WATER RESOURCES RESEARCH, VOL. 32, NO. 10, PAGES 3161–3171, OCTOBER 1996

Mineral nitrogen transformations in and under seasonal snow in a high-elevation catchment in the Rocky Mountains, United States

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Abstract. In an effort to understand sources of nitrate (NO_3^-) in surface waters of high-elevation catchments, nitrogen (N) transformations in and under seasonal snow were investigated from 1993 to 1995 on Niwot Ridge, an alpine ecosystem at 3,500 m located in the Colorado Front Range of the Rocky Mountains. Ammonium (NH_4^+) and NO_3^- labeled with ^{15}N applied as nonconservative tracers to the snow showed no evidence of nitrification in the snowpack. Furthermore, NH_4^+ movement through the amended snowpack was highly correlated with a conservative chloride tracer ($r^2 = 0.99$). In an unamended snowpack NH_4^+ concentrations in meltwater before contact with the ground were highly correlated with NO_3^- concentrations ($r^2 = 0.98$), which is consistent with no nitrification in the snowpack. The isotopically labeled $^{15}NH_4^+$ applied to the snowpack was found in underlying soils, showing that NH_4^+ released from snow can be rapidly immobilized. Resin bag (mixed-bed ion-exchange resins) measurements ($n = 22$) showed that 80% of the mobile inorganic N in unamended subnivial soils was NO_3^-. Measurements of KCl-extractable inorganic N from surface soils showed that highest values were prior to the initiation of snowmelt and lowest values were during the growing season. The natural $\delta^{15}N$ abundance of unamended soils was negative and ranged from -12 to -2, suggesting that atmospheric deposition of $\delta^{15}N$-depleted N is an important component of N cycling in these alpine soils. These results suggest that soil mineralization under seasonal snow, rather than snowmelt release of NO_3^-, may control NO_3^- concentrations in surface waters of high-elevation catchments.

Introduction

Nitrate concentrations in surface waters of high-elevation catchments in the western United States show a characteristic increase in concentration coincident with the initiation of snowmelt runoff [e.g., *Williams and Melack*, 1989]. This annual maximum in NO_3^- concentrations is generally followed by a decrease in concentration to near-detection limits, caused by dilution from snowmelt runoff and assimilation by biota. The source of NO_3^- in surface waters of high-elevation catchments in the western United States is unknown: Effects of N deposition are generally decoupled from the N deposition because of the large variety of N species found in air, deposition, watersheds, and surface waters, as well as the myriad of pathways through which N can be cycled in terrestrial and aquatic ecosystems [*Stoddard*, 1994]. Nitrate concentrations in stream waters are generally consistent with the release of inorganic N from storage in the seasonal snowpack in the form of an ionic pulse and often attributed to release of NO_3^- from snow [e.g., *Williams et al.*, 1995]. *Caine and Thurman* [1990] suggested that meltwater from snow is the major source of NO_3^- in stream waters of the Green Lakes Valley in the Colorado Front Range of the Rocky Mountains and that the surface water system interacts little with vegetation and soils and is effectively decoupled from the alpine pedosphere.

However, recent results reported by *Brooks et al.* [1996] show that N cycling under seasonal snow is much more dynamic than previously documented. Furthermore, *Campbell et al.* [1995] report that in the Loch Vale Watershed in Rocky Mountain National Park of the Colorado Front Range, soils and other shallow groundwater matrices such as boulder fields appear to be important in controlling the surface-water chemistry of high-elevation catchments. Ammonification and nitrification in and under the seasonal snowpack and consequent transport of NO_3^- by infiltrating snowmelt may provide some or all of the NO_3^- in surface waters of high-elevation catchments [e.g., *Williams et al.*, 1995]. In the eastern United States, research in the Adirondacks has shown that the NO_3^- pulse in stream waters during spring runoff is the result in part of snowmelt infiltrating soils and transporting NO_3^- produced by nitrification under the seasonal snowpack to surface waters [*Peters and Driscoll*, 1987; *Rascher et al.*, 1987].

The contribution of snowpack ammonium (NH_4^+) to the annual streamwater pulse of NO_3^- is unknown. Little NH_4^+ is found in surface waters of high-elevation catchments at any time [e.g., *Baron*, 1991; *Stottlemyer and Troendle*, 1992]. Several researchers have suggested that NH_4^+ released from the snowpack is immobilized by microbial activity and/or adsorbed on soil exchange sites as snowmelt infiltrates soils [*Brooks et al.*, 1995; *Williams et al.*, 1995]. However, the general lack of well-developed soils in high-elevation catchments makes this expla-

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Paper number 96WR02240.
0043-1397/96/96WR-02240$9.00

nation problematic. In contrast, *Kendall et al.* [1995] have suggested that NH_4^+ stored in the seasonal snowpack may be transformed to NO_3^- before release in snowmelt.

Recent results add some urgency to understanding the sources of NO_3^- in surface waters of high-elevation catchments in western North America. Concentrations of anthropogenic N in the ambient air of these mountainous areas have increased as much as 30-fold during the last several decades [*Fahey et al.*, 1986]. The resulting increases in wet and dry deposition of N are beginning to change the fundamental nitrate-discharge pattern in high-elevation catchments of the western United States. In the Colorado Front Range, NO_3^- concentrations in many streams now remain elevated throughout the growing season, indicating that these high-elevation catchments have become N saturated [*Williams et al.*, 1996a]. Episodic acidification in small headwater catchments of the Colorado Front Range is associated with NO_3^- in surface waters [*Williams et al.*, 1996b] and may begin to occur in other high-elevation catchments if present levels of anthropogenic pollutants in atmospheric deposition are maintained or increase.

Our objective is to evaluate processes that may contribute NO_3^- to surface waters in a high-elevation catchment in the Colorado Front Range of the Rocky Mountains. We test these hypotheses: (1) nitrification of NH_4^+ to NO_3^- in snow is an important process; (2) NH_4^+ and NO_3^- released from the snowpack are retained in underlying soils; and (3) NO_3^- produced in subnivial soils contributes to NO_3^- in surface waters. To evaluate these hypotheses, we report on the results of several experiments conducted on and near Niwot Ridge including transformations and fate in the snow and underlying soils of isotopically labelled $^{15}NH_4Cl$ and $K^{15}NO_3$ tracers applied to the surface of a natural snowpack; recovery of NH_4^+ and NO_3^- in subnivial resin bags; time series measurements of KCl-extractable soil inorganic N; and measurements of inorganic N in snow meltwater before contact with the ground, in soil solution, and in surface waters.

Site Description

All experiments were conducted on the Niwot Ridge saddle at an elevation of 3,500 m (Figure 1), located in the Colorado Front Range of the Rocky Mountains about 5 km east of the Continental Divide (40°03'N, 105°35'W). This site is a United Nations Educational, Scientific and Cultural Organization (UNESCO) Biosphere Reserve and a Long-Term Ecological Research (LTER) network site. Niwot Ridge is an interflueve and was not glaciated during the Pleistocene. Soils are Cryochrepts and are approximately 2.0 m in depth over granitic parent material. Soil carbon (C) in the top 100 mm of soil ranges from 130 to 200 g kg^{-1}, and soil N pools range from 9 to 15 g kg^{-1} [*Burns*, 1980]. Vegetation at the experimental sites on Niwot Ridge is classified as transitional between moist and dry meadow, and the dominant plant species are the gramminoid *Kobresia myosuroides*, the forb *Acomostylis rossii* (alpine avens), and the gramminoid *Deschamsia caespitosa* (hair grass) in protected microsites. Climate is characterized by long, cool winters and a short growing season (1–3 months). Since 1951, mean annual temperature has been −3.8°C and annual precipitation has been 1,000 mm [*Williams et al.*, 1996b]. Surface water samples were collected from an ephemeral stream that drains Niwot Ridge and the experimental area during snowmelt runoff (Figure 1); this catchment area is about 8 ha. Additional surface water samples were collected from a seasonal stream draining the 8-ha Martinelli catchment about 400 m from the experimental area on Niwot Ridge (Figure 1). The Martinelli catchment has a poorly developed soil structure with little vegetation and is dominated by a late-melting snowpatch [*Caine*, 1989].

