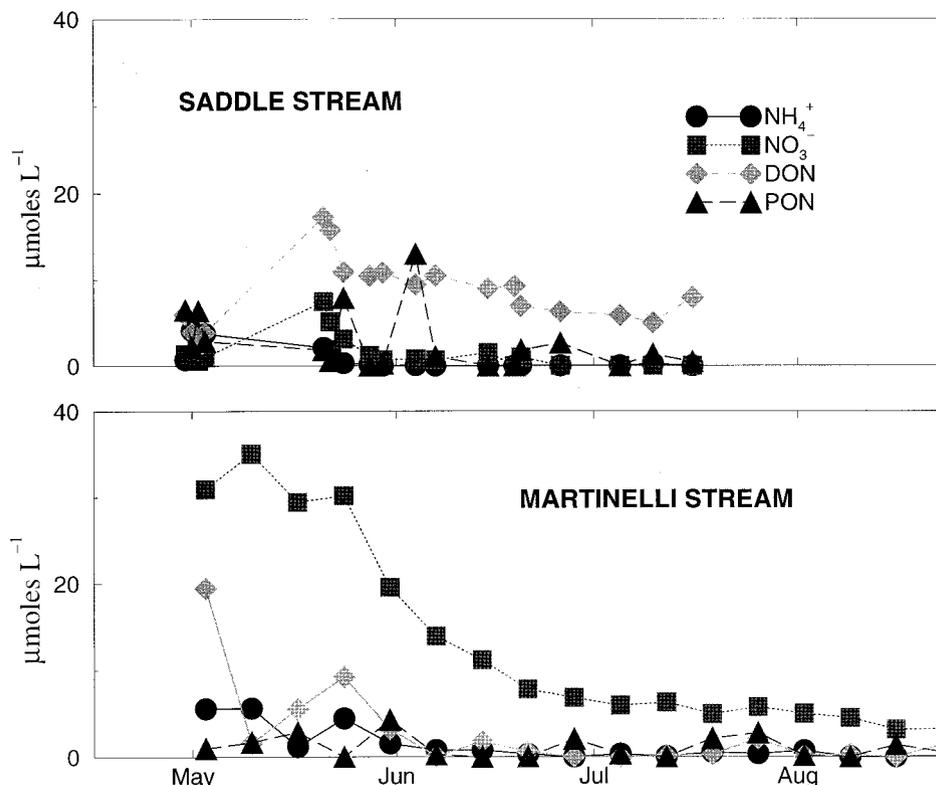
DON ratio with time indicates that the proportion of N in DOM increased with time.

#### 4.3. Landscape Type

There was a striking difference in the magnitude of concentrations of  $\text{NO}_3\text{-N}$  and DON between the Saddle (tundra area) and Martinelli (talus area) streams, adjacent 8 ha catchments on the south side of Niwot Ridge (Figure 1). At both locations,  $\text{NO}_3\text{-N}$  and DON increased on the rising limb of the hydrograph and then decreased rapidly. At the Saddle stream, DON concentrations were always greater than  $\text{NO}_3\text{-N}$  concentrations (Figure 8). The concentrations of DON reached a maximum of  $18 \mu\text{mol L}^{-1}$  at the initiation of snowmelt and then gradually decreased to  $\sim 6 \mu\text{mol L}^{-1}$ . Concentrations of  $\text{NO}_3\text{-N}$  were  $6 \mu\text{mol L}^{-1}$  at the initiation of snowmelt and then quickly decreased toward detection limits. In contrast, at the Martinelli catchment, concentrations of  $\text{NO}_3\text{-N}$  were always greater than concentrations of DON and up to an order of



**Figure 7.** Concentrations of DOC and DON at GL4 in 1998. Note that the scale is different for DOC and DON. Discharge from Figure 5 is overlaid. DOC concentrations show a consistent decrease with time. However, DON concentrations were more variable with time, suggesting that the quality as well as the quantity of DON changed over time.



**Figure 8.** Concentrations of N species in 1996 from Saddle and Martinelli streams, adjacent 8 ha basins that differ by landscape type. Patterns in concentration were similar for the other years.

magnitude higher (Figure 8). Nitrate concentrations were  $\sim 35 \mu\text{mol L}^{-1}$  at the initiation of snowmelt and then gradually decreased to  $\sim 3 \mu\text{mol L}^{-1}$ . The concentrations of DON were  $6 \mu\text{mol L}^{-1}$  at the initiation of snowmelt then decreased quickly toward detection limits. At both catchments,  $\text{NH}_4^+$  and PON concentrations were near detection limits.

