

**CLIMATOLOGICAL AND ELEVATIONAL CONTROLS ON ORGANIC AND
INORGANIC NUTRIENTS IN STREAM WATERS, BOULDER CREEK WATERSHED,
COLORADO FRONT RANGE**

By

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ABSTRACT

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Climatological and Elevational Controls on Organic and Inorganic Nutrients in Stream Waters, Boulder Creek Watershed, Colorado Front Range

Thesis directed by Professor Mark W. Williams

Due to short growing seasons, sparse vegetation, thin soils, and a harsh climate, the biota of high elevation ecosystems throughout the Colorado Front Range are sensitive to disturbance. These ecosystems are subject to two major drivers of environmental change: directional changes in climate and increasing inorganic nitrogen (N) deposition in wetfall. By analyzing long term climate records and water chemistry data, we investigate the role of climate and N deposition in determining nitrate export from Green Lakes Valley in the Colorado Front Range. We found that streamwater nitrate concentrations observed at the Green Lakes 4 (GL4) outlet have significantly increased by $0.27 \mu\text{eq L}^{-1} \text{yr}^{-1}$ between 1985 and 2009. In contrast, there was not an increasing nitrate trend at the subalpine site. Comparing solute chemistry before and after the regional drought that began in 2000, we show a 114% increase in sulfate concentrations, an 82% increase in calcium and a 42% increase in silica concentrations at GL4, suggesting that flowpaths switch towards an increasing contribution from rock glacier melt during dry years. Simple mass balance models indicate that there is a net gain of nitrate between the two highest elevation sites of approximately $0.22 \text{ moles NO}_3^- \text{ m}^{-1} \text{ d}^{-1}$, suggesting high nitrification potential in the recently exposed alpine soils. These findings confound emission policies and associated water quality improvement efforts, as climate change and cryosphere melt may affect alpine nitrate concentrations as much, or more than atmospheric deposition trends.

The Landscape Continuum Model (LCM) is a conceptual framework for how mountain ecosystems accumulate and redistribute exogenous and endogenous materials, emphasizing the

importance of transport processes and redeposition of nutrients and water. This study tests the LCM by comparing changes in organic and inorganic nutrients in stream waters of headwater catchments along an elevational gradient in the Colorado Front Range. Water samples were simultaneously collected at four gauged headwater catchments, ranging in elevation from 1830 to 3500 m, and analyzed for nitrogen, carbon, and base cation chemistry. Weathering rates, as measured by dissolved silica concentrations, decreased exponentially with increasing elevation, but the relative contributions of different primary materials to the solute load did not change systematically with elevation. We report a strong shift from a dominance of inorganic nutrients in the alpine to greater organic contributions below treeline as indicated by the decreasing nitrate concentrations (21.36 to 0.85 μeqL^{-1}) and increasing dissolved organic carbon concentrations (0.36 to 10.41 mg C L^{-1}) with decreasing elevation. Solute yields did not demonstrate similar patterns, as local geomorphic and climate characteristics confounded general elevation trends. This study expands the scope of the original LCM to include elevation, climate, and geomorphic controls that, in turn, drive the landcover characteristics that account for the difference in solute concentrations and fluxes. The updated conceptual model also provides a useful framework to assess the implications of future disturbances such as mountain pine beetle infestation, increased N deposition and warming air temperatures.

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Climate Change and Biogeochemical Cycling in Green Lakes Valley, Colorado Front Range, USA

Abstract

Due to short growing seasons, sparse vegetation, thin soils, and a harsh climate, the biota of high elevation ecosystems throughout the Colorado Front Range are sensitive to disturbance. These ecosystems are subject to two major drivers of environmental change: directional changes in climate and increasing inorganic nitrogen (N) deposition in wetfall. By analyzing long term climate records and water chemistry data, we investigate the role of climate and N deposition in determining nitrate export from Green Lakes Valley in the Colorado Front Range. We found that nitrate concentrations observed at the Green Lakes 4 (GL4) outlet have significantly increased by $0.27 \mu\text{eq L}^{-1} \text{yr}^{-1}$ between 1985 and 2009. In contrast, there was not an increasing nitrate trend at the subalpine Albion site. Comparing solute chemistry before and after the regional drought that began in 2000, we show a 114% increase in sulfate concentrations, an 82% increase in calcium and a 42% increase in silica concentrations at GL4, suggesting that flowpaths switch towards an increasing contribution from rock glacier melt during dry years. Simple mass balance models indicate that there is a net gain of nitrate between the two highest elevation sites of approximately $0.22 \text{ moles NO}_3^- \text{ m}^{-1} \text{ d}^{-1}$, suggesting high nitrification potential in the recently exposed alpine soils. These findings confound emission policies and associated water quality improvement efforts, as climate change and cryosphere melt may affect alpine nitrate concentrations as much, or more than atmospheric deposition trends.

1.1 Introduction

Mountain ecosystems provide important ecosystem services worldwide, such as clean water, wood, minerals, livestock forage, and recreation (Price 2006; Körner and Spehn 2002). Alpine regions are one of Earth's most extensive extreme environments, present on all seven continents (Williams et al., 2007). Due to short growing seasons, sparse vegetation, thin soils, and a harsh climate, biota in these alpine systems are at the edge of their environmental tolerance (Williams et al. 2001). Additionally, the complex topography and landscape heterogeneity of these high elevation catchments make it challenging to quantify and explain observed changes in aquatic nutrient fluxes (Seastedt et al. 2004).

In this study, we address the interplay between two major drivers of environmental change in the Front Range of the Colorado Rockies: climate change and atmospheric deposition of inorganic nitrogen. Warming temperatures are likely responsible for the unprecedented rates of mountain glacier retreat worldwide (Meier et al., 2007; Cannone et al., 2008; Racoviteanu et al., 2008). In the western US, warmer temperatures have resulted in decreases in the proportion of precipitation falling as snow (Knowles et al. 2006), decreases in 1 April snowpack snow-water equivalent (SWE) (Mote 2006), and earlier runoff during the spring snowmelt period (Cayan et al., 2001; McCabe & Clark 2005; Regonda et al., 2005; Stewart et al., 2005). Diaz and Eischeid (2007) found that the mean annual air temperature for the warmest month from 1987-2006 in the western US was greater than the Köppen classification of 10°C for 73% of areas classified as having alpine climates, placing the persistence of alpine tundra at risk.

In the western United States, anthropogenic emissions of NO_x (nitrogen oxides) and NH₃ (ammonia) from energy generation activities, transportation, industry, and agricultural activities

contribute to deposition of dissolved inorganic nitrogen ($\text{DIN} = \text{NO}_3^- + \text{NH}_4^+$) in high-elevation watersheds (Baron & Campbell, 1997; Williams and Tonnesson 2000). Deposition data indicate that DIN in wetfall has increased steadily over much of the Rocky Mountains in recent years (Fenn et al., 2003; Burns, 2003). Regional patterns of nitrate concentrations and $\delta^{15}\text{N}\text{-NO}_3^-$ values suggest that atmospheric deposition of inorganic N may affect the amount of nitrate in lakes through indirect processes such as enhanced nitrification (Nanus et al., 2008).

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 conditions are the overarching control on ecosystem processes at a broad scale, further confounding researchers' attempts to quantify how N deposition alone impacts ecosystem function. Several studies have suggested that for mountain areas, climate effects may exceed those of atmospheric deposition (Meixner et al., 2004; Rogora et al., 2007). For example, there may be enhanced weathering and N-mineralization under a warmer climate (Rogora et al., 2003; Hong et al., 2005); leading to increased N export to surface waters (Henriksen and Hessen, 1997). In the northern Rocky Mountains, Saros et al. (2010) report that nitrate concentrations were an order of magnitude higher in high-elevation lakes fed by glacial meltwaters and snowmelt compared to those fed only by snowmelt, attributing the higher nitrate concentrations to glacial meltwater contributions. Baron et al. (2009) report that observed recent increases of nitrate concentrations in the Loch Vale watershed are the result of melting ice from glaciers and rock glaciers in that catchment, which perhaps increase net nitrification of the newly exposed barren soils.

Here we investigate the role of climate and N deposition in determining nitrate export from the Green Lakes Valley in the Colorado Front Range. During 1983–2007, average annual

air temperatures in the watershed increased $1.08^{\circ}\text{C decade}^{-1}$ ($p < 0.01$) (Clow, 2010). Moreover, annual precipitation in Colorado from 2000 to 2003 was below the long-term average for the state, with 2002 one of the driest and hottest years on record (Pielke et al., 2005). Concurrent with this climate forcing was increasing DIN concentrations in wetfall. Through the examination of long term data records and the construction of simple mass balance models, we investigate the spatial and temporal changes in nitrogen biogeochemistry in Green Lakes Valley. Specifically, we address the following four questions: (1) How has nitrate export changed since 1985? (2) What is the impact of drought on alpine stream nitrate dynamics? (3) What is the role of mountain glaciers on nitrate dynamics in Green Lakes Valley, and (4) How do in-stream nitrogen dynamics vary between alpine and subalpine sites?

1.2 Site Location

Green Lakes Valley (40 03' N, 105 35' W) is an east-facing, high-elevation alpine catchment in close proximity to large scale urban and agricultural activities in the Denver-Boulder-Fort Collins area. Elevations range from over 4,000 m at the Continental Divide to 3,250 m at the outlet of the valley with a total drainage area of 700 ha (Figure 1.1). Green Lakes Valley is a municipal water source for the city of Boulder and is designated as a UNESCO Biosphere Reserve. Public access has been restricted since the 1950's, 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 a variety of environmental studies have been conducted since the early 1950's. The continental, high-mountain climate of Green Lakes Valley has been recorded continuously at the D1

meteorological station (Figure 1.1) on Niwot Ridge for over 50 years and for shorter periods on the valley floor. Mean annual temperature at D1 is -3.7°C (Williams et al., 1996b).

The 9-ha Arikaree glacier (ARIK) sits at the head of the valley and is a source of North Boulder Creek (Figure 1.1). Mass balance measurements have been made on the Arikaree Glacier beginning in the mid-1960's (Caine, *in preparation*). The outflow of the Arikaree glacier drains into the Navajo bench (NAV), which is a braided first-order stream located on a "shelf" above Green Lake 5 (GL5) at an elevation of 3750 m. In turn, discharge from GL5 drains into Green Lake 4 (GL4), where discharge has been measured continuously since the early 1980's during the ice-free season. Discharge from a lobate rock glacier (RG5), located in the talus foot zone on the north-facing side of Kiowa Peak at an elevation of 4,000 m, adjacent to GL5 and approximately 8 ha in area, has been collected for chemical analyses since the late 1990's. Discharge from a blockfield (here-on called 'talus' to be consistent with Liu et al. (2004)) on the east face of Niwot Ridge has also been sampled since the late 1990's (e.g. Williams et al., 2006). Two other talus sites above GL5 (EN.4L and KIO.SW) with intermittent discharge are sampled on a weekly basis during snowmelt. The upper basin above GL4 is defined by steep slopes, glacial cirques, permanent snowfields, exposed bedrock, talus outcrops, sparse vegetation, and undeveloped soils; characteristics shared by other alpine areas in the region. There is high spatial variability in snow depth mainly due to redistribution by wind (Erickson et al., 2005).

Bedrock in the upper basin is composed of Precambrian schists and gneisses, the Silver Plume quartz monzonite, and Audubon-Albion stock (Williams et al., 2006). GL4 is a typical alpine headwater catchment in the Colorado Front Range where active and inactive rock glaciers are indicative of underlying permafrost (Janke, 2005). Patterned ground and active solifluction lobes are also common in parts of Niwot Ridge and Green Lakes Valley, especially on ridgelines

(Fahey, 1973). Permafrost has been verified above 3500 m on Niwot Ridge (Ives and Fahey, 1971) and more recently by geophysical methods near Green Lake 5 (Leopold et al., 2008).

In contrast to Green Lake 4, the Albion (ALB) site is located below the series of Green Lakes at the treeline ecotone between alpine and subalpine landscapes. This lower section has more extensive vegetation and soil cover, and less exposed bedrock compared to the upper valley. Finally, The 8-ha Martinelli catchment represents a 1st order, snow-field dominated catchment and its outlet is at an elevation of 3,380m (Figure 1.1). The Martinelli catchment has a poorly developed soil structure, little vegetation, and a deep winter snow cover (Caine, 1989). The smaller catchment area limits groundwater storage and almost 80% of streamflow is composed of snowmelt event water (Liu et al., 2004). In contrast to GL4, MART does not contain any glacial sources or permafrost due to its southern aspect and lower elevation.

