

# Pathways for nitrate release from an alpine watershed: Determination using $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$

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[1] Snowpack, snowmelt, precipitation, surface water, and groundwater samples from the Loch Vale watershed in Colorado were analyzed for  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate to determine the processes controlling the release of atmospherically deposited nitrogen from alpine and subalpine ecosystems. Although overlap was found between the  $\delta^{15}\text{N}_{(\text{NO}_3)}$  values for all water types ( $-4$  to  $+6\text{‰}$ ), the  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values for surface water and groundwater ( $+10$  to  $+30\text{‰}$ ) were usually distinct from snowpack, snowmelt, and rainfall values ( $+40$  to  $+70\text{‰}$ ). During snowmelt,  $\delta^{18}\text{O}_{(\text{NO}_3)}$  indicated that about half of the nitrate in stream water was the product of microbial nitrification; at other times that amount was greater than half. Springs emerging from talus deposits had high nitrate concentrations and a seasonal pattern in  $\delta^{18}\text{O}_{(\text{NO}_3)}$  that was similar to the pattern in the streams, indicating that shallow groundwater in talus deposits is a likely source of stream water nitrate. Only a few samples of surface water and groundwater collected during early snowmelt and large summer rain events had isotopic compositions that indicated most of the nitrate came directly from atmospheric deposition with no biological assimilation and release. This study demonstrates the value of the nitrate double-isotope technique for determining nitrogen-cycling processes and sources of nitrate in small, undisturbed watersheds that are enriched with inorganic nitrogen. *INDEX TERMS:* 1806 Hydrology: Chemistry of fresh water; 1871 Hydrology: Surface water quality; 1803 Hydrology: Anthropogenic effects; 1854 Hydrology: Precipitation (3354); *KEYWORDS:* nitrogen, oxygen, isotopes, alpine, watershed, deposition

## 1. Introduction

[2] Atmospheric deposition of anthropogenic nitrogen exceeds ecosystem nutrient demand in undisturbed ecosystems in some areas of North America and northern Europe, resulting in nitrogen saturation of watersheds and export of inorganic nitrogen in surface waters. The Front Range of Colorado receives annual atmospheric deposition of nitrogen at a rate of 3–6 kg/ha. This amount is greater than in most areas of western North America but less than in other areas of the world where nitrogen saturation has been identified. Nitrate is exported year-round in surface waters of undisturbed alpine/subalpine catchments in the Front Range of Colorado [Williams *et al.*, 1996a; Baron and Campbell, 1997], indicating that these ecosystems are more sensitive to nitrogen deposition than the forested ecosystems that have been studied in eastern North America and Europe [Baron *et al.*, 1994; Fenn *et al.*, 1998; Campbell *et al.*, 2000].

[3] Processes controlling nitrogen “leakage” from alpine systems are very different from those in deciduous forests of North America and Europe [Fenn *et al.*, 1998; Campbell *et al.*, 2000]. In deciduous forests, nitrogen saturation begins when the capacity of plants and microbial communities to assimilate atmospherically deposited nitrogen is exceeded [Stoddard, 1994; Aber *et al.*, 1998]. The original hypothesis was that because alpine water-

sheds contain little soil and vegetation, they act as “Teflon basins,” flushing most of the atmospherically deposited nitrogen into surface waters with little opportunity for assimilation or attenuation of nitrogen [Williams and Melack, 1991]. More recently, it has been recognized that substantial biogeochemical cycling occurs in alpine ecosystems, even in areas dominated by bedrock or talus deposits [Williams *et al.*, 1997; Campbell *et al.*, 2000].

[4] Although nitrogen-cycling processes can be measured in various ways at the plot scale, their relative importance at the watershed or ecosystem scale is difficult to determine, particularly in heterogeneous systems such as alpine catchments. Water and solute flux measurements allow for indirect determination of net transformations of nitrogen at the catchment scale, placing some boundaries on the magnitude of various processes. However, the flux measurements do not reveal individual processes that occur during ecosystem nitrogen cycling.

[5] The  $\delta^{15}\text{N}$  of nitrate has been used in numerous studies to determine sources of nitrogen in groundwater and surface water affected by agricultural land uses [Kendall, 1998]. This approach is successful because the primary agricultural sources of nitrogen, fertilizer and animal waste, usually have distinct isotopic signatures of nitrogen. Use of  $\delta^{15}\text{N}$  to identify sources and cycling of nitrogen in undisturbed watersheds has not been as successful because the two predominant sources of nitrate in these waters, atmospheric deposition and soil microbial processes, have  $\delta^{15}\text{N}_{(\text{NO}_3)}$  values that have substantial overlap. However,  $\delta^{18}\text{O}_{(\text{NO}_3)}$  has been useful in

separating atmospheric and microbial sources of nitrate in undisturbed watersheds affected by elevated deposition of nitrogen [Durka *et al.*, 1994; Kendall *et al.*, 1995; Kendall, 1998; Burns and Kendall, 2002].

[6] Previous biochemical and bacteriological studies have shown that nitrate produced by microbial nitrification in laboratory cultures derives two oxygens from water molecules and one oxygen from atmospheric  $\text{O}_2$  [Andersson and Hooper, 1983; Kumar *et al.*, 1983; Hollocher, 1984]. If these oxygens are incorporated without any fractionation, and the  $\delta^{18}\text{O}$  of water and  $\text{O}_2$  are known, the  $\delta^{18}\text{O}$  of microbial nitrate can be calculated, as shown:

$$\delta^{18}\text{O}_{(\text{NO}_3)} = 2/3 \delta^{18}\text{O}_{(\text{H}_2\text{O})} + 1/3 \delta^{18}\text{O}_{(\text{O}_2)}$$

[7] For waters that have  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$  values in the normal range of  $-25$  to  $+4\%$ , and  $\delta^{18}\text{O}$  values (query addition) of soil  $\text{O}_2$  gas that are equivalent to those of atmospheric  $\text{O}_2$  (about  $+23\%$ ) [Kroopnick and Craig, 1972], the  $\delta^{18}\text{O}_{(\text{NO}_3)}$  formed from in situ nitrification of ammonium should be in the range of  $-10$  to  $+10\%$ . This model is dependent on four critical assumptions: (1) The proportions of oxygen from water and  $\text{O}_2$  are the same in soils as observed in laboratory cultures, (2) no fractionation results from the incorporation of oxygen from water or  $\text{O}_2$ , (3) the  $\delta^{18}\text{O}$  of water used by the microbes is identical to that of the bulk soil water, and (4) the  $\delta^{18}\text{O}$  of the  $\text{O}_2$  used by the microbes is identical to that of atmospheric  $\text{O}_2$ .