Methods

Nitrogen Transformations in Snow

N tracer experiments. Tracers were applied to the snow in 1994 and 1995 in an experimental effort to determine if NH_4^+ in snow is transformed to NO_3^- before release from the snowpack. In both years, three treatments were applied in separate 2 × 4 m plots: $^{15}NH_4Cl$, $K^{15}NO_3$, and a KCl control, with each plot separated by a distance of 5 m and located on the same elevational contour to prevent mixing of tracers caused by lateral flow of meltwater through the snowpack; the experimental area in 1995 was about 70 m from the experimental area of 1994 (Table 1, Figure 1). On April 19, 1994, and prior to surface melt, the NH_4^+ and NO_3^- salts were added as 10 atom percent ^{15}N at the rate of 5 g m^{-2}; an equivalent amount of KCl salt was added to the control plot. On April 27, 1995, and prior to surface melt, NH_4^+ and NO_3^- salts were added to separate plots as 99 atom % ^{15}N at the rate of 0.50 g m^{-2}; a similar amount of KCl salt was added to the control plot (Table 1). Tracers were dissolved in 2 L of distilled water and applied to the snow surface with a hand sprayer following the protocol of *Bales et al.* [1993]. The location of tracer addition to the snowpack was marked with threads placed on the snow surface. Lateral movement of water through snow was evaluated qualitatively by placing visible food-coloring dye on the snow surface after snowmelt and destructively sampling; these dye tracers were located about 50 m from the experimental plots and on the same elevational contour as the experimental plots (Figure 1). Duplicate samples were collected in all tracer plots, and mean values are presented.

Snow samples. Snow samples from both amended and natural snowpacks were collected for chemical content following the protocol of *Williams and Melack* [1991a]. Snow pits were dug weekly to biweekly from the snow surface to the ground at the downhill edge of the experimental plots. Snow samples were collected using beveled PVC tubes (50 mm diameter, 500 mm long) that had been soaked in 10% HCl and then rinsed at least five times with deionized water. Vertical, contiguous cores were collected, in increments of 200 to 400 mm depending on location of tracers, from the snow-air interface to the snow-ground interface. Snow was transferred from the cores into new polyethylene bags and transported 4 km to our analytical facilities the same day as collection. Snow pits were refilled after each sampling episode to minimize changes in melt rates and meltwater flow through snow.

Snowpack meltwater. Release of NH_4^+ and NO_3^- from the unamended snowpack was investigated in 1994 and 1995 by collecting snowpack meltwater in 1-m^2 snow lysimeters before contact with the ground following the protocol of *Bales et al.* [1993]. Meltwater flowed by gravity from the snow lysimeters about 5 m into a subnivian laboratory. Meltwater discharge was measured continuously in tipping buckets, conductance was measured continuously using an inline conductance meter, and grab samples were collected about daily and analyzed for NO_3^- and NH_4^+ concentrations. The lysimeter array, subnivian laboratory, and unamended snowpacks were located about 60 m NW of the amended snow plots (Figure 1).

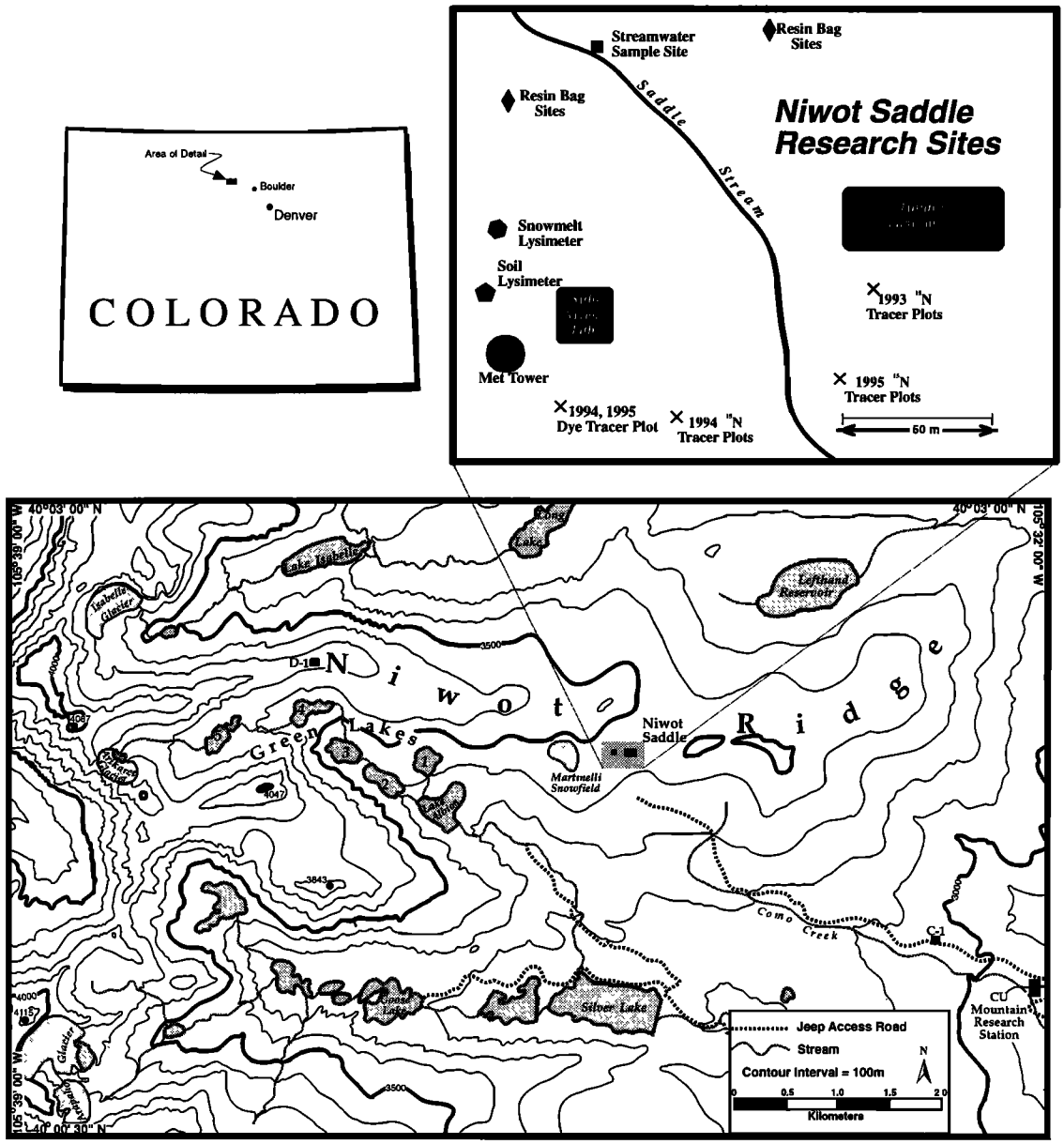

Figure 1. Topographic map of the Green Lakes Valley and Niwot Ridge and enlargement of the experimental study area on the Niwot Ridge saddle.