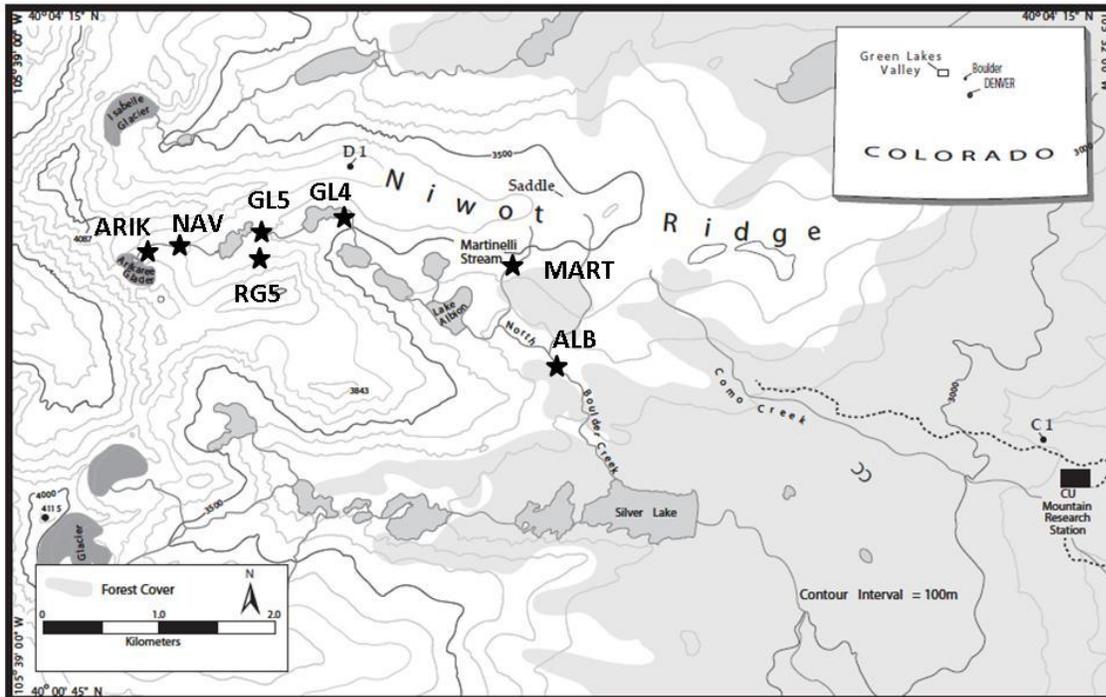


Figure 1.1: Site location map of Green Lakes Valley. Temperature and precipitation are measured at D1 and C1 climate stations. Weekly grab samples of surface water (locations marked by stars) are collected for chemical analyses along the hydrologic axis of the catchment during the ice free season at the Arikaree Glacier (ARIK), Navajo bench (NAV), Green Lake 5 (GL5), the Green Lake 5 Rock Glacier (RG5), Green Lake 4 (GL4), Albion (ALB), and Martinelli (MART). Precipitation chemistry is measured at the Niwot Saddle as part of the National Atmospheric Deposition Program (NADP).

1.3 Methods

1.3.1 Sample Collection and Analysis

This study utilizes a long-term data set collected by the Niwot Ridge LTER program, including daily air temperature and precipitation, weekly wet deposition chemistry, weekly stream chemistry, and daily discharge (available at <http://culter.colorado.edu/NWT/>). Seasonal discharge has been measured continuously since 1982 at GL4, ALB, and MART from approximately 1 May to 30 October. Rating curves were developed from weekly stage height

readings at NAV and measured GL4 discharge, providing a rough estimate of discharge at this site (Williams & Caine, 2001). Streams and subglacial water were sampled as grab samples from about 1 May to 30 October, with collection beginning in 1984 for all stream sites and in the mid to late 1990's for the rock glacier and subglacial waters. Weekly sampling of wet deposition chemistry was initiated in 1984 at the Niwot Ridge site by the National Atmospheric Deposition Program/National Trends Network

(<http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=CO02>).

All water samples were analyzed for pH, acid-neutralizing capacity (ANC), conductance, major ions and dissolved silica (Si), following the protocols presented by Williams et al. (2006; 2007; 2009). Routine measurements of dissolved organic carbon (DOC) began in 1998. The yields of chemical species were estimated as the product of measured concentrations and the accumulated water discharge for weekly intervals centered on the day of sampling. Seasonal volume-weighted mean (VWM) concentrations for individual species were calculated as seasonal mass flux divided by seasonal discharge.

1.3.2 Statistical Methods

Long-term trends of conductance, ANC, Ca^{2+} , NO_3^- , SO_4^{2-} , Si and DOC were analyzed using the nonparametric seasonal Kendall test (Helsel and Hirsch, 1992). Concentrations were first adjusted for flow using a multiple linear regression model. In this case, a season was 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 a long term trend. Simple linear regression was used to determine the significance of correlations between climate and nitrate concentrations. Multiple regression analyses were

also conducted to determine the combined effects of air temperature and N deposition on streamwater chemistry. The Mann-Whitney U-procedure was used to test for differences in chemical and hydrological observations for the 1985-1999 and 2000-2009 sampling periods. This is a commonly used nonparametric test of whether two samples of observations come from the same distribution. Significant differences were determined at the $\alpha = 0.05$ level and are noted with asterisks in tables and figures.

1.3.3 Evaluating Gains and Losses of DIN along Stream Reaches

Four reaches within Green Lakes Valley were modeled to estimate gains and losses of nitrate and ammonium: Arikaree to Navajo (ARIK-NAV), Navajo to the outlet of Green Lake 5 (NAV-GL5), outlet of Green Lake 5 to outlet of Green Lake 4 (GL5-GL4), and outlet of Green Lake 4 to Albion (GL4-ALB) (Barnes, unpublished data). Discharge measurements are made at 3 of the sites within the watershed (NAV, GL4, ALB) and were estimated for the remaining sites (ARIK, GL5) using a ratio of watershed sizes with the closest site as follows, where A is the catchment area and Q is discharge (Eq. 1 and Eq. 2).

$$\text{Eq. 1: } Q_{\text{ARK}} = \frac{A_{\text{ARK}}}{A_{\text{NAV}}} * Q_{\text{NAV}}$$

$$\text{Eq. 2: } Q_{\text{GL5}} = \frac{A_{\text{GL5}}}{A_{\text{GL4}}} * Q_{\text{GL4}}$$

Daily discharge is not available prior to 2000 for NAV and thus our estimates of solute gains and losses for the upper reaches (ARIK-NAV and NAV-GL5) are confined to this period.

The gains or losses of a solute (S_i) within a reach were calculated using the following equations:

$$\text{Eq. 3 (no lateral flow): } S_i = Q_{ds} * C_{ds} - Q_{us} * C_{us}$$

$$\text{Eq. 4 (with lateral flow): } S_i = Q_{ds} * C_{ds} - (Q_{us} * C_{us} + \Delta Q * C_{us})$$

Where Q is the daily discharge ($\text{m}^3 \text{d}^{-1}$), C is the solute concentration with us and ds designating the upstream and downstream sites, respectively, S represents the gain or loss of solute i ($\text{moles} * \text{d}^{-1}$) with i designating the specific solute (nitrate or ammonium). Results were then normalized to the length of the reach ($\text{moles} \text{m}^{-1} \text{d}^{-1}$) or reported as a percentage change relative to the upstream site, with negative values representing a loss of a solute and positive values representing a gain. The simplicity of this model relies on the fact that there are no tributaries entering North Boulder Creek within the confines of these reaches and thus any incoming water is from groundwater or meltwater (snow, glacial, or permafrost). Given that there are few measurements for the inorganic nitrogen concentrations within the lateral influx of water to each reach, two assumptions were made in an effort to provide boundaries to the estimates of in-stream gains and/or losses: (1) incoming water simply dilutes the upstream flux, i.e. there is no inorganic nitrogen in the water (Eq. 3) or (2) the inorganic nitrogen concentrations in lateral flow are equal to the upstream site (Eq. 4). In the latter case the lateral fluxes were calculated using solute concentrations from the upstream site and the difference in discharge (ΔQ) between the boundary sites of a given reach.

1.4 Results

1.4.1 Long-Term Data

Precipitation and Stream Discharge

The mean annual precipitation at the alpine D1 climate station of 119 cm yr^{-1} from 1985 to 2009 (Figure 1.2) was almost twice that of the 64 cm yr^{-1} at the subalpine C1 station. While there were no significant long-term trends in annual precipitation at either climate station ($p > 0.05$), mean annual precipitation has declined during the 1985-2009 period. Since 1985, the mean annual precipitation has declined 1.66 mm yr^{-1} at D1 and 2.32 mm yr^{-1} at C1. This decline in annual precipitation is driven in large part by a regional drought from 2000 to 2007, with 2002 having the lowest annual precipitation values since 1985 (Figure 1.2).

Specific discharge at GL4 averaged 91 cm yr^{-1} for the period 1985-2009, almost twice that of the 54 cm yr^{-1} at ALB. At both sites, specific discharge declined with the regional drought that started in 2000 (Figure 1.2). Similarly, the stream discharge at ALB averaged 54 cm yr^{-1} , just below the mean annual precipitation at the C1 climate station (64 cm yr^{-1}). Annual discharge at both GL4 and ALB in 2002 was among the lowest in the long-term discharge record, reflecting the low precipitation that year.

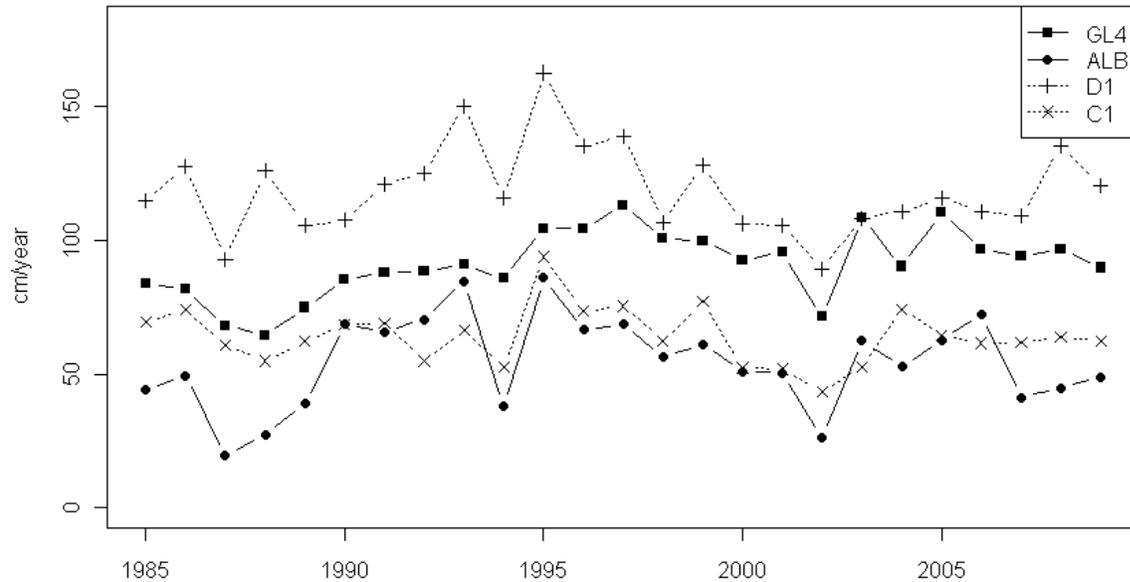


Figure 1.2: Times series (1985-2009) of stream discharge, in cm yr^{-1} , from GL4 and ALB, and annual precipitation, in cm yr^{-1} , from the D1 (3770 m) and C1 (m) climate station.

Nitrogen Deposition

There was a significant increase ($p < 0.01$) in the wet deposition of DIN at the Saddle site at the rate of $0.19 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ between 1985 and 2009 (Figure 1.3). Annual VWM nitrate concentration has more than doubled from less than $10 \mu\text{eq L}^{-1}$ in 1985 to over $20 \mu\text{eq L}^{-1}$ in 2000 ($0.24 \mu\text{eq L}^{-1} \text{ yr}^{-1}$, $p < 0.05$). Similarly, the ammonium concentrations have increased five-fold, from less than $3 \mu\text{eq L}^{-1}$ in 1985 to over $15 \mu\text{eq L}^{-1}$ in 2004 ($0.28 \mu\text{eq L}^{-1} \text{ yr}^{-1}$, $p < 0.05$). Annual deposition of DIN peaked in 2000 at $9.4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. Annual deposition of DIN has decreased since 2000 (Figure 1.3), driven by the decrease in annual precipitation associated with the beginning of the drought.