[8] Under natural conditions some of these assumptions may be violated. Several field studies have reported  $\delta^{18}\text{O}$  values of soil microbial nitrate that are as much as  $5\%$  higher than the theoretical maximum value of  $+10\%$ , with various explanations hypothesized [Amberger and Schmidt, 1987; Aravena *et al.*, 1993; Wassenaar, 1995; Kendall *et al.*, 1995; Kendall, 1998; Seiler, 1999; Mayer *et al.*, 2001; Burns and Kendall, 2002]. On the basis of an evaluation of many studies, Kendall [1998] concluded that  $+15\%$  is a more appropriate upper value for  $\delta^{18}\text{O}$  of microbial nitrate and suggested that microbial fractionation of ambient  $\text{O}_2$  during respiration is a likely explanation for the higher values. Recent experimental work by Mayer *et al.* [2001] resulted in microbial nitrate values as high as  $+15\%$  and indicated that the ratio of oxygens derived from water versus those derived from  $\text{O}_2$  gas may vary from the theoretical ratio depending on ambient conditions and nitrification mechanisms.

[9] The precise value of the soil microbial end-member probably varies somewhat in time and space, even in small watersheds. However, as long as the variability is small relative to the separation between  $\delta^{18}\text{O}$  of nitrate from atmospheric deposition and microbial nitrification,  $\delta^{18}\text{O}$  can be useful for determining relative contributions of the two sources. For this study we used a range of  $0$  to  $+15\%$  for the composition of microbial nitrate.

[10] The “double-isotope” technique was used first by Böttcher *et al.* [1990] to determine sources of nitrate in groundwater down-gradient from an agricultural area. Durka *et al.* [1994] later determined sources of nitrate in an undisturbed watershed in Bavaria, Germany, where  $\delta^{18}\text{O}_{(\text{NO}_3)}$  in atmospheric deposition ranged from  $+50$  to  $+75\%$ , whereas  $\delta^{18}\text{O}_{(\text{NO}_3)}$  in spring water ranged from  $+10$  to  $+40\%$ . Studies were begun at several U.S. Geological Survey (USGS) research watersheds in 1993 to determine whether the double-isotope technique could be used to determine relative contributions of nitrate from atmospheric deposition and soil processes in North American watersheds. Early results demonstrated that the technique was useful and that isotopic signatures from specific sources of nitrate were similar among three North American watersheds and the German watershed [Kendall *et al.*, 1995].

[11] In this investigation,  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate are used in conjunction with conventional measurements of water and nitrogen flux and  $\delta^{18}\text{O}$  of water to (1) determine sources of nitrate in precipitation, groundwater, and surface water; (2) trace fluxes and transformations of nitrogen along hydrologic flow paths; and (3) link plot-scale measurements of ecosystem processes to catchment-scale flux measurements.

## 2. Site Description

[12] The Loch Vale watershed is located in Rocky Mountain National Park in the northern Front Range of Colorado and has been the focus of ecosystem research since 1981. A map, photographs, and description of the watershed can be found at <http://co.water.usgs.gov/lochvale/>, and a detailed description of the physical setting and biogeochemistry of the Loch Vale ecosystem is given by Baron [1992]. Elevation of the Loch Vale watershed ranges from  $3050$  to  $4026$  m. The entire watershed consists of  $83\%$  bare rock, boulder fields, snow, and ice;  $11\%$  alpine ridge (tundra);  $5\%$  forest; and  $1\%$  subalpine meadow [Baron, 1992]. Climate is typical of midcontinent high-elevation zones; annual average precipitation is  $110$  cm, of which  $65$ – $80\%$  falls as snow [Baron and Denning, 1993]. Strong westerly winds redistribute low-density snow during the winter months, removing snow from ridge-top tundra and depositing it on slopes near the valley floor.

[13] The two subbasins of Loch Vale, Andrews Creek ( $183$  ha) and Icy Brook ( $326$  ha), each have an average slope of  $33$ – $34$  degrees; more than half of each basin area has a slope greater than  $30$  degrees. The basins are primarily alpine; less than  $1\%$  of their areas are forested and less than  $20\%$  of their areas are covered by vegetated soil. Processes controlling major-ion chemistry in the two subbasins are discussed by Campbell *et al.* [1995]. Because of subtle differences in microclimate, hydrology, geology, landscape-type distribution, and vegetative cover, the Icy Brook catchment retains  $45\%$  of total annual inorganic nitrogen deposition, compared with  $29\%$  for Andrews Creek [Campbell *et al.*, 2000; Clow and Sueker, 2000].

[14] Two springs emerging from talus deposits were sampled to determine the role of talus in streamflow generation and nitrogen export: Andrews Spring, located at the base of south facing talus deposits near the Andrews Creek stream gage, and Spring 19, located at the base of north facing talus deposits near the Icy Brook stream gage. Talus deposits consist of poorly sorted colluvial material resting at the angle of repose beneath cliffs and couloirs; they are sparsely covered with patches of poorly developed soil and vegetation. The talus deposits have high permeability, but the drainage areas for the individual springs are undetermined because of uncertainty in the underlying bedrock surface topography.

## 3. Methods

[15] Sample volumes of  $10$ – $20$  L were needed when the study began in order to produce the  $200$   $\mu\text{mol}$  of nitrate needed for analysis of both  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  by dual-inlet mass spectrometry. Because access to the study area is limited to foot travel (hiking, skiing, and snowshoeing), transport of water samples to the laboratory prior to processing was impractical. Methods were developed to collect the nitrate on ion exchange columns in the field, addressing the need for practicality while taking precautions to prevent nitrate transformations during sample processing.