A synoptic survey of water content from ephemeral streams draining talus and tundra landscape types in Green Lakes Valley was conducted during snowmelt runoff in 1998 (Figure 9). Nutrient concentrations in tundra ( $n = 20$ ) and talus ( $n = 18$ ) landscape types paralleled the patterns found in the Martinelli and Saddle streams. Mean  $\text{NO}_3\text{-N}$  concentrations in talus of  $20 \mu\text{mol L}^{-1}$  were twice that of the  $10 \mu\text{mol L}^{-1}$  found in tundra areas ( $p = 0.001$ ). In contrast, DON concentrations of  $8 \mu\text{mol L}^{-1}$  from tundra areas were 4 times the mean concentrations of  $2 \mu\text{mol L}^{-1}$  from talus areas ( $p < 0.001$ ). Similarly, DOC concentrations were greater in tundra areas compared to talus areas ( $p < 0.001$ ). There was no significant difference by landscape type for either  $\text{NH}_4\text{-N}$  or PON ( $p > 0.05$  for both).

## 5. Discussion

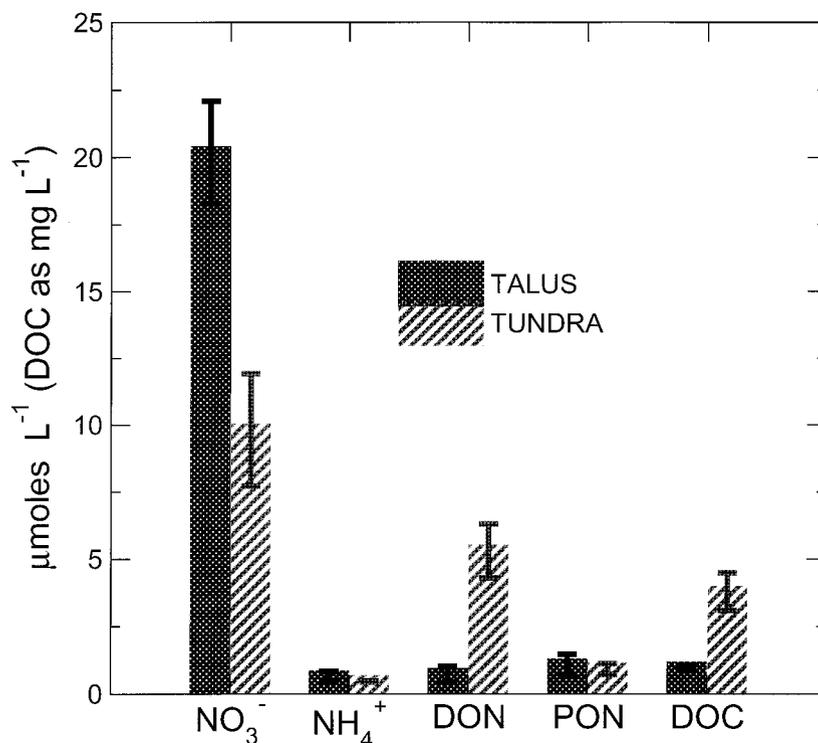
### 5.1. Mass Balance

Organic N fluxes in wet deposition appear to be large enough to warrant routine analysis in deposition monitoring programs at high elevations (question 1 from section 1). Similarly, organic N was an important component of N export in stream water (question 2). For the 3 years of mass balance measurements a substantial amount of total N was composed of organic N in both precipitation (11–19%) and stream water

(17–27%). While there was net retention of N in the basin, little of this N accretion was due to net retention of organic N. These results suggest previous studies of N retention in high-elevation ecosystems may have overestimated net N retention by not measuring organic N in precipitation and basin outflow (question 3) [Brooks *et al.*, 1999a; Campbell *et al.*, 2000a; Sickman and Melack, 2001]. Although the immediate importance of organic N does not appear to be as important as inorganic N, organic N is potentially bioavailable [e.g., Seitzinger and Sanders, 1997] and must be considered in any mass balance analysis of N flux for high-elevation catchments.

