

Thawing glacial and permafrost features contribute to nitrogen export from Green Lakes Valley, Colorado Front Range, USA

Rebecca T. Barnes · Mark W. Williams ·
Jordan N. Parman · Ken Hill · Nel Caine

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Abstract Alpine ecosystems are particularly susceptible to disturbance due to their short growing seasons, sparse vegetation and thin soils. Increased nitrogen deposition in wetfall and changes in climate currently affect Green Lakes Valley within the Colorado Front Range. Research conducted within the alpine links chronic nitrogen inputs to a suite of ecological impacts, resulting in increased nitrate export. The atmospheric nitrogen flux decreased by $0.56 \text{ kg ha}^{-1} \text{ year}^{-1}$ between 2000 and 2009, due to decreased precipitation; however alpine nitrate yields increased by 40 % relative to the previous decade (1990–1999). Long term trends indicate that weathering products such as sulfate, calcium, and silica have

also increased over the same period. The geochemical composition of thawing permafrost, as indicated by rock glacial and blockfield meltwater, suggests it is the source of these weathering products. Furthermore, mass balance models indicate the high ammonium loads within glacial meltwater are rapidly nitrified, contributing $\sim 0.5\text{--}1.4 \text{ kg N ha}^{-1}$ to the growing season nitrate flux from the alpine watershed. The sustained export of these solutes during dry, summer months is likely facilitated by thawing cryosphere providing hydraulic connectivity late into the growing season. This mechanism is further supported by the lack of upward weathering or nitrogen solute trends in a neighboring catchment which lacks permafrost and glacial features. These findings suggest that reductions of atmospheric nitrogen deposition alone may not improve water quality, as cryospheric thaw exposes soils to biological and geochemical processes that may affect alpine nitrate concentrations as much as atmospheric deposition trends.

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R. T. Barnes
Department of Geological Sciences, University
of Colorado, Boulder, CO 80303, USA

R. T. Barnes (✉)
Institute of Marine and Coastal Sciences, Rutgers, State
University of New Jersey, New Brunswick, NJ 08901,
USA
e-mail: becca.barnes@gmail.com

M. W. Williams · J. N. Parman · K. Hill · N. Caine
Department of Geography and Institute of Arctic
and Alpine Research, University of Colorado, Boulder,
CO 80309-0450, USA

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Introduction

Alpine systems are very susceptible to environmental change due to their short growing seasons, sparse vegetation, thin soils, and a harsh climate (Williams

et al. 2002). Additionally, the complex topography and landscape heterogeneity of these catchments makes it challenging to quantify and explain changes in aquatic nutrient fluxes (Seastedt et al. 2004).

Warming temperatures are likely responsible for unprecedented rates of mountain glacier retreat worldwide (e.g. Meier et al. 2007). In the western U.S., warmer air temperatures have decreased the proportion of precipitation falling as snow (Knowles et al. 2006), decreased early snowpack snow-water equivalent (Mote 2006), and led to earlier runoff during snowmelt (e.g. Clow 2010; Regonda et al. 2005). Diaz and Eischeid (2007) found that in the western U.S. mean annual air temperature for the warmest month from 1987 to 2006 was greater than the 10 °C Koppen classification for 73 % of areas classified as having alpine climates, placing the persistence of alpine tundra at risk.

Anthropogenic emissions of NO_x (nitrogen oxides) and NH_3 (ammonia) from energy production, transportation, industry, and agricultural activities contribute to deposition of dissolved inorganic nitrogen ($\text{DIN} = \text{NO}_3^- + \text{NH}_4^+$) in high-elevation watersheds in the western U.S. (Baron and Campbell 1997; Williams and Tonnessen 2000). Deposition data indicate that DIN concentrations in wetfall have increased steadily over much of the Rocky Mountains in recent decades (e.g. Burns 2003). This increase of DIN in wetfall at high elevation in the Colorado Rocky Mountains has resulted in this area becoming N-saturated (Williams et al. 1996a), leading to higher concentrations of nitrate in surface waters (Baron et al. 1994; Williams and Tonnessen 2000), and shifted phytoplankton nutrient limitation from predominant nitrogen (N) and joint N and phosphorus (P) limitation to predominant P limitation (Elser et al. 2009). An outstanding question remains: is increased nitrate in surface waters of high-elevation catchments in the Colorado Rockies from nitrate in wetfall directly transported to surface waters, or is it a result of net nitrification induced by DIN in wetfall?

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 on ecosystem processes (Baron et al. 2009). Ollinger et al. (2003) suggest that climate is the overarching control on ecosystem processes, confounding researchers' attempts to quantify ecosystem effects of N deposition and several studies report

climate effects exceeding those of atmospheric deposition (e.g. Meixner et al. 2004; Rogora 2007). For example, there may be enhanced weathering and N-mineralization under a warmer climate (Hong et al. 2005), leading to increased N export to surface waters (Henriksen and Hessen 1997). In the northern Rockies, Saros et al. (2010) report significantly greater nitrate (NO_3^-) concentrations in glacial and snowmelt fed lakes compared to those collecting snowmelt alone. Similarly, Baron et al. (2009) report that recent NO_3^- concentration increases in Loch Vale watershed result from melting ice in permafrost and rock glaciers. In Green Lakes Valley (GLV), 45 years of glacial mass balance and climate data show that recent increases in summer air temperature have resulted in the Arikaree Glacier crossing a threshold that will likely result in its disappearance in the next several decades (Hoffman et al. 2007). Finally, a recent synthesis suggests that climate change impacts on nitrogen transport and processing will be driven mostly by alteration in hydrology (Baron et al. 2012).

Here we investigate the nexus between changing climatic conditions and N deposition in GLV in the Colorado Front Range. From 1983 to 2007, average annual air temperatures in GLV increased $1.08 \text{ }^\circ\text{C decade}^{-1}$ (Clow 2010) leading to a 15 positive degree-day year^{-1} increase (Caine 2010). Long-term precipitation records show a decrease in annual precipitation starting in 1999; with 2002 being one of the driest and hottest years on record (Pielke et al. 2005) and cumulative precipitation in 2000–2003 being below the long-term average. Further evidence of a change in precipitation can be seen by examining the snow depth surveys, conducted at maximum accumulation that began in 1997 (Erickson et al. 2005), the lowest mean snow depth of 123 cm was recorded in 2002 (Williams et al. 2006). In addition to changing amounts of precipitation, evaluation of long-term discharge records show that the date of centroid of discharge in GLV has occurred earlier, changing at a rate of $-0.2 \text{ day year}^{-1}$ at GL4 and $-0.6 \text{ day year}^{-1}$ at MART (Hill 2008), suggesting that snowmelt is occurring earlier in the season. Collectively, these observations point to a warmer and drier GLV from 2000 to 2009, as compared to the previous two decades. Thus, despite increases in DIN concentrations in precipitation, atmospheric N deposition has generally decreased over the last decade in GLV. We evaluate the effects of warming and drying on the spatiotemporal variability

of nitrogen biogeochemistry in GLV through the examination of long-term stream chemistry and cryospheric data.

Methods

Site location

GLV is a 700-ha east-facing, high-elevation (3,250–4,000 m) alpine catchment in close proximity to large-scale urban and agricultural activities in the Denver–Boulder–Fort Collins area (Fig. 1). As Boulder's municipal water source, GLV has had restricted public access since the 1950s, leaving the watershed relatively undisturbed. The northern drainage divide is Niwot Ridge, a Long-Term Ecological Research (LTER) area and National Atmospheric Deposition Program (NADP) site where environmental research has been conducted since the early 1950s. The continental, high-mountain climate of GLV has been recorded continuously since the 1950s at alpine D1 (3,700 m) and subalpine C1 (3,021 m) meteorological stations on Niwot Ridge; with a mean annual temperature of $-3.7\text{ }^{\circ}\text{C}$ (Williams et al. 1996b).

The 9-ha Arikaree glacier (ARK) sits at the head of GLV and is the source of North Boulder Creek (Fig. 1), which starts as a braided first-order stream at the Navajo (NAV) bench below ARK, flowing into a series of lakes, including Green Lake 4 (GL4). The GL4 watershed (225-ha) is defined by steep slopes, glacial cirques, semi-permanent snowfields, exposed bedrock, talus outcrops, sparse vegetation, and undeveloped soils; characteristics shared by other alpine areas in the region. Bedrock in GLV is composed of Precambrian schists and gneisses, the Silver Plume quartz monzonite, and Audubon–Albion stock (Williams et al. 2006). Permafrost has been verified above 3,500 m on Niwot Ridge (Ives and Fahey 1971) and more recently near Green Lake 5 (GL5; Leopold et al. 2008) and in the GL4 watershed (Janke 2005). In addition to ARK, three rock-glacier/blockfield sites have been sampled: an 8-ha lobate rock glacier (RG5) at the foot of the north-facing side of Kiowa Peak and two blockfield sites above GL4 (EN.4L and KIO.SW, Fig. 1). Previous research has shown that about 65 % of the discharge from GL4 in the mid 1990s is older water from groundwater and blockfield areas and the remaining 35 % is new snowmelt (Liu et al. 2004).