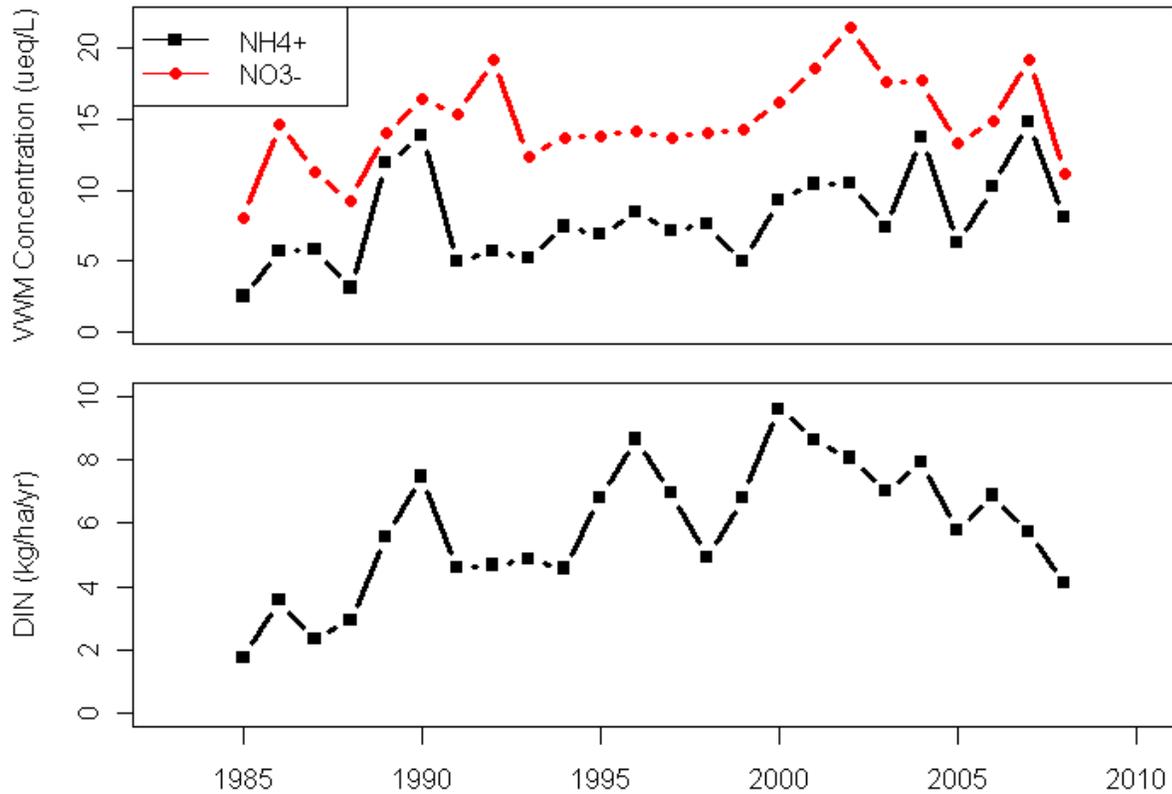


Figure 1.3: Time series of wet atmospheric deposition concentrations of ammonium and nitrate in μeqL^{-1} at the Saddle NADP site (3520m) and total annual DIN deposition ($\text{kg ha}^{-1}\text{yr}^{-1}$) for the period 1985-2009.

Stream Chemistry

Concentrations and yields of geochemical weathering products increased over the study period at GL4 and ALB (Figure 1.4). The trend of increasing annual VWM concentrations of calcium, sulfate, and silica is driven in part by a large increase associated with the drought years. For example, at GL4, annual VWM concentrations of sulfate increased from about $40 \mu\text{eq L}^{-1}$ in

the mid-1990's to over $100 \mu\text{eq L}^{-1}$ in 2000. Somewhat surprising, yields of geochemical weathering products increased throughout the study period, even with the recent drought (Table 1.1). Calcium at GL4 increased significantly ($p < 0.01$) at a rate of $0.63 \text{ kg ha}^{-1} \text{ yr}^{-1}$ with a mean value of $14.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$. Similarly, the other weathering products increased significantly with a $1.13 \text{ kg ha}^{-1} \text{ yr}^{-1}$ increase in sulfate ($p < 0.01$) and a $0.22 \text{ kg ha}^{-1} \text{ yr}^{-1}$ increase in silica ($p < 0.01$). ALB also demonstrated significant ($p < 0.01$) increasing trends in weathering product yields, with a $0.35 \text{ kg ha}^{-1} \text{ yr}^{-1}$ increase in calcium, $0.40 \text{ kg ha}^{-1} \text{ yr}^{-1}$ increase in sulfate, and a $0.19 \text{ kg ha}^{-1} \text{ yr}^{-1}$ increase in silica yield. The rates of increase in yield were less at ALB than at GL4 for all weathering solutes.

At GL4, the annual VWM concentration of nitrate over the study period averaged $15.0 \mu\text{eq L}^{-1} \text{ yr}^{-1}$, compared to $6.13 \mu\text{eq L}^{-1} \text{ yr}^{-1}$ at ALB (Figure 1.4). There was a significant increase in the VWM concentration of nitrate at GL4 over time ($p < 0.05$) of $0.27 \mu\text{eq L}^{-1} \text{ yr}^{-1}$. In contrast, the lower elevation ALB site demonstrated a significant decreasing trend in nitrate concentrations of $0.15 \mu\text{eq L}^{-1} \text{ yr}^{-1}$ ($p < 0.05$). The annual yield of $\text{NO}_3^- \text{ N}$ measured at the GL4 site increased significantly at a rate of $0.06 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for the period 1985-2009 ($p < 0.005$) with a mean yield of $1.94 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Table 1.1). In contrast to the increasing trends at GL4, there was no significant change in nitrate yields at ALB (Table 1.1) and the mean value of $0.49 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ was only 25% of that of GL4. As with the geochemical weathering products, at GL4 there appears to be an increase in both the concentration and flux of nitrate starting in 2000. However, that trend does not appear at the ALB site.

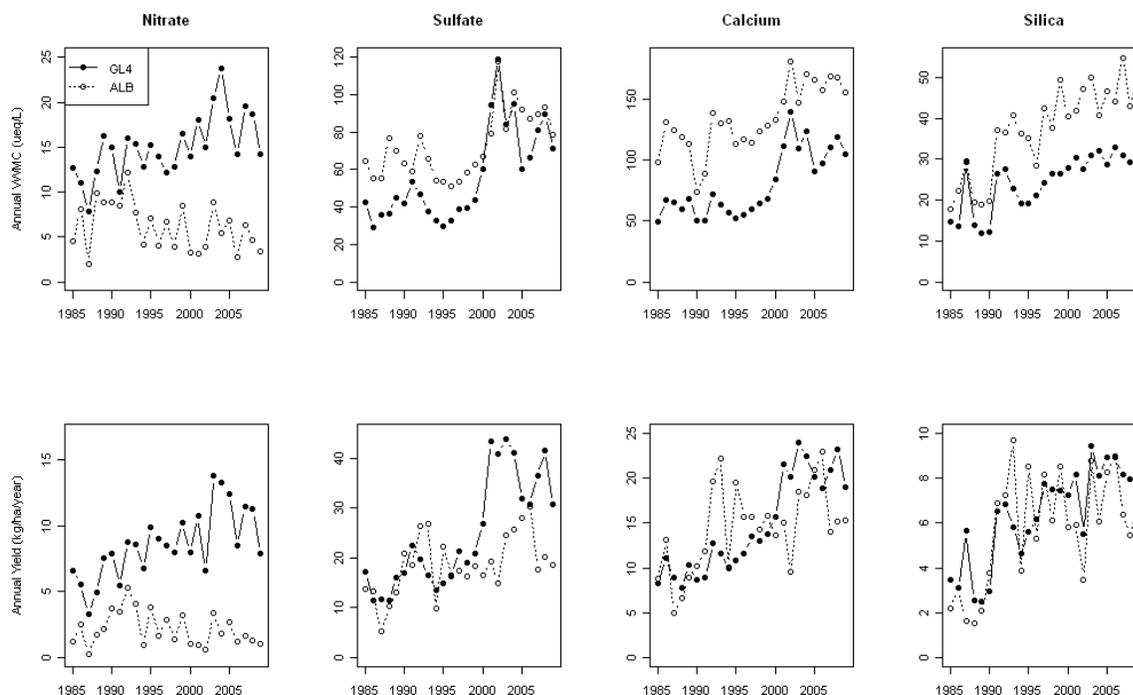


Figure 1.4: Annual volume-weighted mean concentrations ($\mu\text{eq L}^{-1}$) and annual yield ($\text{kg ha}^{-1} \text{yr}^{-1}$) of nitrate-N, sulfate, calcium and silica at GL4 (black circles) and ALB (white circles).

Table 1.1: Seasonal Kendall trends in yields of select solutes ($\text{kg ha}^{-1} \text{yr}^{-1}$) for GL4 and ALB. Significance trends are shaded ($p < 0.05$).

Site	Period Begin	Parameter	Yield Trend (kg/ha/year)						
			Annual	MAY	JUNE	JULY	AUG	SEPT	OCT
GL4	1985	Ca^{2+}	0.63	0.16	0.15	0.10	0.08	0.08	0.09
GL4	1985	$\text{NO}_3^- \text{N}$	0.06	0.02	0.01	0.01	0.01	0.01	0.01
GL4	1985	SO_4^-	1.13	0.29	0.25	0.16	0.17	0.18	0.17
GL4	1985	Si	0.22	0.05	0.05	0.05	0.03	0.03	0.03
ALB	1985	Ca^{2+}	0.35	0.09	0.01	0.09	0.09	0.06	0.06
ALB	1985	$\text{NO}_3^- \text{N}$	-0.01	0.00	-0.01	-0.00	0.00	0.00	0.00
ALB	1985	SO_4^-	0.40	0.11	-0.08	0.13	0.12	0.08	0.08
ALB	1985	Si	0.19	0.05	0.03	0.06	0.03	0.02	0.02

Multiple regression tests were evaluated to try to explain the annual variance in nitrate values at the two sampling sites. In this simple model, mean annual temperature, DIN fluxes in

wet deposition, and DIN concentrations in wet deposition were used as explanatory variables. However, this multiple regression failed to significantly explain the differences in nitrate yields throughout the study period. At GL4, the model explained only 16% of the variance ($p = 0.28$), and at ALB only 14% ($p = 0.35$). Simple linear regressions of the individual variables were also not significant.

1.4.2 Drought Condition Comparison

In order to assess how the water chemistry changes in response to drought conditions, we followed the protocol of Baron et al. (2009) and separated the long-term sampling period into two periods corresponding to wet and dry years. The first period from 1985-1999 corresponded to relatively wet years, while the second period from 2000- 2009 commences at the start of the prolonged drought in the study area (Figure 1.2). At GL4, we find that the nitrate - N yield increased by 40% during the drought, from a mean of 1.7 to 2.3 kg N ha⁻¹ yr⁻¹ (Table 1.2). The sulfate yield increased 126% from 16.7 to 36.7 kg ha⁻¹ yr⁻¹, while the calcium yield increased 92% from 10.7 to 20.6 kg ha⁻¹ yr⁻¹. In contrast to GL4, nitrate - N yield at ALB between the 1985-1999 and 2000-2009 study periods decreased by 40%, from a mean of 0.58 to 0.35 kg N ha⁻¹ yr⁻¹. The weathering product yields at ALB followed the same increasing patterns seen at GL4, although the percent change was not as large. The sulfate yield increased 30% from 16.6 to 21.5 kg ha⁻¹ yr⁻¹, while the calcium yield increased 24% from 13.2 to 16.3 kg ha⁻¹ yr⁻¹.

At the smaller MART catchment, the nitrate yields during the drought decreased by 44%, from 2.39 to 1.35 kg N ha⁻¹ yr⁻¹ (Table 1.2). This is a similar percent decrease as observed at ALB and opposite the trend at GL4. In contrast to the increasing trends at ALB and GL4, sulfate yield at MART decreased by 49% from an annual mean of 9.74 to 5.01 kg ha⁻¹ yr⁻¹. The

calcium yield also decreased by 26% at MART from 10.7 to 7.9 kg ha⁻¹ yr⁻¹, indicating that the geochemical weathering processes occurring during drought years at MART are different from the chemical weathering processes at GL4 and ALB.

Table 1.2.: Mean annual yield (kg ha⁻¹ yr⁻¹) and percent change over time of select solutes for 1985-1999 and 2000-2009 periods.

Solute	Green Lake 4			Albion			Martinelli		
	1985-1999	2000-2009	% change	1985-1999	2000-2009	% change	1985-1999	2000-2009	% change
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

1.4.3 Elevational Gradient and Nitrogen Concentrations

Annual VWM nitrate concentrations along an elevational gradient in Green Lakes Valley demonstrated a general increasing trend both with elevation and time (Figure 1.5). The lowest mean annual nitrate concentrations for the 1985-2009 study period of 6.1 µeq L⁻¹ were found at ALB, the lowest elevation site. Moving up the elevational gradient, the mean annual nitrate concentrations increase from 15.0 µeq L⁻¹ at GL4 to 17.3 µeq L⁻¹ at GL5. The two highest elevation sites have higher nitrate concentrations than any of the other sites along the gradient, with NAV having a significantly ($p < 0.05$) higher annual mean concentration of 28.1 µeq L⁻¹ compared to 18.5 µeq L⁻¹ at ARIK. The annual VWM concentrations of nitrate increased significantly ($p < 0.05$) during the post-2000 period at all sites with the exception of the lower elevation ALB site.

The historic ammonium concentrations did not demonstrate an elevational trend (Figure 1.5). In general, ammonium concentrations were near detection limits except at ARIK. The

greatest historic mean annual concentrations were consistently found at ARIK, with a sharp increase during the post-2000 period. The mean annual concentration in 2002 at ARIK ($22.1 \mu\text{eq L}^{-1}$) was an order of magnitude greater than the next greatest ammonium concentration at GL5.