### 5.2. Concentrations

**5.2.1. Snow.** The presence of a seasonal snowpack does appear to influence the storage and release of organic N to the underlying terrain (question 4). Both DON and PON were released from the seasonal snowpack in the form of an ionic pulse. One cause of the ionic pulse is that larger molecules such as  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  do not fit into the crystalline lattice of ice and hence are adsorbed on the outside of snow grains [Bales, 1992]. Consequently, the first fraction of meltwater percolating through the snowpack leaches the larger solute molecules stored on the outside of snow grains. The larger size of the DON and PON molecules relative to solutes such as  $\text{NO}_3^-$  and  $\text{NH}_4^+$  suggest that the concentration factor for DON and PON would be greater than for  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . Our results bear this out, with both DON and PON having higher values of the  $C_i/C_a$  ratio ( $\sim 20$ ) compared to inorganic N (5–15). However, analytical uncertainty caused by the relatively low values of DON and PON in the snowpack may have influenced the large magnitude of their concentration ratios.



**Figure 9.** A synoptic survey in 1998, which showed significant differences in NO<sub>3</sub>-N, DON, and DOC between tundra and talus landscape types but not for NH<sub>4</sub>-N or PON. Error bars are one standard error.

The higher concentrations of DON in snow with time and, to a lesser extent, PON suggest that the snowpack acts as a trap or filter for organic debris transported by wind from nearby areas that are becoming snow-free. Several researchers have shown that seasonal snowpacks accumulate aeolian deposition, particularly in the spring and summer when surrounding areas become snow-free, and the presence of liquid water in the snowpack increases the “stickiness” of the snowpack. For example, Caine [1974], Thorn and Darmody [1980], and Litaor [1987] have shown that late season snowpacks are efficient collectors of aeolian sediments. Clow *et al.* [1997] has shown that aeolian deposition is an important source of calcium to high-elevation catchments. Williams *et al.* [2000] report that late lying snowpacks in the Green Lakes Valley are characterized by pockets of organic matter located on the snow surface at spatial distances of centimeters to meters. Our results suggest that late lying snowpacks capture organic debris transported by wind from nearby areas and may provide an additional source of organic N to the underlying terrain. Note that this release of organic N from snow occurred in May and June and was not included in mass balance calculations for atmospheric deposition of N, which used NADP measurements for this period.

Biological activity within the snowpack may play a role in the storage and release of organic N. It is unlikely that biological activity influences the early season pulse of organic N in snowpack meltwaters. Brooks *et al.* [1993] have shown that there is very little microbial biomass in cold and dry snowpacks at high elevation in the Rocky Mountains, with concentrations generally  $<10^4$  cells mL<sup>-1</sup>. However, microbial activity increases dramatically in wet, draining, and thin ( $<1$  m deep) snowpacks, with concentrations of microbial biomass  $>10^9$  cells mL<sup>-1</sup> [Brooks *et al.*, 1993]. *Chlamydomonas nivalis* and other

microbes migrate from underlying soils up into the snowpack at this time and may have a large effect on both organic and inorganic N concentrations.

**5.2.2. Rainfall.** Seasonal increases in concentrations of inorganic and organic N in wet fall for late summer rains may be a result of the predominance of upslope conditions which transport pollutants from the Front Range urban corridor to high-elevation areas. Williams *et al.* [1996a] and Williams and Tonnessen [2000] have shown that annual atmospheric deposition of inorganic N in wetfall to Niwot Ridge has been increasing at the rate of 0.32 kg ha<sup>-1</sup> yr<sup>-1</sup>. The source of this increase in N deposition in wet fall is unknown. A recent analysis of NADP data at Niwot Ridge shows that the pH of precipitation is lowest in August and September. The synoptic climatology of these acidic events was characterized by weak circulation and anticyclonic conditions, suggesting atmospheric buildup of pollutants from local sources, such as the urban corridor along the Front Range [Losleben *et al.*, 2000]. The increased fluxes of organic N in precipitation at this time are consistent with the production of either organic nitrates or amine N in the Front Range [Neff *et al.*, 2001], potentially a fruitful area for additional research.

We did not include estimates of dry deposition of N because of the difficulty in measuring this flux. However, if dry fall of inorganic N falls into the range of 25–50% of wet fall, as suggested in section 3, it would be 2–4 times that of organic N in wet fall, causing the percentage of organic N in annual atmospheric deposition of N to decrease. The percentage of organic N in stream export of total N would then increase compared to inputs of organic N in atmospheric deposition of total N in wet fall.