Nitrogen Transformations in Soils Under Snow

N tracer experiments. Interactions between inorganic N released from snow and underlying soils was investigated by collecting soil samples and analyzing for the ^{15}N content of total soil N in the N tracer plots in 1994 and 1995 (Table 1). Experimental plots were moved each year to insure there was no contamination of soils from the N tracer applied the previous year (Figure 1). An additional ^{15}N tracer experiment was conducted in 1993. The single treatment in 1993 consisted of applying $^{15}NH_4Cl$ to the snow surface prior to melt as 99 atom percent ^{15}N at a rate of 0.05 g m^{-2}. Soil samples under the snowpack in the tracer plots were analyzed for ^{15}N of total soil N at weekly to monthly time periods for all 3 years. At each sampling date, snow pits were dug to the soil surface, and three to five soil samples about 50 mm in diameter were collected from each tracer plot. Each soil sample was collected only from thawed soils; thaw depth under the snowpack generally varied from 30 to 80 mm. Soil surface temperature and thaw depth were taken manually at the bottom of snow pits using either an Omega temperature probe (±0.1°C) or a Tel-Tru thermometer (±0.2°C). Additionally, in 1993 surface litter samples were collected from a 50 × 50 mm area in the tracer plot concurrently with soil samples. Soil and litter samples were dried at

Table 1. Parameters for Tracer Experiments, 1993–1995

Year	Treatment	Atom Percent	Tracer Amount, g m^{-2}	Maximum Snow Depth, m
1993	$^{15}NH_4Cl$	99	0.05	0.8
1994	$^{15}NH_4Cl$, KCl, $K^{15}NO_3$	10	5.0	2.1
1995	$^{15}NH_4Cl$, KCl, $K^{15}NO_3$	99	0.5	1.3

60°C to constant weight, ground to 200 mesh, and subsampled for analysis by a C/N analyzer coupled to an isotope ratio mass spectrometer [*Burke et al.*, 1990]. Recovery of ^{15}N tracer in the amended soil plots was calculated as the change in ^{15}N content of soil or litter total N before and after melt multiplied by the amount of total soil or litter N.

Subnivial soil N. Mobile inorganic N moving through the top 50 mm of unamended and snow-covered soil was measured with paired ion-exchange resin bags, following the protocol of *Brooks et al.* [1996]. The paired resin bags were installed at the soil surface and at a depth of 50 mm at 24 sites that ranged from shallow to deep snowpack conditions. Resin bags were installed in the autumn when snow began accumulating and collected as sites became snow free. At the soil surface, resin bags were placed in 35-mm-diameter acid-washed PVC tubes which extended 30 mm above the soil into the snowpack and were open at the top but isolated from the soil by silicone sealant. Companion bags were buried at each site at a depth of 50 mm in 35-mm-diameter acid-washed radiator hose. These tubes were open both at the top and bottom and designed to measure inorganic N moving through the top 50 mm of soil. Net production of mobile, inorganic N in snow-covered soils was calculated as the difference between surface and buried resin bags at each of the 24 sites. Resin bags (16–50 mesh) contained 20 mL (wet volume) of mixed cation and anion exchange resins loaded with H^+ or OH^- with a total exchange capacity of 0.57 meq mL^{-1} [*Binkley and Matson*, 1983]. In 1994 an index of subnivial N cycling was estimated from the change in KCl-extractable N over time. At each sampling date in 1994 when N tracers were sampled in snow pits, snow pits in the control plots were dug to the soil surface, and five soil samples were collected from thawed soils to be analyzed for KCl-extractable NO_3^- and NH_4^+ following the protocol of *Brooks et al.* [1996].

Soil and Surface Water Inorganic N

Zero-tension soil lysimeters were installed on September 12, 1994, about 2 m from the snow lysimeters in a duplicated array at depths of 100, 300, and 500 mm, following the protocol of *Litaor* [1993]. They were constructed of halved 400-mm sections of PVC pipe 250 mm in diameter, capped on one end, and plumbed to drain into a 1-L storage bottle connected to the surface with tygon tubing. After construction, lysimeters were rinsed copiously with distilled water, soaked in distilled water for 24 hours, rinsed again, and then installed horizontally into the side wall of a soil pit which was immediately refilled; NH_4^+ and NO_3^- concentrations in rinse water were below detection limits. Zero-tension soil lysimeters were sampled about weekly starting when free water became available during snowmelt in late June 1995, providing about 9.5 months of equilibration time for the soil lysimeters. Surface waters of the Saddle and Martinelli streams were collected as grab samples at daily to weekly sampling frequency. Water samples were collected in polyethylene bottles soaked with DI water overnight and then rinsed copiously five times; bottles were further rinsed three times with sample water at the time of collection. Samples were transported the same day as collection to our wet chemistry laboratory and treated the same as melted snow samples.

Laboratory Analyses

All water and snow samples were analyzed for *p*H, acid-neutralizing capacity (ANC), conductance, major ions, and reactive silicate (Si). Chemical analyses followed this protocol for all water samples including snow samples. Snow samples were stored frozen (−20°C) for 1–2 months until analysis. Blank samples of distilled, deionized water were stored in the bags for the same amount of time and showed no significant contamination from the bags [*Williams et al.*, 1992]. Snow samples were placed in covered polyethylene buckets and melted at room temperature. Ammonium was determined colorimetrically within 24 hours of melting for snow samples and after collection of water samples, on a Lachat flow injection analyzer using a phenolate reaction enhanced by nitroprusside; detection limit was 9.8 $\mu g\ N\ L^{-1}$ (0.7 $\mu eq\ L^{-1}$) and precision was 2.7%. ANC was also measured immediately after melting for snow or return to the laboratory for water samples using the Gran titration technique. Subsamples were immediately filtered through prerinsed (300 mL), 47-mm Gelman A/E glass fiber filters with an approximately 1-μm pore size. Filtered samples were stored in the dark at 4°C for subsequent analyses within 1 to 4 weeks. Anions were measured using ion chromatography (Dionex DX 500) employing chemical ion suppression and conductivity detection. The detection limit for NO_3^- was 1.4 $\mu g\ N\ L^{-1}$ (0.1 $\mu eq\ L^{-1}$), and precision was 1.5%. Snow samples from the ^{15}N tracer experiments were immediately refrozen until diffused for isotopic N analysis by mass spectrometry.

Soil samples were processed for NH_4^+ and NO_3^- within 12 hours of returning from the field. Fresh soils were sieved and homogenized using a 2-mm sieve. Subsamples of this soil were extracted with 2N KCl (1:5, weight: volume) by shaking at 250 rpm for 60 min and allowing to sit at room temperature for 18 hours. These extracts were filtered through prerinsed (300 mL distilled water) Whatman #1 filter paper, and aliquots were analyzed on the Lachat autoanalyzer. Ammonium was analyzed as in snow; NO_3^- was analyzed using a sulfanilamide reaction following reduction to nitrite on a cadmium column. Ion exchange resin bags were air dried, and inorganic N extracted as in soil samples.

We followed the protocol developed by *Brooks et al.* [1989] for sequential diffusion of NH_4^+ and NO_3^- for atom percent ^{15}N of snow samples. Snow was melted and placed in a closed container with MgO added to buffer the solution to a *p*H of approximately 10.5. Ammonium was volatilized to NH_3, which was diffused on a filter paper disk acidified with $KHSO_4$ and suspended above the solution on a stainless steel wire. After a 6-day incubation, the filter paper was removed, dried in a desiccator, and wrapped in a tin capsule for analysis. After a 24-hour period during which containers with melted snow were left open to allow any remaining NH_3 to volatilize, a fresh acidified paper disk was added to the container, Devarda's alloy was added to reduce NO_3^- to NH_4^+, and the containers were closed and incubated for an additional 6-day period and then treated as above. The diffusion technique was designed to prepare aliquots of 20 mL containing 60 ± 10 μg of inorganic N. Concentrations of inorganic N in many snow samples were less than this amount; these samples were spiked with a known atom percent ^{15}N (0.400) to bring the inorganic N content up to the acceptable range. The recovery of N after diffusion was 80% for standards, 85% for NO_3^-, and 83% for NH_4^+. The small error in atom percent ^{15}N for NH_4^+ and NO_3^- diffused onto the filter paper discs has been shown to cause isotopic fractionation on the order of 1 to 2% [*MacKown et al.*, 1987] and does not alter the conclusions drawn in this paper.

