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Landscape-level nitrogen import and export in an ecosystem with complex terrain, Colorado Front Range

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Abstract Knowledge of import, export, and transport of nitrogen (N) in headwater catchments is essential for understanding ecosystem function and water quality in mountain ecosystems, especially as these ecosystems experience increased anthropogenic N deposition. In this study, we link spatially explicit soil and stream data at the landscape scale to investigate import, export and transport of N in a 0.89 km^2 site at the alpine-subalpine ecotone in the Front Range of the Rocky Mountains, Colorado, U.S.A. For two of the major N inputs to our site, N deposition in the snowpack and N fixation, a complementary relationship was found across the study site, with greater abundance of N-fixing plants in areas with less snow and substantial snow inputs in areas with low N fixer abundance. During the initial phases of snowmelt, mixing model end members for oxygen isotopes in nitrate (NO_3^-) indicated that a substantial quantity of NO_3^- is transported downhill into the forested subalpine without being assimilated by soil microbes. After this initial pulse, much less NO_3^- entered the stream and most but not all of it was microbial in origin. Rising δ^{15}N in stream NO_3^- indicated greater influence of fractionating processes such as denitrification later in the season. NO_3^- from both atmospheric and microbial sources was not exported from our site because it was consumed within the first several hundred meters of the stream; ultimately, N exports were in the form of dissolved organic nitrogen (DON) and particulate N (PN). The results of this study suggest that the highest elevation dry alpine meadows rely more heavily on N fixation as an N source and experience less of the effects of anthropogenic N deposition than mid and lower elevation areas that have more snow. Our data also suggest that mid-elevation krummholz, moist meadows, and talus slopes are exporting N as NO_3^- shortly after the onset of snowmelt, but that this NO_3^- is rapidly consumed as the stream flows through the subalpine forest. This consumption by assimilation and/or denitrification currently provides a buffer against increased inorganic N availability downstream.

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Introduction

Mountain ecosystems are important sources of fresh water and the quality of this water can depend in part on nitrogen (N) import, export, and transport in headwater catchments (Alexander et al. 2007; Jassby et al. 1994). Understanding import and export of N in mountain ecosystems is essential for understanding both N availability and the effects of increasing anthropogenic N deposition (Fenn et al. 2003; Weathers et al. 2006; Williams et al. 1995). Our current understanding of N import and export is based primarily on point estimates (Bowman 1992; Bowman et al. 1996; Williams et al. 1998) or on integrated estimates from hydrologic data (Brooks et al. 1999; Johnson et al. 2000). While these estimates provide a valuable foundation for understanding these processes, more detailed measurements that take spatial heterogeneity into account are likely to reveal important biogeochemical phenomena at larger scales, especially in the complex terrain of mountain ecosystems (Weathers et al. 2000, 2006). To uncover these phenomena and better understand long-term N balance, we need to link terrestrial and aquatic biogeochemical processes using landscape-level data (Fisher et al. 2004). In this study, we use spatially explicit estimates of N deposition and N fixation as well as stream chemical and isotopic analyses to examine landscape-level N input, transport, and export in a 0.89 km^2 alpine-subalpine site.

Prior to anthropogenic N deposition, N fixation by plants (via *Rhizobia* spp.) was the dominant annual input of N to southern Rocky Mountain ecosystems (Bowman et al. 1996; Sievering 2001; Williams & Tonnessen 2000). Current estimates of N inputs now indicate that N deposition and N fixation inputs are approximately equal in the Front Range of the Rocky Mountains, with N fixation accounting for around half of the inputs, atmospheric deposition on the snowpack accounting for one quarter, and wet and dry atmospheric deposition during the snow-free season accounting for the remaining quarter (Fisk et al. 2001; Sievering 2001). Bowman et al. (1996) estimated that N fixation rates in different plant communities varied from 127 mg m^{-2} $year^{-1}$ in wet meadows to 810 mg m^{-2} $year^{-1}$ in fellfields depending on N-fixer abundance and production rates in those plant communities. Despite the importance of spatial variation in N inputs to mountain ecosystems, few spatially explicit data are available for N fixation rates, atmospheric deposition rates, and the relationship between these two sources. In this study, we use geostatistical data to generate spatially explicit estimates of N fixation and N inputs from snow and use these estimates to explore the spatial relationship between these two sources.

Over the winter, atmospherically deposited N at our study site builds up in the snowpack primarily as dissolved inorganic N (DIN: NO_3^- and NH_4^+) and undergoes little chemical transformation (Williams et al. 1996). During snowmelt, this DIN enters the ecosystem as an "ionic pulse" (Williams et al. 1995). Headwater stream samples often show very low NH_4^+ (Williams et al. 1995; Williams et al. 2001), which may be due to rapid assimilation by plants and soils (Yano et al. 2010). Thus NO_3^- is the dominant form of DIN found in these streams, and early season pulses of NO_3^- have been observed in multiple ecosystems (Bernal et al. 2006; Brooks and Williams 1999; Williams et al. 1995). One of the key uncertainties concerning these early season NO_3^- pulses is the source of the NO_3^- in stream waters. High levels of organic matter in headwater streams but not in snow suggest that the source water for these streams is subsurface flow (Hood et al. 2003; Hornberger et al. 1994). Further evidence for infiltration of snowmelt into the subsurface comes from mixing model analyses of isotopic and geochemical tracers (Williams et al. 2009). Infiltration of snowmelt water to the subsurface before export to streams has led to the hypothesis that the source of stream NO_3^- is leached microbial NO_3^- from soils (Williams et al. 1996). The alternative is that the NO_3^- may come from unprocessed, atmospherically deposited N in snow (Williams et al. 1995). With increased N deposition, this distinction in NO_3^- sources to streams is important because it determines the extent to which anthropogenic N may affect plants and soils in addition to downstream waterways.