In contrast to GL4, the Albion (ALB) site is located below the series of lakes at the ecotone between alpine and subalpine (Fig. 1). This lower section has more extensive vegetation and soil cover, compared to the upper valley. The 8-ha Martinelli (3,380 m) catchment represents a 1st-order, snow-field dominated catchment (Fig. 1). The Martinelli (MART) catchment has poorly developed soils, little vegetation, deep winter snow cover (Caine and Swanson 1989), and limited groundwater storage resulting in event water contributing almost 80 % of streamflow (Liu et al. 2004). In contrast to GL4, MART does not contain any glacial features or permafrost due to its southern aspect and lower elevation.

Sample collection and analysis

This study utilizes long-term data collected by the Niwot Ridge LTER, including daily air temperature, precipitation, stream discharge, and weekly wet deposition and stream chemistry. Discharge has been measured continuously since 1982 at GL4, ALB, and MART from May through October. The duration of discharge and stream chemistry measurements varies from year to year due to access to the site, e.g. some years may have 1 week of data for May and October while other years have three or more weeks. Rating curves developed from 30 years of stage height readings at GL5 and NAV and discharge measurements at GL4 were used to estimate discharge at GL5 and NAV. Stage heights taken approximately four times per week at the ungauged sites (GL5 and NAV) ensure that these rating curves can capture seasonal changes in the relationship between discharge at these sites and the downstream gauged site (GL4), however uncertainty still exists and this could amount to $\pm 10\%$ (Williams and Caine 2001). Cumulative weekly discharge at ARK was estimated by scaling the measured flows at NAV by the estimated proportions of surface snow and ice in the two basins. More specifically when there was 100 % snow cover above NAV, the flow at ARK was calculated to be proportional to the drainage areas, when the only snow and ice in the NAV catchment is the ARK the flow at NAV is set equal to that of the meltwater flow of the glacier (ARK). Given the nature of this extrapolation, the flow at ARK is less certain than at other sites throughout the watershed; in some cases this uncertainty could be up to $\pm 30\%$.

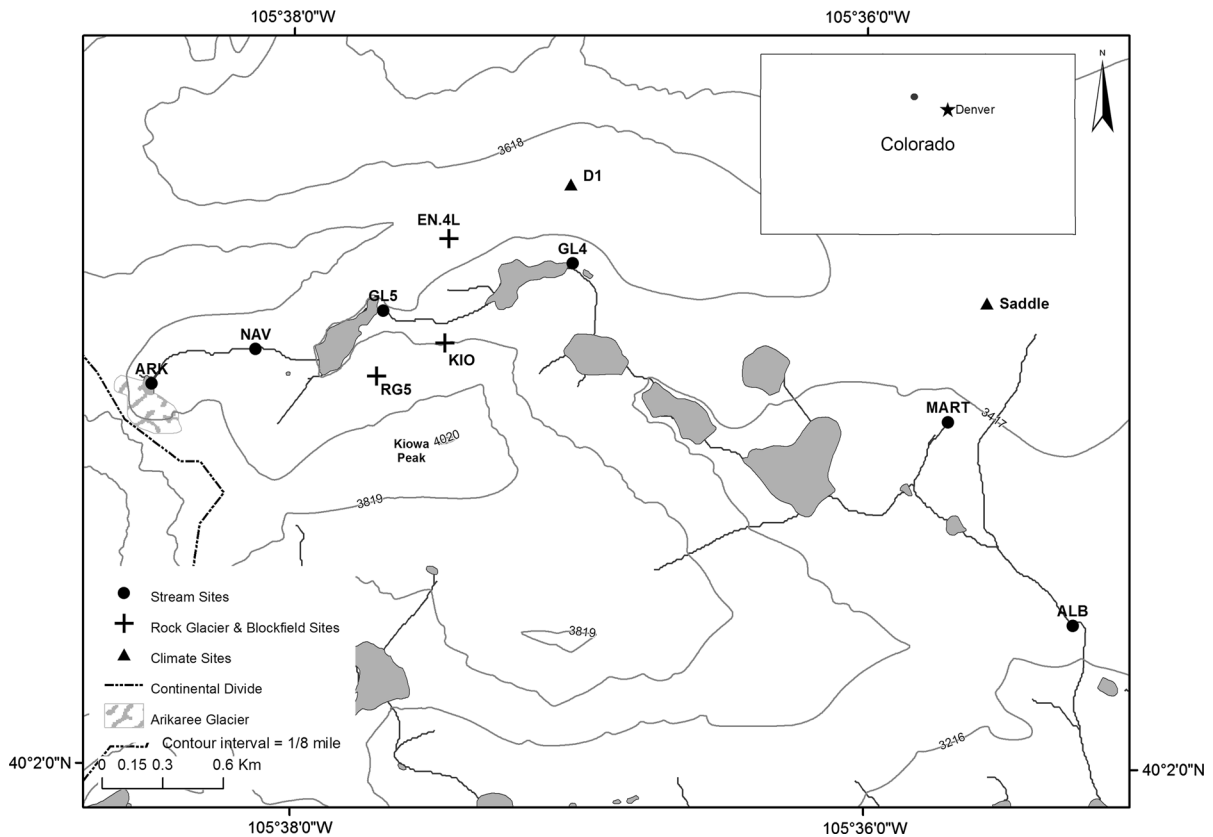


Fig. 1 Site location map of Green Lakes Valley. Temperature and precipitation are measured at climate stations D1, Saddle, and C1 (not shown, 3021 m). Weekly water samples were collected at the ARK, Navajo bench (NAV), Green Lake 5

(GL5), Rock Glacier (RG5), Green Lake 4 (GL4), Albion (ALB), and Martinelli (MART). Stream flow gauging stations are located at GL4 and ALB. Water samples from blockfield features started in the 1990s at KIO and EN.4L

Streams (NAV, GL4, GL5, ALB), glacial melt (ARK), rock glacier (RG5), and blockfield (KIO, EN4L) waters were sampled weekly for chemical content from May through October, with collection beginning in 1984 for all stream sites and the glacial meltwater and in the mid to late 1990s for the rock glacier and -blockfield waters. The NADP initiated weekly sampling of wet deposition chemistry in 1984 at the Saddle site (3,500 m). All water samples were analyzed for pH, acid neutralizing capacity (ANC, measured via gran titration), conductance, major ions and dissolved silica (Si), following the protocols presented by Williams et al. (2006). Routine measurements of dissolved organic carbon (DOC) began in 1998. Chemical yields were estimated as the product of concentrations and the accumulated water discharge for weekly intervals centered on the day of sampling. Volume-weighted mean (VWM) concentrations for

individual species were calculated as annual mass flux divided by annual discharge.

Statistical methods

Long-term trends in the concentration and flux of calcium (Ca^{2+}), nitrate (NO_3^-), sulfate (SO_4^{2-}), and silica (Si) at GL4, MART, and ALB were analyzed using the nonparametric seasonal Kendall test (Helsel and Hirsch 1992). To assess long-term trends, seasons were defined as a month, with the sample closest to the midpoint of the month used for the test. By controlling for monthly, i.e. seasonal, variation in concentration this test can assess the presence or absence of long term trends. In addition, this test allows us to determine if any long-term trends are being driven by certain parts of the sampling period (i.e. a given month); this is especially important given that the

sampling period at these sites varies from year to year due to changes in access. Analysis of variance (ANOVA) was used to test for differences in the chemical observations for the wet (1985–1999) and dry (2000–2009) sampling periods. Significant differences were determined at the $p < 0.05$ level.

Mass balance model

Given the documented role of in-stream processing of nitrogen species within small streams (e.g. Bernal et al. 2012; Hall et al. 2009; Hubbard et al. 2010; Peterson et al. 2001), it is likely that nitrification, uptake, and removal (e.g. denitrification) contribute to the observed differences between sites and that these rates have change over space and time. To estimate how in-stream processes change within the alpine portion of GLV, three reaches were modeled using the historical database to estimate gains and losses of NO_3^- , ammonium (NH_4^+), and a conservative tracer (chloride, Cl^-) within stream reaches. Three reaches were defined by sampling locations within the watershed: Arikaree to Navajo (ARK–NAV), Navajo to the outlet of Green Lake 5 (NAV–GL5), and the outlet of Green Lake 5 to outlet of Green Lake 4 (GL5–GL4). Regular discharge estimates are not available prior to 2000 for NAV and thus our estimates of solute gains and losses are confined to post-2000. In addition, due to variability in the duration of discharge measurements each year, the analysis is confined to the months of June through September. Weekly flux estimates for ARK, NAV, GL5, and GL4 were calculated using weekly chemical measurements ($\mu\text{mol L}^{-1}$) and weekly average discharge values ($\text{m}^3 \text{day}^{-1}$).

