

# Climate-induced changes in high elevation stream nitrate dynamics

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## Abstract

Mountain terrestrial and aquatic ecosystems are responsive to external drivers of change, especially climate change and atmospheric deposition of nitrogen (N). We explored the consequences of a temperature-warming trend on stream nitrate in an alpine and subalpine watershed in the Colorado Front Range that has long been the recipient of elevated atmospheric N deposition. Mean annual stream nitrate concentrations since 2000 are higher by 50% than an earlier monitoring period of 1991–1999. Mean annual N export increased by 28% from 2.03 kg N ha<sup>-1</sup> yr<sup>-1</sup> before 2000 to 2.84 kg N ha<sup>-1</sup> yr<sup>-1</sup> in Loch Vale watershed since 2000. The substantial increase in N export comes as a surprise, since mean wet atmospheric N deposition from 1991 to 2006 (3.06 kg N ha<sup>-1</sup> yr<sup>-1</sup>) did not increase. There has been a period of below average precipitation from 2000 to 2006 and a steady increase in summer and fall temperatures of 0.12 °C yr<sup>-1</sup> in both seasons since 1991. Nitrate concentrations, as well as the weathering products calcium and sulfate, were higher for the period 2000–2006 in rock glacier meltwater at the top of the watershed above the influence of alpine and subalpine vegetation and soils. We conclude the observed recent N increases in Loch Vale are the result of warmer summer and fall mean temperatures that are melting ice in glaciers and rock glaciers. This, in turn, has exposed sediments from which N produced by nitrification can be flushed. We suggest a water quality threshold may have been crossed around 2000. The phenomenon observed in Loch Vale may be indicative of N release from ice features such as rock glaciers worldwide as mountain glaciers retreat.

*Keywords:* atmospheric deposition, climate change, Loch Vale, microbial activity, nitrogen, rock glaciers, Rocky Mountain National Park, weathering

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## Introduction

Fully one-third of the world's legally protected areas are in mountains (Körner *et al.*, 2005). Partly due to their inaccessibility, many mountain environments are among the least disturbed on Earth by direct human encroachment, including land use change. In spite of their protected status, mountain ecosystems are highly vulnerable to changes in climate, pollutant and nutrient inputs. Complex topography, harsh climates, and short growing seasons all combine to reduce the ability of mountain ecosystems to withstand disturbances that affect physical structure (e.g. soil and slope stability) and biological communities. The great landscape-scale heterogeneity of

high mountain areas also makes it difficult to explain observed phenomena: forest, tundra, talus and block fields with little vegetation, stored ice in glaciers, rock glaciers, which are cryic features made up of unconsolidated rubble cemented with ice, and permafrost all contribute to the cycling and flux of nutrients.

In this paper, we present the juxtaposition of two widespread disturbances: climate change and atmospheric nitrogen (N) deposition. Climate change is affecting mountain areas worldwide (IPCC, 2007; Meier *et al.*, 2007) and increasing atmospheric deposition of N occurs over so much of the Earth's surface that the cumulative effect amounts to global-scale change (Turner *et al.*, 1990; Galloway *et al.*, 2004). In the high mountain environment of the Colorado Front Range the co-occurrence of climate change and N deposition complicates the identification of N deposition effects. In other mountain regions there may be additional ramifications, such as eutrophication.

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In both the western United States and the European Alps the warmest mean annual temperatures have occurred after 2000 (Diaz & Eischeid, 2007; Cannone *et al.*, 2008). Analysis of extant records for the western United States found that the mean annual temperature of the warmest month over the 20 years from 1987 to 2006 exceeded the Köppen classification threshold of 10 °C for 73% of areas currently classified as having alpine climates, threatening their persistence (Diaz & Eischeid, 2007). Climate warming is affecting the proportion of precipitation that falls as rain vs. snow (Stewart *et al.*, 2005), inducing earlier mountain snowmelt (Knowles *et al.*, 2006), causing plant and animal species to shift their distributions northward or up in elevation (Parmesan, 2006; IPCC, 2007; Cannone *et al.*, 2008), and increasing the occurrence of temperature-related disturbances such as wildfire and insect outbreaks (Hicke *et al.*, 2006; Westerling *et al.*, 2006). Mountain glaciers are melting at unprecedented rates worldwide (Granshaw & Fountain, 2006; Meier *et al.*, 2007; Cannone *et al.*, 2008).

Atmospheric deposition has long been recognized as a source of pollution to mountain ecosystems (Körner *et al.*, 2005), and there is an extensive literature on the contribution of N to eutrophication and acidification. Enhanced rain-out of pollutants with orographic precipitation contributes to the influence of air pollution on mountain ecosystems (Ollinger *et al.*, 1993; Weathers *et al.*, 2006). Atmospheric N deposition contributes to increased N concentrations in plant tissues and soils, increased soil microbial activity, and changes in the flora of the alpine tundra (Körner *et al.*, 2005; Bowman *et al.*, 2006). Additions of very low quantities of nutrients to oligotrophic mountain aquatic systems, especially N and phosphorus, have been shown to transform algal species assemblages and increase primary productivity of mountain lakes and streams worldwide (Jassby *et al.*, 1995; Sickman *et al.*, 2003; Wolfe *et al.*, 2003; Bergström & Jansson, 2006; Enders *et al.*, 2008). Nitrate (NO<sub>3</sub><sup>-</sup>) concentrations in mountain streams are changing worldwide, with some papers reporting increases (Rogora *et al.*, 2001; Rogora, 2007) and others strong interannual variability (Park *et al.*, 2003; Watmough *et al.*, 2004). Stream NO<sub>3</sub><sup>-</sup> concentrations have declined in northeastern US mountain regions recently for reasons that are not entirely clear, but may be associated with climate phenomena or reforestation (Fitzhugh *et al.*, 2003; Goodale *et al.*, 2003; Hong *et al.*, 2005; Kahl *et al.*, 2004; McLaughlan *et al.*, 2007).

A few authors have addressed the coupled interactions of climate change and atmospheric N deposition on ecosystems, but most papers to date have been theoretical (Baron *et al.*, 2000; Park *et al.*, 2003; Herman *et al.*, 2007; Judd *et al.*, 2007; Rogora, 2007). Atmospheric N deposition increased from ~1950 to 2000 in the

Colorado Front Range mountains with many concurrent ecological and biogeochemical responses (Baron *et al.*, 2000; Burns, 2003). Yet, as the examples from New England suggest, changing climatic conditions can confound interpretation of environmental response, and climate is the over-riding control on ecosystem processes at broad scales (Ollinger *et al.*, 1993). We observed a linear increase in temperature over time, and a large and sudden increase in the concentration of inorganic N and N export from a high-elevation stream in a long-term research watershed in Rocky Mountain National Park. Measured inorganic N values in streams since 2000 are the highest observed since monitoring began in 1982. This paper explores the synchronous change in stream chemistry and climate to evaluate the relative roles of atmospheric N deposition and climate. Our objective was to use multiple lines of evidence from a long-term ecosystem research study to address the causal mechanisms for changes to mountain aquatic environments.