In this study, we use a technique based on the oxygen isotopic ratios in NO_3^- to determine the source of stream NO_3^- (Bohlke et al. 2003; Kaiser et al. 2007; Michalski et al. 2002). Oxygen isotopic values are typically reported on the standard δ-scale with permil (‰) units: $\delta = R_{sample}/R_{reference} - 1$ where R represents the elemental $^{17}O/^{16}O$ or $^{18}O/^{16}O$ ratios in the sample and in the Standard Mean Ocean Water (SMOW) (Bohlke et al. 2003). Historically, $\delta^{17}O$ was rarely measured because most oxygen-bearing species—including those derived from microbial processes—follow a relationship between $\delta^{17}O$ and $\delta^{18}O$ that is described by the *terrestrial fractionation line* in which $\delta^{17}O \approx 0.52 * \delta^{18}O$. However, in the atmosphere, NO_3^- is the end product of the oxidation by ozone (O_3) of NO_x (NO_x = NO and NO_2, with the anthropogenic emissions originating from the combustion products of fossil fuels) and shows a significant positive deviation from the terrestrial fractionation line. A linear approximation of this deviation is annotated as $\Delta^{17}O = \delta^{17}O - 0.52 * \delta^{18}O$ (see Thiemens 2006 for a review). $\Delta^{17}O$ in non-polar atmospheric NO_3^- generally ranges from 20 to 35‰ (Morin et al. 2009). In contrast to atmospheric NO_3^-, $\Delta^{17}O$ in microbial NO_3^- has a value of 0 (Michalski et al. 2004). In this study, we use these two distinct $\Delta^{17}O$ signatures as end members in a mixing model to determine the source of stream NO_3^-.

Once NO_3^- enters headwater streams, it is often rapidly transformed to dissolved organic N (DON), particularly if the surrounding ecosystem is N limited (Peterson et al. 2001; Williams et al. 2009). NO_3^- is consumed by a variety of processes including denitrification, in-stream assimilation, and assimilation by riparian vegetation (Bernal et al. 2006; Bernhardt et al. 2005). These processes may, however, be overwhelmed by the large stream flows associated with storms or snowmelt, leading to early season pulses of NO_3^- (Hall et al. 2009). While the chemistry of many headwater streams has been studied, spatially explicit measurements along the upper reaches (first several hundred meters) of headwater streams at the alpine-subalpine ecotone are less common and are not often evaluated alongside measurements of soil properties in the surrounding terrestrial environment. In other ecosystems, combining spatially explicit N cycling data from aquatic and terrestrial parts of the ecosystem has been an effective approach for understanding phenomena such as riparian buffer zones in agricultural systems (Lowrance 1992; Pinay et al. 1993).

The goal of this study is to improve our understanding of landscape-level N import and export in an ecosystem with complex terrain. We focus on a subset of N import and export processes to address three key unanswered questions: (1) How are N inputs from the snow pack related to N inputs from N fixation across the landscape? (2) To what extent are N inputs from the snow pack assimilated by soil microbes before reaching streams? and (3) Once N reaches a headwater stream, to what extent is it consumed or transformed in the upper reaches of the stream?

Methods

Study site

The study site is a 0.89 km^2 area in the headwaters of Como Creek. The site is situated at the alpine-subalpine ecotone within the Niwot Ridge Long Term Ecological Research (LTER) site in the Front Range of the Rocky Mountains, Colorado, USA (Fig. 1). The Niwot Ridge landscape includes both an elevation gradient (3,290–3,510 m a.s.l.) from the subalpine forest to the alpine tundra as well as a topographic/snow gradient of snow depth and snow cover duration that varies with landscape slope (0–22°) and aspect in relation to the prevailing westerly winds (Seastedt et al. 2004). The canopy cover is 4% willow and other shrubs, 24% tree cover, and 72% herbaceous. The highest elevations in the study site are characterized by dry meadow alpine tundra vegetation and the lowest elevations are densely forested with mature *Picea engelmannii* and *Abies lasiocarpa* trees. The mid elevations contain a mosaic of krummholz trees, talus slopes and moist meadow tundra. C:N ratios in the study site are higher in the subalpine forest than they are in the higher elevations at our site (Darrouzet-Nardi 2010). The site also contains small seasonal wetlands and is drained by several intermittent streams that typically run May through July. The largest of these streams has a well defined channel along its entire length and was used for all water samples presented in this study (Fig. 1). There is some evidence of denitrification in

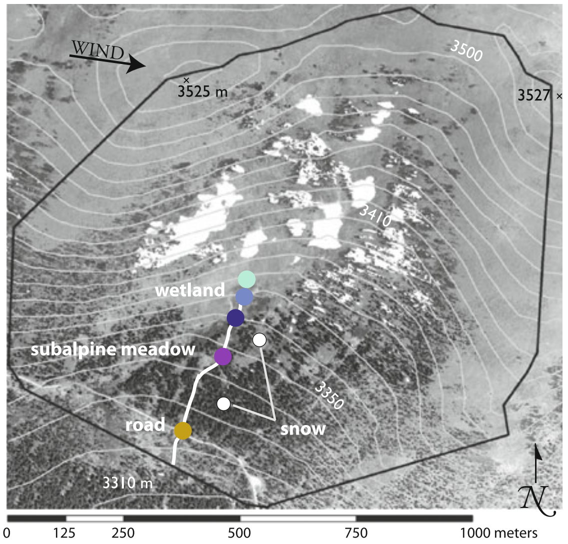

Fig. 1 Aerial photo of the study site, which is on Niwot Ridge in the Front Range of the Rocky Mountains, Colorado, USA (40.0490°, −105.5730°). Photo taken in 2002 (USGS 2004). The black polygon delineates the study site. The predominant wind direction is shown by the arrow in the *upper left*. The contour interval is 10 m. The *white patches* are snow, the *darker areas* are trees, and the *gray areas* are tundra. The *white line* indicates the stream channel in which the intermittent stream flows. The *colored circles* indicate stream sampling locations, the top three being the upper, mid and lower wetland sites. The two smaller white circles indicate the snow pit sampling locations. Two snow pits were dug at the northern location on different dates

or near the stream channel, particularly in the wetland where the stream channel originates (Darrouzet-Nardi and Bowman, *unpublished data*).