The isotopic content of N was analyzed at the Agricultural

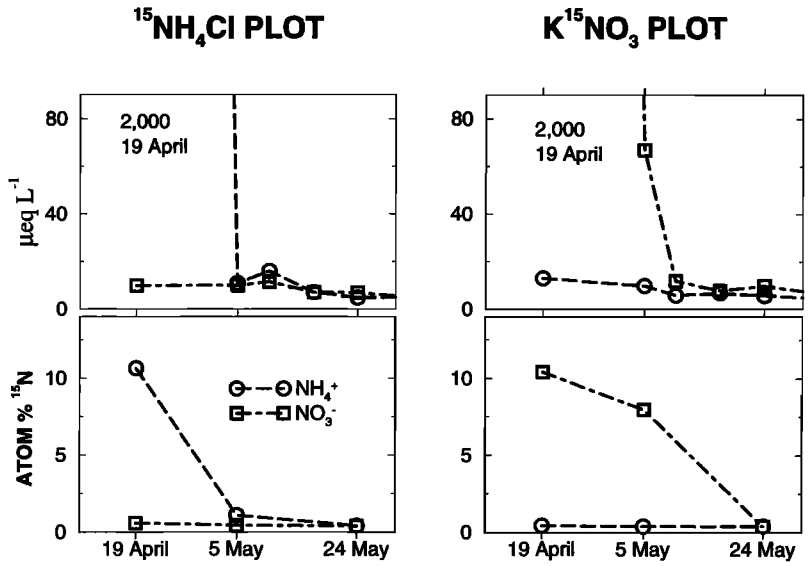

Figure 2. Volume-weighted mean concentrations of NH_4^+ and NO_3^- and atom percent ^{15}N values of NH_4^+ and NO_3^- in snow from $^{15}NH_4Cl$ and $K^{15}NO_3$ experimental plots in 1994 ($n = 2$). Ammonium concentrations in the ammonium treatment plot and NO_3^- concentrations in the nitrate treatment plot were both greater than 2,000 μeq L^{-1} on April 19 and are off the scale of this figure.

Research Service/USDA in Fort Collins using an automated C/N analyzer connected to an isotope ratio mass spectrometer [*Burke et al.*, 1990]. Analytical precision for any individual mass spectral analysis of samples containing near normal ^{15}N abundance was ±0.0005 atom percent ^{15}N. As an example of analytical reproducibility for ^{15}N content of soil samples shown in Figure 6, atom % ^{15}N (mean and standard deviations) for five replicate soil samples collected in June 1994 was 0.3646 ± 0.0005 for the control plot, 0.3640 ± 0.0002 for the NH_4^+ plot, and 0.3641 ± 0.0003 for the NO_3^- plot.

Results

Nitrogen Transformations in Snow

N tracer experiments. Maximum snow depth in the three treatment plots in 1994 varied from 2.05 to 2.15 m and was measured during the last week in April. Tracers were applied to the snow surface on April 19. Surface melt started about May 1, and the snowpack became isothermal at 0°C about May 3. There were no rain-on-snow events and little snowfall during the experimental period in 1994. The melt rate in 1994 was much faster than normal, as clear, warm sunny days resulted in a consistent positive energy balance [*Williams et al.*, 1996b]. Because of the very fast melt rate, we were unsure of the vertical location of the tracer in the snowpack and therefore bulked snow samples into a single integrated snow sample from each snowpit. Volume-weighted mean concentrations for both NO_3^- and NH_4^+ in the control pit on April 19 were about 10 μeq L^{-1}. In contrast, NH_4^+ concentrations in the ammonium treatment plot and NO_3^- concentrations in the nitrate treatment plot were both greater than 2,000 μeq L^{-1} on April 19 and then rapidly decreased with the initiation of snowmelt on about May 1 (Figure 2).

The increase of NH_4^+ and NO_3^- concentrations in treatment plots of more than 2 orders of magnitude compared to NH_4^+ and NO_3^- concentrations in control plots should push the system toward nitrification of NH_4^+ or reduction of NO_3^- if these processes are important in seasonal snowpacks. On May 5, NH_4^+ concentrations in the ammonium treatment plot were only slightly elevated above control plot concentrations at 12 μeq L^{-1} while NO_3^- concentrations in the nitrate treatment plot of 65 μeq L^{-1} were about 6-fold that of control concentrations. By May 24, tracer concentrations in both treatment plots were at background amounts of about 8 μeq L^{-1}. These concentration patterns suggest that the tracers either moved rapidly through the snowpack to underlying soils or moved laterally through the snow and out of the sampling area.

If the added NH_4^+ was nitrified to NO_3^-, we should find NO_3^- concentrations in the ammonium plot elevated above NO_3^- concentrations in the control plot, and, similarly, if the added NO_3^- is reduced to NH_4^+ we should find NH_4^+ concentrations in the nitrate plot elevated above NH_4^+ concentrations in the control plot. In both treatment plots, concentrations of the nontracer N species were the same as in the control plot, suggesting no transformations of inorganic N in the snowpack. By similar reasoning, increased atom percent ^{15}N should be found in nontracer inorganic N species if oxidation or reduction processes of N are important in snow.

The snowpack was sampled on three dates for the ^{15}N content of NO_3^- and NH_4^+: prior to the initiation of snowmelt on April 19, after the initiation of snowmelt on May 5, and near the end of snowmelt on May 24 (Figure 2). The atom percent ^{15}N in controls for both ammonium and nitrate tracer plots was about 0.400, the spiked value of N during diffusions. On all sampling dates the atom percent ^{15}N content of the nontracer N species was the same as controls, about 0.400. The ^{15}N content on the first sampling date, April 19, was about 10 atom percent ^{15}N for NO_3^- in the nitrate plot and for NH_4^+ in the ammonium plot (Figure 2). On May 5, $^{15}NH_4^+$ was 1.097 atom percent ^{15}N in the ammonium plot and $^{15}NO_3^-$ was 7.97 atom percent ^{15}N in the nitrate plot, compared to 0.400 atom percent ^{15}N for controls, indicating that most of the tracer species in each snowpit was from the applied tracers. On May 24 the atom percent ^{15}N for all N species in all pits was the same as

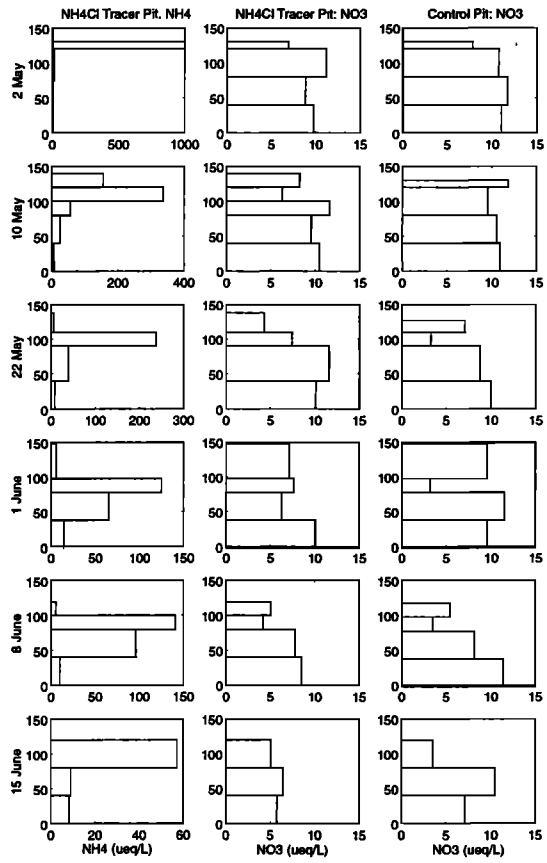

Figure 3. A time series of NH_4^+ and NO_3^- concentrations in snow as a function of snow depth, from May 2 through June 15, 1995. The first column is NH_4^+ concentration in the $^{15}NH_4Cl$ tracer snowpit, the second column is NO_3^- concentration in the $^{15}NH_4Cl$ snowpit, and the third column is NO_3^- concentration in the control snowpit. The x axis is concentration (μeq L^{-1}), and y axis is snow depth (centimeters above snow-ground interface); note that the x axis range changes with date for NH_4^+ in the NH_4Cl snow pit. There was no significant difference in NO_3^- concentrations between NH_4Cl and control snow pits ($p = 0.41$, $n = 25$).

that for the controls. Again, these results suggest that there was no oxidation or nitrification of NH_4^+ and that NO_3^- was not reduced in the snowpack. The ^{15}N values for tracer N species are consistent with concentration values that show no transformations of inorganic N in the snowpack.