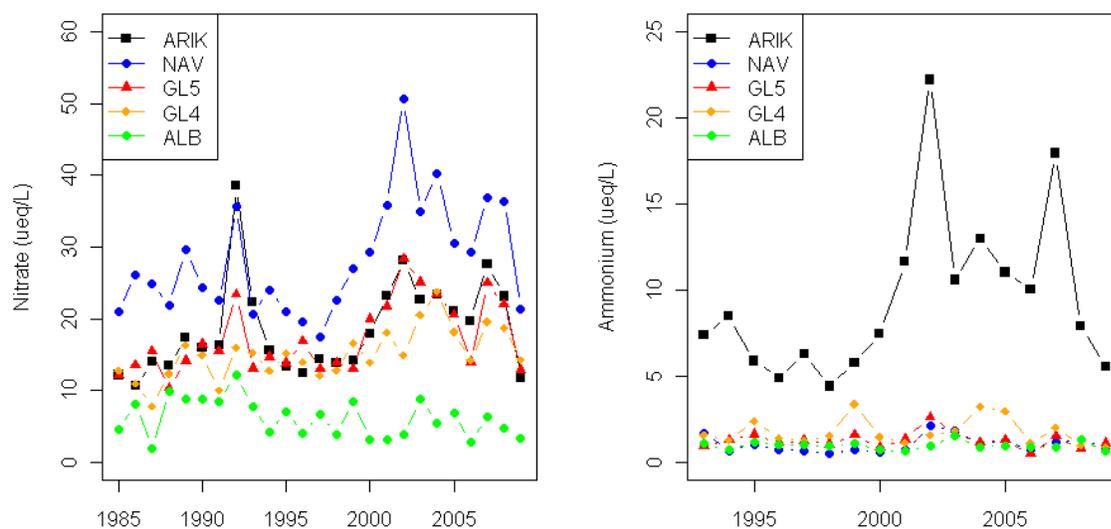


Figure 1.5: Historical nitrate and ammonium concentrations (μeqL^{-1}) for ARIK, NAV, GL5, GL4, and ALB (decreasing in elevation). Values are annual volume-weighted means for GL4 and ALB and arithmetic annual means for ARIK, NAV, and GL5.

1.4.4 Evaluating Gains and Losses of DIN along Stream Reaches

Mass balance models indicate that there is a net gain of nitrate between ARIK and NAV of approximately $0.22 \text{ moles NO}_3^- \text{ m}^{-1} \text{ d}^{-1}$ (Figure 1.6). Between NAV and GL5, the model shows a switch to a net loss of nitrate, though the magnitude of the loss is smaller than the losses between GL4 and ALB. There is a similar loss of $0.24 \text{ moles NO}_3^- \text{ m}^{-1} \text{ d}^{-1}$ between GL5 and GL4, but the greatest losses occur between GL4 and ALB. Of the five months modeled (June-September), the losses were greatest during June ($1.7 \text{ moles NO}_3^- \text{ m}^{-1} \text{ d}^{-1}$). Later in the season

during baseflow conditions (August and September), the losses are not as great in all reaches.

The higher nitrate losses earlier in the season are likely due to greater amounts of nitrate entering the system from snowmelt, which generally occurs in June.

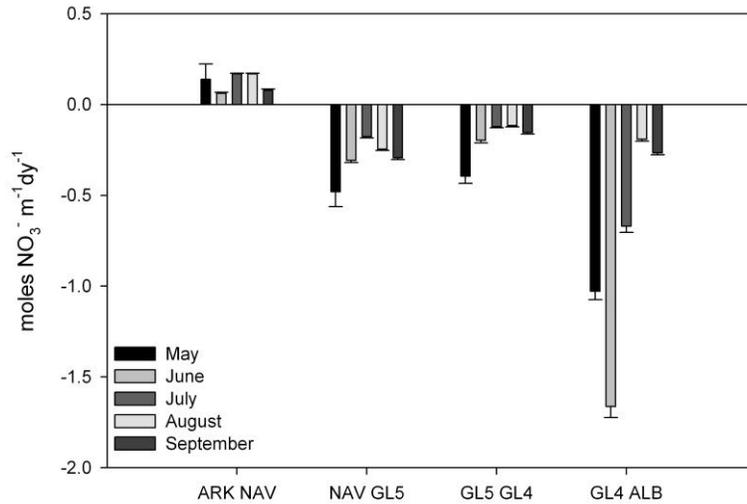


Figure 1.6: Change in fluxes of nitrate in moles N m⁻¹d⁻¹ at four reaches along North Boulder Creek between 2000-2009, assuming lateral inputs to stream with concentrations equal to that of the upstream site. Error bars indicate the variability within a given month throughout the time period (Barnes, *written communication*).

We evaluated potential nitrification of ammonium to nitrate in the reach between ARIK and NAV (Figure 1.7) from July to September by comparing the changes in nitrate and ammonium from our mass balance model. The loss of ammonium was significantly correlated with the increase in nitrate (slope = -1.01, $p < 0.001$) between July and September from 2000 to 2009. This strong negative relationship suggests the nitrification of ammonium to nitrate between ARIK and NAV. The relationship between changes in nitrate and ammonium are not present in June, suggesting that the biological controls associated with ammonium removal and nitrate production may vary due to snowpack conditions and the onset of snowmelt in the spring that contributes to high flow conditions.

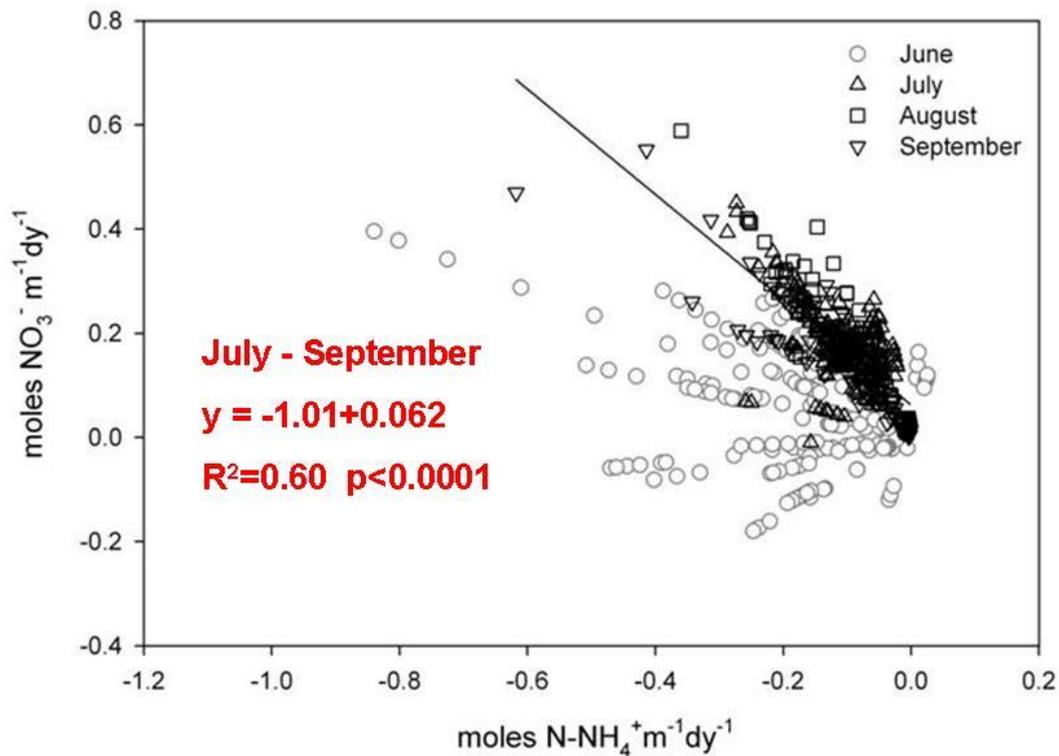


Figure 1.7: Plot of change in nitrate versus ammonium in moles $\text{m}^{-1} \text{ d}^{-1}$ in the stream reach between ARIK and NAV. Negative values imply a loss of the solute and positive values correspond to the production of the solute. Data points are estimated daily values from June-September during the 2000-2009 period (Barnes, *written communication*).

Simple mass balance modeling indicated that the amount of nitrate lost to in-stream processes between GL4 and ALB increased significantly from 1990 to 2009 (Barnes, unpublished data) (Figure 1.8). Average annual in-stream losses of nitrate between GL4 and ALB were bounded between -0.046 moles $\text{N m}^{-1} \text{ d}^{-1}$ (assuming lateral input waters with nitrate concentrations equal to the outflow of GL4) and -0.054 moles $\text{N m}^{-1} \text{ d}^{-1}$ (assuming no lateral input of nitrate) ($p < 0.005$).

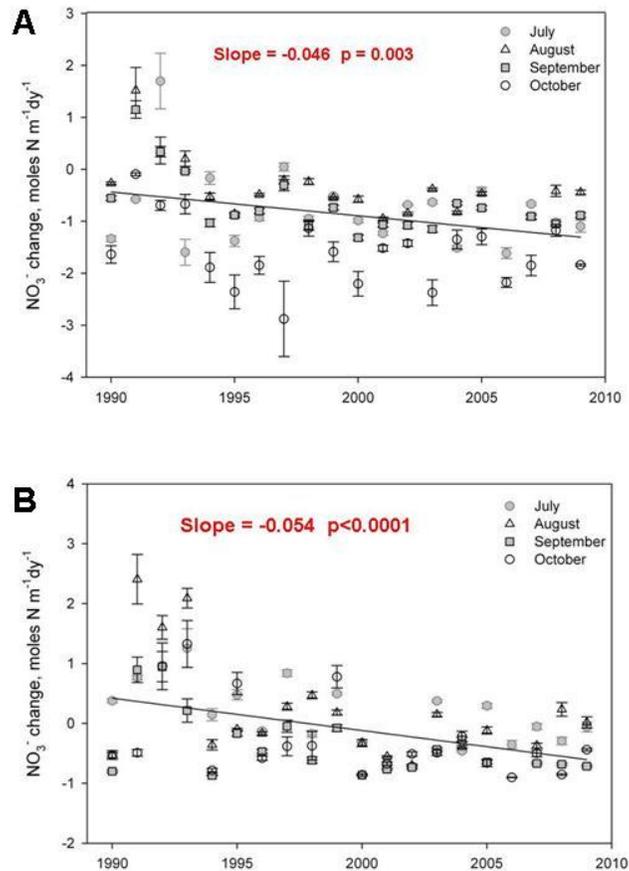


Figure 1.8: Time series of change in mass of nitrate in moles N m⁻¹d⁻¹ during baseflow months (July-October) from 1990-2009 between GL4 and ALB assuming A) lateral inputs of nitrate with concentrations equal to the concentrations at GL4 and B) assuming no lateral inputs of nitrate (Barnes, *written communication*).

1.5 Discussion

There is ample evidence that the elevated stream water nitrate concentrations in high-elevation catchments throughout the Colorado Front Range observed between 1985 and 2009 are caused, in part, by increased atmospheric deposition of inorganic nitrogen (Baron et al., 2000; Burns, 2003). However, the streamwater concentrations of nitrate in Green Lakes Valley (GL4, ALB, and MART) have remained high despite a post-2000 decrease in atmospheric deposition of inorganic N at the D1 climate station. These findings compel us to look for other causal

mechanisms that might contribute to the elevated nitrate concentrations in streamwaters, most notably climate-driven changes to the physical environment including cryosphere melting and temperature-driven changes in N-cycling throughout the alpine and subalpine landcover regions.

1.5.1 Changing Flowpaths and Geochemical Weathering

Chemical and isotopic mixing models suggest that snowmelt is the dominant source of water to MART, while discharge at GL4 is a mixture of groundwater, talus water, and snowmelt (Liu et al., 2004). Additionally, Liu et al (2004) found that the source waters of MART remain constant, yet change within the GL4 catchment in response to differences in climate conditions, particularly drought. This evidence indicates that the flowpaths at GL4 are more sensitive to changes in climate than the MART catchment.

Increasing geochemical weathering product concentrations and fluxes at GL4 in the dryer post-2000 period support the hypothesis that the upper Green Lakes Valley may already be responding to climate change. The Piper diagram demonstrates that the dry period annual mean concentrations of base cations tend to shift towards the rock glacier melt signature (Figure 1.9). Past research at Niwot Ridge (Williams et al., 2006) has shown that air temperature warming promotes the dissolution of pyrite, epidote, chlorite, and minor calcite with the precipitation of silica and goethite, resulting in a unique rock glacier outflow signature. Our results are consistent with this study as warm, dry periods drive the chemical signature of GL4 surface waters towards this rock glacier end-member, suggesting increased glacier melt contributions to stream flow.