## Methods

### *Site description*

The Loch Vale Watershed (LVWS) is a 660 ha alpine/subalpine catchment located in Rocky Mountain National Park. LVWS extends southwest to northeast with elevation ranging from approximately 4000 m at the Continental Divide to 3100 m at the gaged outlet of The Loch, a subalpine lake (Fig. 1). Proportionally, LVWS is comprised of 1% surface water, 1% wetlands, 1% permanent snow and glaciers, 6% old-growth Engelmann spruce-subalpine fir forest, and 11% alpine. Fully 80% of LVWS is exposed rock and talus, of which 3% may overlie rock glaciers (Baron, 1992; Clow *et al.*, 2003). The bedrock found within LVWS is 80% biotite gneiss and 20% Silver Plume Granite (Cole, 1977). Dissolution of bedrock minerals, including biotite, plagioclase, pyrite, and microcrystalline calcite influences surface water chemistry in LVWS (Mast *et al.*, 1990). Biogeochemical and meteorological monitoring since 1982 has addressed watershed-scale ecosystem processes, particularly as they respond to atmospheric deposition (Baron, 1992; Baron *et al.*, 2000; Campbell *et al.*, 2000).

### *Data collection and analysis methods*

Data used for this study include daily air temperature and precipitation, weekly wet deposition chemistry, weekly stream chemistry, and daily discharge. Routine weekly stream sample collection began in 1991, and we present results from 1991 through 2006. Time series of temperature, precipitation, wet deposition chemistry, and stream discharge reveal dynamic characteristics of the mountain environment. We group stream chemistry

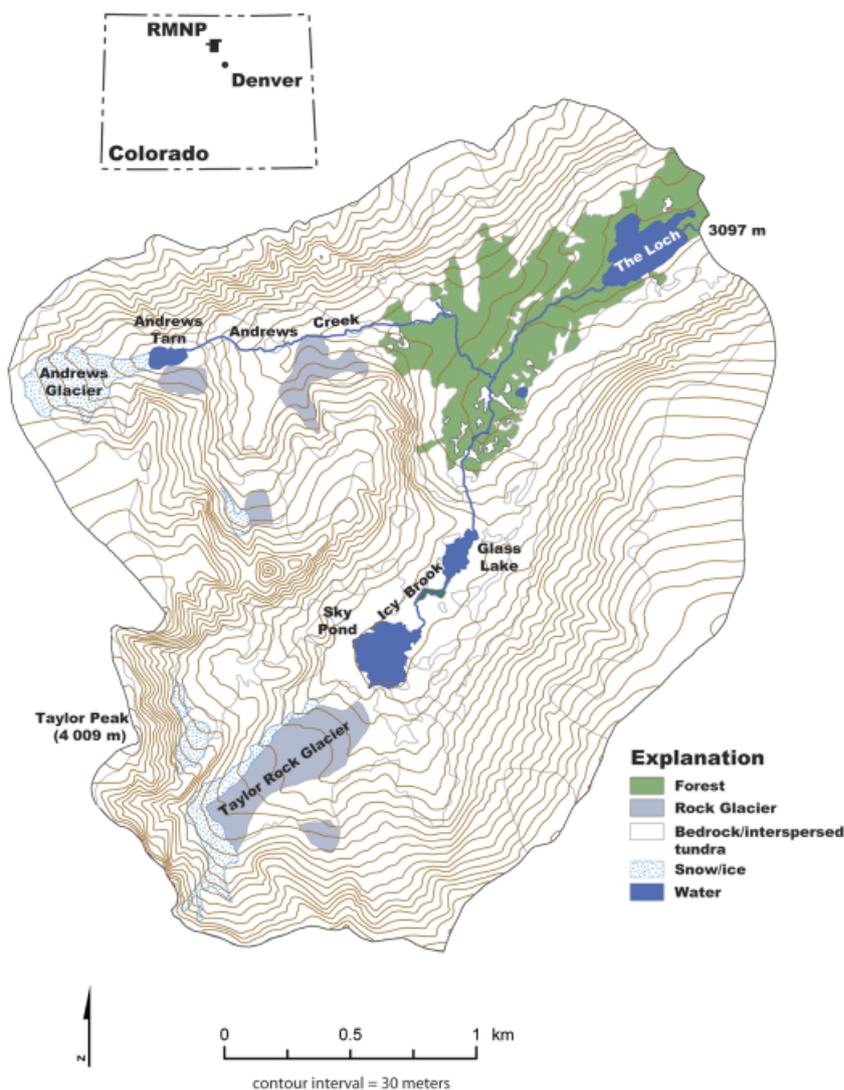


Fig. 1 Map of 660 ha Loch Vale watershed, Rocky Mountain National Park, CO, USA.

data into two unequal periods of samples that were collected during 1991–1999 and those collected during 2000–2006. This is because of our inclination to use the longest time period possible for evaluation. Chemical concentrations before 2000 demonstrated seasonal variability but no directional trends and a lower inter-annual variability than water collected after 2000. The nonparametric Mann–Whitney *U*-test allows for comparison of unequal and irregularly distributed data, as described below. All data except temperature data are reported for water years October 1 to September 30; temperature is reported for annual and seasonal periods, with the seasons divided as winter (DJF), spring (MAM), summer (JJA), and fall (SON). We used the absolute daily minimum and maximum values and the means of all daily measurements for this study.

Daily precipitation and weekly wet deposition chemistry were measured at the National Atmospheric Deposition Program/National Trends Network CO98 Loch Vale site (<http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=CO98>). Precipitation was captured in an alter-shielded Belfort rain gage (Bigelow *et al.*, 1990; Allstott *et al.*, 1999).

Stream samples were collected weekly throughout the year and analyzed according to standard methods (<http://www.nrel.colostate.edu/projects/lvws/pages/accesstodata/fieldlabmethods.htm>). Data reported for the period 1991–2006 include conductivity,  $\text{Ca}^{+2}$ ,  $\text{NO}_3^-$ -N,  $\text{SO}_4^{-2}$ ,  $\text{SiO}_2$ , and DOC. Less regular sampling of other stream locations, including the Sky Pond inlet, has occurred since 1983. Sky Pond inlet collections occurred only during the months June–September. Data quality

was evaluated using field blanks, co-located field duplicates, charge balance calculations, and comparisons of theoretical conductance with measured conductance (Allstott *et al.*, 1999; Botte & Baron, 2004).

Discharge has been measured at 3050 m at The Loch outlet since 1983 with a Parshall flume, stilling well, datalogger, and backup strip chart. Flow values are compared with those calculated from weekly stage heights, and periodically to those from hand-held meters (Botte & Baron, 2004). There is continuous flow through the year.