A similar tracer experiment was attempted in 1995, with the difference that snow samples were not analyzed for ^{15}N content. The 1995 melt season was much different than that of 1994. Maximum snow depth when the tracer was applied on April 27 was about 130 cm. New snow fell intermittently throughout the experiment and the tracers were generally buried 40 to 50 cm below the snow surface (Figure 3). Meltwater began infiltrating from the snow surface after May 2, and the snowpack became isothermal at 0°C between May 10 and 22. In contrast to 1994, NH_4^+ added to the ammonium tracer plot on April 27, 1995, persisted in the snowpack through the last sampling date on June 15, 1995 (Figure 3). Ammonium concentrations in the tracer layer decreased from 1400 μeq L^{-1} on May 2 to 57 μeq L^{-1} on June 15 (Figure 3). After the initial snow pit was sampled on May 2, NH_4^+ concentrations below the tracer layer were generally above background concentrations of NH_4^+ as infiltrating meltwater slowly transported the NH_4^+ tracer toward the base of the snowpack. On June 15 the thread marking the tracer application was on the snow surface and sampling was discontinued.

Nitrate concentrations in the ammonium snow pit showed no response to the NH_4^+ augmentation. Nitrate concentrations for all layers on all dates in the NH_4Cl snowpit ranged from 4.2 to 11.6 μeq L^{-1} with a mean of 7.8 $\pm$ 2.9 μeq L^{-1}, similar to NO_3^- concentrations in the control pit, which ranged from 3.2 to 11.8 μeq L^{-1} with a mean of 8.4 $\pm$ 2.9 μeq L^{-1} (Figure 3). A simple t test showed that there was no significant difference between NO_3^- concentrations in the control snow pit and the NH_4Cl snow pit ($p = 0.41$, $n = 25$). Ammonium in the KNO_3 plot showed a similar pattern of no transformation from NO_3^-, with no significant difference between NH_4^+ in the KNO_3 plot and the control plot ($p = 0.38$, $n = 25$). These results are consistent with the 1994 experiments and suggest that transformations of NH_4^+ and NO_3^- in the snowpack are not important processes.

Ammonium in the ammonium tracer plot in 1995 moved through the snow pit at the same rate as Cl^- (Figure 4). Chloride was chosen as a tracer because it undergoes few if any chemical reactions or biological transformations and thus acts as a conservative tracer of water movement through snow. A simple linear regression analysis between Cl^- and NH_4^+ for all snow layers with NH_4^+ concentrations greater than natural levels of about 10 μeq L^{-1} shows that NH_4^+ was significantly related to Cl^- ($NH_4^+ = 3.73 + 0.96\ Cl^-$, $r^2 = 0.99$, $p \ll 0.0001$, $n = 15$). The y intercept of 3.73 was not significantly different than 0 ($t = 0.33$, $p = 0.74$). The slope of 0.96 for this line is slightly less than 1, indicating that there may be a slight loss of NH_4^+ relative to Cl^-. A similar test, but one for all snow layers with Cl^- concentrations greater than 10 μeq L^{-1}, gives similar results ($r^2 = 0.99$, $p \ll 0.0001$, $n = 15$). The high correlation between NH_4^+ and Cl^- concentrations in layers with tracer salt strongly indicates that the rate and magnitude of NH_4^+ transport through the snowpack is the same as Cl^-,

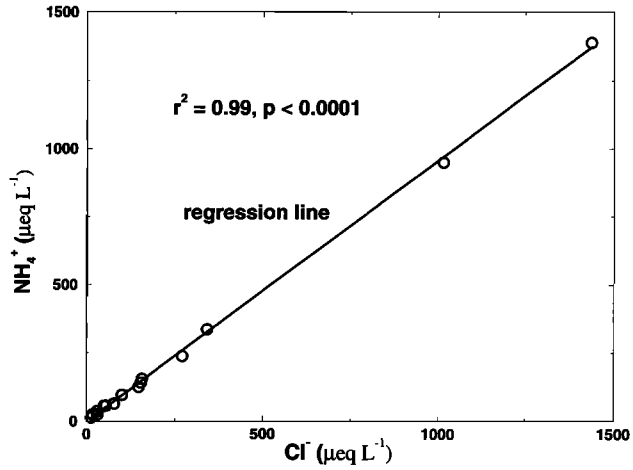

Figure 4. Regression plot of Cl^- and NH_4^+ concentrations in the NH_4Cl snowpit from 1995 for all layers and all dates with NH_4^+ concentrations greater than background levels (>10 μeq L^{-1}). Ammonium concentrations were significantly related to Cl^- concentrations, indicating that NH_4^+ was transported through the snowpack at the same rate as a conservative tracer such as Cl^- ($r^2 = 0.99$, $p < 0.0001$, $n = 15$).

again suggesting that within-snowpack transformations of NH_4^+ are not important.

Snowpack meltwater. The release of NH_4^+ and NO_3^- from a natural snowpack in 1995 also provides no indication of nitrification within the snowpack. A time series of NH_4^+ and NO_3^- concentrations in meltwater before contact with the ground shows that these solutes were released as an ionic pulse (Figure 5). The maximum concentration of NH_4^+ in meltwater was 130 μeq L^{-1} compared to initial bulk snowpack concentrations of 6.2 μeq L^{-1}, a concentration factor of 21. The maximum concentration of NO_3^- in meltwater showed a similar pattern, with a maximum meltwater concentration of 210 μeq L^{-1}, about 20 times that of initial bulk snowpack concentrations of 10.6 μeq L^{-1}. Concentrations of both solutes then decreased rapidly with time. A simple linear regression analysis (Figure 5) shows that NO_3^- concentrations in meltwater were highly correlated with NH_4^+ concentrations ($NO_3^- = 4.42 + 1.5\ NH_4^+$; $r^2 = 0.98, p \ll 0.001, n = 20$). Nitrate concentrations in meltwater were 1.5 times NH_4^+ concentrations; similarly, NO_3^- concentrations in bulk snow were 1.7 times NH_4^+ concentrations. Furthermore, the NH_4^+: NO_3^- molar ratio in snow of 0.6 was similar to the molar ratio in spring deposition of 0.6 at the colocated NADP site. Snow lysimeter results from 1994 show a lower magnitude ionic pulse but pattern similar to that of 1995 [*Williams et al.*, 1996b]. These results suggest that NO_3^- and NH_4^+ release from the seasonal snowpack was conservative and that nitrification of NH_4^+ or reduction of NO_3^- did not occur.