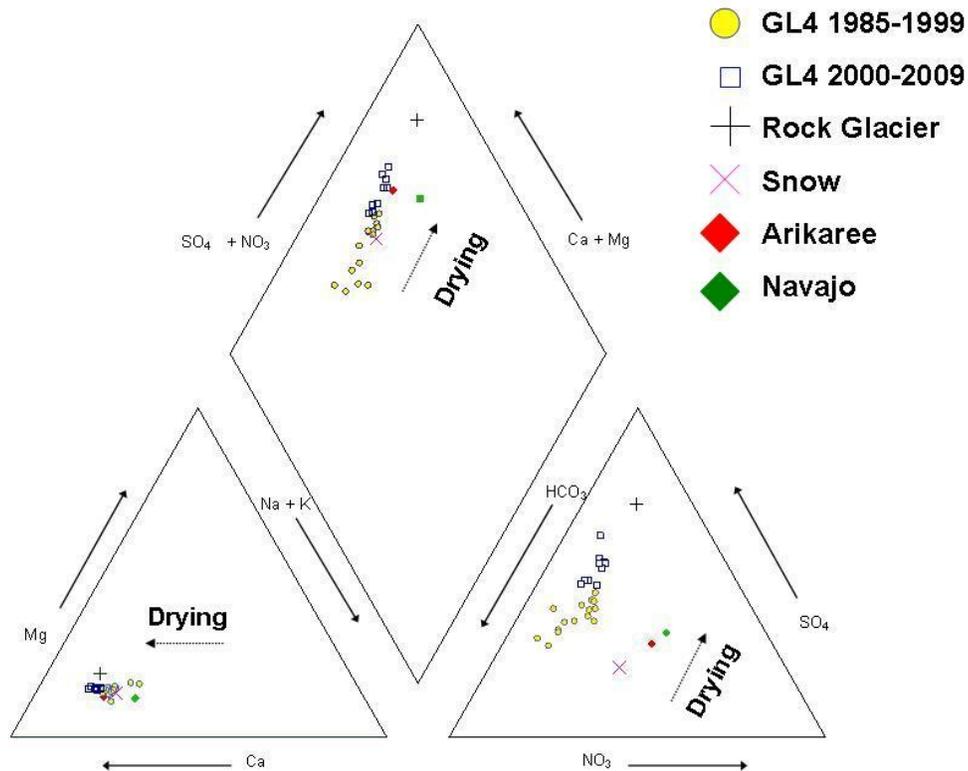


Figure 1.9: Piper diagram for GL4, RG5 and talus chemistry from 1985-2009. The 1985-1999 period (yellow circles) was characterized by lower temperatures and higher precipitation than the 2000-2009 period (blue boxes). Note: The HCO_3^- value in this figure is actually the measured ANC.

Others have offered a mechanism explaining increases in weathering reactions, proposing that melting permafrost can serve as a potential source of water during dry years and during the summer months after snowmelt (Baron et al., 2009). Our findings are consistent with this proposed mechanism, as base cation concentrations show large increases in the post-2000 drought period, especially during the late summer months after snowmelt. Calcium concentrations at GL4 increased 92% in the post-2000 drought period, a much greater percent increase than reported at the Sky Pond inlet in the Loch Vale watershed (33%). This greater increase could be due to a greater contribution from rock glacier meltwater at GL4. Here, moisture derived from permafrost melting may provide a sufficient vector for transporting

nutrient-rich material from talus slopes and the rock glacier into the surface waters within the upper Green Lakes Valley, generating a rapid chemical response in stream waters.

Research conducted in Europe supports this concept linking climate to increased weathering rates in alpine catchments. Rogora et al. (2003) determined that warmer temperatures and reduced snow cover contributed to increasing trends in conductivity, base cations, and sulfate throughout alpine lakes in the Italian Alps. Additionally, Wögrath and Psenner (1995) found that in lakes with a lithologic sulfate source, concentrations increased in warmer summer months due to accelerated warming. In the central European Alps, Thies et al. (2007) showed that increasing calcium, magnesium, and sulfate concentrations in lake water are due primarily to warming temperatures promoting rock glacier melt, as opposed to atmospheric deposition trends or catchment geology. At the GL4 site, the chemical changes suggest that the catchment is experiencing similar rock glacier melt and that the warmer and dryer climate may be contributing to a significant shift in flowpaths in the form of cryosphere melt.

The MART site offers a test of this idea. MART does not contain ice features such as permafrost, glaciers, and rock glaciers. In contrast to GL4 and ALB, there is no concomitant increase in calcium, magnesium and sulfate during the drought years. Rather, fluxes of these solutes decline during the drought years. Thus, melting of ice features such as permafrost and rock glaciers appears to explain the increase in base cations during the drought years.

1.5.2 Increasing Nitrification Potential

Nitrogen deposition at Niwot Ridge has increased at a greater rate as compared to other NADP monitoring locations within the Rocky Mountains (Burns, 2003) and the region

experiences greater deposition loads than most other high-elevation sites throughout the United States (Williams & Tonnessen, 2000; Baron et al., 2009; NADP, 2010). However, despite recent decreases in N deposition loads to the watershed starting in 2000, nitrate concentrations have continued to increase at GL4 (Figure 1.4). For further insight, we turn to climatic controls to try to explain these elevated nitrate concentrations.

Over the past decade, there has been considerable research illustrating the relationship between climate change and concentrations of N in surface waters. Hong et al. (2005) utilized a dynamic N model (SINIC) that incorporated both climatic and hydrological variables to show that mineralization and nitrification rates between wet and dry periods explained ten times more variability than differences in atmospheric wet deposition at the Hubbard Brook Experimental Forest. They concluded that warm periods accelerate nitrate loss to surface waters, due in large part to increased rates of N mineralization. Similarly, Meixner et al. (2004) showed that the difference in modeled concentrations of ANC between wet and dry years was close to ten times greater than the change due to doubling atmospheric deposition within the Sierra Nevada range, again suggesting the relative importance of climate change compared to atmospheric N deposition. Lastly, Murdoch et al. (1998) presented strong empirical evidence correlating increases in mean annual temperature and greater nitrate concentrations in the Catskill Mountains.

Our findings support the Hong et al. (2005) concept of mineralization and nitrification rates as primary drivers of nitrate leaching to streamwaters. During drought years, it appears that barren soils in the upper basin of Green Lakes valley are freed via glacier retreat and permafrost melt. The greatest historic ammonium concentrations were observed at ARIK, the highest elevation site in Green Lakes Valley. This ammonium can either be taken up by vegetation,

absorbed on ion exchange sites, or nitrified. The high concentrations of nitrate at NAV downstream from ARIK, the 1:1 relationship between ammonium loss and nitrate gain between the sites, and the lack of vegetation support the hypothesis of nitrification as a source of nitrate at NAV. This is consistent with other studies that have shown that high nitrification potential is correlated with stream water nitrate concentrations (Christ et al., 2002; Hong et al., 2005). Previous isotopic work in a nearby watershed found that the majority of stream water nitrate was derived from microbial nitrification and not directly from atmospheric deposition (Campbell et al. 2002).

Given that nitrification appears to be the integral step in N leaching, we can assess the mechanism by which climate influences mineralization and nitrification rates. Murdoch et al. (1998) suggest that soil microbes play a major role in transforming nitrogen derived from deposition into mobile nitrate that can leach into surface waters. They found that the mineralization and nitrification activity associated with microbes increased with warmer temperatures, as the optimum temperature for these processes is typically higher than those observed in the field. Therefore, an increase in ambient air temperatures could lead to greater rates of nitrification and nitrate export. Past work in the Green Lakes Valley has shown that there is a great deal of microbial activity in tundra soils and talus fields that nitrifies ammonium and produces mobile nitrate (King et al., 2008; Nemergut et al., 2008). In fact, the moist environments inside talus fields promote algal and fungal growth that facilitates the cycling of nitrogen even during the winter months under snowpack (Ley et al., 2004). Given the documented microbial activity in Green Lakes Valley, increases in temperature could further enhance microbial production, potentially resulting in the observed increased nitrate leaching.

Hong et al. (2005) concluded that the cumulative interaction of climatic factors was sufficient to explain most features of the long-term pattern of stream water nitrate concentrations. They argued that climatic influence cannot be revealed by analyzing individual climatic variables, but when taken as a whole and over a longer study period, climate does play an important role. Thus the lack of any significant relationships between N deposition and/or temperature and nitrate concentrations at GL4, ALB, and MART does not necessarily mean that climate does not play a role.

Our nitrate export percent change results are similar to findings from the neighboring Loch Vale watershed in Rocky Mountain National Park. We found a 40% increase in nitrate export between the 1985-1999 (mean 1.7 kg N ha⁻¹yr⁻¹) and 2000-2009 (mean 2.3 kg N ha⁻¹yr⁻¹) periods. This is higher than the 31% percent increase reported at Loch Vale by Baron et al. (2009) between the 1991-1999 (2.0 kg N ha⁻¹yr⁻¹) and 2000-2006 periods (2.8 kg N ha⁻¹yr⁻¹). The higher percent difference at GLV is most likely due to the difference in sampling periods, as we included six more years (1985-1990) in the pre-drought period and three additional years (2007-2009) in the post-drought period calculations.

Further downstream at the ALB site, we did not observe any significant increases in nitrate concentrations. Conversely, there is a small, but statistically significant decrease of 0.15 µeq L⁻¹ in annual volume-weighted concentrations for the 1985-2009 study period. Figure 1.5 clearly demonstrates the decreasing nitrate concentrations moving down elevation. This sharp decrease in inorganic N across the alpine/subalpine ecotone has been documented at Niwot Ridge by Hood et al. (2003b), attributed to the catchment retention of nitrate as the areal extent of soil and vegetative cover increases. In addition to this terrestrial retention of inorganic

nitrogen, the stream itself has potential to process added inputs of inorganic nitrogen from the alpine portions of the catchment. Peterson et al. (2001) found that headwater streams frequently retain and transform more than 50% of the inputs of DIN from their watersheds. North Boulder Creek also has a high surface to volume ratio, promoting faster uptake and processing of N and removing nitrate via biological assimilation and denitrification within channelized flow.

1.5.3 Presence of Ice Features such as Glaciers

Saros et al. (2010) demonstrate that the presence of glaciers on alpine watersheds in the central Rocky Mountains more strongly influences nitrate concentrations in high-elevation lake ecosystems than any other geomorphic or biogeographic characteristic. Our results are consistent with their findings, with our highest nitrate concentrations at the NAV site just below the Arikaree Glacier. It is worth noting that the maximum concentration of nitrate of about $17 \mu\text{eq L}^{-1}$ that they report is well-below the $51 \mu\text{eq L}^{-1}$ at our NAV site. This difference may be in part because our DIN deposition values of near $10 \text{ kg N ha}^{-1}\text{yr}^{-1}$ are about three times the $2 - 3.5 \text{ kg N ha}^{-1}\text{yr}^{-1}$ they report for their sites in the central Rockies.

Saros et al. (2010) then hypothesize that relatively high sublimation and evaporation rates on glaciers in alpine regions appear to concentrate nitrate in these environments, prior to delivering high nitrate meltwaters to downstream aquatic ecosystems. They also suggest that the higher nitrate concentration of glacial meltwater relative to seasonal snowpack melt may also be due, in part, to its reduced contact with watershed soils where microbial communities may rapidly assimilate any available inorganic nitrogen. Our results are not consistent with these hypotheses.

The low concentrations of ammonium at all sites except ARIK (less than $5 \mu\text{moles L}^{-1}$) are consistent with previous reports that ammonium is relatively immobile in these high-elevation environments (Brooks et al., 1996; Baron and Campbell, 1997; Williams et al., 2001). Ammonium in snowmelt and rain is quickly removed from water moving through the subsurface environment in these high-elevation catchments by biological assimilation and adsorption on ion exchange sites. The high ammonium concentrations in the outflow of the Arikaree Glacier are anomalous. At this site, water is sampled before it has been in contact with rock and ground surfaces, and so it is analogous to sampling a large snowmelt lysimeter. The high values of ammonium in the outflow of the Arikaree Glacier are likely the result of an ionic pulse (Williams et al., 2007). Ammonium values of about $25 \mu\text{moles L}^{-1}$ compared to bulk snow values of about $5 \mu\text{moles L}^{-1}$ are similar to the concentrations in snowpack meltwater before contact with the ground at the Saddle site on Niwot Ridge, which ranged from 5 to 15 times bulk snowpack values (Williams et al., 2001). Similarly, nitrate values at ARIK show similar enhancement relative to bulk snowpack values and are consistent with the release of nitrate in the form of an ionic pulse from the glacier. However, ammonium is rapidly immobilized within several hundred meters at the ARIK site, where ammonium values are near detection limits and we see a large corresponding increase in nitrate. Nitrification of ammonium to nitrate may be one explanation for these changes in solute concentration between the ARIK and NAV sites. Our results suggest that microbial processes may be more important in these areas than suggested by Saros et al. (2010).

1.5.4 Stoichiometric Controls

A recent study by Taylor and Townsend (2010) offers additional insight into the differences in nitrate concentrations between the alpine and subalpine sites. They propose that across a wide range of environments, dissolved organic carbon to nitrate ratios ($\text{DOC}:\text{NO}_3^-$) strongly influence nitrate accumulation or uptake by regulating a host of microbial processes that couple carbon and nitrogen cycling. 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 nitrate in the system. Figure 1.10 demonstrates that this may be occurring in Green Lakes Valley at certain high elevation sites. Nitrate concentrations on the y-axis are highly correlated with elevation; for example, the rock glacier (RG5) values around $100 \mu\text{eq L}^{-1}$ are at 4,000 meters. High nitrate concentrations are observed when the $\text{DOC}:\text{NO}_3^-$ drops below 3.5, particularly in the talus (EN.4L and KIO.SW) and rock glacier (RG5) sites. These sites are carbon limited, resulting in little N assimilation, driving the systems toward net nitrification. In contrast, due to increased soil and vegetative cover, there is more organic carbon available at the ALB site, allowing this critical ratio to rapidly rise above 20 and resulting in an N-limited system with little nitrate. The $\text{DOC}:\text{NO}_3^-$ at GL5 and GL4 are near the threshold of 3.5, showing that the lower elevation of the alpine is at the threshold of moving from nitrogen to carbon limitation.