#### Statistical treatment of data

The Mann–Whitney *U*-procedure was used to test for differences in chemical and hydrological observations pre- and post-2000 (Sokal & Rohlf, 2003). Mann–Whitney *U* is a commonly used nonparametric test of whether two samples of observations come from the same distribution and is appropriate for testing the null hypothesis that samples are drawn from the same population when the data are not normally distributed. Significant differences were determined at the  $p \leq 0.05$  level and noted with asterisks in tables and figures.

## Results

#### Observed physical changes

No trends were observed in mean maximum, mean, or mean minimum annual temperatures over the period 1991–2006 (Fig. 2a). The mean annual temperature of 1.5 °C was the same as reported by Baron *et al.* (1994) for the years 1983–1992. There were, however, significant warming trends in summer (JJA) means, and specifically for July, where the mean JJA and July temperatures increased by 0.12 and 0.22 °C yr<sup>-1</sup> (Fig. 2d and f). The increase in July minimum temperatures of 0.18 °C yr<sup>-1</sup> was also significant (Fig. 2f). Mean fall (SON) temperatures increased by 0.12 °C yr<sup>-1</sup>, but were not the result of specific monthly trends (Fig. 2e).

There was no trend in winter (DJF) mean and minimum temperatures from 1991 to 2006, but maximum temperatures declined significantly by 0.13 °C yr<sup>-1</sup> (Fig. 2b). While there were no significant trends in spring (MAM) temperatures, note that the mean MAM temperature fluctuated around 0 °C (Fig. 2c).

The 1991–2006 mean annual precipitation of 104 cm was similar to the annual mean of 102 cm reported by Baron *et al.* (1994). Precipitation declined significantly by 2.3 cm yr<sup>-1</sup> from 1991 to 2006, corresponding with a regional dry period but not a long-term trend, because precipitation is highly variable in the Colorado Front Range (Ray *et al.*, 2008) (Fig. 3).

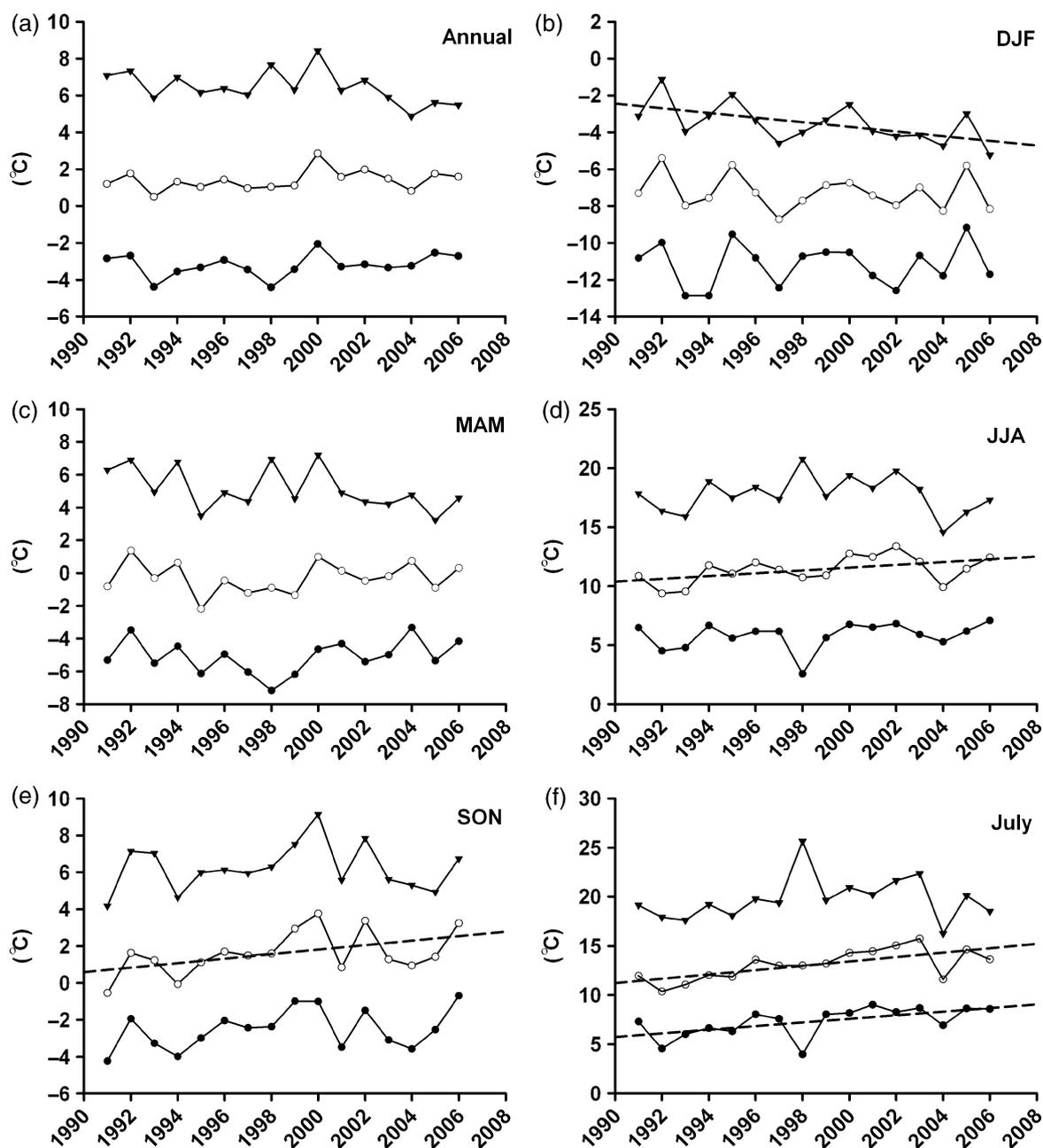
Stream discharge averaged 77 cm yr<sup>-1</sup> for the period 1991–2006 and there was a slight decline of 0.9 cm yr<sup>-1</sup> in annual flow (Fig. 3). The amount of measured discharge nearly equaled or exceeded measured precipitation in 2000, 2003, and 2006.

#### Observed chemical changes

There was an increase in concentration of total inorganic N (NH<sub>4</sub><sup>+</sup>-N + NO<sub>3</sub><sup>-</sup>-N) in wet deposition of 0.01 mg N L<sup>-1</sup> yr<sup>-1</sup> between 1991 and 2006, which is similar to the trend reported by Baron (2006) for the period 1984–2002 (Fig. 4a). The difference between the means in precipitation N concentrations between 1991–1999 and 2000–2006, 0.27 and 0.35 mg N L<sup>-1</sup>, respectively, was significant. Because there was less than average precipitation in the period post-2000, wet N deposition (the product of concentration and precipitation) that averaged 3.08 kg N ha<sup>-1</sup> yr<sup>-1</sup> between 1991 and 1999, was lower (3.03 kg N ha<sup>-1</sup> yr<sup>-1</sup>) for the period 2000–2006, but the differences were not significant (Fig. 4a).