Nitrogen Transformations in Soils Under Snow

N tracer experiments. Our original hypothesis with the addition of $^{15}NH_4Cl$ to snow in 1993 was that the isotopically labeled $^{15}NH_4^+$ would be retained in litter after release from the snowpack. Maximum snowpack depth in 1993 was 0.80 m and occurred at the time tracer was applied (Table 1). However, the ^{15}N content of litter at all sampling dates was not significantly different than the control content of 0.3610 atom percent N at $\alpha = 0.05$, and our original hypothesis was not supported (Figure 6). In contrast, the ^{15}N value of soil gradually increased throughout the snowmelt season, reaching

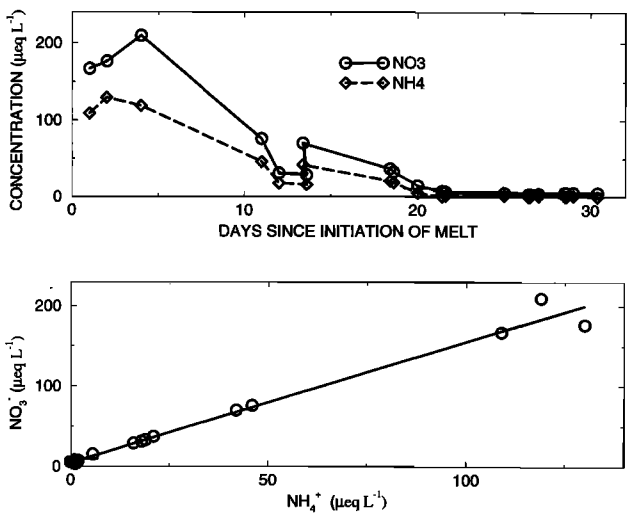

Figure 5. A time series of NH_4^+ and NO_3^- concentrations in meltwater before contact with the ground (top) and regression analysis between the two solutes (bottom).

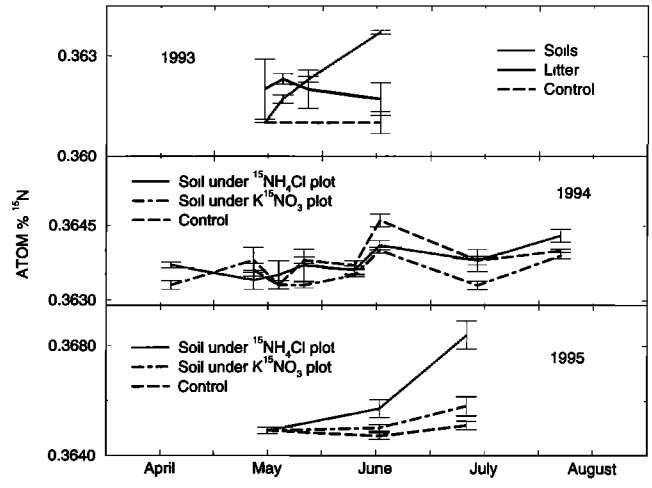

Figure 6. Atom percent ^{15}N values and standard error for total soil N under alpine snowpacks to which isotopically labeled N was applied (n ranges from 3 to 5 per sample). The tracer in 1993 was $^{15}NH_4Cl$, and samples were analyzed for total soil N and litter in treatment and control plots. In both 1994 and 1995, $^{15}NH_4Cl$, $K^{15}NO_3$, and KCl (control) were added in separate plots and total soil N was analyzed for ^{15}N.

0.3637 atom percent N on June 15, and was significantly higher than the control value ($p < 0.0001$) on that date. About 82% of the ^{15}N tracer added to snow was recovered in soils. The almost complete recovery of the isotope tracer in soils in 1993 indicates that most snowmelt infiltrates soils and NH_4^+ released from storage in the seasonal snowpack is assimilated by soil biota and/or adsorbed on soil exchange sites. An interesting result is that the coefficient of variance (CV) for total soil ^{15}N decreased from 32% to 13% with time, suggesting a more homogeneous distribution of labeled N in soils over time. A possible explanation for this pattern of decreasing variance in ^{15}N is rapid cycling of the labeled N by an active microbial population.

The success of our 1993 experiment encouraged us to try the more elaborate tracer experiment in 1994 in a different location so that there would be no contamination from the 1993 experiment. Litter samples were not collected, on the basis of our results from 1993. The control plot of ^{15}N in soil in 1994 was 0.3638 atom percent N, higher than the 0.3610 atom percent N in soil from the control plot in 1993. In 1994, there was no significant change at the $\alpha = 0.05$ level in the ^{15}N content of soils in either the NH_4^+ or NO_3^- tracer plots relative to controls (Figure 6). We believe that the lack of recovery of ^{15}N in soils in 1994 was because of lateral flow paths within the deeper snowpack. Dye tracers applied to the top of the snowpack after snowmelt about 50 m from the tracer plots showed that the dye penetrated to a depth of only centimeters in the snow before moving laterally on the order of tens of meters. Our time series measurements of inorganic N concentrations in the snowpack of our experimental plots are consistent with the lateral transport of NH_4^+ and NO_3^- tracers away from the experimental plots (Figure 2). Lateral flow within the snowpack and transport away from our sampling plots is a possible explanation for the lack of recovery of ^{15}N in soils in 1994.

We repeated the 1994 experiment in 1995 with lower sampling frequency for soils, moving the location again to avoid contamination from the previous tracer experiments. In con-

Table 2. Inorganic N Amounts in Snow*, in Soil Surface Resin Bags, and in Buried Soil Resin Bags, 1994

	NO_3^-, mg N m^{-2}	NH_4^+, mg N m^{-2}	TIN, mg N m^{-2}	Percent NO_3^-
Snow	300	85	385	78
Surface	276 ± 59	110 ± 18	387	71
Soil	904 ± 240	266 ± 21	1171	77
Mobile N	628 ± 257	156 ± 32	784 ± 274	80

*Snow values are from *Williams et al.* [1996b].
Amounts for resin bags are mean and standard error (n = 22). TIN, total inorganic N (NO_3^- + NH_4^+).

trast to 1994, in 1995 the tracers persisted in the snowpack throughout the snowmelt season (Figures 2 and 3). The control plot of ^{15}N in soil in 1995 was 0.3649 atom percent ^{15}N, higher than the atom percent ^{15}N in either 1994 or 1993, reflecting differences in natural ^{15}N abundance in different plots and different years. The ^{15}N content of soil gradually increased throughout the snowmelt season in both plots, on June 9 reaching 0.3684 atom percent N in the NH_4^+ plot and 0.3658 atom percent N in the NO_3^- plot (Figure 6). The ^{15}N content in the ammonium plot was significantly greater than in the control plot (p = 0.02), while the nitrate plot was not significantly different than the control plot (p = 0.10). Recovery rates of tracers were low, 5% in the ammonium plot and 2% in the nitrate plot. The ^{15}N enrichment in the NH_4^+ plot is consistent with the results from 1993 and indicates that NH_4^+ released from the snowpack can be retained in soils. The slight ^{15}N enrichment in the NO_3^- tracer plot indicates that some NO_3^- released from the snowpack may be retained in soils.

The natural abundance of ^{15}N in soils at Niwot is depleted compared to many other soils. The natural abundance of nitrogen is expressed in the conventional delta (δ) notation as parts per mil, defined as

$$\delta^{15}N = \frac{^{15}N/^{14}N(\text{sample}) - {}^{15}N/^{14}N(\text{standard})}{^{15}N/^{14}N(\text{standard})} \times 1000,$$

where the standard is atmospheric N_2 (0.3663 atom % ^{15}N). The $\delta^{15}N$ values for control soils at Niwot Ridge from 1993 to 1995 were strongly negative, ranging from −12 to −2 (n = 45). Most soils are enriched in ^{15}N compared to atmospheric N_2, for example, mean $\delta^{15}N$ was +9.2 ± 2.1 for 124 agricultural soils in 20 states [*Shearer et al.*, 1978]. However, unpublished results from alpine soils in the Snowy Range of southern Wyoming show $\delta^{15}N$ values similar to those of Niwot Ridge, ranging from −4 to −7 (A. Mosier, Agricultural Research Service, Fort Collins, Colorado, personal communication, 1995). Nitrogen cycling in alpine soils may be much different than in many other ecosystems.