N inputs

Two N input sources—N fixation and snow inputs—were quantified using spatially explicit techniques across the study site. To quantify N-fixer abundance, vegetation surveys were done at 604 locations within the study site using a 1 m^2 point-intercept quadrat with 81 points (9 × 9) per quadrat during July and August of 2008 and 2009. The locations of these quadrats were haphazardly chosen along either transects or as the centroids of tessellated polygons that covered the entire study site (for more details see Darrouzet-Nardi 2010). At each of the 81 points in the quadrats, any plants that were present were recorded, counting multiple hits if present. Plants present but not intersecting any of the 81 points were marked as "trace." For each of these 604 locations, % cover of N fixers was calculated as the number of hits of three N fixing plants divided by the number of points in the quadrat (81). The three N fixing plants were *Trifolium dasyphyllum*, *Trifolium parryi*, and *Dryas octopetala*. *D. octopetala* was rare, only occurring in several small patches. Snow depth was manually surveyed at 501 locations across the study site using graduated metal poles on March 31-April 2, 2008, the approximate time of maximum snow depth in 2008, following the protocols of Erickson et al. (2005). For snow depth locations, 80% were on a regularly spaced triangular grid covering the entire study site and 20% were randomly located. Kriging for both N fixer abundance and snow depth were done using ordinary kriging with a spherical variogram model in ArcGIS 9.2 (ESRI) using the package Geostatistical Analyst (ESRI).

To evaluate the combined effects of these two input sources, the percent N-fixer cover and snow depth were converted to estimates of N input quantities with units of mg N m^{-2} $year^{-1}$ and then added together. Snow input was calculated by multiplying snow depth by snow density and concentration of N in the snow. Previous studies have shown that homogeneity of nutrient concentrations in the snowpack and snowpack density across the landscape are reasonable assumptions (Williams et al. 2001; Williams and Melack 1991). The snow density value was measured in a snowpit within the study site on April 11, 2008 (Fig. 1, northern snow sampling point). The total nitrogen (TN) value was the mean of three snow (two in close proximity on different dates) pits sampled within the study site at maximum snow depth (Table 1). N inputs from N fixation were measured using the approach in Bowman et al. (1996): percent cover of N-fixers were multiplied by net primary production in an alpine area with ~100% plant cover, percent N in *Trifolium* tissues, the percent of N annually resorbed by *Trifolium*, and the percent N that *Trifolium* derives from fixation. For net primary production, we use a measured value from a moist meadow near the study site in 1994, 410 g m^{-2} $year^{-1}$ (Fisk et al. 1998). In Fisk et al. (1998), various measurements are presented of net primary production in alpine plant communities over several years; the moist meadow value was chosen because moist meadows at this

Table 1 Concentrations of N pools in snowpack (μmol L^{-1}) and isotopic composition of NO_3^- (‰), based on three snowpits dug within the study area

Location	Date	NO_3^-	$\Delta^{17}O$- NO_3^-	$\delta^{18}O$- NO_3^-	$\delta^{15}N$- NO_3^-	NH_4^+	DIN	DON	TDN	PN	TN
Northern	2004-03-20	9.3	28.9	76.3	0.9	6.6	15.9	0.0	15.9	0.0	15.9
Northern	2004-03-25	7.3	28.7	76.0	−1.1	5.5	12.8	1.0	13.8	0.0	13.8
Southern	2004-03-26	10.0	28.2	76.1	2.5	6.9	16.9	0.0	16.9	0.0	16.9
	mean ± *SE:*	8.9 ± 0.8	28.6 ± 0.2	76.1 ± 0.1	0.8 ± 1.0	6.3 ± 0.4	15.2 ± 1.2	0.3 ± 0.3	15.5 ± 0.9	0.0 ± 0.0	15.5 ± 0.9

The locations refer to the two snow sampling locations shown in Fig. 1

DIN dissolved inorganic N, *DON* dissolved organic N, *TDN* total dissolved N, *PN* particulate N, *TN* total N

study site were the areas in which ~100% plant cover was found in the vegetation surveys, with wet meadows typically having >100% and dry meadows having less. The variation measured by Fisk et al. (1998) was 280–600 g m^{-2} $year^{-1}$ and these measurements included both above and belowground production. Bowman et al. (1996) measured *Trifolium* in six alpine plant communities and determined that the %N in tissues ranged from 2.03 to 2.72%. Their median value of 2.33% is used here. We also used estimates of N resorption (40%) and reliance on fixed N (90%) from Bowman et al. (1996). A study in the Alps found a similarly high reliance of alpine legumes on fixed N (Jacot et al. 2000).

N transport and exports

To evaluate the transport, aquatic processing, and export of N from the study site, five sites along the largest intermittent stream were monitored for stream chemistry on eight dates from May 21, 2008 to July 29, 2008 (Fig. 1). These water samples—as well as the snow samples described above—were collected using a standard Niwot Ridge LTER protocol and analyzed at the Kiowa wet chemistry laboratory run by the Niwot Ridge LTER program. The protocols used are presented in Williams et al. (2006) and Williams et al. (2009). All samples were filtered with 0.45 μm glass fiber filters for stream samples and 1.0 μm Nuclepore filters (Whatman) for snow samples. NH_4^+ was measured on an OI Analytical Spectrophotometric Flow System IV Analyzer with a detection limit of 0.13 μeq L^{-1}. NO_3^- was measured on a Metrohm 761 Compact Ion Chromatograph with a detection limit of 0.02 μmol L^{-1}. Total dissolved N (TDN) concentrations on filtered samples were determined by using potassium persulfate digestion to oxidize all forms of N into NO_3^-. The digested samples for TDN were then measured on an OI Analytical Spectrophotometric Flow System IV Analyzer with a detection limit of 0.45 μmol L^{-1} and precision of 1.39%. DON was calculated by subtracting measured total dissolved inorganic N from TDN. The same digestion and measurements were done on unfiltered samples to estimate total N (TN). Particulate N (PN) was calculated by subtracting TDN from TN. In cases where there were small inconsistencies in the additivity of the fractions due to methodological differences and subsample to subsample variation, we used DIN over TDN and TDN over TN.