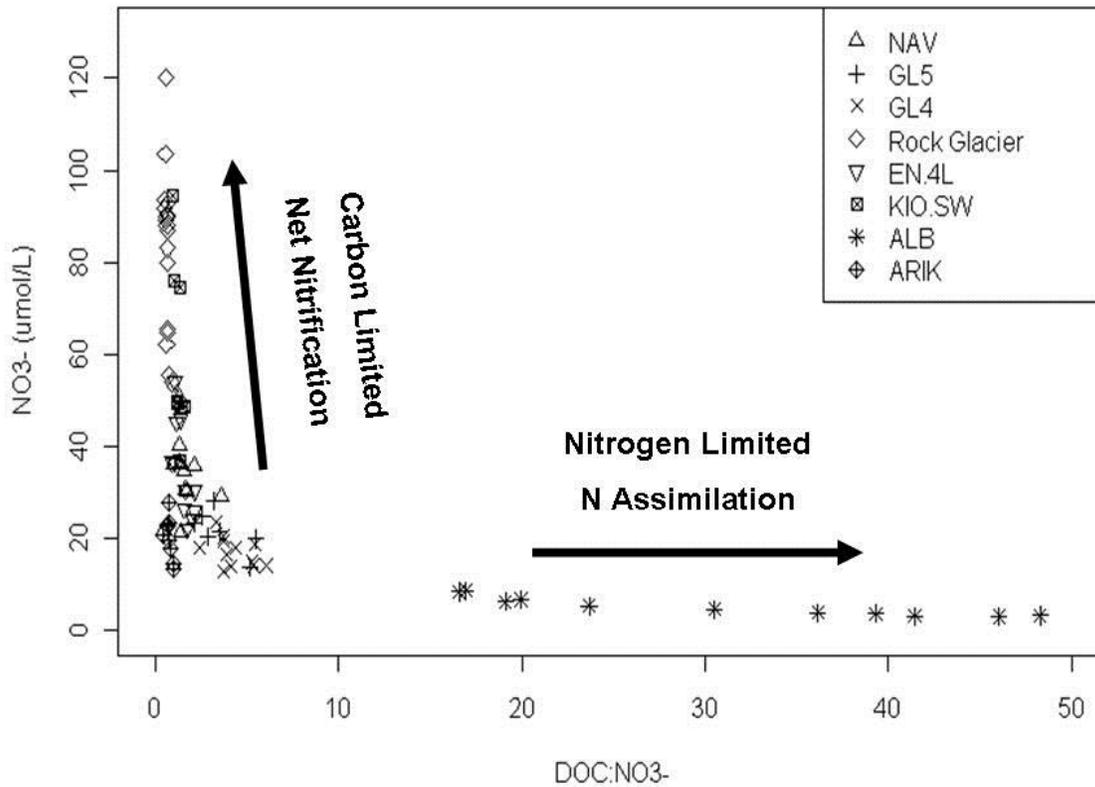


Figure 1.10: Scatterplot of NO_3^- vs. DOC: NO_3^- ratio for eight sites in Green Lakes Valley. Values are volume-weighted annual means for GL4 (n=10) and ALB (n=10), and arithmetic annual mean concentrations for NAV (n=10), GL5 (n=10), Rock Glacier (n=10), EN.4L (n=5), KIO.SW (n=5), and ARIK (n=5).

1.5.5 Nitrate Dynamics in a Warming Climate

Typically, the primary connectivity between terrestrial soils and surface waters occurs during the spring snowmelt season, with warmer summer temperatures restricting soil moisture in high-elevation catchments and reducing the likelihood of N export (Monson et al., 2002) in the absence of summer storms strong enough to saturate soils (Williams et al., 2007). However, as mentioned earlier, other mechanisms such as permafrost melt may facilitate the export of

inorganic nitrogen in the drier months. Even in the winter months, when cold temperatures and snow cover reduce the opportunity for solute flushing, nitrate values remain higher than expected. Clow et al. (2003) showed that there is groundwater flow year-round in these alpine catchments, although these inputs are primarily derived from talus fields, not tundra soils from which you might expect to see elevated solute concentrations. Melt from rock glaciers and permafrost may provide insight into the year-round persistence of high solute concentrations; with melt water mixing with groundwater forming the surface waters in these catchments. Liu et al. (2004) demonstrated that this is likely occurring as flowpaths in the upper Green Lakes Valley shift towards stronger rock glacier inputs in the summer months. Our findings support this concept of year-round hydraulic connectivity facilitating the export of nitrate, with increasing nitrate concentrations at GL4 during every month in the post-2000 drought period.

Studies have shown that high latitude catchments characterized by discontinuous permafrost near or at the 0° isotherm tend to have higher concentrations of inorganic N in surface waters (Jones et al., 2005). A Williams et al. (2006) conceptual model for Niwot Ridge proposes that summer warming allows the 0° isotherm separating frozen surfaces from liquid water to lower into the rock glacier by the end of summer. The associated melt water and groundwater are more likely to come into contact with mineral surface areas within the glacier, thereby enhancing weathering. The increase in weathering base cations at GL4 and ALB appears to validate this model, but rock glacier and permafrost melt also has strong implications for nitrification and N-export. Warmer temperatures have been correlated with high inorganic N and weathering product concentrations in alpine areas of Switzerland and the Rocky Mountains, suggesting that much of the atmospherically-deposited N is nitrified before it reaches surface waters (Lafreniere and Sharp, 2005; Rogora, 2007; Williams et al., 2007). This nitrification

could be due to the presence of active microbes in rock glacier outflows and sediment pockets within talus fields (Williams et al., 2007; Ley et al., 2004). Thus, the observed increases in nitrate concentrations may be climatically-induced, a result of melting ice in rock glaciers that flushes from microbially active sediments.

1.5.6 Uncertainties

It is important to note that this study does not address a potentially significant nutrient contribution to Green Lakes Valley: dry deposition. Neff et al. (2008) have documented an increase in aeolian dust deposition in the western US, linked to human activities such as grazing (Neff et al., 2005). Neff et al. (2008) showed that mineral aerosols from the dust provide significant inputs into the biogeochemical cycles of high elevation ecosystems, such as a more than five-fold increase in calcium. Most of this aeolian deposition occurs as dust on snow events (Ley et al., 2004, Painter et al., 2007). In addition to the mineral inputs associated with aeolian deposition, dust has been shown to contribute to earlier snowmelt by decreasing the albedo on the snowpack surface (Painter et al., 2007). The NADP collectors used in this study only collect wet deposition, thus the contribution from dry deposition is not accounted for as an input, though surely some portion of the stream water nutrient flux can be attributed to these aeolian deposition events. The role that dry deposition may play in the biogeochemical cycling of nutrients in mountain ecosystems merits further research and quantification.

1.6 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 MART and GL4 allows for isolation of the effects of rock glacier and permafrost melt on surface water chemistry, with strong evidence of increased weathering product and nitrate concentrations 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 an increasing contribution of cryosphere melt to surface waters. In contrast, there is no melting or potential melting at the lower elevation sites, indicating that the biogeochemical cycling within these sites are less susceptible to a warming climate. In addition, the lower elevation sites do not appear to be carbon limited, thus limiting the extent of net mineralization and nitrification that drives nitrate leaching in the alpine sites above. These findings, taken in combination, confound emission policies and associated water quality improvements, as climate change and glacier melt may effect nitrate concentrations as much, or more than atmospheric deposition trends.

Acknowledgments

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**Are All Headwater Catchments the Same?
Elevational Controls on Organic and Inorganic
Nutrients in Headwater Catchments in Boulder Creek Watershed,
Colorado Front Range**

Abstract

The Landscape Continuum Model (LCM) is a conceptual framework for how mountain ecosystems accumulate and redistribute both exogenous and endogenous materials, emphasizing the importance of transport processes and redeposition of nutrients and water. This study tests the LCM by comparing changes in organic and inorganic nutrients in stream waters of headwater catchments along an elevational gradient in the Colorado Front Range. Water samples were simultaneously collected at four gauged headwater catchments, ranging in elevation from 1830 to 3500 m, and analyzed for nitrogen, carbon, and base cation chemistry. Weathering rates, as measured by dissolved silica concentrations, decreased exponentially with increasing elevation, but the relative contributions of different primary materials to the solute load did not change systematically with elevation. We report a strong shift from a dominance of inorganic nutrients in the alpine to greater organic contributions below treeline as indicated by the decreasing nitrate concentrations (21.36 to $0.85 \mu\text{eqL}^{-1}$) and increasing dissolved organic carbon concentrations (0.36 to $10.41 \text{ mg C L}^{-1}$) with decreasing elevation. Solute yields did not demonstrate similar patterns, as local geomorphic and climate characteristics confounded general elevation trends. This study expands the scope of the original LCM to include elevation, climate, and geomorphic controls that, in turn, drive the landcover characteristics that account for the difference in solute concentrations and fluxes. The updated conceptual model also provides a useful framework to assess the implications of future disturbances such as mountain pine beetle infestation, increased N deposition and warming air temperatures.

2.1 Introduction

Due to their close proximity to the Denver-Boulder metropolitan region and agricultural areas to the east, high elevation watersheds in the Colorado Front Range are exposed to disproportionately high rates of inorganic nitrogen (N) deposition (Baron et al., 2000; Heuer et al., 2000). The aquatic and terrestrial systems in these areas are particularly sensitive to even small changes in N deposition due to relatively sparse vegetation, thin soils, and short growing seasons that result in conditions in which biota exist at the razor's edge of environmental tolerance (Williams et al., 1998). Alpine areas are already experiencing shifts in ecosystem structure and function (Seastedt et al., 2004). More specifically, traditionally N-limited high elevation ecosystems are approaching the initial stages of nitrogen saturation, fundamentally transforming the biogeochemical cycles that are integral to ecosystem health (Williams et al., 1996a). Given the ecosystem shifts already observed, it is increasingly important to more fully understand how mountain landscapes' hydrological and biogeochemical cycles respond to two major drivers of global change: atmospheric nitrogen deposition and changes in climate.

In order to gain a better understanding of how mountain ecosystems are potential bellweathers of global change, it is useful to outline a conceptual model of how these high-elevation ecosystems accumulate and redistribute both exogenous material derived from the atmosphere and endogenous material that comes from the mountains themselves. Several studies have proposed such models, recognizing that changes in water and nutrient inputs rarely occur in a uniform fashion across the landscape. While some researchers emphasize the spatial heterogeneity in topography (Billings, 1973) and soil development (Burns and Tonkin, 1982) in

determining zones of accumulation and redistribution, others more explicitly address physical transport via fluvial networks (Vannote et al., 1980) and material spiraling (Fisher et al., 1998).

Perhaps the most appropriate conceptual model for high elevation ecosystems, the Landscape Continuum Model (LCM), was developed by Seastedt et al. (2004) in order to predict “hot spots” and tipping points in both alpine and subalpine areas of mountain catchments. The LCM emphasizes the downward transfer of water and nutrients via physical transport vectors such as rivers, wind, rockslides, and avalanches. The unique spatial heterogeneity of landscape cover within the watershed determines where inorganic and organic materials are likely to accumulate or be exported further downstream (Figure 2.1). In particular, the LCM predicts that in response to increased N deposition, high elevation headwater catchments along the Colorado Front Range should exhibit high concentrations of nitrate and low concentrations of dissolved organic carbon.

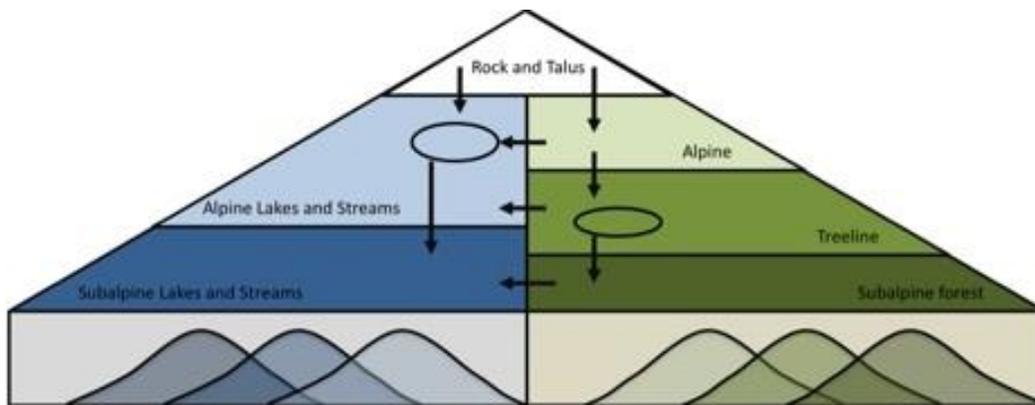


Figure 2.1: The Landscape Continuum Model (Seastedt et al., 2004) views high elevation ecosystems as being influenced primarily by climatic and topographic drivers. It links terrestrial systems to each other (green), and to aquatic ecosystems as well (blue). Complex topography creates unique transport processes across a heterogeneous landscape that result in “hot spot” areas of accumulation and attenuation. In this conceptual diagram, the circles represent likely areas of dissolved inorganic nitrogen accumulation, e.g. at treeline and in alpine lakes and streams (Figure adapted from Williams et al., 2010: LTER Renewal).