### 3.1. Sample Collection: Atmospheric Deposition

[16] Snowpack samples were collected in early April of each year by excavating a snow pit to the ground surface and carving a column of uniform dimensions from a clean pit face throughout the

depth of the snowpack [Ingersoll, 1995]. Snowpack samples were stored in 60-L polyethylene carboys buried in the snowpack, which remained at 0°C and in the dark until samples were melted. Samples were melted by placing the carboys in a sunny area for 2–3 days during May or June. The 60 L of snow yielded approximately 20 L of water, which were immediately filtered and processed in the field.

[17] Snowmelt samples were collected from a snowmelt lysimeter with an area of 6.1 m<sup>2</sup> that was installed on top of a large flat rock. The lysimeter consisted of a polypropylene-lined pan that drained into a 60-L polyethylene carboy. The lysimeter was located at approximately 3200 m elevation on a SE aspect; therefore the timing of melt at the site was early compared with the timing in many other parts of the watershed. Samples were collected every 1–4 days when snow was melting in May, and a 1-L subsample for chemical composition and  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$  was taken to the lab and processed within 24 hours. A 20-L subsample was buried in the snowpack, where it was stored fully or partially frozen until being processed with the snowpack samples.

[18] Bulk precipitation samples were collected every 1–3 weeks in a 60-L polypropylene carboy which was open during spring season (when snow or rain could fall) and covered with nylon screen during summer and early fall to exclude detritus and insects. Samples were transported to the laboratory, filtered within 24 hours, and refrigerated until a composite sample of 10–20 L had accumulated.

### 3.2. Sample Collection: Streams and Talus Springs

[19] The chemical composition of streams and the two intensively sampled springs was determined from grab samples collected weekly to monthly during the open-water season (May–October) and intermittently during the snow cover season (November–April). Autosamplers were used occasionally for more frequent sampling. During 1995, grab samples were collected from various springs and seeps emerging from talus deposits located throughout the Loch Vale watershed.

[20] Nitrate isotope samples of surface water and groundwater were collected in 10- to 20-L collapsible polyethylene carboys. During winter and early spring, water samples were collected and stored in the snowpack until above-freezing air temperatures allowed processing. During warmer seasons most samples were filtered and processed immediately in the field, although some samples were transported to the laboratory for filtering and processing the following day.

### 3.3. Sample Processing and Analysis

[21] Filtered (0.45  $\mu\text{m}$ ), unpreserved, refrigerated aliquots were analyzed for nitrate concentration by ion chromatography (standard error was 0.5  $\mu\text{eq/l}$ ) in the U.S. Geological Survey research laboratory in Boulder, Colorado. Unfiltered, unpreserved, unrefrigerated samples collected in 30-mL glass vials with poly-seal caps were used to analyze for  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$  in the U.S. Geological Survey stable isotope laboratory in Menlo Park, California.

[22] Nitrate isotope samples were passed through a 0.45- $\mu\text{m}$  filter by gravity feed or a battery-powered peristaltic pump. A subsample was collected for analysis of nitrate concentration, and the sample volume was measured volumetrically or by weight to calculate total nitrate in the sample. Samples were then gravity fed through ion exchange columns [Chang *et al.*, 1999] at a rate of 0.5–1 L/h. Most samples were left for 1–3 days before disassembling columns, although occasionally the columns were left in the field for 1–2 weeks.

[23] A 1994 pilot study of nitrate isotopes in Loch Vale and other undisturbed watersheds [Kendall *et al.*, 1995] used a methodology that originally was designed for waters such as agricultural and urban runoff that have relatively high nitrate concentrations [Silva *et al.*, 2000]. Although the method used in the pilot study was successful and nitrate isotope values were similar to those in this study, capture of nitrate on the anion exchange resin was difficult because the column frequently became clogged by dissolved organic material (DOM). Although DOM concentrations were low, substantial organic material accumulated in the upper part of the columns as the 20 L of sample water passed through the resin.

[24] The collection method used in this study was modified specifically for use on low-ionic-strength waters that have low nitrate concentrations. The method is described in detail by Chang *et al.* [1999]; the main differences between the method used in the pilot study and the method used in this study were that in this study (1) a cation column was placed in series before the anion column to capture cations, acidify the sample, and protonate the DOM (reducing its affinity for the anion resin); (2) cation and anion columns were larger, with more ion exchange resin; and (3) the anion resin had a coarser mesh and varied during the study: AG1X resin was used in 1995 and AG2X resin was used in 1996–1997. The AG2X resin was preferred over the AG1X resin because it has lower affinity for DOM as well as for nitrate and other anions [Chang *et al.*, 1999]. The lower-affinity resin is sufficient to capture all of the nitrate while releasing some of the DOM that clogged the columns in the pilot study. It was also easier to extract the nitrate from the lower-affinity resin for analysis.