To investigate the source of stream NO_3^-, we examined oxygen and nitrogen isotopic ratios in stream and snow NO_3^-. Sufficient NO_3^- for $\Delta^{17}O$ analysis (triplicates at 100 nmol) was present in 20 of the 39 stream samples collected. While no samples from the 'road' sampling site (Fig. 1) had sufficient NO_3^- for analysis, the other four sites had sufficient levels during at least some parts of the season (no 'road' sample was collected on the first sampling date due to deep snow covering the stream). To achieve the necessary NO_3^- concentration for analysis, all samples were concentrated on 0.3 mL of anionic exchange resin (BioRad AG 1-X8, chloride form) and eluted with 5 × 2 mL of a 1 M NaCl solution with 100% recovery (Frey et al. 2009). For the 20 stream samples that had a sufficient amount of NO_3^-, NO_3^- isotopic composition ($\Delta^{17}O$, $\delta^{18}O$, $\delta^{15}N$) was determined using an on-line bacterial method and mass spectrometry (Kaiser et al. 2007; Morin et al. 2009). Briefly, 100 nmol of NO_3^- are converted to gaseous N_2O by the denitrifying bacteria *Pseudomonas aureofaciens* in anaerobic conditions. N_2O is then decomposed on a gold surface heated at 900°C (Kaiser et al. 2007). This decomposition of N_2O produces a mixture of O_2 and N_2 that is then separated by gas chromatography and injected in an Isotope Ratio Mass Spectrometer (IRMS; Thermo Finnigan MAT 253). This mass spectrometer has a peak jump feature that permits the measurement of the comprehensive isotopic composition of NO_3^- on the same sample. We used a bulk approach to correct for any isotopic effect that may have occurred throughout the analytical procedure (see supporting online material in Morin et al. 2009). The raw values of the international reference materials USGS-32, USGS-34 and USGS-35 are compared to their accepted values following the "identical treatment" recommendations. The accuracy of the method for the presented results is 0.43‰ and is calculated as the standard deviation of the residuals from a linear regression between measured standards and their expected values.

Using the $\Delta^{17}O$ values, we used a two-member mixing model to partition the contribution of snow and soil NO_3^- sources to the intermittent stream. The first end member in the mixing model was the $\Delta^{17}O$ of NO_3^- from three snow samples collected in late March near the origin of the intermittent stream channel. These snow samples were analyzed at the same time as the stream samples. This value was also evaluated against the documented atmospheric range of 20–35‰ (Morin et al. 2009). The second end member is the $\Delta^{17}O$ of NO_3^- formed by microbial processes such as nitrification, which is known to be 0‰ (Michalski et al. 2004). Using our measured relationship between $\Delta^{17}O$ and $\delta^{18}O$, we also evaluated our microbial end member against a previously used end member of $\delta^{18}O = 15‰$ in Nanus et al. (2008). Because the anomaly in the oxygen isotopes of NO_3^- are only generated in the atmosphere and are not influenced by mass-dependent fractionations as they would in the biological production of NO_3^-, the $\Delta^{17}O$ value can be viewed as a specific isotopic tracer of atmospheric NO_3^-. Thus, $\Delta^{17}O$ is a direct measurement of the relative level of atmospheric NO_3^- in ecosystems (Michalski et al. 2004). A large pool of atmospheric NO_3^- is released from storage in the winter snowpack during the snowmelt period with the same isotopic characteristics. The melting snowpack can be seen as a tracer experiment that releases atmospheric NO_3^- to our ecosystem. We use these characteristics of NO_3^- pools (atmospheric and soil) to estimate residence time of NO_3^- and the proportion of NO_3^- in our study site that is of atmospheric origin.

Results

N import from fixation and snow

The dry alpine meadows in the higher elevations received very little snow; the dense forest in the lower part of the study site received a relatively consistent 1–2 m of snow; and the intermediate krummholz areas received the most variable inputs (0–4 m; Fig. 2). Average snow depth at the time of measurement (March 31–April 2) across the study site was 0.99 m. The snow density measured in a snowpit on April 11, 2008 was 384 kg m^{-3}. The total nitrogen (TN) values in the three snowpits were 13.9, 15.9, and 16.9 µmol N l^{-1}, with a mean of 15.5 µmol N l^{-1}. Of this N, about 60% was NO_3^- and 40% was NH_4^+; there were trace amounts of DON (Table 1). For the estimates of N inputs from snow across the study site, the mean value of