To achieve water balance between the upstream and downstream site of each reach, it was assumed that additional water was gained from minor tributaries, soil water, groundwater, and periglacial features. The three reaches have a few minor incoming tributaries, estimated at less than 10 % of the flow, which originate from the east face of Arikaree Peak, the south side of Niwot Ridge, and from RG5, however these systems are not gauged and there are no discharge estimates. To estimate the net processing of NO_3^- and NH_4^+ , assumptions needed to be made about the concentration of these solutes in the incoming water. Incoming water could simply dilute the upstream flux, i.e. N concentrations equal zero

(Eq. 1). Alternatively, incoming water brings additional solutes; two sets of estimates of NO_3^- , NH_4^+ , and Cl^- concentrations were made in an effort to provide an upper limit to the lateral influxes: (1) incoming water had solute concentrations equal to that at the upstream site or (2) incoming water had solute concentrations equal to rock glacier (RG5) chemistry (Eq. 2). In the latter cases, lateral water fluxes were calculated by multiplying the appropriate solute concentration by and the difference in discharge (ΔQ) between the boundary sites of the reach. Gains or losses of a solute (S_i) within a reach were calculated using the following mass balance equations:

$$S_i = Q_{ds} * C_{ds} - Q_{us} * C_{us} \quad (1)$$

$$S_i = Q_{ds} * C_{ds} - (Q_{us} * C_{us} + \Delta Q * C_{g \text{ or } us}), \quad (2)$$

where Q is the weekly discharge ($\text{m}^3 \text{day}^{-1}$), C is the solute concentration with *us*, *ds*, and *g* designating the upstream, downstream, and rock glacier sites, respectively, S represents the gain or loss of solute i ($\text{mol} * \text{day}^{-1}$) with i designating the specific solute (NO_3^- , NH_4^+ , Cl^-). Results were then normalized to the length of the reach ($\text{mol m}^{-1} \text{day}^{-1}$), with negative values representing a loss of solute and positive values representing a gain, making them comparable between reaches.

The assumption of using the upstream site's chemistry to characterize the lateral water influx is based on studies documenting the positive relationship with streamwater DIN concentrations and elevation in GLV downstream of NAV (e.g. Hood et al. 2003). For example, Hood et al. (2003) found that concentrations of NO_3^- decrease by a factor of five from NAV to ALB to a subalpine site below Silver Lake, from an annual average of 27 to 7.9 to 4.5 $\mu\text{mol L}^{-1}$, respectively. The third possibility, using rock glacier chemistry as a proxy for periglacial contributions, allows us to estimate the net amount of in-stream processing occurring if these features are the source of additional water to the stream. A sensitivity analysis was performed to determine the uncertainty of gains and losses due to in-stream processes in a given reach; this analysis used the following uncertainties for discharge estimates: ± 30 % at ARK, ± 10 % at NAV and GL5, and ± 5 % at GL4. By examining the results of the Cl^- mass balance, we can determine which assumption regarding the incoming water N chemistry best fits the stream reach.

Results

Precipitation, temperature, and stream discharge

Precipitation at Niwot Ridge varies with both space and time. For example, the mean annual precipitation at the alpine D1 climate station, 119 cm year⁻¹ was almost twice that of the 64 cm year⁻¹ at the subalpine C1 station. Mean annual precipitation has declined during the 1985–2009 period by 1.66 mm year⁻¹ at D1 and 2.32 mm year⁻¹ at C1, driven in large part by a regional drought from 2000 to 2007 (Fig. 2b). These declines resulted in a significantly ($p < 0.05$) less precipitation from 2000 to 2009 as compared to 1985–1999 at both D1 and C1. In addition to drier conditions, GLV has also steadily warmed from 1985 to 2009, as indicated by mean annual temperatures increasing by 0.5 °C per decade at D1 (Fig. 2a).

Water yield at GL4 averaged 91 cm year⁻¹ for the period 1985–2009, almost twice that of the 54 cm year⁻¹ at ALB. Both sites saw a decline in volume after 2000 corresponding with the regional drought. However, when comparing average annual discharge from 1985 to 1999 with that of 2000–2009, there was no statistical difference between periods. Discharge at MART averaged 92 cm year⁻¹ for 1985–2009. Annual discharge at MART showed a significant 40 % decrease ($p = 0.005$) between the 1985–1999 (110.2 cm year⁻¹) and 2000–2009 (66.4 cm year⁻¹) periods.

Nitrogen deposition

There was a significant increase ($p < 0.01$) in DIN concentrations in wet deposition between 1985 and 2009 (Fig. 2c). However individually, annual VWM NO₃⁻ and NH₄⁺ concentrations did not show significant trends ($p > 0.05$), due to significant decreases in NO₃⁻ since 2000, at a rate of 1 μM year⁻¹ ($p = 0.0001$, NADP 2013). While annual VWM NH₄⁺ concentrations have also decreased in recent years, there is no consistent trend. Long-term trends are driven by concentration trends prior to 2000, when NO₃⁻ concentrations more than doubled from <10 μM in 1985 to over 20 μM in 2000 and NH₄⁺ concentrations demonstrated a fivefold increase, from <3 μM in 1985 to over 15 μM in 2004 (NADP 2013). These trends in concentration combined with a general decrease in precipitation since 2000, resulted in annual

deposition of DIN peaking in 2000 at approximately 9 kg N ha⁻¹ year⁻¹ (NADP 2013; Fig. 2d).

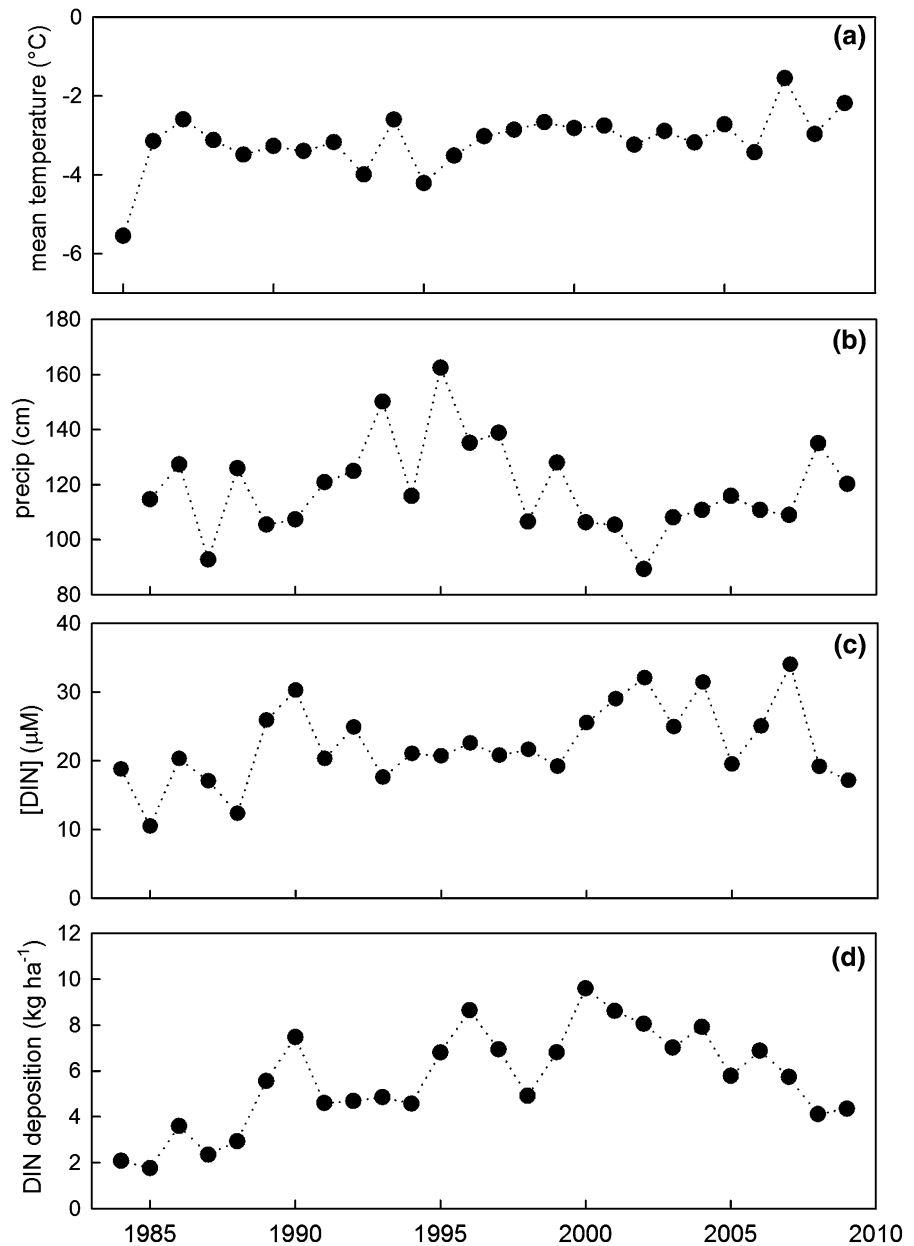
In addition to nitrogen, atmospheric deposition delivers calcium and sulfate to these catchments. Calcium concentration and total deposition steadily increased over the study period by 3.1 mg L⁻¹ year⁻¹ and 1.6 kg ha⁻¹ year⁻¹, respectively (NADP, 2013, Fig. S1). Recent work by Brahney et al. (2013) documents increased calcium deposition throughout the intermountain West due to increased mineral aerosol emission likely caused by increased aridity and human activities. In contrast to calcium, sulfate concentrations in atmospheric deposition have decreased steadily over the last 30 years (NADP, 2013, Fig. S1).