**5.2.3. Outputs.** The dominance of NO<sub>3</sub>-N in stream water exports was somewhat unexpected. The dominance of or-

ganic N is common in watersheds where both inorganic and organic N have been measured in annual stream water export [e.g., *Chapman et al.*, 1998; *Campbell et al.*, 2000b]. Recent measurements of inorganic and organic N at 10 high-elevation catchments in the Lake Tahoe basin show that organic N comprises ~90% of the total N in annual stream water export [*Coats and Goldman*, 2001]. The dominance of  $\text{NO}_3\text{-N}$  in stream water exports at GL4 may be in part because of elevated amounts of inorganic N in atmospheric deposition. *Sickman et al.* [2001] recently summarized inorganic N inputs and outputs for 28 high-elevation catchments in the Sierra Nevada and Rocky Mountains. They report that mean loading of inorganic N in wet fall to the Rocky Mountains of  $3.6 \text{ kg ha}^{-1} \text{ yr}^{-1}$  was double the  $1.8 \text{ kg ha}^{-1} \text{ yr}^{-1}$  for the Sierra Nevada and inorganic N yield in the Rocky Mountains of  $1.1 \text{ kg ha}^{-1} \text{ yr}^{-1}$  was about twice that of the  $0.69 \text{ kg ha}^{-1} \text{ yr}^{-1}$  for the Sierra Nevada. High-elevation catchments in the Rocky Mountains appear to have increased export of  $\text{NO}_3\text{-N}$  as a response to increasing amounts of inorganic N in atmospheric deposition.

The quantity and character of DON export in stream waters did change over time (question 5). Little is known about sources of DON in stream waters and changes over time. In most biomes, soils and vegetation of the catchment are the primary sources of DOM to a stream [*Thurman*, 1985]. Microbial degradation and litter decay mobilize carbon and N. DOC concentrations generally decrease with depth in the soil profile because of podzolization [*McDowell and Wood*, 1984], chemical adsorption, and biological degradation [*Meyer and Tate*, 1983], with very low concentrations of terrestrial DOC in groundwaters that contribute to streamflow. Most DOC thus enters stream systems as a result of the flushing of catchment soils as rain or snowmelt events cause the water table to rise and flow through the upper soil horizons [*Foster and Grieve*, 1982; *Meyer and Tate*, 1983; *Mulholland et al.*, 1990]. Consequently, DOC concentrations in Rocky Mountain streams generally increase on the ascending limb of the hydrograph, peak prior to maximum discharge, then decrease rapidly on the recession limb of the hydrograph [*Lewis and Grant*, 1979; *Hornberger et al.*, 1994; *Boyer et al.*, 1997].

Our measurements of DOC are consistent with the results for streams in the Rocky Mountains. However, DON concentrations at the outflow of GL4 were not related to DOC concentrations, nor did they follow the temporal pattern of DOC. It is worth noting that *Coats and Goldman* [2001] report a temporal pattern in DON concentrations for high-elevation streams in the Lake Tahoe basin that is similar to GL4. In contrast, *Campbell et al.* [2000b] found no seasonal trends in their study of DON in the northeastern United States. Thus it appears that ecological controls on DON export in Green Lakes Valley may be different than for DOC.

One potential explanation for the decrease in the DOC:DON ratio with time at the outflow of GL4 may be that the sources of DON changed over time. The residual organic compounds from decomposition in terrestrial systems are generally well constrained. The resulting soil humic material is generally composed of 3–6% N, composed primarily of proteinaceous and heterocyclic residues or moieties [*Schulten and Schnitzer*, 1998]. The DOM leached to aquatic ecosystems from terrestrial ecosystems is primarily in the form of fulvic acids, the leaky faucet hypothesis. These fulvic acids are relatively recalcitrant from a bioavailability viewpoint, generally hydrophobic and <5000 daltons in size, with an N content ranging from 0.5 to 3% [*McKnight et al.*, 1985]. The DOC:DON ratios of ~40

that we report for the rising limb of the hydrograph at the outflow of GL4 are consistent with a terrestrial source of DOM at that time that is recalcitrant from a bioavailability standpoint.

The combination of a decrease in the DOC:DON ratio along with an increase in concentrations of DON in the late summer and fall months suggests that the source of DON in the Green Lakes basin may be changing with time. For example, fulvic acids in streams derived from aquatic microbial and algal material have distinctly different chemical characteristics than that derived from terrestrial plants and soil [*McKnight et al.*, 1991]. Thus fulvic acids produced by microbial activity in aquatic ecosystems have less aromaticity and higher N content than terrestrially derived fulvic acids [*McKnight et al.*, 1994]. In-stream/in-lake sources of DON may have become a more important source of DON in the summer and fall months than terrestrial sources in the GL4 basin. Recent work has shown that the fluorescence excitation emission matrices (EEMs) of fulvic acids derived from the degradation of microbial material have distinctive characteristics compared to fulvic acids from plant and soil material [*McKnight et al.*, 2001]. Hence measuring the fluorescence of humic DOM provides the opportunity to determine the relative contributions from terrestrial and aquatic sources, and to interpret seasonal changes in total DON and in nonhumic DON in a biogeochemical context.