The mean annual stream NO<sub>3</sub><sup>-</sup>-N concentration measured at The Loch outlet increased significantly from 0.23 mg NO<sub>3</sub><sup>-</sup>-N L<sup>-1</sup> in 1991–1999 to 0.34 mg NO<sub>3</sub><sup>-</sup>-N L<sup>-1</sup> in 2000–2006 (Table 1; Fig. 4b). The amount of N flux at The Loch outlet also increased significantly over time; total stream N export averaged 2.0 kg N ha<sup>-1</sup> yr<sup>-1</sup> before 2000 and 2.8 kg N ha<sup>-1</sup> yr<sup>-1</sup> in subsequent years. There was no trend in either NH<sub>4</sub><sup>+</sup>-N (mean = 0.01 mg N L<sup>-1</sup>, SD = 0.02 mg N L<sup>-1</sup>) or dissolved organic N (DON, mean = 0.04 mg L<sup>-1</sup>, SD = 0.06 mg L<sup>-1</sup>). Concentrations of both Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>-S were greater by about 0.25 mg L<sup>-1</sup> post-2000 (Table 1). The flux of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>-S similarly increased significantly in the years 2000–2006; mean total Ca<sup>2+</sup> flux was 9.5 kg ha<sup>-1</sup> yr<sup>-1</sup> from 1991–1999 and 11.8 kg ha<sup>-1</sup> yr<sup>-1</sup> from 2000–2006, and the pre- and post-2000 values for SO<sub>4</sub><sup>2-</sup>-S were 3.6 and 4.9 kg S ha<sup>-1</sup> yr<sup>-1</sup>, respectively. In contrast, there was no significant difference in SiO<sub>2</sub> concentrations or fluxes (1991–1999 flux of 13.2 kg SiO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup> vs. 2000–2006 flux of 13.4 kg SiO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>). DOC concentrations were 0.26 mg L<sup>-1</sup> lower after 2000, and DOC fluxes also were lower (10.9 vs. 9.8 kg DOC ha<sup>-1</sup> yr<sup>-1</sup> for the pre- and post-2000 periods, respectively). The DOC: NO<sub>3</sub><sup>-</sup>-N mass ratio was 45.2% lower post-2000 than before due to higher NO<sub>3</sub><sup>-</sup>-N, but also lower DOC concentrations (although DOC was not significantly lower).

The outlet to The Loch is below treeline (Fig. 1). Stream chemistry there is influenced by inputs from alpine and subalpine land cover, as well as in-lake processes from The Loch, Glass Lake, Sky Pond, and Andrews Tarn – all small lakes that lie above The Loch outlet. We compared the chemistry from The Loch outlet with chemistry at the Sky Pond inlet, an alpine



**Fig. 2** Time series of mean maximum (solid triangles), mean (open circles), and mean minimum (closed circles) temperatures 1991–2006 from LVWS, in °C, for (a) annual; (b) winter (DJF); (c) spring (MAM); (d) summer (JJA); (e) fall (SON); and (f) July. Only significant ( $p < 0.05$ ) trend lines are shown. Equations for the trend lines are as follows: DJF  $Y = -0.126x + 248.135$ ,  $R^2 = 0.32$ ; JJA  $Y = 0.118x - 223.401$ ,  $R^2 = 0.24$ ; SON  $Y = 0.122x - 41.662$ ,  $R^2 = 0.24$ ; July mean  $Y = 0.222x - 430.766$ ,  $R^2 = 0.35$ ; July minimum  $Y = 0.184x - 359.719$ ,  $R^2 = 0.48$ .

stream at 3322 m. The Sky Pond inlet drains directly from Taylor Rock Glacier into an alpine lake.

Nitrate-N concentrations at the Sky Pond inlet were markedly greater than sample locations further downstream, and the mean 2000–2006 concentration ( $0.52 \text{ mg NL}^{-1}$ ) was significantly greater than the mean for 1991–1999 ( $0.40 \text{ mg NL}^{-1}$ ; Table 1). Mean  $\text{Ca}^{+2}$ ,

$\text{SO}_4^{-2}\text{-S}$ , and  $\text{SiO}_2$  concentrations at the Sky Pond inlet were not as high as measured at The Loch outlet, but mean concentrations were higher for the period 2000–2006 than the period 1991–1999. Another alpine tributary, Andrews Creek, routinely contributes higher concentrations of  $\text{SO}_4^{-2}\text{-S}$ , and  $\text{SiO}_2$  to LVWS than Icy Brook, the stream draining from Sky Pond, and explains the

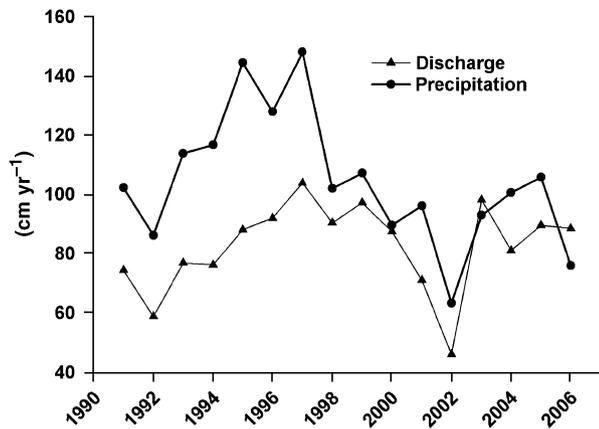


Fig. 3 Time series of annual precipitation and stream discharge, in  $\text{cm yr}^{-1}$ , from Loch Vale watershed, from water years 1991–2006.

higher concentrations at the Loch outlet (Campbell *et al.*, 1995). Dissolved organic carbon concentrations were lower at the Sky Pond inlet than at The Loch outlet, and were not different between the two periods, but the ratio of DOC to  $\text{NO}_3^-$ -N was less by 70% after 2000 (Table 1).

While stream  $\text{NO}_3^-$ -N concentrations measured at The Loch outlet increased in most seasons after water year 2000, it was most pronounced in the fall and winter months of September through January, and during May and June snowmelt (Fig. 5a). The post-2000 increase in stream N fluxes occurred primarily during spring snowmelt when discharge was high (Fig. 5b).

All solutes collected from the Sky Pond inlet except DOC displayed the same seasonal concentration pattern: high June, low July, and high August and September (Fig. 6a). For all solutes except DOC, the post-2000 monthly mean concentrations from the Sky Pond inlet were greater than pre-2000 concentrations. The differences between pre- and post-2000 concentrations were least pronounced for July samples, and, for conductivity and the weathering products  $\text{Ca}^{+2}$ ,  $\text{SO}_4^{-2}$ , and  $\text{SiO}_2$ , the concentration differences were most pronounced in late summer months of August and September. Not all differences were significant, partly due to the small sample size and high variability. Nitrate-N was significantly greater only in July.