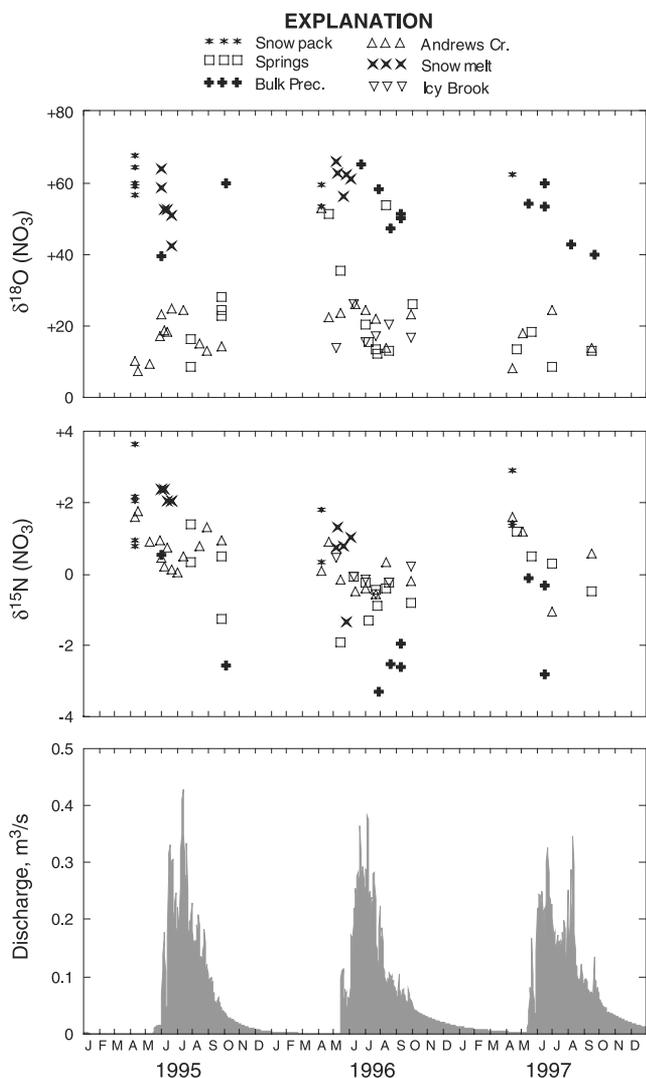
[25] After columns were disassembled, anion exchange columns were refrigerated in the laboratory for up to 2 years before nitrate was extracted and analyzed for  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  via the methods described by Silva *et al.* [2000]. Isotope analysis was performed on a Finnigan Mat 251 stable isotope mass spectrometer. Standard error of analysis for laboratory standards of  $\text{KNO}_3$  was  $\pm 0.05\%$  for  $\delta^{15}\text{N}_{(\text{NO}_3)}$  and  $\pm 0.2\%$  for  $\delta^{18}\text{O}_{(\text{NO}_3)}$ . Field replicate samples collected as part of a related study had a standard error of  $\pm 0.22\%$  for  $\delta^{15}\text{N}$  ( $n = 16$ ) and  $\pm 0.58\%$  for  $\delta^{18}\text{O}$  ( $n = 18$ ); the mean of the absolute differences between replicate pairs was 0.38% for  $\delta^{15}\text{N}$  values and 1.6% for  $\delta^{18}\text{O}$  values [Battaglin *et al.*, 2001].

## 4. Results

[26] Values of  $\delta^{18}\text{O}_{(\text{NO}_3)}$  in atmospheric deposition (snowpack, snowmelt, and bulk precipitation) were distinct from values in water from streams and talus springs (Figures 1 and 2). The  $\delta^{15}\text{N}_{(\text{NO}_3)}$  values were not distinct between the different water types. The  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$ , nitrate concentration, and  $\delta^{18}\text{O}_{(\text{NO}_3)}$  for Andrews Creek and Spring 19 are presented for 1996 in order to compare the hydrology and biogeochemistry of surface water and groundwater (Figure 3). Most of the values of  $\delta^{18}\text{O}_{(\text{NO}_3)}$  from streams and talus springs indicated most of the nitrate had undergone microbial nitrification rather than come directly from atmospheric deposition (with no prior biological assimilation and release) (Figures 1, 2, and 4). A more detailed discussion of each component of the hydrologic system follows.

### 4.1. Atmospheric Deposition

[27] Atmospheric deposition (snowpack, snowmelt, and bulk precipitation) had high  $\delta^{18}\text{O}_{(\text{NO}_3)}$  (+40 to +70‰) and a range of moderate to low  $\delta^{15}\text{N}_{(\text{NO}_3)}$  values (–4 to +4‰) (Figure 1). The  $\delta^{15}\text{N}_{(\text{NO}_3)}$  of bulk precipitation collected during spring and summer was generally lower (–4 to +1‰) than that found in the winter



**Figure 1.** Time series of  $\delta^{18}\text{O}_{(\text{NO}_3)}$  (‰),  $\delta^{15}\text{N}_{(\text{NO}_3)}$  (‰), and Andrews Creek discharge ( $\text{m}^3/\text{s}$ ).

snowpack (0 to +4‰). The  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values in the summer bulk precipitation (+40 to +65‰) were similar to or slightly lower than those in the winter snowpack (+50 to +70‰). The nitrate isotope values for atmospheric deposition are within the wide range of values reported in previous studies, clustering near a peak of relatively high values identified for North America that appear to reflect a mixture of anthropogenic sources of nitrate [Kendall, 1998].

**4.2. Nitrate Release From the Snowpack**

[28] The earliest snowmelt samples in 1995 had nitrate isotopic compositions similar to those of the winter snowpack, and subsequent snowmelt samples had decreasing  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$ , reflecting greater contributions of nitrate from the springtime precipitation (Figure 1). Precipitation amount during April and May (after routine sampling of the snowpack) nearly equaled the amount that accumulated in the winter snowpack during November–March. The spring precipitation was mostly in the form of snow and was sampled in a bulk precipitation collector in early June. Spring precipitation  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  values were lower than values in the winter snowpack (+40‰ in spring versus +55 to

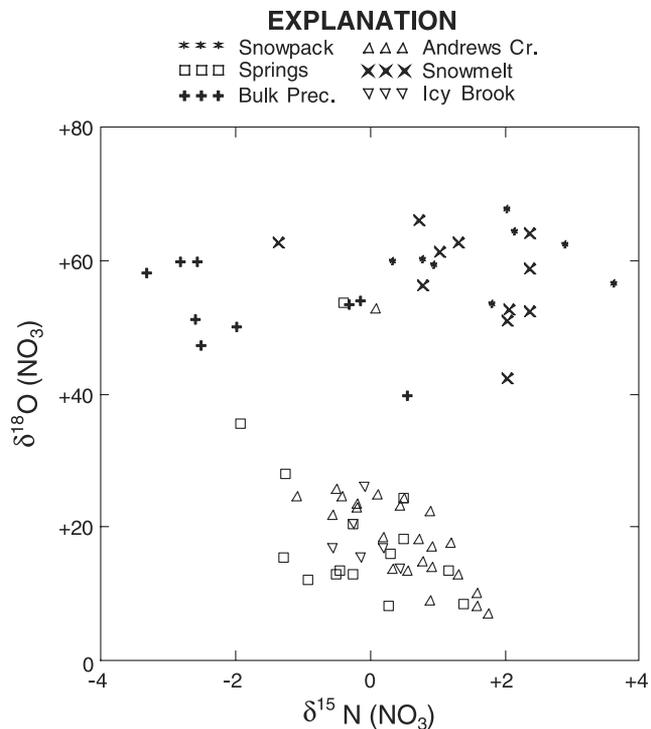
+65‰ in winter for  $\delta^{18}\text{O}$ , and +0.5 in spring versus +0.3 to +2.2‰ in winter for  $\delta^{15}\text{N}$ ).