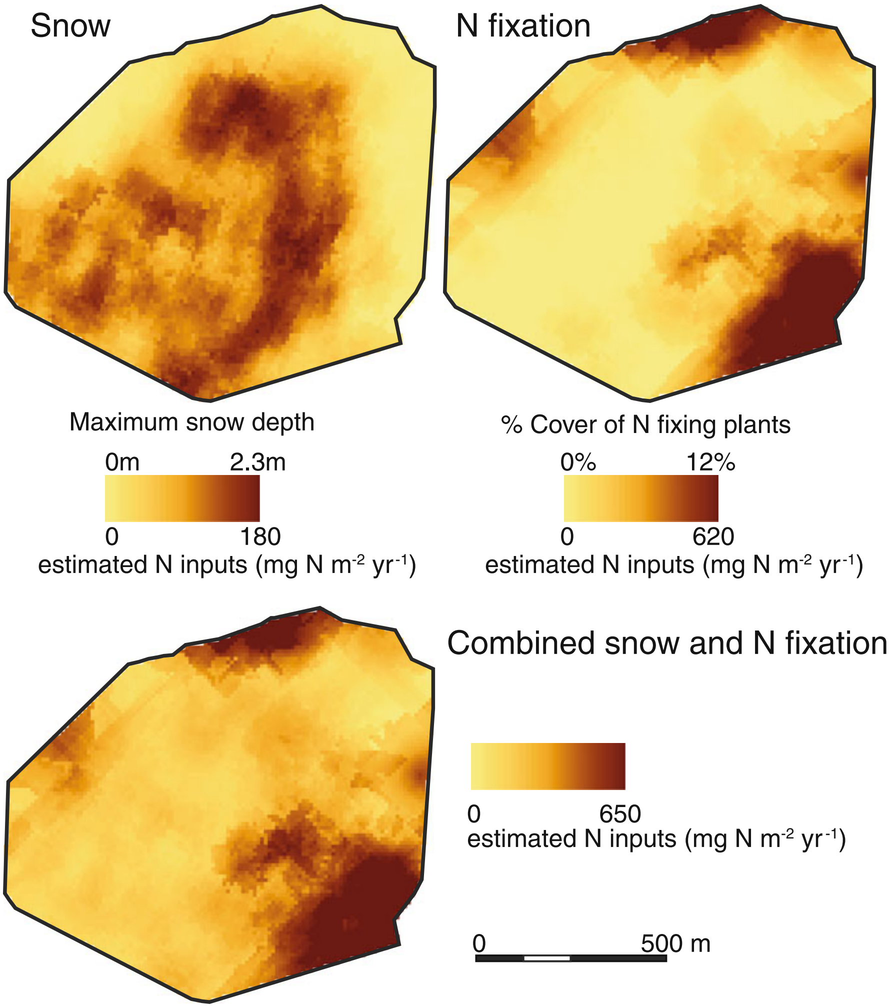

Fig. 2 N inputs to the study site from atmospheric deposition on snow (*top left*), N fixation (*top right*), and their sum (*bottom*). The colored gradients are stretched to snow depth, percent cover of N fixers, and combined N inputs for the three maps respectively; the estimates of N inputs for the snow map and N fixation map are thus on a different scale than the combined map. Maps were created using kriging to interpolate 501 depth measurements (snow) and 604 vegetation quadrats (N fixation). Note that the maximum *interpolated* snow depths and N fixer cover values shown here (2.3 m and 12%) are lower than the maximum *measured* values (4 m and 41%). See methods for calculations of N inputs based on these data. Together, these two inputs have been estimated to account for about 75% of total N inputs to the ecosystem, with the remaining 25% accounted for by wet and dry deposition during the snow-free season

15.5 μmol N l^{-1} was used. The utility of this value was supported by 52 snow pits dug during the winter and spring of 2008 across the Niwot Ridge and adjacent Green Lakes Valley area, for which the median TN value was 14.5 μmol N l^{-1} with 90% of all values being between 10 and 20 μmol N l^{-1} (NWT LTER database: http://culter.colorado.edu/NWT/). Using these snow depths and N concentrations, the total input of N from snow across the study site was estimated to be 83 mg N m^{-2} $year^{-1}$.

A complementary relationship was observed between snow depth and N fixer abundance (Figs. 2, 3). N fixer abundance was patchy, with high abundances in patches at the northern and southeastern edges of the study site (Fig. 2). Using these abundances and the physiological characteristics of N fixers from the literature, total input of N from N fixers across the study site was estimated to be 124 mg N m^{-2} $year^{-1}$. The mean percent cover of N fixers in areas where snow was shallower than

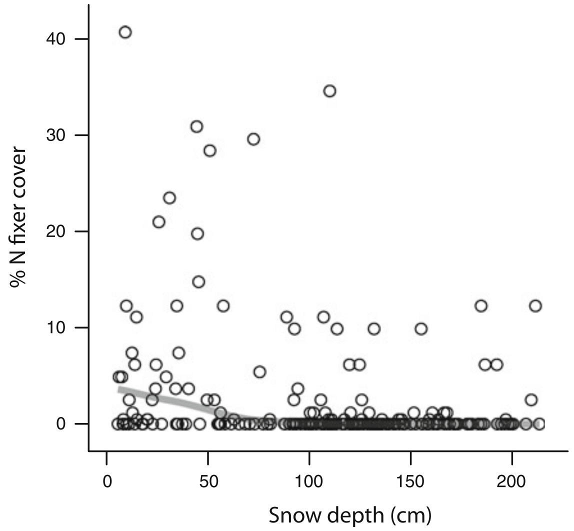

Fig. 3 Relationship between measured values of N fixer abundance and kriged values of snow depth. $n = 203$. The gray line is a loess (local regression) curve with $\alpha = 2/3$ and a first degree polynomial (Chambers and Hastie 1992). The loess curve illustrates the greater abundance of N fixers in areas with <50 cm snow cover

50 cm was 6.0 ± 2.9% (mean ± 95%CI) and the mean percent cover of N fixers in areas where snow was deeper than 50 cm was 1.4 ± 0.7%. In areas with snow <50 cm, 25 of the 45 surveyed plots (56%) had greater than a trace amount of N fixers (trace defined as presence of the species, but no hits with the point-intercept quadrat) while in areas with >50 cm, 25 of the 196 plots (13%) had greater than trace amounts. Substantial heterogeneity remained when the inputs from these two sources were combined due to the large patches of N fixers. However, few areas in our study site had both low snow inputs and low N fixer abundance (Fig. 2).

N transport and export

In 2008, snowmelt within our study site began in early May and continued through mid July. The higher elevation alpine meadows had little snowpack at the onset of melt and were snow free in early May; the subalpine forest was snow free by late June; and the mid-elevations within the site became snow free in mid July. The distribution of late-season snow in 2002, which is similar interannnually, can be seen in Fig. 1. The intermittent stream began flowing in mid May. Though we did not measure stream flow, flow was highest shortly after the stream began flowing and then tapered off throughout the season until it stopped flowing at the end of July.

The highest levels of both DON and DIN in the intermittent streams were seen in our first sample on May 21, shortly after the onset of stream flow (Fig. 4). At that time, DIN was almost entirely in the form of NO_3^-. NH_4^+ was undetectable except in the sample collected on May 21 in the upper wetland adjacent to melting snow where it was 7.0 μmol l^{-1}, similar to the value of nearby snow: 6.6 μmol l^{-1} (Table 1). Throughout the season, higher levels of NO_3^- were found in the wetland sites (upper, middle, and lower) than in the downstream subalpine meadow and road sites. This was particularly true on the first