Subnivial soil N. Resin bag results show that NO_3^- was much more mobile than NH_4^+ in subnivial soils (Table 2). Twenty-two of the twenty-four pairs of resin bags were recovered. Nitrate (276 mg N m^{-2}) and NH_4^+ (110 mg N m^{-2}) amounts in surface resin bags were similar to average NO_3^- (300 mg N m^{-2}) and NH_4^+ (85 mg N m^{-2}) amounts in the seasonal snowpack at maximum accumulation. However, NO_3^- in soil resin bags (904 mg N m^{-2}) was significantly higher than NO_3^- in surface resin bags (p = 0.01), and NH_4^+ in soil resin bags (266 mg N m^{-2}) was significantly higher than NH_4^+ in surface bags (p < 0.0001). Mobile inorganic N produced by subnivial processes was calculated as the difference between soil and surface resin bags. The mobile NO_3^- amount of 628 mg N m^{-2} was significantly greater than the mobile NH_4^+ amount of 156 mg N m^{-2} (p = 0.05). Nitrate accounted for 80% of the mobile soil inorganic N of 784 mg N m^{-2}.

Measurements in 1994 of KCl-extractable inorganic N in soils from underneath snow and during the growing season provide an index of temporal changes in soil nitrogen cycling and suggest that subnivial N dynamics were of similar or greater magnitude compared to the growing season. Both soil NH_4^+ and NO_3^- amounts were highest under the soil prior to the initiation of snowmelt, then decreased under snow after the initiation of snowmelt and were lowest during the growing season (Figure 7). The 64% decrease in soil NO_3^- from 109 mg N m^{-2} prior to snowmelt on April 19 to 39 mg N m^{-2} after the initiation of snowmelt on May 10 was significant (p = 0.006), while the 21% decrease in NH_4^+ from 1060 mg N m^{-2} prior to snowmelt on April 19 to 831 mg N m^{-2} after the initiation of snowmelt was not significant (p = 0.193). It is worth noting that soil inorganic NH_4^+ amounts under snow were higher than resin bag amounts while soil inorganic NO_3^- amounts were lower than resin bag amounts (Table 2), consistent with the production of mobile soil NO_3^- which may be flushed by infiltrating snowmelt into surface waters.

Soil and Surface Water Inorganic N

On the basis of the results from 1994, we began collecting soil water samples for inorganic N in 1995. Nitrate was found in soil solution and NH_4^+ was below detection limits. We began collecting soil water samples from the zero-tension soil lysimeters in 1995 when snow depth decreased to about one m. Ammonium concentrations at all depths for all sampling dates were near or below detection limits. Nitrate concentrations at all depths on the first sampling date were about 50 μeq L^{-1} and then decreased with time (Figure 8). At the 100- and 300-mm depths, concentrations decreased to near detection limits after snow melt. In contrast, concentrations at 500 mm increased after reaching a low of 26 μeq L^{-1} on July 6. ANC and Si concentrations ranged from 59 to 151 μeq L^{-1}, showing

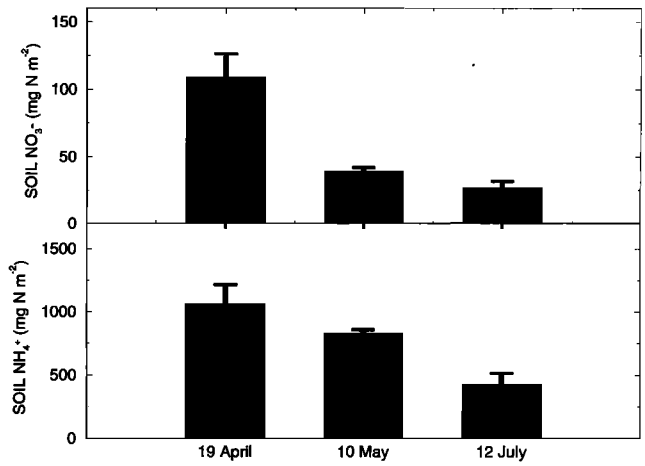

Figure 7. A comparison of KCl-extractable NH_4^+ and NO_3^- (mean and standard error) from soil cores in 1994, under the snowpack and before the initiation of snowmelt on April 19 (n = 7), under snow and after the initiation of snowmelt on May 10 (n = 3), and during the snow-free growing season, on July 12 (n = 9).

no pattern with either time or depth. These high NO_3^- values from zero-tension lysimeters during and immediately following snowmelt are similar to those reported by *Litaor* [1993] for the Green Lakes Valley and consistent with NO_3^- in buried resin bags (Table 2).

In contrast to the large concentrations of NO_3^- in soil solution, NO_3^- concentrations in surface waters collected 20 m away remained near detection limits throughout snowmelt (Figure 8). Nitrate concentrations in the ephemeral stream draining the experimental area were generally about 1 μeq L^{-1}, with a maximum of 2.5 μeq L^{-1} (Figure 8). However, NO_3^- concentrations in the stream draining the Martinelli catchment about 400 m SW of the Niwot saddle stream had a maximum concentration of near 60 μeq L^{-1} at the initiation of snowmelt runoff and then gradually decreased over time (Figure 8).

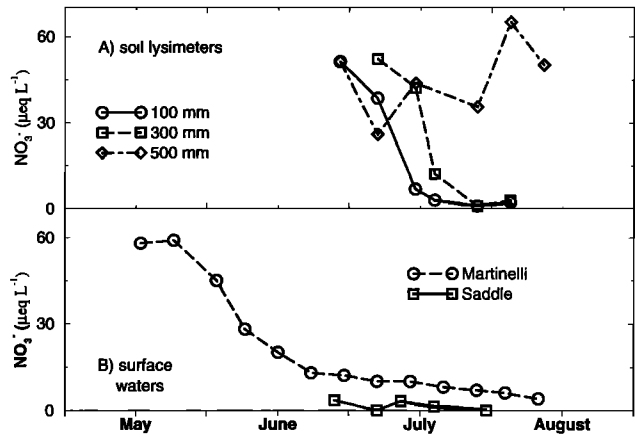

Figure 8. Nitrate concentrations in (a) zero-tension soil lysimeters and (b) surface streams during snowmelt runoff in 1995.

Discussion

Transformation of NH_4^+ to NO_3^- in seasonal snowpacks of high-elevation areas does not appear to be an important process. Our results from both natural and amended snowpacks show no significant changes in NH_4^+ or NO_3^- amounts prior to release from snow and in meltwater. D. H. Campbell et al. (United States Geological Survey, unpublished data, 1995) have sampled NH_4^+ and NO_3^- in snow meltwater before contact with the ground at the Loch Vale watershed in Rocky Mountain National Park and found no significant difference between meltwater concentrations and snowpack concentrations of either NH_4^+ or NO_3^-. Furthermore, *Brooks et al.* [1993] investigated biological activity in seasonal snow for two high-elevation sites in the Rocky Mountains and report insufficient microbial populations to cause significant changes in the inorganic N concentrations of snow. *Williams and Melack* [1991b] also report that in the Sierra Nevada, NH_4^+ concentrations in snowpack meltwater before contact with the ground were consistent with the storage and release of NH_4^+ from seasonal snow in the form of an ionic pulse.

Ammonium released from snow appears to be immobilized in underlying soils. *Preston et al.* [1990] report a 95% total recovery rate and 81% recovery in soils for $^{15}NH_4^+$ applied to snow in a forested ecosystem in British Columbia with much lower recovery rates for $^{15}NO_3^-$, similar to our results. The lack of NH_4^+ in soil waters at Niwot Ridge is consistent with retention of NH_4^+ by soils from infiltrating snowmelt. *Williams et al.* [1993] have shown that up to 100% of the first fractions of snowmelt runoff infiltrates soils before contributing to surface flow, presenting the opportunity for NH_4^+ to be immobilized through a combination of physical and biological processes in soils. *Kendall et al.* [1995] have analyzed NO_3^- from surface waters for the isotopic content of both nitrogen and oxygen to discriminate atmospheric and basin contributions of NO_3^- to surface waters in the Rocky Mountains and suggest that much of the NO_3^- in surface waters appears to be N from atmospheric deposition that has been assimilated and mineralized in the time period of months to a year. Our results suggest that NH_4^+ released from snow and retained in soils may be a potential source of stream water NO_3^- in subsequent years.