There was some similarity in monthly patterns from The Loch outlet, although August and September concentrations did not differ as dramatically from July as at the Sky Pond inlet (Fig. 6b). The post-2000 increase in  $\text{NO}_3^-$ -N was significant in all months;  $\text{Ca}^{+2}$  had significantly higher concentrations in August and September at The Loch outlet in common with the Sky Pond inlet, and  $\text{SO}_4^{-2}$  was significantly higher in July and August at The Loch outlet in common with the Sky Pond inlet. Conductivity increased significantly at The

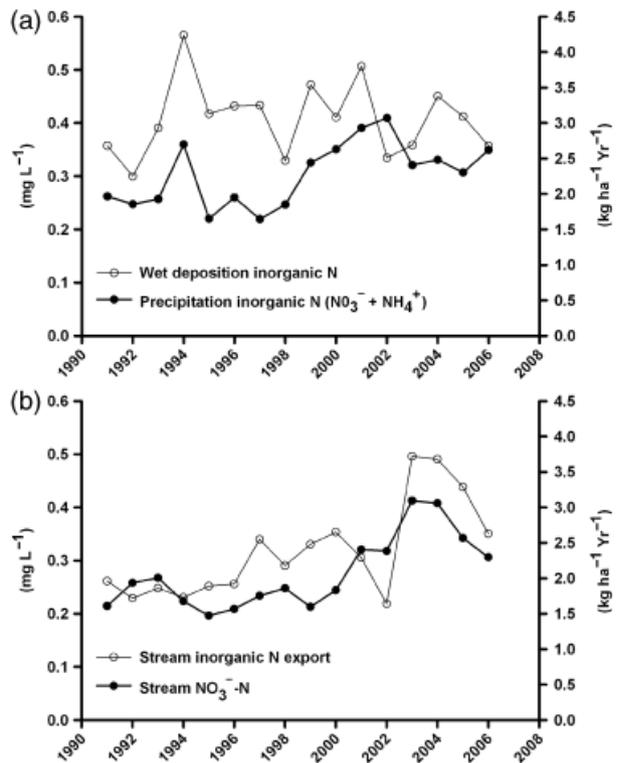


Fig. 4 Time series of (a) annual volume-weighted mean stream precipitation inorganic N concentrations ( $\text{NO}_3^-$ -N +  $\text{NH}_4^+$ -N, in  $\text{mg L}^{-1}$ ) and wet inorganic N deposition ( $\text{kg ha}^{-1} \text{yr}^{-1}$ ), and (b) inorganic N concentrations ( $\text{NO}_3^-$ -N, in  $\text{mg L}^{-1}$ ) and stream inorganic N ( $\text{NO}_3^-$ -N +  $\text{NH}_4^+$ -N) export ( $\text{kg ha}^{-1} \text{yr}^{-1}$ ) from Loch Vale watershed, Rocky Mountain National Park.

Loch outlet in post-2000 August and September, June DOC declined significantly, and there was no significant change in  $\text{SiO}_2$ .

## Discussion

There is little question that high stream nitrate concentrations and many other biological and ecological changes in the Colorado Front Range observed from 1991 to 2006 were caused by atmospheric deposition of N compounds (Baron *et al.*, 2000; Burns, 2003; Bowman *et al.*, 2006). The dramatic increase in  $\text{NO}_3^-$ -N concentrations (30% and 50% more concentrated at the Sky Pond inlet and The Loch outlet, respectively), however, and N export (an increase of 40% at the Loch outlet) since 2000 was not only caused by atmospheric deposition. While precipitation N concentrations have increased gradually over time, mean annual wet inorganic N deposition has remained near  $3.0 \text{ kg ha}^{-1} \text{yr}^{-1}$  since 1991.

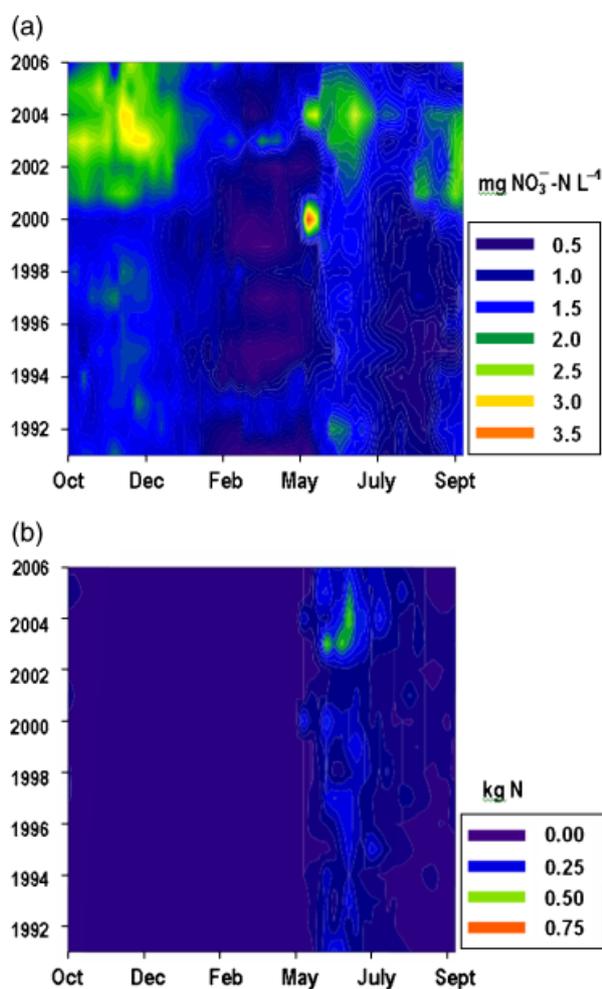
Stream N export from LVWS increased on average by  $0.8 \text{ kg N ha}^{-1} \text{yr}^{-1}$  since 2000. We looked for causal mechanisms to explain the sudden increase in N flux,

**Table 1** Annual mean concentration ( $\text{mg L}^{-1}$ ), standard deviation (in parentheses), and percent change over time of calcium ( $\text{Ca}^{2+}$ ), sulfate sulfur ( $\text{SO}_4^{2-}\text{-S}$ ), silica ( $\text{SiO}_2$ ), nitrate-nitrogen ( $\text{NO}_3^-\text{-N}$ ) and dissolved organic carbon (DOC) for the Sky Pond inlet and The Loch outlet of Loch Vale watershed for 1991–1999, and 2000–2006 periods