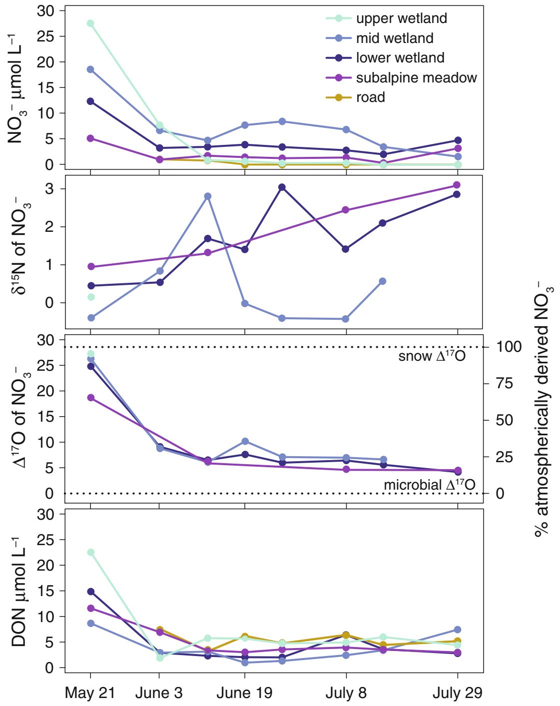

Fig. 4 Concentrations of NO_3^-, isotopic signature of nitrogen ($\delta^{15}N$) and oxygen in NO_3^- ($\Delta^{17}O$), and concentrations of dissolved organic N (DON) throughout the summer of 2008 in the intermittent stream. The color of the plotting *symbols* and *lines* indicate the locations of the samples within the study site (see legend in *top left* and Fig. 1). The results of the two-member mixing model for the two sources of NO_3^- is shown on the right side of the $\Delta^{17}O$ panel. The *dotted lines* are reference lines for the two end members: atmospherically derived NO_3^- and microbially derived NO_3^-. No $\Delta^{17}O$ or $\delta^{15}N$ measurements are available for samples with very low concentrations of NO_3^-

sampling date, in which a clear reduction in NO_3^- was seen as the meltwater flowed downstream from the top to the bottom of the wetland and then to the subalpine meadow (Fig. 4). NO_3^- concentrations dropped by just over half (27.5–12.4 μmol l^{-1}) from the upper to the lower wetland, suggesting that the distance traveled by an average NO_3^- molecule (nitrate uptake length) was about 60 m. The $\delta^{15}N$ of the NO_3^- in the three snow samples was inconsistent, ranging from −1.1 to 2.5 (Table 1). Likewise, the repeated samples at the mid wetland site showed no clear trend throughout the season, ranging from −0.4 to 2.9, with a peak at the mid wetland site on June 12 and a peak at the lower wetland site on June 26 (Fig. 2). However, in both the lower wetland and the subalpine meadow, an upward trend was observed throughout the season (Fig. 2). Sample $\delta^{15}N$ at these two sites rose from 0-1‰ on May 21 to 3‰ on July 29.

NO_3^- in the three snow samples showed a consistent $\Delta^{17}O$ signal, with a mean ± SE of 28.6 ± 0.2‰ (Table 1). These values were within the expected atmospheric range of 20-35‰. A strong positive relationship was observed between $\Delta^{17}O$ and $\delta^{18}O$ ($r^2 = 0.99$; Fig. 5). The intercept of a linear regression between these two isotopic ratios (the $\delta^{18}O$ value at which $\Delta^{17}O = 0$) indicated that the microbial $\delta^{18}O$ signature in our samples was consistently around –3‰. The mixing model indicated that samples collected in the wetland area on May 21 (just after the intermittent stream began to flow) contained NO_3^- derived almost entirely (95% in upper wetland) from atmospherically produced NO_3^- (Fig. 4). However, this percentage was decreased to 92% over the horizontal distance of 31 m to the mid wetland site and 87% over the distance of 68 m to the lower wetland site. By the time water had reached the subalpine meadow 167 m below the stream origin, the mixing model indicated that the portion of NO_3^- that was atmospherically derived dropped to 65%.

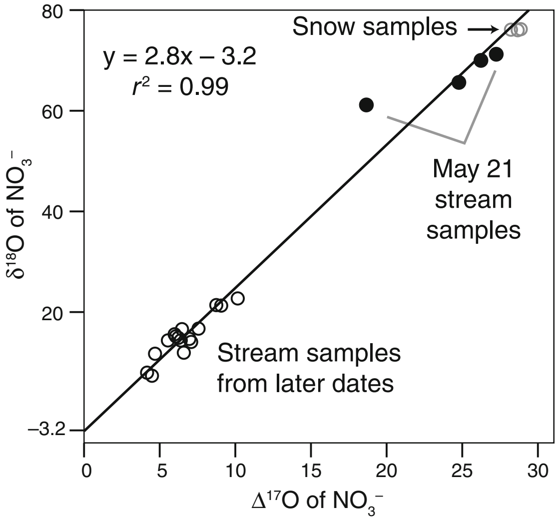

Fig. 5 Relationship between $\Delta^{17}O$ of NO_3^- and $\delta^{18}O$ of NO_3^-. $n = 20$. Snow samples, stream samples collected on May 21, and all other stream samples are separated by plotting symbol color (*gray circles*, *filled black circles*, and *open black circles*). Linear regression slope, intercept, and correlation coefficient are shown in the *upper left*

Beginning on the second sampling date, June 3, most measurements of $\Delta^{17}O$ come from the mid and lower wetland sites, which were the only sites with sufficient NO_3^- for analysis. At those sites, the soil had become the dominant source of NO_3^-, with the mixing model indicating that 21% of the remaining NO_3^- was atmospherically derived on June 3. This percentage stayed relatively constant, dropping to 15% by July 29, the last date on which the stream was sampled. The $\Delta^{17}O$ of NO_3^- decreased over the measurement period with consistent values at each site for a given date (Fig. 4), showing a homogeneity of the decrease process over the study site. These data can be fitted with an exponential equation: $\Delta^{17}O(t) = 19e^{(-0.15t)} + 6$, where the inverse of the decay constant, 0.15^{-1}, describes the characteristic turnover time of NO_3^- in the catchment (i.e., the average time for the atmospheric NO_3^- to be incorporated into the local biogeochemical cycles), 6.6 days in this case. At the steady state when snowmelt has stopped, $\Delta^{17}O$ equaled ~5‰ which can be compared to the 28.6‰ of the snow NO_3^-. These values suggest that atmospheric deposition (dry and wet) represent ~17% of the NO_3^- present in the catchment during this steady state period because 5‰ is 17% of the difference between the two end members, 0‰ (microbial) and 28.6‰ (atmospheric).