The natural ^{15}N abundance in soils at Niwot is consistent with atmospheric deposition of N being a very important component of the N cycle in these alpine soils. *Vitousek et al.* [1989] report that nonnitrogen fixing plants in Hawaii had negative $\delta^{15}N$ values ranging from -10.1 to $+0.7$, similar to values in Niwot soils of -12 to -2. Further, soils at the Hawaiian location showed a gradient in $\delta^{15}N$ abundance that corresponded with foliar $\delta^{15}N$ values, with negative values in the youngest soils which became enriched and positive with increasing age of soils. *Vitousek et al.* [1989] suggest that inputs of ^{15}N-depleted nitrogen from precipitation coupled with very low nitrogen outputs cause the strongly negative $\delta^{15}N$ values of early successional sites in Hawaii. At Niwot the strongly negative $\delta^{15}N$ values of soil suggest that snowpack release of N is an important component of soil N and supports the suggestion of *Kendall et al.* [1995] that much of the NO_3^- in surface waters is from atmospheric deposition of N that has been assimilated, ammonified, and nitrified before transport to streams.

Nitrogen cycling in snow-covered soils of alpine ecosystems appears to be very dynamic compared to the growing season. Previous research at Niwot Ridge [*Fisk and Schmidt*, 1995] and in the Sierra Nevada [*Williams et al.*, 1995] has shown that net mineralization rates over the entire snow season from first accumulation to meltout are low to negative. At Niwot Ridge large amounts of KCl-extractable inorganic N were produced in snow-covered soils prior to snowmelt in 1994. Soil inorganic N then decreased in snow-covered soils after the initiation of snowmelt and was lowest during the growing season. These results are consistent with previous experiments conducted at Niwot Ridge in 1993 which showed high rates of net mineralization under the snow and prior to snowmelt that ranged from 2 to 6 g N m^2, followed by immobilization after the initiation of snowmelt [*Brooks et al.*, 1996]. In contrast, net mineralization during the summer at Niwot Ridge is much lower, at about 1 g N m^2 [*Fisk and Schmidt*, 1995].

Nitrification of mineralized N under seasonal snow in alpine ecosystems prior to snowmelt also appears to be an important process. After subtracting inorganic N released from snow, soil resin bags in 1994 collected more NO_3^- than NH_4^+ (Table 2), in contrast to much larger amounts of KCl-extractable NH_4^+ in soil cores (Figure 7). Resin bags in soils sample the soil solution passing through resin bags, with little contribution from diffusion [*Binkley*, 1984]. Moreover, *Binkley* [1984] reports that in forest soils NO_3^- mobility exceeded that of NH_4^+ by about 30-fold. Our resin bag results are consistent with greater NO_3^- mobility in soil solution compared to NH_4^+ and are indicative of high rates of nitrification under the snowpack. Ammonifi-

cation and nitrification under snow and prior to the initiation of snowmelt may be much larger than during the summer season in alpine ecosystems.

The factors controlling the balance among ammonification, nitrification, and immobilization in subnivian soils are poorly understood. Freeze/thaw processes in the fall most likely contribute to high rates of ammonification and nitrification under snow. In a survey of freezing and its effect on chemical and biological properties of soils, *Edwards and Cresser* [1992] provide evidence that freezing increases nitrification. Increased freeze/thaw activities may partially explain the high amounts of NO_3^- in buried resin bags (Table 2). Cell lysis caused by freeze/thaw processes may release labile carbon and N compounds from ruptured cell membranes, providing substrate for microbial activity. Measurements of high rates of CO_2 flux under snow by *Sommerfeld et al.* [1993] and by *Brooks et al.* [1996] provide evidence that microbial activity is an important process in snow-covered soils. *Schimel et al.* [1995] have proposed a similar process of microbial activity to account for a flush of mineral N as Arctic soils thaw.

The high amounts of KCl-extractable inorganic N in subnivian soils prior to the start of snowmelt may be in part because vegetation is dormant and assimilation of N by vegetation lags behind gross N mineralization. However, once snowmelt starts, assimilation by vegetation and increases in microbial biomass may cause immobilization of N and explain the decreases we report in soil inorganic N. *Salisbury* [1985] found several subalpine and alpine herbaceous species that either remain green all winter or turn green prior to melt-out, including *Acomastylis rossii*, *Ranunculus adoneus*, and *Erythronium grandiflorum; Kimball et al.* [1973] were able to document the synthesis of chlorophyll under snow. Furthermore, *Mullen and Schmidt* [1993] report that the snow buttercup *Ranunculus adoneus* begins N uptake under snow by utilizing a preexisting root system that is heavily infected with a "dark septate" fungi (see work by *Walker et al.* [1996] for a review of this subject). Vegetation and soil dynamics under snow, particularly after the initiation of snowmelt and before melt-out, need much more investigation.

A possible explanation for the large amounts of NO_3^- in surface waters of the Martinelli catchments and low amounts of NO_3^- in the stream draining the Niwot saddle may be differences in soil development and vegetation extent. Soil processes, particularly microbial activity, may be producing large amounts of NO_3^- under snow in both catchments. However, the greater soil and vegetation development at Niwot Ridge may result in biological assimilation of NO_3^-. At Niwot Ridge, NO_3^- may be somewhat mobile in the soil solution but be assimilated by vegetation before subsurface water contributes to streamflow. At the Martinelli catchment the reduced amount of soil and vegetation may tip the balance such that nitrification exceeds assimilation and NO_3^- in subsurface water is transported to surface streams by infiltrating meltwater. Furthermore, reduced levels of primary production at the Martinelli catchment may favor nitrification by reducing labile carbon substrates for microbial activity. The suggestion that surface waters are isolated from the pedosphere in alpine catchments [*Caine and Thurman*, 1990] needs to be revisited.

Conclusions

Our results show that nitrification of NH_4^+ in the seasonal snowpack of an alpine ecosystem is not an important process. However, subnivial N cycling was much more dynamic than previously thought. The production of inorganic N in snow-covered soils prior to snowmelt was significantly greater than snowmelt inputs. Both snowmelt and soil N were immobilized after the initiation of snowmelt.

These results suggest several new avenues for investigation. Recent reports of elevated fluxes of CO_2 through snow suggests that microbial activity under snow in alpine ecosystems is much greater than previously thought. Direct measurements of microbial biomass are needed to substantiate this idea. The fate of NH_4^+ released from snow and retained in soils is unknown; the relative importance of biological assimilation versus inorganic adsorption by soil exchangers demands attention.

The idea that NO_3^- in surface water of alpine ecosystems is from snowmelt and not soils needs to be revisited. It is quite possible that ammonification and nitrification under snow and prior to snowmelt are ubiquitous in alpine ecosystems. Studies similar to this one need to be conducted to see how site-specific these results may be. An intriguing hypothesis is that NO_3^- export from the subsurface environment in alpine ecosystems is controlled by the balance between gross mineralization and assimilation. Areas with more developed soils and/or extensive vegetation may have more assimilation and less NO_3^- export from the subsurface. In contrast, areas with less developed soils and/or extensive vegetation may have less assimilation and greater NO_3^- export from the subsurface. Nitrate production and export from areas generally regarded as biologically unimportant, such as talus and colluvium, may be important contributors of subsurface NO_3^- to surface waters.

Acknowledgments. T. Bardsley, D. Cline, M. Rikkers, A. Loveland, B. Cress, and C. Seibold provided field and laboratory assistance. T. Davinroy provided Figure 1. Funding assistance was provided by the National Park Service Air Resources Division, NASA Earth Observing System grant NAGW-2602, and by National Science Foundation grant DEB 9211776 to the NWT LTER site. The ^{15}N analysis was supported by USDA/ARS. Thanks to three anonymous reviewers who carefully read the manuscript and who provided helpful and constructive advice.

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(Received December 1, 1995; revised July 12, 1996;
accepted July 17, 1996.)