[29] In 1996 most snow fell prior to collection of snowpack samples, and the snowmelt nitrate isotopic composition was similar to that of the snowpack, except in one sample collected on 29 May. That sample had a low  $\delta^{15}\text{N}$  value (−1.4‰), similar to values in summer rainfall (Figure 1). Approximately 6.5 cm of precipitation fell during the preceding week, so the composition of that sample was likely dominated by late-spring precipitation rather than winter snowfall. Meltwater was not sampled in 1997.

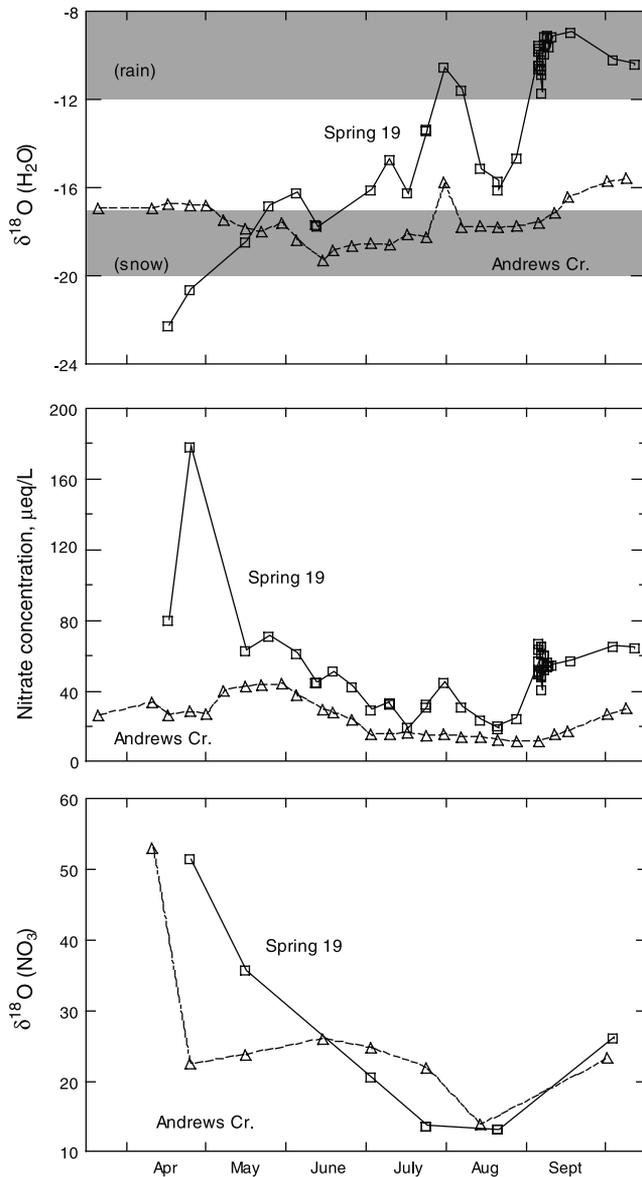
**4.3. Stream Water**

[30] Discharge in Andrews Creek began to rise in May and peaked in late June or early July during all three years (Figure 1). The seasonal pattern of  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$  for 1996 indicated most of the water in the stream originated as snowmelt, with a trend toward slightly greater contributions from rainfall during late summer and fall (Figure 3). Concentrations of nitrate in stream water in 1996 were moderate prior to snowmelt, peaked in late May, decreased through the summer, and rose again in the fall (Figure 3). The seasonal patterns of  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$  and nitrate concentration presented for 1996 were typical of other years as well.

[31] The streams (Andrews Creek and Icy Brook) had  $\delta^{15}\text{N}_{(\text{NO}_3)}$  values that ranged from −1 to +2‰ and  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values that ranged from +10 to +25‰ throughout most of the year (Figure 1). A few higher  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values occurred during peak snowmelt and rain events. The values in stream water were similar to those in groundwater and distinct from those in atmospheric deposition. The nitrate isotopic composition of the stream water was sensitive to time of sampling relative to snowmelt. A sample collected during April 1996 from Andrews Creek had a  $\delta^{18}\text{O}_{(\text{NO}_3)}$  value that was nearly identical to those in atmospheric deposition (snowpack, snowmelt, and bulk precipitation) (Figure 1), suggesting that direct



**Figure 2.** The  $\delta^{18}\text{O}_{(\text{NO}_3)}$  (‰) versus  $\delta^{15}\text{N}_{(\text{NO}_3)}$  (‰) in all samples, 1995–1997.



**Figure 3.** Time series for Andrews Creek and Spring 19, 1996: (a)  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$  (‰), (b) nitrate concentration ( $\mu\text{eq/L}$ ), and (c)  $\delta^{18}\text{O}_{(\text{NO}_3)}$  (‰). Shaded areas represent range of  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$  values for summer rainfall and winter snowpack samples collected in Loch Vale watershed.

snowmelt was entering the stream by overland flow or shallow subsurface flow paths at this time. A similar event was detected in Andrews Creek during early snowmelt in 1994 [Kendall *et al.*, 1995]. At this time of year, discharge is very low and even small amounts of localized snowmelt may have a large effect on stream water chemical composition. In 1995 and 1997 none of the stream samples had  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values greater than +25‰, suggesting that pulses of snowmelt-dominated nitrate in streams are likely of short duration and/or frequency.

[32] In late summer, streamflow usually receded to base flow conditions (Figure 1), and nitrate concentrations increased somewhat (Figure 3). Low temperatures below freezing are common by September, causing plant demand for nitrogen to decrease; however, soil and subtalus temperatures fall more slowly than air

temperatures, so soil microbial activity continues. Low  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values (+15 to +25‰) indicated most of the nitrate in the stream at this time has been cycled through microbial processes (Figures 1 and 3).