The LCM was developed from research conducted at the Niwot Ridge Long-Term Ecological Research (NWT LTER) site in the Colorado Front Range (Bowman & Seastedt, 2001). To illustrate, streamwater concentrations of nitrate decrease moving down an elevational gradient from 3700 m to 2800 m (Hood et al., 2003b). In contrast, concentrations of dissolved organic carbon increased with decreasing elevation (Seastedt et al., 2004), and were derived primarily from autochthonous parent material (Hood et al., 2003a and Hood et al., 2005). These and other findings (Heuer et al., 1999; Baron et al., 2000; Campbell et al., 2000; Williams & Hood, 2001) have demonstrated the unique manner in which alpine headwater catchments accumulate or export water and nutrients and how increased N deposition alters the biogeochemical cycles of these high-elevation ecosystems. While the mechanisms and effects of nitrogen saturation in temperate ecosystems have been widely studied in the northeast United States (e.g. Aber et al., 1989; Aber et al., 1998; Boxman et al., 1998; Goodale et al., 2000) and Europe (Durka et al., 1994; Dise et al., 1998), little research has evaluated nutrient concentrations in stream waters along an elevational gradient extending from the alpine to the plains. Hood et al. (2003b) demonstrated that soil and vegetation characteristics play an integral role in determining the fate of inorganic and organic nitrogen in high-elevation catchments, but similar work has not been conducted in the Colorado Rocky Mountains in subalpine, montane and foothills ecosystems.

This study combines two traditional conceptual frameworks; the physical transport controls common in hydrological models and the biogeochemical perspective that emphasizes substrate constraints on reaction potential. By combining these two frameworks, we can gain insight as to how hydrological and biogeochemistry processes interact at the catchment scale. Here, we evaluate whether the LCM can be extended from alpine ecosystems to down-gradient

subalpine, montane, and foothill ecosystems by comparing changes in organic and inorganic solutes in stream waters of headwater catchments along an elevational gradient in the Colorado Front Range. We ask these questions: (a) are there systematic changes in chemical weathering with elevation, where elevation is a surrogate for several variables such as physical erosion rate, soil thickness, vegetation type, and temperature (e.g. Zobrist and Drever 1992), and (b) are there similar changes in inorganic and organic nutrients in streamwaters with elevation.

For (a), we can evaluate two hypotheses: (1) At higher elevations, thinner soils and lower temperatures will result in less chemical weathering; (2) At higher elevations weathering will be more selective such that weathering of minor, reactive phases such as calcite and amphiboles rather than feldspars will be the dominant source of solutes. For (b), we ask: (1) Are all headwater catchments the same along an elevational gradient in terms of nutrient concentrations? (2) How does the character of dissolved organic matter (DOM) change with elevation?

2.2 Site Location

The Boulder Creek Watershed is about 1160 km² in area and drains the Colorado Front Range from the Continental Divide (4120m) to the eastern plains (1480m) (Figure 2.2). Here we focus on four headwater catchments of the Boulder Creek Watershed: Green Lakes Valley, Como Creek, Gordon Gulch, and Betasso. Research activities at these sites are supported by a combination of the NWT LTER program and the Boulder Creek Critical Zone Observatory (BC-CZO). The watershed encompasses four climatic zones – alpine, subalpine, montane and foothills (Table 2.1). The underlying bedrock is similar among the four catchments, Precambrian crystalline rock that is primarily quartz monzonite, with small percentages of gneiss and schists (Bridge, 2000).

Table 2.1: Sampling site descriptions with site abbreviation, elevation at the basin outlet (m), catchment area (ha), dominant landscape type with percent of forest cover, mean annual air temperature (°C), mean annual precipitation (mm) and percentage of precipitation that falls as snow. Mean air temperature and precipitation values are 10-year averages from 1998-2008.

Site	Abbreviation	Elevation (m)	Catchment Area (ha)	Landscape Type/ (% Forest Cover)	Mean Annual Air Temperature (°C)	Mean Annual Precipitation (mm)	% of Precipitation that falls as snow
Green Lake 4	GL4	3550	221	Alpine (0.09%)	-3.7	1000	85
Como Creek	CC	2910	664	Subalpine (81%)	3.90	800	70
Gordon Gulch	GG	2588	101	Montane (68%)	4.03	456	59
Betasso	BET	1810	45	Foothills (55%)	10.69	475	-----

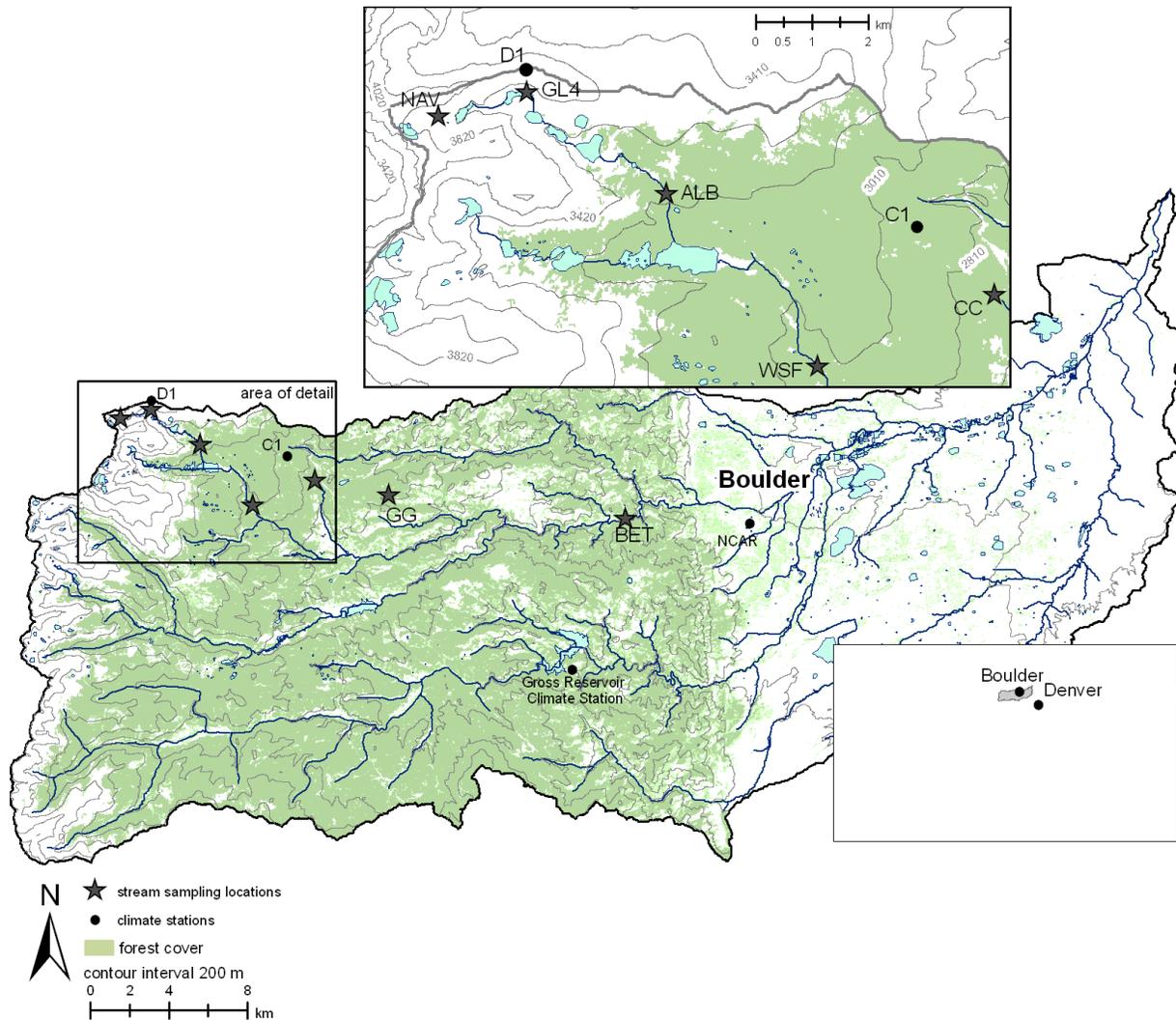


Figure 2.2: Map of Boulder Creek watershed with stream sampling locations (stars) and climate station site (circles). In the Green Lakes Valley, NAV and GL4 are in the alpine portion of the catchment, ALB is at treeline and WSF and CC are in forested subalpine areas. The two Boulder Creek Critical Zone Observatory (CZO) sites (GG and BET) are located in the montane and foothills climatic zones, respectively (Barnes, unpublished data).

The Green Lake 4 (GL4) catchment is 221 ha in area and forms the headwaters of North Boulder Creek. The basin is characterized by a continental climate with a mean annual

temperature of -3.8°C and annual precipitation of about 1000 mm (Williams et al. 1996b), 80% of which falls in the form of snow (Caine, 1996). Niwot Ridge forms the northern boundary of the basin, where climate stations and other instruments are operated by the NWT LTER program. The GLV was glaciated during the Pleistocene and contains glacial and periglacial features such as rock glaciers, along with a string of paternoster-type lakes. The entire valley is contained within the City of Boulder Watershed and public access has been restricted for the past 80 years, resulting in a relatively pristine watershed, protected from recreational disruption. Discharge and water quality have been measured during the ice-free season from about 1985 to present. We also present samples collected for water quality above and below the outlet of GL4 at Navajo (NAV), Albion (ALB) and the Watershed Flume (WSF) along the hydrologic axis of North Boulder Creek (Figure 2.2).

Como Creek (CC) originates on the southeast flank of Niwot Ridge approximately 8 km east of the Continental Divide (Figure 2.2). The catchment falls within the Niwot Ridge Biosphere Reserve and ranges in elevation from 2900 m to 3560 m with an area of 664 ha. The mean annual temperature is 4°C and mean annual precipitation is 800 mm (Monson et al. 2002). The catchment lies atop Pinedale glacial till, resulting in thin soils on top of a deep sediment layer. Approximately 80% of the catchment is below treeline and is primarily subalpine coniferous forest dominated by Engelmann spruce (*Picea engelmannii*), subalpine fir (*Abies lasiocarpa*), limber pine (*Pinus flexilis*) and lodgepole pine (*Pinus contorta*), with some aspen (*Populus tremuloides*). A weir is located at the mouth of the basin at an elevation of 2900 m. Importantly, the Como Creek watershed differs from the nearby Green Lakes Valley in two respects: (1) there are no lakes in the catchment, and (2) there are no talus, exposed bedrock, steep cliffs, or rock glaciers.

Gordon Gulch (GG) is a montane ecosystem, 101 ha in area, and lies within the Arapahoe National Forest and joins North Boulder Creek approximately 16 km below Green Lakes Valley (Figure 2.2). This site lies within the low relief post-Laramide surface below the glacial limit (Bradley, 1987). Weathered rock profiles up to 15 m thick are found in this slowly evolving landscape (Isherwood & Street, 1976; Dethier & Lazarus, 2005). The site is mostly forested and was not affected by Pleistocene glaciation like the Green Lakes Valley. The south-facing slopes are dominated by *Pinus ponderosa*, while the cooler north-facing slopes are a *Pinus ponderosa* – *Pinus contorta* mix. The lowest sample site, Betasso (BET) is 45 ha in area and representative of a foothill montane environment with steep forested slopes composed primarily of *Pinus ponderosa* and *Pinaceae pseudotsuga*, drained by an intermittent stream, and with numerous rock outcroppings. These steep slopes were formed over the last ~5 million years by renewed bedrock channel incision progressing headward from the plains, cutting into the post-Laramide surface (Anderson et al., 2006). This area is situated in the lower portion of Boulder Canyon, approximately 10 km west of the City of Boulder (Figure 2.2). Measurements of water quantity and quality for both GG and BET commenced in the summer of 2008 with the start of the BC-CZO.

2.3 Methods

2.3.1 Climatology

Climate data has been recorded at the D1 and C1 stations on Niwot Ridge since the early 1950's. D1 is located in alpine tundra at an elevation of 3700 m, 2.6 km from the Continental Divide. The C1 climate station is located in subalpine forest at an elevation of 3,005 m, 9.7 km east of the Continental Divide. Climate data for GG is represented by the Gross Reservoir

station at an elevation of 2,309 m, and compiled from the Western Regional Climate Center (<http://www.wrcc.dri.edu>). For BET, we used the climate data compiled from the National Center for Atmospheric Research (NCAR) climate station (1670 m), which has continuous measurements since 1893. For all climate station sites, we report the 2009 annual precipitation and mean annual temperatures and compare 2009 to the ten-year average from 1998-2008.