Stream chemistry

Concentrations and yields of geochemical weathering products increased over the study period at GL4 and ALB (Fig. 3). The trend of increasing annual VWM concentrations of Ca²⁺, SO₄²⁻, and Si was driven in part by an increase during drought years. For example, at GL4, SO₄²⁻ annual VWM concentrations increased from ~20 μM in the mid-1990s to over 50 μM in 2000. Interestingly, geochemical weathering product yields also increased throughout the study period (Fig. 3), despite the decrease in discharge during the drought years. Calcium yield at GL4 increased significantly ($p < 0.01$) at a rate of 0.63 kg ha⁻¹ year⁻¹. Similarly, other weathering products increased significantly ($p < 0.01$) with a 1.13 kg ha⁻¹ year⁻¹ increase in SO₄²⁻ and a 0.22 kg ha⁻¹ year⁻¹ increase in Si. ALB also demonstrated significant ($p < 0.01$) increasing trends in weathering product yields, with a 0.35 kg ha⁻¹ year⁻¹ increase in Ca²⁺, 0.40 kg ha⁻¹ year⁻¹ increase in SO₄²⁻, and a 0.19 kg ha⁻¹ year⁻¹ increase in Si yield (Fig. 3). Seasonal Kendall tests indicate that these yields statistically increased for each month of sampling (May through October) at GL4 over the course of the study period. In contrast, Ca²⁺, SO₄²⁻, and Si yield trends at ALB were driven by increases during August and September; indicating that when flow is dominated by snowmelt (June and July) there were no statistical yield changes.

Concentration and yield trends of geochemical weathering products at MART were inconsistent, with both Ca²⁺ and Si concentrations increasing over time while SO₄²⁻ concentrations decreased (Fig. 3). Ca²⁺

Fig. 2 Atmospheric deposition in Green Lakes Valley. Time series of **a** mean annual temperature ($^{\circ}\text{C}$) at D1 (3,739 m) **b** precipitation (cm) at D1, **c** DIN concentration of wet deposition (μM) and **d** the total annual wet deposition of DIN (kg ha^{-1}) at the Saddle NADP site (3,520 m) for 1985–2009. Precipitation was corrected to account for blowing snow as discussed in Williams et al. (1998)



and Si concentrations increased at a rate of 0.34 and $0.99 \mu\text{M year}^{-1}$, respectively, with maximum concentrations coinciding with the lowest precipitation years in 2003 and 2004 (Fig. 3c, d). In contrast, SO_4^{2-} concentrations statistically decreased at a rate of $-0.30 \mu\text{M year}^{-1}$ with SO_4^{2-} yields decreasing within the catchment at a rate of $-0.27 \text{ kg ha}^{-1} \text{ year}^{-1}$ (Fig. 3b). Seasonal Kendall tests indicate that the decrease in SO_4^{2-} yield from MART was driven by the early part of the sampling period; May and June,

given that later in the year yield decreases were not significant. While annual Si and Ca^{2+} yields did not show consistent trends over time, seasonal Kendall tests indicate that Ca^{2+} yields increased significantly in June and August, while Si yields increased from June to August over the study period.

The annual VWM NO_3^- concentrations increased significantly ($p < 0.001$) at GL4, at a rate of $0.27 \mu\text{M N year}^{-1}$, while NO_3^- VWM concentrations decreased at ALB ($p = 0.07$) and MART

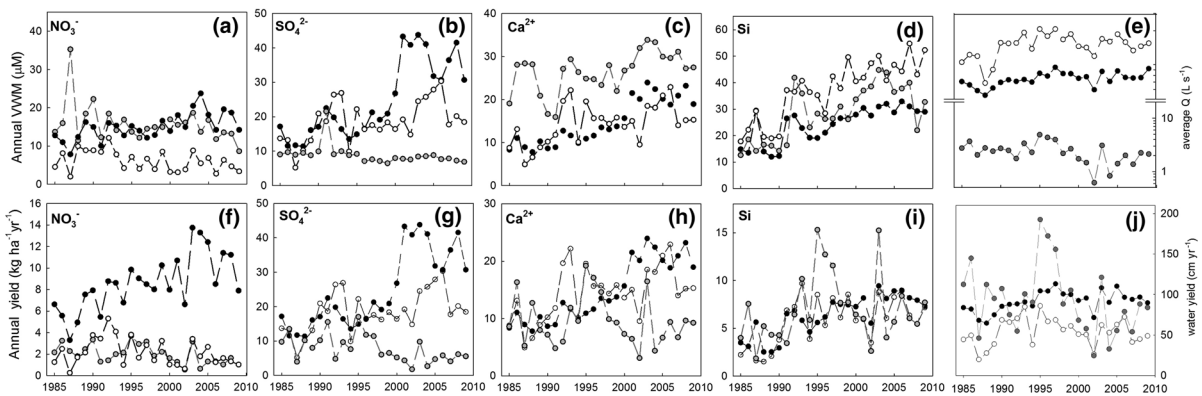


Fig. 3 Annual volume-weighted mean concentrations (μM) and annual yield ($\text{kg ha}^{-1} \text{ year}^{-1}$) of NO_3^- (a, f), SO_4^{2-} (b, g), Ca^{2+} (c, h), and Si (d, i) at GL4 (black circles) and ALB (open circles) and MART (grey circles). The annual average stream

discharge for each stream (e) and water yield (j) are provided for reference. Note the change in y-axis scale between solutes, discharge and water yield measurements

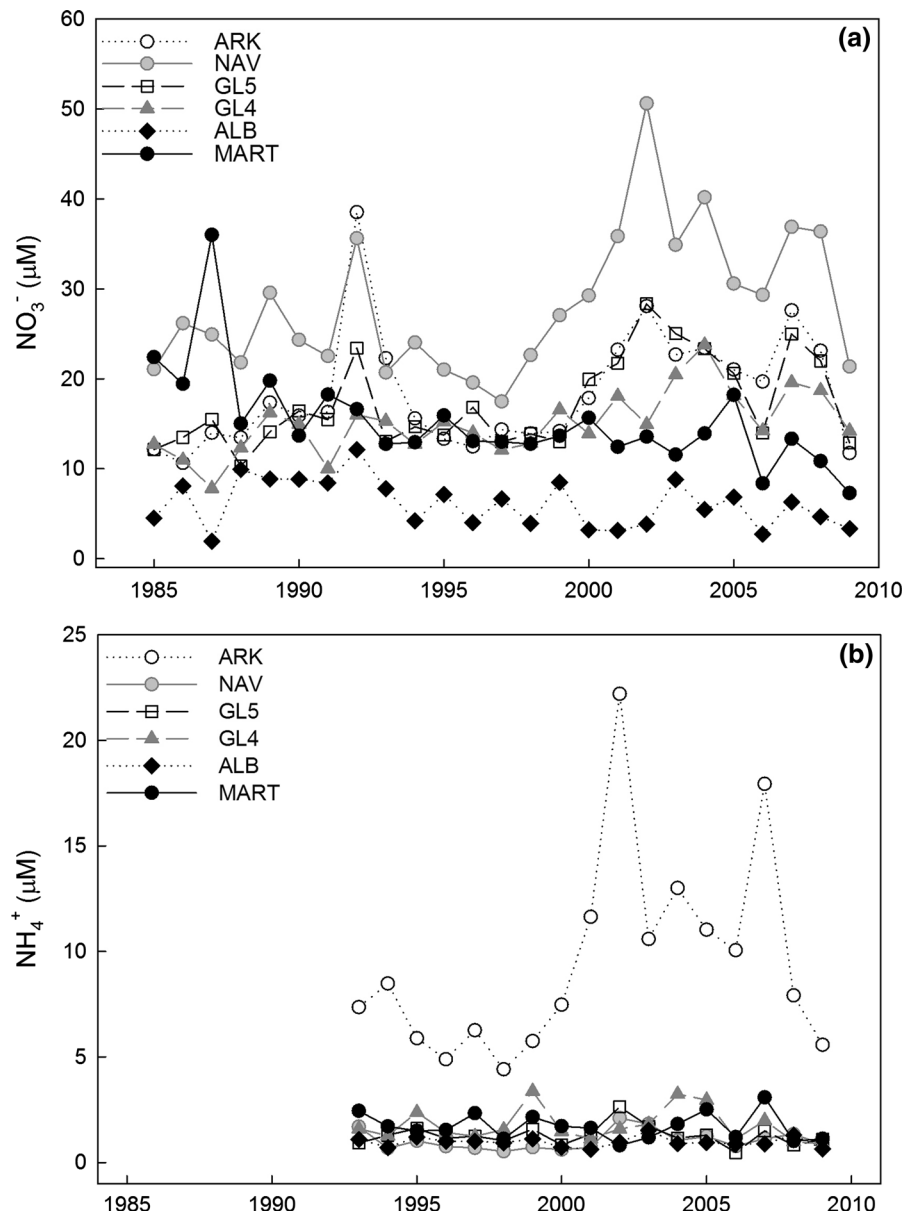
($p = 0.05$) at a rate of $0.13 \mu\text{M N year}^{-1}$ and $0.15 \mu\text{M N year}^{-1}$, respectively (Fig. 3a). The annual yields of NO_3^- at GL4 also increased significantly ($p < 0.005$); with ALB showing no significant change and MART showing a decrease ($p = 0.01$) (Fig. 3f). Seasonal Kendall tests indicate that the NO_3^- yields increased statistically in all months except July (May, June, August–October) in GL4 and showed no statistical changes in ALB with the exception of the month of June. In MART, NO_3^- yields statistically decreased in the months from July to September, driving the overall decreasing trend of NO_3^- export from this catchment.