### 5.3. Ecosystem Controls

The export of organic N in talus and tundra landscape types was the inverse of  $\text{NO}_3\text{-N}$  export (question 6). The process-level controls on DON concentrations and fluxes in surface waters of most biomes are still poorly understood despite the apparent importance of DON as a vector for N export. DOM can be produced and consumed by micro organisms or plants and can be stabilized or solubilized on and off of soil surfaces [*McDowell and Wood*, 1984; *Kielland*, 1994; *Kaiser et al.*, 1996]. This suite of competing reactions greatly complicates interpretation of the regulation of DOM fluxes at the ecosystem scale. Recent research in Hawaii suggests that organic and inorganic components of N flux from soils are regulated by different factors and that DON fluxes are somewhat decoupled from immediate microbial demand for N [*Neff et al.*, 2000]. However, research that shows a relationship between DOC fluxes and soil heterotrophic activity as measured by  $\text{CO}_2$  emissions suggests that terrestrial productivity and the production of humic DON may be coupled [*Brooks et al.*, 1999b].

The differences in concentration of the various N species by landscape type provides potential insight into ecological controls on N export. Talus areas are characterized by an active microbial population, a carbon-limited environment, large inputs of inorganic N from snowmelt, and relatively low amounts of N assimilation by biota [*Williams et al.*, 1997]. High rates of nitrification and low amounts of assimilation result in talus areas having the potential to export large amounts of  $\text{NO}_3\text{-N}$  relative to tundra areas [*Williams et al.*, 1997; *Campbell et al.*, 2000a]. The ratio of 10 for inorganic N to organic N in stream waters draining talus areas compared to 1.5 for tundra areas suggests that  $\text{NO}_3\text{-N}$  export may be directly related to microbial activity. In contrast, the higher amounts of organic N in tundra areas compared to talus areas suggest that DON export may be related to the C and N stock in underlying soils. These different ecological controls on  $\text{NO}_3\text{-N}$  and DON export may then explain why the ratio of inorganic N to organic N in

**Table 2.** Comparison of the Ratio of Dissolved Inorganic N (DIN) to Organic N (ON) From a Number of Biomes With Differing Amounts of Atmospheric Deposition of N

Site	Number of Basins	DIN:ON	Biome	Reference
Chile	31	0.05	forested	<i>Hedin et al.</i> [1995]
Finland (north)	11	0.23	forested	<i>Kortelainen et al.</i> [1997]
Finland (south)	12	0.41	forested	<i>Kortelainen et al.</i> [1997]
Hubbard Brook	9	0.8	forested	<i>Campbell et al.</i> [2000b]
Tahoe Basin	10	0.1	alpine/subalpine	<i>Coats and Goldman</i> [2000]
Emerald Lake	1	0.67	alpine	<i>Williams et al.</i> [1995]
Green Lake 4	1	3.8	alpine	this paper

annual stream water export may be a good indicator of the N status of ecosystems.

In contrast to  $\text{NO}_3\text{-N}$  and DON, concentrations of  $\text{NH}_4\text{-N}$  and PON from the Saddle and Martinelli streams were always low and showed little variation with discharge. These results suggest that controls on the export of these N species were different than for  $\text{NO}_3\text{-N}$  and DON. One potential reason may be that export of  $\text{NH}_4\text{-N}$  and PON is controlled more by abiotic processes than  $\text{NO}_3\text{-N}$  and DON. As snowmelt and rain infiltrate into the subsurface of high-elevation catchments,  $\text{NH}_4\text{-N}$  and PON may be adsorbed on ion exchange sites. Results from the synoptic survey are consistent with this hypothesis, as concentrations of  $\text{NH}_4\text{-N}$  and PON were always low and did not differ significantly by landscape type.

Our results are generally consistent with the hypothesis that DON functions as a leak of N from terrestrial ecosystems to aquatic ecosystems (question 7). The export of organic N may be relatively constant within a given biome. As ecosystems start to switch from N-limited systems to N-saturated systems, export of  $\text{NO}_3\text{-N}$  may increase at a much faster rate than organic N. Hence the ratio of inorganic N to organic N in stream waters may increase as a particular ecosystem becomes N-saturated.