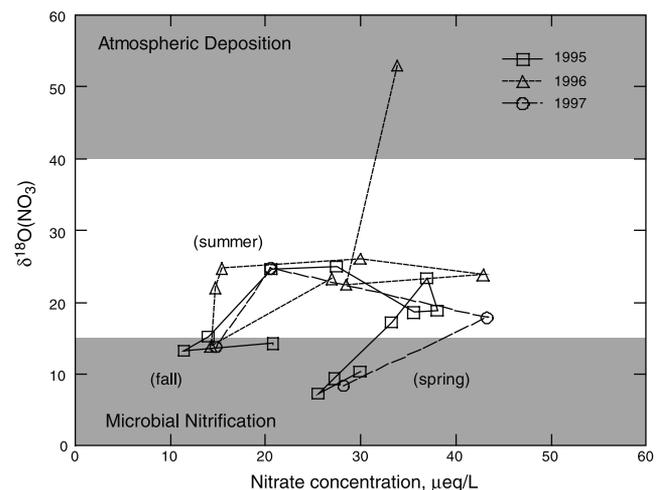
**4.4. Talus Springs**

[33] In 1995, groundwater samples were collected from talus springs during two periods from five different sites. Nitrate concentrations ranged from 24 to 64  $\mu\text{eq/L}$ , and  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values were from +10 to +27‰ (Figure 1), indicating predominantly microbial nitrate.

[34] In 1996, only two sites, Spring 19 and Andrews Spring, were sampled for talus groundwater. Samples from Spring 19 were collected prior to substantial snowmelt in order to characterize premelt waters in talus deposits. Spring 19 data are presented with Andrews Creek data in order to compare seasonal patterns in the surface water and groundwater systems (Figure 3). Although Andrews Spring is closer to the Andrews Creek sampling site, both springs are representative of waters draining numerous talus deposits in these alpine watersheds, and Spring 19 was chosen because more data were available from the early snowmelt period.

[35] A sample collected from Spring 19 in late April 1996 (Figure 3) had very high nitrate concentrations (178  $\mu\text{eq/L}$ ) as well as other major ions including sulfate and chloride in proportions roughly equivalent to those in atmospheric deposition. The  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$  values indicated Spring 19 was fed primarily by snowmelt during the spring season, and  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values were similar to those in atmospheric deposition. Both nitrate concentration and  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values decreased as snowmelt proceeded.

[36] Midsummer  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values in Spring 19 were generally +10 to +20‰, indicating predominantly microbial nitrate, with little or no contribution of nitrate directly from snowmelt or rainfall. A rain event during late July/early August produced a peak in  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$ , indicating that rain was the dominant source of water in the spring for a brief period; however, nitrate concentrations changed only slightly. No nitrate isotope samples were collected during that period. After the event,  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$  values in Spring 19 returned to pre-event values before increasing rapidly in September. The high  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$  values in September indicated that the small amount of flow at that time originated primarily as summer rainfall. Both nitrate concentration and  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values



**Figure 4.** The  $\delta^{18}\text{O}_{(\text{NO}_3)}$  (‰) versus nitrate concentration ( $\mu\text{eq/L}$ ) in Andrews Creek, 1995–1997.

also increased slightly, probably reflecting a decrease in biological uptake in response to lower temperatures.

[37] The  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values in Andrews Spring were generally similar to those in Spring 19. However, a sample from Andrews Spring collected during a rainy period in mid-August 1996 had  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values that indicated a pulse of nitrate directly from atmospheric deposition (Figure 1). In the absence of intense event sampling, the magnitude and duration of these short-term changes are uncertain. In 1997, four samples were collected from Andrews Spring, and all indicated that microbial nitrification was the dominant source of nitrate in the spring, even during snowmelt.

## 5. Discussion

[38] The  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  values of nitrate for each water type (rain, snow, snowmelt, stream water, and talus springs) were consistent during 1995–1997 (Figure 1) and similar to values reported for 1994 [Kendall *et al.*, 1995]. Differences in the ranges of isotopic composition of similar sample types between years were only about 1‰ for  $\delta^{15}\text{N}$  and 5‰ for  $\delta^{18}\text{O}$ , even though interannual differences in hydrologic and biogeochemical processes were evident in the seasonal patterns of  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  values.

### 5.1. Nitrate in Atmospheric Deposition

[39] In this study the seasonal pattern in  $\delta^{15}\text{N}_{(\text{NO}_3)}$  of bulk precipitation (with low values during spring and summer) likely is caused by differences in storm types and sources of nitrogen oxide emissions for the Colorado Front Range [Baron and Denning, 1993]. Winter precipitation at Loch Vale is dominated by synoptic weather systems with westerly airflow; these air masses are affected by regional nitrogen oxide emissions that include transportation, industrial, and agricultural sources. Spring and summer precipitation is affected by the same regional mixture, plus a variable component of easterly flow with a somewhat different mixture of source categories from eastern Colorado and nearby states. The relation between nitrate isotopic composition and sources of nitrate in atmospheric deposition in the Rocky Mountain region merits further investigation.

### 5.2. Ammonium in Atmospheric Deposition

[40] Atmospheric deposition of inorganic nitrogen in the Front Range is made up of substantial amounts of dissolved ammonium in addition to nitrate. In water years 1992 through 1997, annual volume-weighted mean concentrations of ammonium averaged 39% of total inorganic nitrogen in wetfall [Campbell *et al.*, 2000] (see also National Atmospheric Deposition Program (NRSP-3)/National Trends Network, 1999, Illinois State Water Survey, Champaign, available at <http://nadp.sws.uiuc.edu>). Export of ammonium is insignificant in the Loch Vale watershed, and export of nitrate is slightly greater than total inputs of nitrate in atmospheric deposition, suggesting that at least some of the ammonium in atmospheric deposition may be assimilated, mineralized, and nitrified to nitrate that is exported in streamflow [Campbell *et al.*, 2000].