Annual VWM NO_3^- concentrations also varied spatially, generally increasing with elevation within GLV (Fig. 4a). The lowest mean annual NO_3^- concentration for the study period was found at ALB ($6.1 \mu\text{M}$), the lowest elevation site; while the greatest concentrations were found at NAV (mean = $28.1 \mu\text{M}$). Interestingly, the annual VWM concentrations of NO_3^- decreased from the NAV stream site to ARK glacial meltwater. Given this pattern and the general trend of stable or increasing flows between ARK and NAV, an additional source of NO_3^- , from in-stream processing or lateral inputs, must occur between these sites. The annual VWM concentrations of NO_3^- increased sharply during the drought years (2000–2003) at all sites, with the exception of ALB and MART (Fig. 4a). Annual VWM NH_4^+ concentrations were highest at ARK ($9.4 \mu\text{M}$) and with a peak value of $22.2 \mu\text{M}$ in 2002 (Fig. 4b). The higher NH_4^+ concentrations at ARK have been attributed to snowmelt release of NH_4^+ and the

lack of interaction with soils, i.e. minimal opportunity for biological uptake and/or soil sorption, prior to sampling (Hood et al. 2003). The annual VWM NH_4^+ concentrations were always below $4 \mu\text{M}$ at all other sites, with little spatial variation.

In order to assess how water chemistry changes in response to drought, we followed the protocol of Baron et al. (2009), separating data into two periods corresponding to wet (1985–1999) and dry (2000–2009) years, in order to account for differing periods of record we only used data from June through September. At GL4, the NO_3^- , SO_4^{2-} , and Ca^{2+} concentrations increased significantly ($p < 0.003$) between the two periods by 32, 110, and 37 %, respectively (Table 1). At ALB weathering product concentrations increased significantly ($p < 0.0001$), SO_4^{2-} and Ca^{2+} concentrations increased by 45 and 37 %, respectively; but NO_3^- concentrations declined ($p = 0.03$) between the two periods by 31 % (Table 1). Similar to ALB, MART NO_3^- concentrations declined during the drier period (by 13 %) but the weathering product concentrations did not show consistent trends, with SO_4^{2-} concentrations decreasing by 19 % and Ca^{2+} concentrations significantly increasing ($p < 0.001$) by 24 % (Table 1). For the most part the change in solute yields between the two periods was consistent with concentration changes. At GL4, the NO_3^- yield increased ($p = 0.006$) by 40 % during the drought, from a mean of 1.7 to $2.3 \text{ kg ha}^{-1} \text{ year}^{-1}$ and SO_4^{2-} and Ca^{2+} yields also increased ($p < 0.001$) by 126 and 92 %, respectively (Table 1). In contrast, NO_3^- yield at ALB decreased

Fig. 4 Historical **a** NO_3^- (μM) and **b** NH_4^+ (μM) values for ARK, NAV, GL5, GL4, ALB, and MART. Values are annual VWM with the exception of ARK, where an arithmetic mean is reported. Note that NO_3^- data starts in 1984, while NH_4^+ was not measured regularly until 1993



($p = 0.04$) by 40 % over the same period, while yields of SO_4^{2-} and Ca^{2+} increased, though the increase in Ca^{2+} yield was not significant at $p < 0.05$ (Table 1). At the MART catchment without permafrost or glacial features, the NO_3^- , SO_4^{2-} and Ca^{2+} yields decreased significantly by 44 % ($p = 0.002$) and 49 % ($p = 0.001$), respectively during the drought years (Table 1). Despite the increase in Ca^{2+} concentrations over the same period, Ca^{2+} yields decreased 26 %, though not significantly ($p = 0.10$) (Table 1).

Model results: in-stream gains and losses

In order to estimate both the flux of nitrogen coming into the reach (from upstream and lateral inputs); it is necessary to determine incoming water fluxes. Given the uncertainty in the discharge estimates and thus the amount of water gained in each reach, the maximum range of values was determined and half of that range is presented here (average \pm half the range). From 2000 to 2009, the stream reach from ARK to NAV gained

Table 1 Mean annual concentration (μM), yield ($\text{kg ha}^{-1} \text{ year}^{-1}$), and percent change over time of select solutes for Green Lake 4 (GL4), Albion (ALB), and Martinelli (MART) catchments for the wet (1985–1999) and dry (2000–2009) climatic periods

Solute	Green Lake 4			Albion			Martinelli		
	1985–1999	2000–2009	% Change	1985–1999	2000–2009	% Change	1985–1999	2000–2009	% Change
Concentration									
NO_3^-	13.3	17.6	32*	7.0	4.8	-31*	16.6	14.5	-13
SO_4^{2-}	19.5	41.0	110*	30.7	44.4	45*	19.4	15.8	-19
Ca^{2+}	30.18	54.76	81*	58.4	80.0	37*	48.4	59.8	58*
Yield									
NO_3^-	1.7	2.3	40*	0.6	0.4	-40*	2.4	1.4	-44*
SO_4^{2-}	16.7	37.7	126*	16.6	21.5	30*	9.7	5.0	-49*
Ca^{2+}	10.7	20.6	92*	13.2	16.3	24	10.7	7.9	-26

Significant changes ($p < 0.05$) are noted with an asterisk

$15,944 \pm 8629 \text{ m}^3 \text{ day}^{-1}$ or $0.05 \pm 0.03 \text{ m day}^{-1}$, NAV to GL5 gained $46,024 \pm 11029 \text{ m}^3 \text{ day}^{-1}$ or $0.05 \pm 0.02 \text{ m day}^{-1}$, and GL5 to GL4 gained $25,973 \pm 13,022 \text{ m}^3 \text{ day}^{-1}$ or $0.03 \pm 0.02 \text{ m day}^{-1}$. The water balance downstream of ARK was the most uncertain due to lack of precise estimates in glacial meltwater flows. This uncertainty was propagated through the mass balance model to calculate gains and losses of solutes.

The Cl^- mass balance results reveal that for ARK–NAV the water coming in via lateral inputs (i.e. from soil water, groundwater, small tributaries, snow melt) to the reach most closely resembles the solute profile of ARK, the upstream site, and not the rock glaciers. Average change in Cl^- between the sites was $0.04 \pm 0.07 \text{ mol m}^{-1} \text{ day}^{-1}$ when lateral input concentrations are set equal to that of the upstream site. In contrast if lateral inputs were set to have a concentration of zero, the average change in Cl^- was $-0.12 \pm 0.16 \text{ mol m}^{-1} \text{ day}^{-1}$ and if the lateral inputs are set to the concentration profile of the rock glacier the average change in Cl^- is $0.11 \pm 0.09 \text{ mol m}^{-1} \text{ day}^{-1}$. Similarly, the Cl^- results for the other two reaches showed the same pattern: the estimated change in Cl^- was smallest when it was assumed that concentration profile of water gained within the reaches was similar to the upstream site. For NAV to GL5, change in Cl^- averaged 0.01 ± 0.04 , -0.15 ± 0.08 , and $0.09 \pm 0.06 \text{ mol m}^{-1} \text{ day}^{-1}$ for lateral inputs equal to the upstream site, rock glacier, and zero, respectively. For GL5 to GL4, change in

Cl^- averaged 0.01 ± 0.06 , -0.14 ± 0.15 , and $0.08 \pm 0.04 \text{ mol m}^{-1} \text{ day}^{-1}$ for lateral inputs equal to the upstream site, rock glacier, and zero, respectively. From these results we determined that assuming the concentration of water gained by each reach was equal to that of the upstream site most closely matches the long term observations. However, this does not exclude the idea of the mixing of multiple sources, specifically the dilution of the rock glacier signature by talus waters and/or snow; therefore the following discussion will focus on the results from the model which assumes that the lateral inputs of water have nitrogen concentrations similar to that of the upstream site, but the implications of rock glacier, blockfield, and talus water contributions will also be discussed.