Solute	Sky Pond inlet ( $\text{mg L}^{-1}$ )		% change	The Loch outlet ( $\text{mg L}^{-1}$ )		% change	Export from The Loch outlet ( $\text{kg ha}^{-1} \text{yr}^{-1}$ )	
	1991–1999	2000–2006		1991–1999	2000–2006		1991–1999	2000–2006
Years	1991–1999	2000–2006		1991–1999	2000–2006		1991–1999	2000–2006
Conductivity	9.48 (1.90)	15.46(3.73)	63.1	14.22 (4.10)	18.29 (5.32)	28.6	na	
$\text{Ca}^{2+}$	1.15 (0.35)	1.53 (0.54)*	33.0	1.72 (0.52)	2.00 (0.58)	16.3	9.48 (1.91)	11.76 (2.42)*
$\text{NO}_3^-\text{ N}$	0.40 (0.14)	0.52 (0.24)*	30.9	0.23 (0.02)	0.34 (0.06)*	47.8	2.03 (0.40)	2.84 (0.76)*
$\text{SO}_4^{2-}\text{-S}$	0.50 (0.19)	0.72 (0.34)	45.0	0.65 (0.20)	0.86 (0.28)	32.3	3.64 (0.63)	4.85 (1.00)*
$\text{SiO}_2$	1.55 (0.56)	1.90 (0.50)	22.6	2.40 (0.79)	2.44 (0.78)	1.7	13.19 (4.25)	13.40 (6.52)
DOC	0.51 (0.29)	0.53 (0.59)	3.9	1.42 (0.95)	1.17 (0.79)	−17.6	10.93 (3.65)	9.75 (2.39)
DOC: $\text{NO}_3^-\text{ N}$	0.39	0.12	−69.5	1.12	0.61	−45.2	na	

Solute export is shown in  $\text{kg ha}^{-1} \text{yr}^{-1}$ . Conductivity is in  $\mu\text{S cm}^{-1}$ . The last row presents the DOC:  $\text{NO}_3^-\text{ N}$  ratio.

\*Significant differences ( $p = 0.05$ ).



**Fig. 5** Contour plots of (a) weekly stream  $\text{NO}_3^-\text{-N}$ , in  $\text{mg L}^{-1}$  and (b) weekly inorganic N ( $\text{NO}_3^-\text{-N} + \text{NH}_4^+\text{-N}$ ) export from the 660 ha watershed, in  $\text{kg N}$ , by month (ordinate) and year (abscissa) for water years 1991–2006.

including the onset of N saturation in alpine or forest environments; climate-driven changes in alpine, forest, or aquatic N cycling; or climate-driven changes to the physical environment, namely glaciers or rock glaciers.

#### *Contribution of ecological processes to changes in N dynamics*

Most ecosystem N is bound in plant tissue and soil organic matter, and a small amount cycles annually between these pools (Schlesinger, 1997). However, even in strongly N-limited systems there is always some N loss (Vitousek & Howarth, 1991; Perakis & Hedin, 2002). An increase in the leakage of N from soils to surface waters could occur from a change in N cycling between the periods before and after 2000. This could occur by either climate-induced changes in N mineralization rates, plant N uptake rates in forests or tundra during any season, or from the onset of N saturation. Less insulating snow cover has been linked to greater spring N leaching from alpine soils by Brooks *et al.* (1998), but this alone cannot explain nearly year-round increases in  $\text{NO}_3^-\text{-N}$  and weathering products in summer and fall.

Completion of snowmelt in early- to mid-summer coupled with spring and summer evapotranspiration reduces the presence of liquid soil water in mid- to late-summer. Inadequate soil moisture not only restricts the mobility of soluble soil N, it was found to restrict its production by limiting soil microbial activity in studies conducted in a nearby high-elevation forest (Scott-Denton *et al.*, 2003). Additional research conducted in forest stands at Niwot Ridge CO found annual precipitation was markedly lower post-2000, similar to LVWS. Mon-

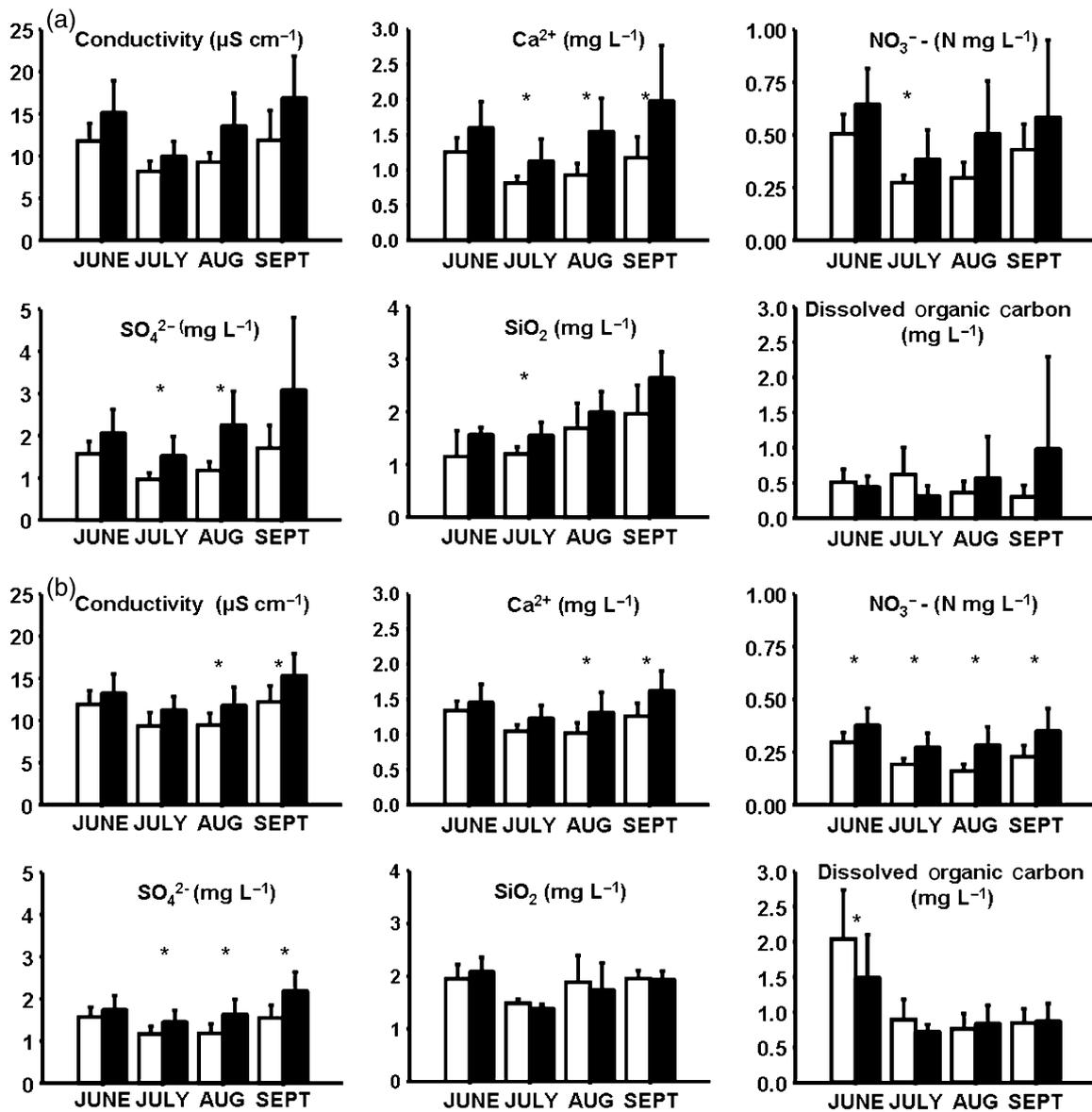


Fig. 6 Mean chemical concentrations are shown by month from (a) the Sky Pond inlet, and (b) The Loch outlet for the period 1991–1999 (left bars) and for the period 2000–2006 (right bars). Asterisks denote significant ( $p = 0.05$ ) differences.