[41] Some studies have suggested that ammonium is nitrified to nitrate before being released from the snowpack [Schaefer and Driscoll, 1993]. In this study, ammonium and nitrate concentrations in the snowpack were similar to those in snowmelt, indicating no net transformation of inorganic nitrogen in the snowpack. An earlier investigation using labeled  $\delta^{15}\text{N}$  also indicated that ammo-

nium from atmospheric deposition is not nitrified in the snowpack but is readily sorbed to exchange sites in soil-like material and later assimilated or nitrified to nitrate [Williams *et al.*, 1996b]. Together, these studies suggest that most of the ammonium in atmospheric deposition contributes to the pool of nitrogen in soil and vegetation and that a portion of this organic nitrogen may eventually be mineralized, nitrified, and exported.

### 5.3. Contribution of Microbially Cycled Nitrate to Stream Water

[42] Although alpine landscapes have sparse vegetation and poorly developed soils, substantial pools of soil nitrogen are available for microbial nitrification [Williams *et al.*, 1997]. Soil nitrate has  $\delta^{15}\text{N}$  values that reflect the atmospheric deposition from which the nitrate was derived and  $\delta^{18}\text{O}$  values characteristic of microbial nitrification (a combination of oxygen from water and  $\text{O}_2$  gas, as discussed in section 1). Both isotopes also may be affected by fractionation that occurs during nitrogen-cycling processes.

[43] The results of this study are similar to a companion study using  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  that was conducted in forested watersheds in the northeastern United States [Burns and Kendall, 2002]. That study also found that most of the nitrate in stream water had an isotopic signature that indicated substantial biological cycling of atmospherically derived nitrogen prior to release from the ecosystem.

[44] Andrews Creek shows a strong counterclockwise pattern of hysteresis when  $\delta^{18}\text{O}_{(\text{NO}_3)}$  is plotted versus nitrate concentration, reflecting changes in amounts and sources of nitrate through the seasons (Figure 4). In 1995 and 1997, samples collected prior to substantial snowmelt had moderate nitrate concentrations (20–40  $\mu\text{eq/l}$ ) and low  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values (less than +15‰) characteristic of microbially cycled nitrate. In 1996 a single early sample appeared to be dominated by snowmelt ( $\delta^{18}\text{O}_{(\text{NO}_3)}$  of +54‰), as was discussed previously. In all years, samples collected on the rising limb of the snowmelt hydrograph (in May or June) had high nitrate concentrations (>35  $\mu\text{eq/l}$ ) and moderate  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values (+15 to +30‰) that indicated contributions both from direct snowmelt and from flushing of microbially cycled nitrate. As snowmelt progressed, concentrations decreased, but the isotopic signature indicated constant proportions of the two sources through late summer. During the summer period, nitrate concentrations in both sources decrease: Atmospherically derived nitrate decreases because of differential elution of snowpack solutes, and microbial nitrate decreases because soil pools have been flushed during early runoff [Brooks *et al.*, 1998]. Nitrate concentrations in stream water are also reduced by aquatic uptake of nitrate, which increases as the snowpack recedes and soil temperatures warm. In late summer the proportion of microbial nitrate again increased, but nitrate concentrations remained lower than in the spring.

[45] The cluster of values for streams and talus springs in Figure 2 suggests a mixing line that extends between a source with high  $\delta^{18}\text{O}_{(\text{NO}_3)}$  and low  $\delta^{15}\text{N}_{(\text{NO}_3)}$  to a source with low  $\delta^{18}\text{O}_{(\text{NO}_3)}$  and high  $\delta^{15}\text{N}_{(\text{NO}_3)}$ . Lumping of different sites and years explains some of the scatter in this cluster; however, the proposed end-member mixing model remains hypothetical. Bulk precipitation collected in spring and summer of all years had high  $\delta^{18}\text{O}_{(\text{NO}_3)}$  and low  $\delta^{15}\text{N}_{(\text{NO}_3)}$  that could comprise one end-member of the mixing line. The high  $\delta^{15}\text{N}_{(\text{NO}_3)}$  for the other end-member could come from nitrate in snow (Figure 1), ammonium in rain and/or snow, or possibly denitrification; the low  $\delta^{18}\text{O}_{(\text{NO}_3)}$  of this end-member would be caused by microbial nitrification. A better understanding

of nitrogen deposition and cycling in various landscapes is needed to establish these end-members.

#### 5.4. Sources of Water and Nitrate

[46] The role of subalpine hydrologic flow paths in controlling hydrologic and chemical fluxes in alpine watersheds has been identified in previous studies [Campbell *et al.*, 1995; Williams *et al.*, 1997; Campbell *et al.*, 2000; Clow and Sueker, 2000]. Mast *et al.* [1995] showed that although most of the water in Andrews Creek was “new water” from snowmelt (based on hydrograph separation using  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$ ), much of that water had been transported along subsurface flow paths prior to reaching the stream, and substantial interaction had occurred with soil or soil-like materials (based on hydrograph separation using dissolved silica).

[47] In this study, although seasonal patterns of  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$  in Spring 19 and Andrews Creek were mostly similar, Spring 19 showed much greater amplitude of change between event water and old water (Figure 3). This was true for both the seasonal snowmelt event and for midsummer rains, indicating a smaller reservoir of water with a shorter hydrologic residence time in the talus. The  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$  of water in Andrews Creek prior to initiation of snowmelt more closely resembled that of snow than rain (Figure 3), suggesting base flow came from a reservoir in which residence time was sufficiently long to integrate snow and rain from the previous season. During peak snowmelt in June and July the source of water in Andrews Creek was almost entirely snowmelt (presumably from the current season). Late summer values were intermediate between snow and summer rainfall. Relatively small seasonal variance in  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$  in Andrews Creek suggests a large reservoir of water and a hydrologic residence time of many months to a year or more.

[48] From peak snowmelt until late summer,  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values indicated more than half of the nitrate in both Andrews Creek and Spring 19 came from microbially cycled nitrate (Figures 1 and 3). This microbially cycled nitrate likely originated as nitrogen in atmospheric deposition (alpine/subalpine plant communities do not fix much nitrogen directly from the atmosphere) but may have been cycled and stored in the ecosystem for months or years before being nitrified and flushed from soil-type matrices during snowmelt.