Mass balance results assuming lateral inputs of N equal to upstream concentrations, indicate that there was a net gain of NO_3^- between ARK and NAV ranging from an average of $0.59 \pm 1.30 \text{ mol m}^{-1} \text{ day}^{-1}$ in June to $1.27 \pm 0.70 \text{ mol m}^{-1} \text{ day}^{-1}$ in July and August from 2000 to 2009 (Fig. 5b). Between NAV, GL5, and GL4, the mass-balance shows a switch to net losses of NO_3^- , ranging from $-0.27 \pm 0.40 \text{ mol m}^{-1} \text{ day}^{-1}$ in July (GL5–GL4) to $-0.74 \pm 0.28 \text{ mol m}^{-1} \text{ day}^{-1}$ in Sept (NAV–GL5); with a general trend towards increasing losses later in the summer when flows are lower (Fig. 5b).

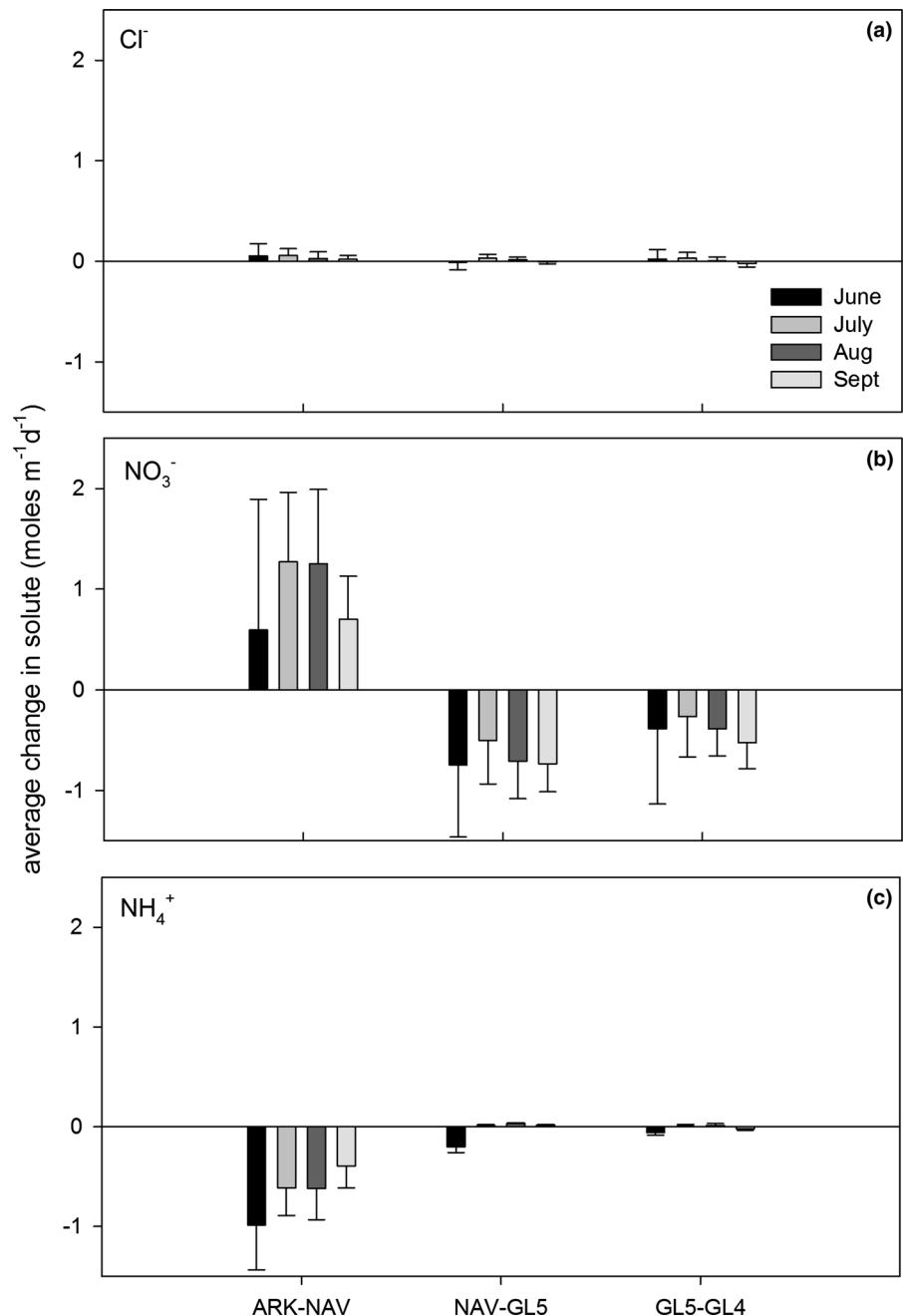
Mass balance results for NH_4^+ assuming lateral stream inputs with NH_4^+ concentrations equal to the upstream site, indicate that there is loss of NH_4^+ between ARK and NAV, ranging from a monthly

average of -0.42 ± 0.22 (Sept) to -0.98 ± 0.45 (June) $\text{mol m}^{-1} \text{day}^{-1}$ (Fig. 5c). The amount of NH_4^+ lost in this reach is significantly greater ($p < 0.001$) than the amount lost in any downstream reach, which had a maximum average monthly loss rate of $-0.5 \pm 0.03 \text{ mol m}^{-1} \text{day}^{-1}$ (June, GL5–GL4).

Discussion

There is ample evidence that the elevated stream NO_3^- in high-elevation catchments throughout the Colorado Front Range are caused, in part, by atmospheric N deposition (Williams et al. 1996a). However, stream concentrations of NO_3^- at GL4 have

Fig. 5 Average change in Cl^- , NO_3^- , and NH_4^+ fluxes ($\text{mol m}^{-1} \text{day}^{-1}$) in North Boulder Creek at three reaches between 2000 and 2009. Calculations assume lateral stream inputs with concentrations equal to upstream site. Error bars indicate the variability of the mean (i.e. one half the range of all model output) at each site for a given month throughout the time period; it should be noted that the majority of this variation is due to uncertainty in the discharge estimates



remained high despite a post-2000 decrease in atmospheric delivery of N. While N leakage from N-saturated soils (Brooks and Williams 1999) could explain the continued increase in alpine export of NO_3^- from GL4, the concurrent decrease in precipitation suggests that this mechanism is unlikely; specifically, with decreased water delivery how would the N in soils be delivered to the stream and how would N yields increase? Thus there are likely other causal mechanisms that contribute to stream NO_3^- concentrations and export; possibly climate-driven changes to the physical environment and N-cycling in alpine and subalpine regions.

Influence of periglacial features on surface water chemistry

Chemical and isotopic mixing models suggest that discharge at GL4 is a mixture of groundwater, blockfield water, and snowmelt; while snowmelt is the dominant source of water to MART (Liu et al. 2004). Given the changing temperature and precipitation one would expect a decrease in snow cover and/or earlier snowmelt at MART; however weekly mapping of snow covered areas revealed no significant trend in the rate of snow cover disappearance over time due to intra- and inter-annual variability. However, there has been an increase in the frequency of completely snow-free summers since the onset of the drought (2000–2009) as compared to the previous period (1985–1999).

Increased GL4 geochemical weathering product fluxes during the drier post-2000 period support the hypothesis that the upper GLV may already be responding to climate change through melting of stored water in permafrost and rock glaciers (Caine 2010). Past research has shown that for the GL5 rock glacier (RG5), warming temperatures promote the dissolution of pyrite, epidote, chlorite, and minor calcite with the precipitation of silica and goethite, resulting in a unique outflow signature (Williams et al. 2006). In addition, recent work in high elevation lakes in Colorado has demonstrated that in cases where SO_4^{2-} is derived primarily from weathering sources, as opposed to atmospheric deposition, concentrations have significantly increased from 1985 to 2008, coinciding with increased temperatures (Mast et al. 2011). Similar to the finding of Williams et al. (2006), Mast et al. (2011) concluded that this SO_4^{2-} was largely derived from pyrite weathering. Comparing

the annual VWM concentrations of ions in GL4 to various source waters demonstrates that during the dry period GL4 chemistry shifted towards the rock-glacier and blockfield melt signature (Fig. 6a), suggesting increased rock-glacier melt and/or permafrost thaw contributions to stream flow. The lack of similar changing ion trends in MART (Fig. 6b) support the idea that increased chemical weathering fluxes at GL4 and ALB are due to thawing of permafrost and melting of glacier ice. This is consistent with the mechanism hypothesized by Baron et al. (2009): thawing permafrost can serve as source water during dry years and summer months after snowmelt. Here, permafrost derived moisture provides a sufficient vector for transporting material from rock glaciers, talus and blockfield slopes into surface waters above GL4.

Research conducted in Europe supports the link between climate and weathering rates in alpine catchments. Warmer temperatures have been linked to increased trends in conductivity, base cations, and SO_4^{2-} in the Italian Alps (Rogora et al. 2003) and Austria (Wograth and Psenner 1995). Similarly, Thies et al. (2007) showed that increasing cation and SO_4^{2-} concentrations in lake water were due primarily to warming temperatures promoting rock-glacier melt, as opposed to atmospheric deposition trends or catchment geology. It is also possible that increased dust deposition could be responsible for increased export of calcium (Brahney et al. 2013) at GL4 and ALB, however if this was the case one would expect similar trends at MART, which were not observed.