son *et al.* (2002) found warmer summer temperatures restricted soil moisture in a subalpine forest at Niwot Ridge by increasing early season evapotranspiration. In June, soils covered with snow or located below snow patches can be wet enough to have free water movement, but by July and August the movement of soil N into surface waters requires summer storms of sufficient magnitude to saturate the soils (Baron, 1992; Williams *et al.*, 2007). From late July to October, when stream  $\text{NO}_3^-$ -N concentrations were elevated in the post-2000 period, both forest N uptake and soil microbial activity were strongly limited by soil moisture, alleviated only by typical summer rain storms, which

were rare in Colorado during this period (Monson *et al.*, 2002; Groisman *et al.*, 2005).

The primary connectivity between terrestrial soils and surface waters occurs during spring snowmelt in the Colorado Rocky Mountains (Baron & Campbell, 1997; Heuer *et al.*, 1999), but stream  $\text{NO}_3^-$ -N concentrations were elevated nearly year round during the 2000–2006 period. Winter temperatures are cold, and snow remains frozen until the spring thaw, thus there is little opportunity for the flushing of soil solutes during the fall and winter. Although there is groundwater input year-round, talus slopes – not tundra or forest soils – are the primary groundwater reservoirs (Clow *et al.*, 2003).

Could Loch Vale ecosystems have crossed an N-saturation threshold? Measured mean soil solution  $\text{NH}_4^+$ -N +  $\text{NO}_3^-$ -N during the growing season in LVWS forest averaged  $0.16 \text{ mg NL}^{-1}$  (SD =  $0.54 \text{ mg NL}^{-1}$ ) during 1996, 1997, and 1999 (Rueth *et al.*, 2003). Repeat measurements from the same locations in 2005 found a mean (SD)  $\text{NH}_4^+$ -N +  $\text{NO}_3^-$ -N of  $0.15$  ( $0.69$ )  $\text{mg NL}^{-1}$  (K. E. Williams, personal communication). The low concentrations of  $\text{NH}_4^+$ -N +  $\text{NO}_3^-$ -N in the Oa and B horizons during the growing season argue against the possibility that forest  $\text{NH}_4^+$ -N +  $\text{NO}_3^-$ -N saturation was responsible for the observed change in stream  $\text{NO}_3^-$ -N. Experiments in nearby alpine areas found that increases in  $\text{NO}_3^-$ -N leaching only occurred at  $\text{NH}_4^+$ -N +  $\text{NO}_3^-$ -N deposition levels above  $20 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (Bowman *et al.*, 2006), far greater than the  $4\text{--}6 \text{ kg wet plus dry N ha}^{-1} \text{ yr}^{-1}$  observed in LVWS over the entire period of record.

Further argument against a major role of alpine and forest processes is that the high  $\text{NO}_3^-$ -N concentrations that accompanied greater N export at The Loch outlet also were observed from the Sky Pond inlet which is virtually above all vegetation. A landscape-level N budget developed for LVWS concluded that forest and alpine areas served as contributing source areas to surface waters only during the period of snowmelt (May through late-July) when there was hydraulic connectivity (Baron & Campbell, 1997). On the other hand, water and solutes supplied from melting rock glaciers at the top of LVWS can mix with groundwater from talus and flow directly into Sky Pond and then downstream (Clow *et al.*, 2003; Williams *et al.*, 2007). The combined evidence strongly suggests N saturation was not the cause of the observed increase in  $\text{NO}_3^-$ -N concentrations or N export.

We did not measure algal productivity consistently over the years since 1991; however, the highest  $\text{NO}_3^-$ -N concentrations were observed at the highest elevations and  $\text{NO}_3^-$ -N concentrations were lower at The Loch outlet, implying consumption along the downstream gradient. The decrease in concentration between high and low elevations was about  $0.2 \text{ mg NL}^{-1}$  for both time periods, supportive of the assumption that algal processes did not change after 2000.

#### *Influence of physical processes on solute dynamics*

Summer and fall mean temperatures increased significantly,  $0.12 \text{ }^\circ\text{C yr}^{-1}$ , from 1991 to 2006. This was especially apparent for the warmest month, July, in which the mean and the mean minimum temperatures increased by  $0.22$  and  $0.18 \text{ }^\circ\text{C yr}^{-1}$ , respectively. The warming, coupled with declining precipitation but not discharge, and discharge that sometimes exceeded

precipitation, brought us to consider the consequences of melting cryosphere. This concept has been raised in several recent publications. Glacier melt patterns in Rocky Mountain National Park are highly responsive to summer temperatures (Hoffman *et al.*, 2007). Janke & Frauenfelder (2008) modeled the response of permafrost to an increase of  $0.5 \text{ }^\circ\text{C}$ , and suggested that 95% of Colorado Front Range permafrost, including rock glaciers, could contract with a  $2.0\text{--}2.5 \text{ }^\circ\text{C}$  warming. Warming already experienced in LVWS (Clow *et al.*, 2003) and the alpine West (Diaz & Eiseheid, 2007) was concluded to have increased the lower limit of permafrost by  $160\text{--}190 \text{ m}$  and reduced the area climatically identified as alpine by nearly three quarters, respectively. Lafrenière & Sharp (2005) observed greater stream flows in a glacial catchment in Alberta during a low winter precipitation – high summer temperature El Niño year. There was greater flow in the El Niño year compared with flow in the same stream in two non-El Niño years, and also greater flow than in a nearby nonglacial stream from which runoff decreased during the El Niño year.

An increase in rock glacier melt activity should increase the concentration of solutes derived from weathering because dilute meltwater in an environment with high rock:water ratios and rock-water contact time significantly enhances weathering (Brown *et al.*, 1996; Lafrenière & Sharp, 2005; Williams *et al.*, 2006; Thies *et al.*, 2007). The weathering products of biotite, plagioclase, pyrite, and trace amounts of calcite released from melting rock glaciers above Sky Pond could produce the concentrations of  $\text{Ca}^{+2}$ ,  $\text{SO}_4^{-2}$ , and  $\text{SiO}_2$  we observed at the Sky Pond inlet in August and September (Mast *et al.*, 1990). Water from Sky Pond flows downstream to The Loch within  $4\text{--}6$  weeks during late summer, increasing concentrations at the Loch outlet as well (Baron, 1992).