[49] In general, the similarity of the seasonal patterns for  $\delta^{18}\text{O}_{(\text{NO}_3)}$  in the talus springs and in the stream water suggests that talus deposits are important source areas of nitrate export, especially during late summer when areas with better developed soil and vegetation may not be exporting nitrogen. These results support the hypothesis that microbial cycling controls the supply of mobile nitrate in groundwater, including the talus deposits [Brooks *et al.*, 1998]. Transport processes are controlled by hydrologic variables such as flow paths, reservoir sizes, and residence times. Thus both biogeochemical and hydrologic processes control export of nitrate in alpine springs and streams. The highest nitrate concentrations in the springs and streams are a combination of flushing of microbially cycled nitrate and nitrate directly from rain or snowmelt.

#### 5.5. Other Potential Sources and Sinks for Nitrogen

[50] Bowman *et al.* [1996] reported substantial input of N to certain alpine landscapes at Niwot Ridge, Colorado, from symbiotic fixation of atmospheric  $\text{N}_2$  gas. Vegetation is more widespread and soils are better developed at Niwot Ridge compared with Loch Vale, and it is believed that  $\text{N}_2$  fixation is not a substantial component of the nitrogen budget in Loch Vale.

However,  $\text{N}_2$  fixation could affect nitrogen budgets in favored areas and merits further investigation.

[51] In 1996, stream nitrate isotope samples were collected from Icy Brook as well as from Andrews Creek (Figure 2). Although more algal uptake of nitrogen occurs in the Icy Brook drainage [Baron and Campbell, 1997; Campbell *et al.*, 2000], significant isotopic fractionation resulting from primary productivity was not evident: The Icy Brook  $\delta^{15}\text{N}_{(\text{NO}_3)}$  values were within the same range as those of Andrews Creek (Figures 1 and 2). Both the concentration data and the isotope data suggest that during most of the runoff season, algal uptake does not substantially affect nitrogen flux in the watershed, although other studies suggested that algal uptake may reduce nitrate concentrations in Sky Pond and downstream in Icy Brook during late winter and early spring [Campbell *et al.*, 1995; Baron and Campbell, 1997].

[52] Denitrification does not appear to substantially affect fluxes of nitrate from surface water or talus springs in the Loch Vale watershed either. If denitrification was important in these systems, a progression toward higher  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values would be expected in the remaining nitrate [Böttcher *et al.*, 1990]. Such a pattern was not evident in double-isotope plots, either in time series from single sites or from multiple sites along a single flow path (Figure 1). The spring waters emerging from the talus deposits are probably well oxygenated during most of the year and denitrification is likely not important. Samples from wells and tension lysimeters in nearby wetlands were often anoxic, but these sites had too little nitrate for isotopic analysis; denitrification may be occurring in the wetland landscapes, but they make up less than 1% of the total watershed area and are not believed to substantially affect watershed fluxes of nitrogen [Campbell *et al.*, 2000]. However, this study indicates the need for a more thorough investigation of temporal and spatial variability in soil N-cycling processes.

## 6. Conclusions

[53] Elevated atmospheric deposition is the source of nitrogen inputs to Colorado Front Range alpine ecosystems, but substantial microbial cycling of nitrogen occurs before it is exported in stream water. The  $\delta^{18}\text{O}_{(\text{NO}_3)}$  of stream water indicates that in most years, more than half of the nitrogen in atmospheric deposition is stored and cycled in the ecosystem before being nitrified and exported from the watershed in streamflow. During late summer, >75% of the nitrate in streamflow is from microbial nitrification rather than directly from atmospheric deposition. In the streams, seasonal changes in nitrate concentration are small relative to changes in the  $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$ , indicating substantial storage and subsequent release of nitrate at timescales greater than those for water. Inorganic nitrogen in atmospheric deposition includes substantial ammonium in addition to nitrate. The ammonium inputs are either assimilated or otherwise retained in the ecosystem, or nitrified and exported as nitrate in stream water.

[54] Much of the nitrate exported in the alpine streams is transported from the talus deposits. Although the talus deposits have little vegetation and soil development, they function much like well-developed soils. Isotopic signatures indicated substantial contributions from microbial nitrification to the nitrate found in both the subalpine waters and in the streams. Only a few isolated samples of stream water and talus springs collected during early snowmelt and summer rain events were dominated by nitrate that came directly from atmospheric deposition.

[55] Elevated levels of nitrogen in atmospheric deposition to the Front Range likely result from local and regional emissions sources such as agriculture and fossil fuel combustion in motor vehicles

and power plants. The consistently higher  $\delta^{15}\text{N}$  of nitrate in the winter snowpack compared with spring and summer bulk precipitation likely reflects a seasonal difference in the mixture of local and regional sources of atmospheric nitrate. Regional patterns in  $\delta^{15}\text{N}$  of nitrate in the snowpack will be examined in future studies to evaluate the potential for determination of sources of nitrate in precipitation using nitrogen isotopes. In contrast to the  $\delta^{18}\text{O}_{(\text{NO}_3)}$  values, which change as nitrogen is cycled through the ecosystem, changes in  $\delta^{15}\text{N}_{(\text{NO}_3)}$  values are relatively small as nitrogen is cycled, and values in streams and talus springs are within the same range as those in atmospheric deposition.

[56] Nitrate mass balance and  $\delta^{15}\text{N}_{(\text{NO}_3)}$  support atmospheric deposition as the primary source of watershed nitrate. The  $\delta^{18}\text{O}_{(\text{NO}_3)}$  indicates that a substantial amount of the nitrate is microbially cycled before being exported from alpine ecosystems. Other studies suggest that terrestrial ecosystems in the Colorado Front Range are being affected by excess nitrogen in deposition [Baron *et al.*, 2000]. Future changes in climate, anthropogenic emissions of nitrogen compounds, or terrestrial nitrogen cycling could affect amounts and sources of nitrate in surface water and groundwater. The nitrate double-isotope technique proved robust in this study for distinguishing between atmospheric and microbial sources of nitrate in runoff from undisturbed watersheds and may be useful for determining future changes in sources of nitrate in the Front Range and for assessing nitrogen-cycling processes in other catchments that exhibit symptoms of nitrogen saturation.

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Note: This .pdf file incorporates a correction of Figures 1 and 2 which was published after the original article.