The ARK and other ice features within GLV may directly contribute NO_3^- to the catchment. Saros et al. (2010) demonstrated that the presence of glaciers within alpine watersheds more strongly influence NO_3^- concentrations in high-elevation lake ecosystems than any other geomorphic or biogeographic characteristic; hypothesizing that relatively high sublimation and evaporation rates on glaciers concentrates N, resulting in high NO_3^- concentration in glacial meltwaters. They did not account for the effects of other periglacial features such as rock glaciers and/or permafrost in their comparison; given that these features often covary with snow glaciers, they could be important contributors to the Saros et al. (2010) observations. Further, reduced contact with watershed soils and microbes may contribute to the higher NO_3^- concentrations in glacial meltwater, relative to seasonal snowpack melt.

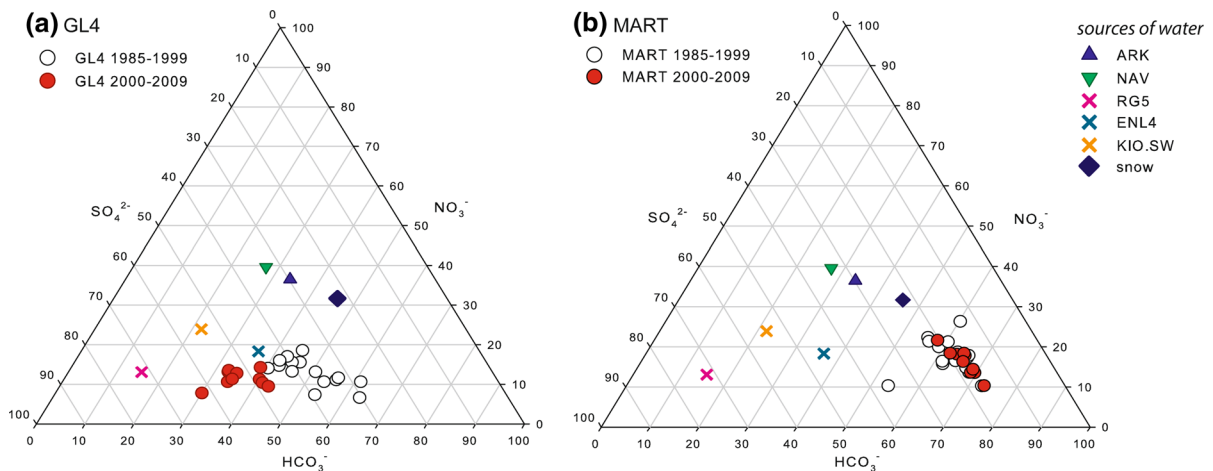


Fig. 6 Ternary diagram for annual VWM of GL4 (a) and MART (b), plotted with possible source waters: the VWM chemistry values for NAV and ARK and mean concentrations for snow (end of winter, prior to melt) and the rock glacier (RG5) from 1985 to 2009. Talus water was characterized by means from shorter time series of data, 2003–2010 for ENL4

and 2010 for KIO.SW. The 1985–1999 period (*open circles*) was characterized by lower temperatures and higher precipitation than the 2000–2009 period (*red circles*). Note: The HCO_3^- value in this figure is actually the measured ANC and axes represent the normalized proportion of the anions and cations for each sample. (Color figure online)

The water at ARK is sampled prior to contact with in situ rock or soil surfaces, thus it is not surprising that NH_4^+ and NO_3^- values are more similar to snowpack concentrations prior to contact with the ground than snow melt (Williams et al. 2001; Williams et al. 2007). While these observations are in line with the hypotheses of Saros et al. (2010), the rapid transformation of NH_4^+ within several hundred meters of ARK (Figs. 4, 7) indicates that microbial processes are also an important contributor to NO_3^- export in glacially fed streams. Further, the direct conversion of NH_4^+ in glacial meltwater to NO_3^- adds between 0.5 and 1.4 kg N ha^{-1} year $^{-1}$ to the GL4 watershed between June and September, amounting to 12–31 % of the annual DIN received via wet deposition in 2009.

In addition to the snow glacier (ARK), thawing permafrost and rock glaciers could also enhance N export. Studies have shown that high latitude catchments characterized by discontinuous permafrost near or at the 0° isotherm tend to have higher DIN concentrations in surface water compared to watersheds with continuous permafrost (Jones et al. 2005). A conceptual model for GLV proposed that summer warming allows the 0° isotherm, separating frozen surfaces from liquid water, to lower into the rock glacier by the end of summer (Williams et al. 2006). This recession exposes fresh mineral surfaces, thereby enhancing geochemical weathering and increasing the

export of ions, as observed at GL4 and ALB (Fig. 3). This process could also increase the export of NO_3^- , due to the presence of active microbes in rock glacier outflows and sediment pockets within talus fields (Ley et al. 2004). Thus, the observed increases in NO_3^- may also be a result of melting ice in rock glaciers flushing microbially active sediments. Finally, thawing cryosphere provides an explanation for the 2 mm year $^{-1}$ increase in discharge at GL4 in October (1984 to present) when temperatures are such that ablation and melting of the snow glacier should be minimal (Hill 2008). Assuming that 50 % of this increased baseflow is derived from thawing periglacial features an additional 1.2–5.9 kg $\text{NO}_3\text{-N}$ enters the stream each year. While this flux does not amount to a large proportion of N entering the system on an annual basis (<0.03 kg N ha^{-1} year $^{-1}$, or less than 1 % of the incoming DIN in wet deposition to GL4), given that the majority of it enters during 1 month of the year, it could make a substantial difference to late season exports.

Increasing nitrification potential

Research has linked changing climatic conditions to N dynamics; for example warm and wet periods accelerate NO_3^- loss to surface waters due in part to increased rates of mineralization (Hong et al. 2005),

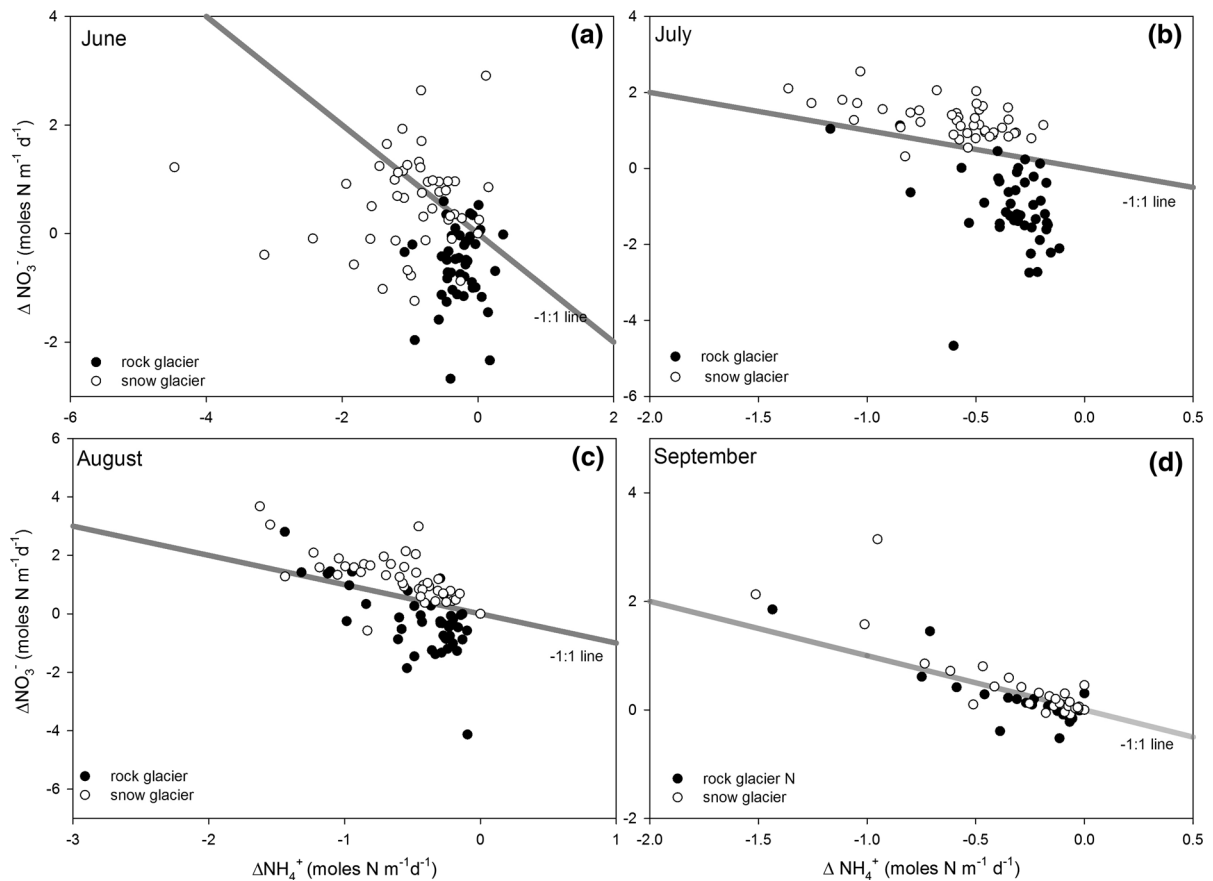


Fig. 7 Monthly relationships between the changes in NO_3^- and NH_4^+ ($\text{mol m}^{-1} \text{day}^{-1}$) between ARK and NAV. Data points are weekly output from the mass balance model, with negative values corresponding to a loss and positive values corresponding to a gain. The *open circles* assume that any water gained by the stream reach has a N chemistry similar to that of the snow glacier (ARK), while *closed circles* assume that the incoming

water has an N chemistry similar to the rock glacier. The *-1:1 line* represents nitrification of incoming NH_4^+ (upstream influx + lateral inputs). Points falling above the *-1:1 line* suggest there are additional NO_3^- sources to the stream, while points below the *-1:1 line* represent biological uptake and/or export of NH_4^+

while higher annual temperatures have been linked to greater stream NO_3^- concentrations (Murdoch et al. 1998). Trends in the long-term data and mass-balance results support the connection between increased air temperatures and altered N cycling.