DON and PN were the dominant forms of hydrologic N export from the study site: the first sample at the road on June 3 showed 87% of N in the form of DON or PN and at all subsequent dates DON and PN were 100% of N export (Table 2). Of these two forms, DON made up the larger fraction, with PN ranging from 0 to 25% of the export on our sampling dates.

Table 2 Concentrations of N fractions (μmol L^{-1}) in stream exports from our study site

Date	NH_4^+	NO_3^-	DIN	DON	TDN	PN	TN
2004-06-03	0	1.1	1.1	7.4	8.5	2.8	11.2
2004-06-12	0	0.8	0.8	3.5	4.3	0	4.3
2004-06-19	0	0	0	6.1	6.1	1.6	7.6
2004-06-26	0	0	0	4.8	4.8	0.8	5.6
2004-07-08	0	0	0	6.3	6.3	0.9	7.2
2004-07-15	0	0	0	4.4	4.4	1.6	6.1
2004-07-29	0	0	0	5.2	5.2	1.0	6.2

Samples were from the ‘road’ site (see Fig. 1)

DIN dissolved inorganic N, *DON* dissolved organic N, *TDN* total dissolved N, *PN* particulate N, *TN* total N

Discussion

N import

Estimates of N inputs from N fixation and snow are similar to previous estimates (Bowman 1992; Bowman et al. 1996; Williams et al. 2001) and thus support the previous finding that these two sources are similar in magnitude at the total ecosystem scale (Fisk et al. 2001; Sievering 2001). However, while the ecosystem totals were similar, the spatially explicit data in this study show a complementary relationship between atmospherically derived inputs of N through snow and N fixer abundance across the landscape. While there are uncertainties due to the assumptions of the calculations of these inputs and heterogeneity in combined inputs is still substantial, the overall pattern appears robust. N fixer abundance is clearly higher in areas with less than 50 cm maximum snow depth while snow inputs provide substantial N in areas with few or no N fixers growing. While we cannot determine the underlying cause of this relationship with the data in this study, we can hypothesize that N fixers are more competitive in areas with less N inputs from snow (Chapin et al. 1994). In addition to lower direct N inputs from the snowpack, soils with less insulation from deep snow are also colder, which may lower N mineralization rates and further contribute to N limitation (Brooks and Williams 1999). This relationship between N fixer abundance and snow depth demonstrates the potential for an increase in N deposition to reduce N fixer abundance by reducing their competitiveness (Suding et al. 2005). If such declines in N fixer abundance did occur, they might create an important negative feedback to increased N availability from N deposition. There is some evidence of declining N fixer abundance on Niwot Ridge: in a repeat survey over 15 years, the percentage of survey plots ($n = 50$) containing at least 20% cover of *Trifolium nanum* dropped from 40 ± 14% in 1981 to 6 ± 11% in 1996 (Korb and Ranker 2001). However, the other two *Trifolium* species did not show such dramatic declines and such declines have not been observed in Long Term Ecological Research (LTER) plots or in N addition experiments (Bowman et al. 2006).

In the present study, we were not able to make spatially explicit measurements of atmospheric inputs during the snow-free season, but consideration of these unmeasured inputs is worthwhile for understanding total N import to this ecosystem. The remaining unmeasured N inputs from wet and dry atmospheric deposition during the snow-free season are estimated to account for one quarter of total N inputs (Sievering 2001). The spatial differences in N inputs shown in this study may be attenuated by the more evenly distributed wet deposition in summer rain, which is likely to be more even across a site of this size and elevation range. In contrast, the pattern of snow inputs may be bolstered by dry deposition that more closely tracks snow depth patterns. Patterns in dry deposition have been evaluated using transects across the alpine-subalpine ecotone on Niwot Ridge (Liptzin and Seastedt 2009). These transects showed that dry deposition (including the estimated one quarter of total ecosystem N inputs) blow away from exposed areas and collects in leeward tree covered areas just as snow does. The heterogeneity in dry deposition, though, may not be as large as in snow: along these transects, snow depths were about eight times higher under trees than in open areas while dry deposition was just three times higher. Ultimately, we wish to know the combined effect of wet and dry deposition across the landscape. One study of total deposition in the southern Appalachian Mountains that was based on lead (Pb) quantities in soils suggests that spatial heterogeneity of deposition is high in similarly sized mountain ecosystems, even with deposition from precipitation (Weathers et al. 2000). These findings suggest that either N inputs in precipitation may be more heterogeneous than expected, or, that heterogeneity in dry deposition leads to heterogeneity of total inputs despite more even inputs from precipitation. Similar data at our study site would provide a valuable addition to our understanding of N imports in alpine-subalpine ecosystems.

N transport and export

The similarity between the isotopic signature (Δ^{17}O) of NO_3^- in snow and NO_3^- in the uppermost reaches of the intermittent stream on our first sampling date suggests that a substantial portion of NO_3^- in the snowpack flows downhill without first being assimilated by plants and soils. For the early season pulse of NO_3^-, this finding is not consistent with the hypothesis of Williams et al. (1996) that stream NO_3^- concentrations are controlled by the balance of soil N assimilation and mineralization, though the hypothesis may still hold later in the season. In findings similar to those presented here, an early-season pulse of non-microbially derived NO_3^- was observed in a nearby rock glacier (Williams et al. 2007) and in a similar ecosystem in the Sierra Nevada mountains (Sickman et al. 2003). The pattern in δ^{18}O values observed within our same study site by Williams et al. (2009) is also consistent with our findings. However, studies in two North American deciduous forests have shown smaller contributions of atmospheric NO_3^- during early snowmelt (Piatek et al. 2005; Spoelstra et al. 2001). The transfer of nutrients from the higher to the lower elevations of the alpine-subalpine ecosystem provides direct support for the Landscape Continuum Model (Seastedt et al. 2004), which hypothesizes that lower elevation ecosystems are subsidized by water and nutrient supplements from higher elevations at the alpine subalpine ecotone. Transport of atmospheric NO_3^- to lower elevations as well as the lower snow depths in the high elevation alpine meadows suggest that the alpine is experiencing proportionally less N enrichment from anthropogenic deposition than the subalpine forest.