We considered whether there was a connection between wet atmospheric deposition of  $\text{Ca}^{+2}$  and  $\text{SO}_4^{-2}$  and the higher stream concentrations. Average annual wet deposition of  $\text{SO}_4^{-2}$  declined post-2000, however, while the average annual  $\text{Ca}^{+2}$  wet deposition increased due to high winter  $\text{Ca}^{+2}$  deposition in 2006 (<http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=CO98>). Because the post-2000 increase in wet  $\text{Ca}^{+2}$  deposition ( $0.70 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ) was much less than the increase in stream  $\text{Ca}^{+2}$  flux ( $2.28 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ), and because  $\text{SO}_4^{-2}$  and  $\text{Ca}^{+2}$  inputs from precipitation trended different directions, we dismissed this possibility.

Higher June and July  $\text{Ca}^{+2}$ ,  $\text{SO}_4^{-2}$ , and  $\text{SiO}_2$  concentrations at the Sky Pond inlet and The Loch outlet in recent years could be artifacts of below-average precipitation causing less dilution of weathering products during snowmelt (Lafrenière & Sharp, 2005). A flow

separation analysis for the Green Lakes Valley, an alpine catchment near LVWS, reported similar water quality among various alpine landforms in June and July, and identified snowmelt and soil water as the primary contributors to summer streamflow (Williams *et al.*, 2006). Divergence in flowpaths among landforms occurred in August and September, when baseflow from rock glaciers took on distinctly different chemical signatures (Williams *et al.*, 2006). The onset of snowmelt did not occur earlier than usual in LVWS post-2000, but there was less snow, higher summer temperatures, and lower June and July stream flow, suggesting earlier transition from snowmelt-dominated water to soil- or groundwater-dominated water. Williams *et al.* (2006) also noted higher June and July concentrations during drier years than in years with more precipitation.

Williams *et al.* (2006) pose a seasonal conceptual model, in which typical summer warming allows the 0° isotherm that separates frozen surfaces from liquid water to penetrate into a rock glacier by late summer. Meltwater and groundwater come into contact with mineral surface area and enhance weathering. With warmer than historic summer temperatures, such as we observed in LVWS, the 0° isotherm is reached earlier in the season, allowing for a longer period during which liquid water is in contact with minerals. Our observations of increased weathering products in recent years support both the conceptual model of Williams *et al.* (2006) and the conclusions of Clow *et al.* (2003) that warming has increased the altitude where permafrost and permanent snow and ice can persist. The observations suggest a water quality threshold may have been crossed around 2000.

#### *Microbial activity*

While melting glacial ice could explain the post-2000 increase in the stream discharge to precipitation ratio and concentrations of weathering products for the late summer and fall, there is evidence in the literature that it also may stimulate nitrification in newly exposed sediments. High concentrations of inorganic N in alpine streams correspond with warm temperatures and increased levels of weathering products in Switzerland and the Canadian Rockies as well as in Colorado (Lafrenière & Sharp, 2005; Rogora, 2007; Williams *et al.*, 2007). Even in bedrock and talus-dominated headwater catchments there is a strong suggestion from isotopic analyses that most N from atmospheric deposition has been nitrified before it reaches high-elevation streams (Campbell *et al.*, 2000; Enders *et al.*, 2008). Direct measurements of glacial ice in Taylor Glacier and Taylor rock glacier show it to have very low NO<sub>3</sub><sup>-</sup>-N concentrations, with late summer values of 0.01 NO<sub>3</sub><sup>-</sup>-N

(Martin, 1994). Active microbes have been found, however, in subglacial waters, intraglacial water veins, surficial glacial holes ('cryoconite holes') and rock glacier outflows from arctic and alpine environments (Mader *et al.*, 2006; Hodson *et al.*, 2007; Williams *et al.*, 2007; Wynn *et al.*, 2007). Several recent studies have documented microbial activity in fine sediment pockets of mountain talus and blockfields (Muldoon, 2003; Ley *et al.*, 2004). Fluorescence properties of DOC from glacier and rock glacier outflow point toward a microbial or aquatic microbial source in both Alberta and Colorado (Lafrenière & Sharp, 2004; Williams *et al.*, 2007). Similarly, enriched δ<sup>13</sup>C in *n*-alkanes from pigments in Sky Pond sediments in recent years strongly suggests increased microbial or lichen activity in the talus or rock glacier upstream (Enders *et al.*, 2008). Increased growth of either microbes or lichens is congruent with warming of high-elevation rock glaciers and talus.

We propose that the observed stream N increases in LVWS are climatically induced, caused by melting ice in glaciers and rock glaciers that has flushed N from microbially active sediments. Williams *et al.* (2007) describe rock glaciers as extreme environments that are dark, cold, and low in organic matter. Increased nitrification would produce an inverse relation between NO<sub>3</sub><sup>-</sup>-N and DOC due to microbial consumption of organic carbon, which is what we and others have found (Williams *et al.*, 2007). At both the Sky Pond inlet and lower-elevation Loch outlet DOC: NO<sub>3</sub><sup>-</sup>-N ratios decreased. An alternative explanation is that the meltwater released from wasting ice is enriched with N derived from surficial cryoconite features. *In situ* microbial activity in either exposed sediments or on the surface of glacier ice merits further study to determine the N source.

The increase in stream NO<sub>3</sub><sup>-</sup>-N resulting from nitrification in newly exposed sediments provides a possible explanation for summer and fall concentrations, but NO<sub>3</sub><sup>-</sup>-N concentrations from samples collected at The Loch outlet increased markedly in nearly all months after 2000. The mean December 2000–2006 concentration was 0.47 mg NO<sub>3</sub><sup>-</sup>-N L<sup>-1</sup> compared with a mean of 0.32 NO<sub>3</sub><sup>-</sup>-N L<sup>-1</sup> and maximum (in 1995) of 0.41 mg NO<sub>3</sub><sup>-</sup>-N L<sup>-1</sup> for 1990–1999. Freeze concentration has been noted by us and others as a winter phenomenon in lakes with extensive ice cover, such as in Antarctica and Greenland (Baron, 1992; Vincent & Howard-Williams, 1994; Willemse *et al.*, 2004). With less overall water available after 2000, one could logically expect increased winter concentrations. Nitrate concentrations decline in late winter due to algal consumption (Spaulding *et al.*, 1993), although NO<sub>3</sub><sup>-</sup>-N was not depleted to the concentration levels observed before 2000.

While our 1991–2006 records are not definitive of climate change, they exemplify what will happen as high elevations become warmer. The phenomenon observed in Loch Vale may be indicative of  $\text{NO}_3^-$ -N produced via nitrification and flushed with meltwater worldwide as mountain glaciers retreat. The increase in  $\text{NO}_3^-$ -N concentration and N export in LVWS after 2000 was quite dramatic and surprising. The unexpected source hampers the ability to detect responses in high-elevation aquatic ecosystems from changes in Colorado N emissions policies. While emissions inventories and wet and dry atmospheric deposition measurements will provide records of a change in emissions and deposition, observations of actual improvements in water quality may be confounded by melting glaciers that provide an additional source of  $\text{NO}_3^-$ -N into high-mountain aquatic ecosystems.

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