There are three possible mechanisms for removing NH_4^+ downstream from ARK: NH_4^+ can either be taken up by vegetation, absorbed on ion exchange sites, or nitrified. The high concentrations of NO_3^- and low concentrations of NH_4^+ at NAV as compared to ARK (Fig. 5a) and lack of vegetation support the hypothesis of nitrification as an important source of NO_3^- to NAV. Comparing the relationship between gains of NO_3^- and losses of NH_4^+ estimated by the model for reach ARK–NAV, suggests that nitrification

of incoming glacier meltwater NH_4^+ is likely an important process in July–September (open circles fall on or parallel to the *-1:1 line*, Fig. 7b–d). This is consistent with tracer study results at NAV showing approximately identical rate coefficients for NO_3^- production and NH_4^+ decay within the stream and neighboring wetland (Miller et al. 2006) and the proposed mechanism to explain decreasing NH_4^+ and increasing NO_3^- concentrations as the meltwater travels from ARK to NAV as discussed by Hood et al. (2003). However, given that water added to the reach between ARK and NAV is probably a combination of sources (i.e. contributions from blockfield-, talus-water, and other periglacial features) it is likely that some of the NH_4^+ is lost via uptake by plants

(black circles parallel but below the $-1:1$ line, Fig. 7b, c) and that additional NO_3^- enters the stream (black circles below the $-1:1$ line, Fig. 7a–c). Additional NO_3^- could be gained via the exposure of barren soils via permafrost thaw and glacier retreat, providing substrate for increased mineralization and subsequent nitrification of produced NH_4^+ to NO_3^- either within the soils or upstream of NAV.

Given that nitrification appears to be the integral step in N leaching, it is important to assess how climate influences mineralization and nitrification rates. Research suggests that temperature dependent soil microbial activity plays a major role in transforming N from deposition into mobile NO_3^- (Murdoch et al. 1998). Furthermore, past GLV research has shown a great deal of microbial activity in tundra soils and talus fields that nitrifies NH_4^+ , producing mobile NO_3^- (Nemergut et al. 2008). In fact, moist environments inside talus fields promote algal and fungal growth, facilitating N-cycling even during winter months under the snowpack (Ley et al. 2004). Therefore, an increase in temperatures could further enhance microbial production, potentially resulting in increased NO_3^- leaching.

Stoichiometric controls on N cycling

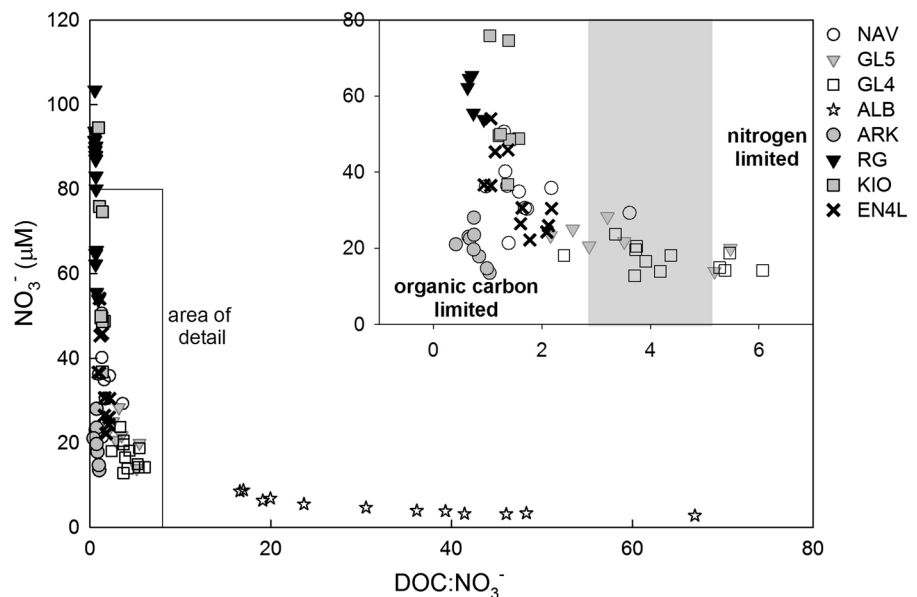
A meta-analysis by Taylor and Townsend (2010) offers additional insight into the spatial patterns of

NO_3^- concentrations in GLV. Their results indicate that across a wide range of environments, DOC to NO_3^- molar ratios ($\text{DOC}:\text{NO}_3^-$) strongly influence NO_3^- accumulation or uptake by regulating a host of microbial processes. When this resource ratio falls below a critical threshold of 3.5 for microbial biomass, the onset of carbon limitation may drive the rapid accrual of NO_3^- in the system. This mechanistic understanding of ecosystem nitrogen processing is in line with our model results and the spatial trends in the long-term data. High NO_3^- concentrations correspond to $\text{DOC}:\text{NO}_3^-$ below 3.5 (Fig. 8), particularly in the blockfield (EN.4L, KIO.SW), rock glacier (RG5), and glacial meltwater (ARK) sites. These sites are carbon limited, resulting in little N assimilation, driving the systems toward net nitrification. In contrast, increased soil and vegetative cover provides more organic carbon at ALB, increasing $\text{DOC}:\text{NO}_3^-$ to above 20, resulting in an N-limited system with little stream NO_3^- . The $\text{DOC}:\text{NO}_3^-$ at GL5 and GL4 are near 3.5, indicating that the lower elevation alpine extent is at the threshold of moving from nitrogen to carbon limitation.

Increased connectivity in a warming climate

Typically, the primary connectivity between terrestrial soils and surface waters occurs during the spring snowmelt season, with warmer temperatures and

Fig. 8 Scatterplot of $\text{DOC}:\text{NO}_3^-$ (μM to μM) ratio versus NO_3^- (μM) for eight sites in Green Lakes Valley. Values are volume-weighted annual means for NAV, GL5, GL4, ALB and arithmetic means for RG, EN.4L, KIO.SW, and ARK. The grey bar in the inset represents the stoichiometric threshold identified by Taylor and Townsend (2010)



reduced summer precipitation restricting soil moisture in high-elevation catchments and reducing the likelihood of N export (Monson et al. 2002). However, as mentioned earlier, other mechanisms such as permafrost thaw may facilitate the export of DIN in drier months. Even in winter months, when cold temperatures and snow cover reduce the opportunity for solute flushing, NO_3^- values remain higher than expected. Clow et al. (2003) showed that groundwater flows year-round in these alpine catchments, although these inputs are primarily derived from talus fields, not the tundra soils from which you might expect elevated solute concentrations. Meltwater from rock glaciers, blockfields and talus slopes may provide insight into the year-round persistence of high solute concentrations; with meltwater mixing with groundwater to form surface waters in these catchments. Liu et al. (2004) demonstrated that this is likely occurring, as flowpaths in upper GLV shift towards stronger rock glacier inputs in the summer months. Our findings support this concept of year-round hydraulic connectivity facilitating the export of NO_3^- , with increasing NO_3^- concentrations at GL4 during every month in the post-2000 drought period.

Conclusions

The historical stream chemistry data provide insight into what the future holds for alpine and subalpine catchments in a warmer world. The comparison between the MART and GL4 catchments allows for isolation of the effects of glacial and permafrost melt to surface water chemistry, providing strong evidence that these cryospheric features are the source of increased weathering products and NO_3^- fluxes later in the growing season. In light of the drier and warmer conditions present in the post-2000 period, GL4 may have crossed a tipping point towards increasing contribution of cryosphere melting to surface waters. In contrast, the MART catchment has not demonstrated a strong correlation between changing climate and stream chemistry likely due to the lack of cryospheric features. The lower elevation subalpine sites (ALB) do not appear to be carbon limited, thus minimizing the extent of net mineralization and nitrification that seem to be driving the nitrate leaching in the higher elevation alpine (e.g. NAV and GL4) sites. These findings, taken in combination, confound

emission policies and associated water quality improvements, as climate change and glacier melt and thawing permafrost may effect NO_3^- concentrations as much, or more than atmospheric deposition trends.

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