The chemistry of the stream water in the wetland suggests that subsurface flow rather than overland flow is the dominant hydrologic source to the intermittent stream, in concordance with other studies of headwater catchment streams (Hood et al. 2003; Hornberger et al. 1994; Williams et al. 2009). The low concentration of NH_4^+ and the high concentration of DON in the stream on our first sampling date suggest that the melt water at that time had been in contact with the soil. NH_4^+, which was found in the snow pack but not the stream water, can bind to the negatively charged soil matrix or be assimilated by plants or microbes. Decomposing soil organic matter provides a source for the DON that is not present in the snow pack. Evidence of soil contact suggests that the atmospheric NO_3^- present in the stream was not removed by soils. In the semiarid chaparral of southern California, another ecosystem experiencing high levels of N deposition, similarly high exports of atmospheric N were observed shortly after peak stream flow (Michalski et al. 2004). This NO_3^- export may indicate a lack of time for NO_3^-—which does not bind to the negatively charged soil matrix—to be immobilized. Later in the season, low or undetectable concentrations of stream DIN suggest that there may still be substantial N limitation during the growing season. The increasing δ^{15}N of these NO_3^- exports later in the season suggest that these NO_3^- pools were affected by processes such as denitrification that are known to discriminate against ^{15}N (Dawson et al. 2002). The Δ^{17}O data suggest a residence time for atmospheric NO_3^- on the order of one week before it is consumed by plants or soil microbes. Pool dilution studies that use direct applications of ^{15}N tracers to soils typically show residence times for inorganic N on the order of one day (Booth et al. 2005). However there is substantial variation in those measurements, and a residence time of one week is not implausible, especially given the cold temperatures during snowmelt.

The δ^{18}O values we observed in snow NO_3^- (76.1 ± 0.1‰) were within the range of values from a previous study of NO_3^- in precipitation in the Rocky Mountains in 2004, in which $\delta^{18}O$ ranged from 71‰ to 78‰ (Nanus et al. 2008). After our first sampling date (May 21)—in which our $\delta^{18}O$ values in stream NO_3^- were close to the snow values—our stream $\delta^{18}O$ values were similar to those observed in lakes: ours ranged from 7.3‰ to 22.7‰ while values in lakes across the Rocky Mountains in 2004 ranged from −5.7‰ to 21.3‰ (Nanus et al. 2008). Nanus et al. (2008) used a conservative estimate of the microbial $\delta^{18}O$ value of 15‰. Based on the additional information from the $\Delta^{17}O$ data in our study, the microbial value appears to be closer to −3‰, indicating a greater atmospheric contribution in some of the lake samples and indicating that the lowest lake values were a good match with the microbial NO_3^- end member. The very close relationship between $\Delta^{17}O$ and $\delta^{18}O$ that we observed ($r^2 = 0.99$) was not observed in the study of the semiarid chaparral in southern California (Michalski et al. 2004), suggesting that $\delta^{18}O$ cannot be used to estimate an accurate microbial end member in all cases.

The NO_3^- that was exported from the alpine areas within our study site was consumed in the intermittent stream over an average distance as short as 60 m, a short distance compared to other similar streams (Lautz & Siegel 2007). On the first sampling date just after snowmelt, the decline in total NO_3^- as well as $\Delta^{17}O$ of NO_3^- in the water flowing from the wetland to the subalpine meadow suggests that some of the NO_3^- was assimilated and then again exported as microbially derived NO_3^-. NO_3^- from both sources was then consumed as the stream flowed through the subalpine forest. The import of inorganic N via snow and export of DON and PN via streams was also documented by Williams et al. (2009). As noted in that study, this transition suggests that terrestrial and/or aquatic parts of the ecosystem are converting inorganic N to DON, likely through biotic assimilation and decomposition. The results of the present study also build upon the results of Williams et al. (2009) with the $\Delta^{17}O$ analyses: the consistent $\Delta^{17}O$ signal across the length of the stream (except on the first sampling date) suggests that NO_3^- removal from the stream is a one-way process and not the result of a negative net flux. This removal of NO_3^- is consistent with the conclusion that the subalpine forest is still strongly N limited, which is also consistent with a documented transition to soils with higher C:N ratios in the subalpine forest (Darrouzet-Nardi 2010). This removal of NO_3^- over a short physical distance in the uppermost reaches of a headwater stream also underscores the importance of these ecosystems in controlling downstream water quality.

The fate of the DIN that is lost from the stream is not certain, but possible fates include denitrification, in-stream assimilation, and assimilation by riparian vegetation (Hall et al. 2009). Direct measurements of NO_3^- loss and N_2O production in wet soils as well as isotopic measurements of soil N in the wetland area are consistent with substantial N losses through denitrification within the study site (Darrouzet-Nardi, *unpublished data*; Filippa et al. 2009). The increasing $\delta^{15}N$ values of NO_3^- in our stream samples are also consistent with gaseous losses of N. Denitrification has also been implicated in other Rocky Mountain headwater streams (Hubbard et al. 2010). However, assimilation by stream biota or riparian vegetation likely also contribute to NO_3^- removal from the intermittent stream. Assimilation by stream biota, particularly in the hyporheic zone, has been shown to contribute to NO_3^- loss in other ecosystems (Hall et al. 2009; Woodward et al. 2009). Depending on the ratio of denitrification to assimilation, denitrification may effectively buffer against downstream effects of increased anthropogenic N deposition. Assimilation by subalpine forests may also provide a temporary buffer until the forest become N saturated.

Conclusion

Our results suggest that the alpine tundra experiences less anthropogenic N deposition than the subalpine forest because (1) the dry meadow alpine areas have less N inputs from the snow pack and (2) deposited N in the mid elevations can flow downhill without being processed by soil microbes. However, less exposure does not necessarily translate into less impact. The results of this study also suggest several mechanisms by which terrestrial and aquatic ecosystems can interact within headwater catchments to buffer against elevated downstream nutrient availability. In the short term, consumption of N by assimilation and/or denitrification in the intermittent stream as it flows through the subalpine forest appears to be performing this function. Over the long term, it is also possible that reductions in N fixers, particularly in the subalpine forest, may partially compensate for increased atmospheric deposition. A better understanding of spatial variation in summer wet and dry deposition as well as in denitrification in soils and streams would be useful next steps in understanding N balance in ecosystems with complex terrain.

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