Our results suggest that the ratio of the annual mass flux of inorganic N to organic N in stream waters may provide an index to evaluate the N status of terrestrial ecosystems from a variety of biomes (question 8). Pristine, forested catchments in Chile have an inorganic to organic N ratio of  $\sim 0.05$  in stream waters (Table 2). In Finland, as atmospheric deposition of inorganic N increases from 3.0 to 4.6  $\text{kg ha}^{-1} \text{yr}^{-1}$  along a latitudinal gradient, the ratio of inorganic to organic N in annual stream water export doubles from 0.23 in the northern part of the country to 0.41 in the southern part of the country. At nine forested catchments in the northeastern United States, where atmospheric deposition of inorganic N is 6–10  $\text{kg ha}^{-1} \text{yr}^{-1}$ , the ratio of inorganic to organic N in annual stream water export increases to 0.8 (Table 2). Similarly, in alpine and subalpine catchments of the Sierra Nevada, where atmospheric deposition of inorganic N is  $< 2 \text{ kg ha}^{-1} \text{yr}^{-1}$ , the ratio of inorganic to organic N is 0.67 or less (Table 2). However, at our alpine site in the Rocky Mountains, where atmospheric deposition is appreciably greater than in the Sierra, the ratio of inorganic to organic N in annual stream water export is much higher than any of the other sites at 3.8.

Ecosystem export of total N varies with vegetation, soils, climate, and other variables [e.g., *Hedin et al.*, 1995; *Kortelainen et al.*, 1997; *Lewis et al.*, 1999]. The export of DON in stream water may be controlled primarily by the standing stock of N in terrestrial soils. This soil reservoir of N may change only slowly

in response to increases in atmospheric deposition of N [*Schimel*, 1986; *Parton et al.*, 1993], resulting in little increase in the export of DON to surface waters. In contrast, soil inorganic N may increase relatively quickly in response to increases in atmospheric deposition through increases in ammonification and particularly net nitrification [*Aber et al.*, 1989, 1998], resulting in a relative large increase in the export of inorganic N to stream waters. Hence the ratio of inorganic N to organic N may provide an index of available N (DIN) to background N (DON) which is independent of the actual magnitude of the fluxes of these N species.

## 6. Conclusions

For the 3 years of mass balance measurements, a substantial amount of total N was composed of organic N in both precipitation (11–19%) and stream water (17–27%). While there was net retention of N in the basin, little of this N accretion was due to net retention of organic N. These results suggest previous studies of N retention in high-elevation ecosystems may have overestimated net N retention by not measuring organic N in precipitation and basin outflow [*Brooks et al.*, 1999a; *Campbell et al.*, 2000a; *Sickman and Melack*, 2001].

The ratio of inorganic N to organic N in annual stream water flux may provide a novel way to evaluate the N status of ecosystems. Our results suggests that  $\text{NO}_3\text{-N}$  export may be controlled by immediate microbial demand, whereas DON export may be related to the standing stock of C and N. Consequently, the ratio of inorganic N to organic N in stream water should increase with increasing inputs of N to catchments from sources such as atmospheric deposition and fertilization. Additional research is warranted to determine if  $\text{NO}_3\text{-N}$  and DON export are related to standard indices of the N content of soils, such as KCl-extractable inorganic N, microbial biomass N, and net ammonification and nitrification. Similarly, soil C:N ratios should be investigated in an effort to understand the relationship between  $\text{NO}_3\text{-N}$  and DON export in stream water and soil fertility.

The presence of snow does influence the storage and release of organic N to the underlying substrate. Both DON and PON appear to be released from the snowpack in the form of an ionic pulse. Late lying snowpacks also appear to act as filters to trap organic matter from nearby areas transported by wind. It is possible that talus areas receive much of their organic matter as aeolian deposition to late lying snowpacks.

Our results suggests that sources of organic N may change with time. The low concentrations of DON and high DOC:DON ratio at the initiation of snowmelt at the outflow of GL4 are consistent with a terrestrial source of highly refractory

DOM. The increase in DON concentrations and decrease in the DOC:DON ratio during low-flow periods suggests that the N content of DOM changes over time. One reason for the change in character of DON may be that sources of DOM changed from humidified and condensed terrestrial sources at the initiation of snowmelt runoff to aquatic sources during the late summer and fall months. Whether this change in the character of DON is to a more labile or refractory form is unknown and deserves additional attention.

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