2.3.2 Stream Sampling

Stream samples were collected as grab samples following the protocol of Williams et al. (2009). Samples were collected weekly during the ice-free season from about May 1 to October in Green Lakes Valley and Como Creek. At GG and BET, samples were collected weekly from April-July 2009 and biweekly on the recession curve of the hydrograph during the later summer and fall (August-October 2009), to provide more samples during the period where the hydrograph was changing the most. Samples were collected in cleaned HDPE bottles after rinsing three times with sample water at the time of collection. Samples were transported within a few hours of collection to the Kiowa Environmental Chemistry Laboratory, where subsamples were immediately filtered through pre-combusted glass fiber filters with a nominal pore size of 0.7 μm and stored in the dark at 4°C prior to analyses. Samples for DOC and fluorescence index (FI) analyses were collected in pre-combusted amber glass bottles with Teflon-lined caps.

2.3.3 Discharge and Yield Calculations

Water level is measured with a pressure transducer and converted to volumetric discharges by empirical rating curves at the outlets of the four catchments. Yields of chemical species were estimated as the product of measured concentrations and the accumulated water

discharge for weekly intervals centered on the day of sampling. Seasonal volume-weighted mean (VWM) concentrations for individual species were calculated as seasonal mass flux divided by seasonal discharge, following the approach of Hood et al. (2003b).

2.3.4 Soil samples

Soil samples were collected during the growing season in early August 2009 following the approach of Hood et al. (2003b) at the same elevation as the stream sample sites, all within 20 m of the stream and each site was chosen to represent terrestrial areas that would likely contribute soil water to stream discharge. Soil samples were collected as five sets of three replicates for each location. Each set consisted of three soil cores composited in a new polyethylene bag collected using a 20-cm soil corer. Soils were processed within twelve hours for KCl-extractable nitrate and ammonium, microbial biomass N, and total C and N, following the protocol in Hood et al. (2003b).

2.3.5 Laboratory Analyses

All water samples were analyzed for pH, acid-neutralizing capacity (ANC), specific conductance, H^+ , NH_4^+ , Ca^{2+} , Na^+ , Mg^{2+} , K^+ , Cl^- , NO_3^- , SO_4^{2-} , Si, DOC, dissolved organic nitrogen (DON) and total nitrogen (TN) at the Kiowa Environmental Chemistry Laboratory in Boulder, CO. Detection limits and instrumentation are as presented in Williams et al. (2009); in general detection limits for all solutes were less than $1 \mu eq L^{-1}$. KCl-extractable nitrate and ammonium in the soil samples were analyzed using the same procedure for stream samples. Total C and N were measured on a CHN analyzer.

The determination of fluorescence properties of the whole water component of the weekly samples, and calculation of the fluorescence index (FI), were as presented in Miller et al. (2006). The fluorescence index (FI) of these whole water samples were compared to an aquatic reference collected from Lake Fryxell in the McMurdo Dry Valleys of Antarctica and the terrestrial reference was from the Suwannee River that drains the Okefenokee swamp in Georgia (McKnight et al., 2001). This FI comparison to the two reference fulvic acids serves as a semi-quantitative analysis of the precursor organic material (terrestrial vs. aquatic) in the headwater catchments.

To further understand dissolved organic matter quality, the DOC content of a small subset of samples was also characterized by 3-dimensional fluorescence, a measure of the fluorescing portion of the DOM pool, using a Fluoromax-3™ fluorometer as described in Wickland et al. (2007). The 3-D excitation-emission matrices (EEMs) were subsequently analyzed via comparison to the PARAFAC model developed by Cory and McKnight (2005). This model attempts to predict the excitation-emission matrices of dissolved organic matter based upon thirteen compounds, seven of which have spectra similar to known quinines (Cory and McKnight, 2005).

Following the methods of Aiken et al. (1992), the streamwater DOM of this small subset of samples was fractionated using resin columns into three groups: larger molecular weight hydrophobic acids (HPOA), smaller molecular weight hydrophilic molecules (HPI), and transphilic acids (TPIA) using Amberlite XAD-8 and XAD-4 resins. The amount of organic matter within each fraction was calculated using the DOC concentration and the sample mass of each fraction and are presented as the percentage of total DOC. Stream water samples were

fractionated in duplicate and average values are presented. The standard deviation of these fractions was $\leq 2\%$. These analyses were not conducted for Como Creek.

2.3.6 *Statistical Methods*

Simple and multiple linear regression analyses were run using the “R” statistical package. The significance level (α) was 0.05 for all statistical analyses. Solute concentrations were also analyzed using a two-way repeated measures analysis of variance. These analyses tested for the response of these parameters among sampling sites (between-subjects effects), and the change over time (within-subjects effects), using time (individual months between May and October) and site as independent variables. Time included six periods, corresponding to the months between May and October.

2.4 **Results**

2.4.1 *Climatology*

Mean annual temperatures from 1998 to 2008 increased with decreasing elevation, from 10.7°C at BET to -3.7°C at D1, a lapse rate of 7.0°C per 1,000 m. The annual mean 2009 temperature for Green Lakes Valley measured at the D1 climate station was -3.2°C, within 15% of the 10-year mean of -3.7°C (Table 2.1). The annual mean temperature at the C1 climate station was 4.3°C, warmer than, but within 15% of the 10-year mean of 3.9°C. The mean temperature at the GG site, as measured at Gross Reservoir was 5.1°C, compared to the long-term mean of 4.0°C. The 2009 mean annual temperature at the NCAR climate station was 12.3°C, slightly warmer than the long-term average of 10.7°C.

In contrast to mean annual air temperature, annual precipitation from 1998 to 2008 generally decreased with decreasing elevation, ranging from 1,000 mm at D1 to 456 mm at GG. The 2009 precipitation at D1 of 1,214 mm was 12.1% higher than the long-term average of 1,000 mm. At C1, the 804 mm of precipitation in 2009 was similar to the long-term average of 800 mm. Below at Gross Reservoir, there was 511 mm of total precipitation in 2009, compared to the long-term average of 456 mm. At the NCAR climate station, total precipitation in 2009 was 459 mm, within two centimeters of the long-term average of 475 mm. It is worth noting that annual precipitation at both GG and BET was less than 64% of the 804 mm recorded at C1. Moving down in elevation from the subalpine forest results in a sharp decrease in annual precipitation. Thus, 2009 was slightly warmer and wetter than the 10-year average.

In general, there was no consistent pattern in the relationship of discharge with elevation. The hydrographs of the high-elevation alpine and subalpine sites are characteristic of snowmelt dominated catchments, with a sharp rising limb followed by a long recession limb after peak discharge (Figure 2.3). However, while the lower montane and foothills sites also exhibited a characteristic snowmelt hydrograph, during the summer months there were also large increases in discharge in response to summer rain events. BET differs from the other catchments in that it is an intermittent stream characterized by discharge only after precipitation events. The specific discharge measurements show a lag in the timing of peak discharge with increasing elevation, with discharge occurring earlier at the lowest elevation sites compared to the higher elevation sites. At the lower elevation sites, BET peaked at 0.09 cm d^{-1} on April 20th and GG peaked at 0.59 cm d^{-1} on April 25th. The CC hydrograph peaked at 0.57 cm d^{-1} more than a month later on June 4th, while peak discharge at the alpine GL4 occurred on June 23rd (1.37 cm d^{-1}).

Total seasonal discharge varied by several orders of magnitude decreasing with decreasing elevation. The total seasonal discharge at GL4 was 1,982,000 m³ compared to 1,283,800 m³ at CC. GG discharge was 241,580 m³, while the smaller and intermittent BET catchment had a total discharge of only 1341 m³.

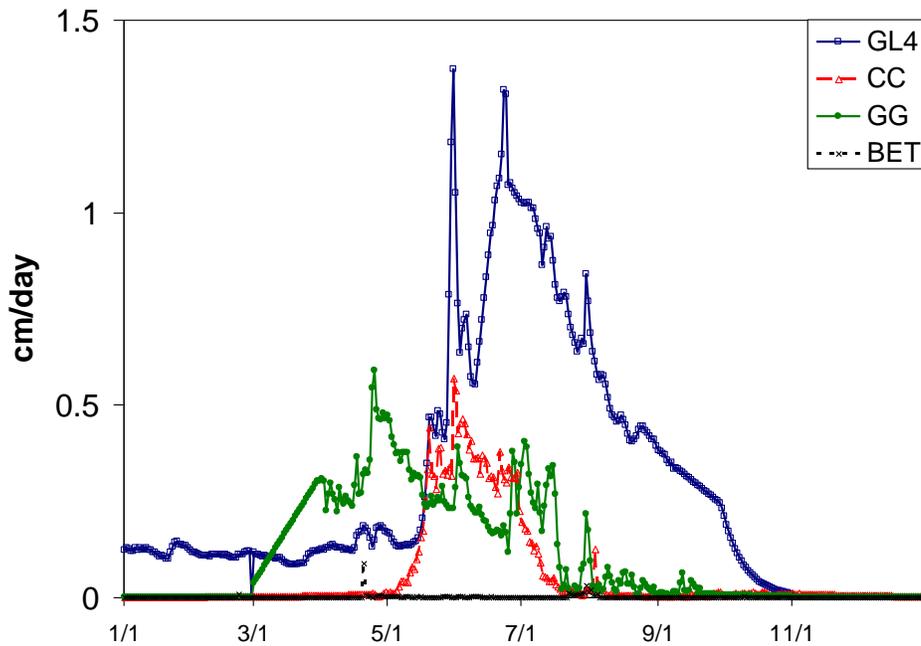


Figure 2.3: Specific discharge in cm d⁻¹ at all gauged sample sites for 2009 calendar year.

2.4.2 Stream Chemistry

Geochemical weathering products

Concentrations of geochemical weathering products increased with decreasing elevation. To illustrate, VWM seasonal concentrations of acid-neutralizing capacity increased by over an order of magnitude from 61 $\mu\text{eq L}^{-1}$ at GL4 to 3130 $\mu\text{eq L}^{-1}$ at BET. Similarly, the concentrations of sodium increased from 17 $\mu\text{eq L}^{-1}$ at GL4 to 453 $\mu\text{eq L}^{-1}$ at BET (Table 2.2). Concentrations

of calcium also showed a large increase as elevation decreased, from $92 \mu\text{eq L}^{-1}$ at GL4 to $2970 \mu\text{eq L}^{-1}$ at BET.

In contrast, geochemical weathering product yields did not show a similar relationship with elevation (Table 2.3). For example, the seasonal export of calcium from GL4 was 17.3 kg ha^{-1} at GL4, only 3.1 kg ha^{-1} at CC, 13.5 kg ha^{-1} at GG, and then decreased to 2.2 kg ha^{-1} at BET. Similarly, the seasonal export of sodium was 3.5 kg ha^{-1} at GL4, 2.4 kg ha^{-1} at CC, 6.1 kg ha^{-1} at GG, and then decreased to 0.1 kg ha^{-1} at BET. Thus, the largest export of calcium occurred at the site with the lowest VWM seasonal concentration, but the largest seasonal discharge. BET, the site with the highest concentrations, had the lowest flux of calcium and sodium.

Table 2.2: Volume-weighted mean seasonal concentrations (May-October 2009) for select solutes in stream waters.

Site	pH	COND $\mu\text{S cm}^{-1}$	ANC $\mu\text{eq L}^{-1}$	NH_4^+ $\mu\text{eq L}^{-1}$	Ca^{2+} $\mu\text{eq L}^{-1}$	Na^+ $\mu\text{eq L}^{-1}$	NO_3^- $\mu\text{eq L}^{-1}$	DON $\mu\text{mol L}^{-1}$	DOC mg L^{-1}	DOC:DON ratio	FI ratio
GL4	6.56	16	61	1.25	93	17	10.5	3.3	0.8	28	1.50
CC	6.93	24	172	0.11	113	73	0.2	10.8	4.8	36	1.38
GG	7.59	72	611	0.71	351	129	3.2	13.7	5.8	39	1.44
BET	8.18	551	3130	0.78	2974	453	0.8	11.8	10.4	73	1.57

Table 2.3: Seasonal export (kg ha^{-1}) for ANC, NH_4^+ , Ca^{2+} , Na^+ , NO_3^- , DON and DOC at the four gauged sampling sites in 2009.

Site	ANC kg ha^{-1}	NH_4^+ kg N ha^{-1}	Ca^{2+} kg Ca ha^{-1}	Na^+ Kg Na ha^{-1}	NO_3^- kg N ha^{-1}	DON kg N ha^{-1}	DOC kg C ha^{-1}
GL4	34.4	0.15	17.3	3.5	1.75	0.54	10.0
CC	11.4	0.01	3.1	2.4	0.01	0.42	14.4
GG	73.0	0.03	13.5	6.1	0.10	0.62	19.0
BET	1.9	<0.01	2.2	0.1	<0.01	0.01	0.2

We evaluated the hypothesis that at higher elevations, thinner soils and lower temperatures will result in less chemical weathering by conducting linear regressions of the concentrations of geochemical weathering products with elevation. For this analysis, we added additional sites along Boulder Creek (NAV, ALB, WSF) to increase our statistical power. Concentrations of base cations (Ca^{2+} , Mg^{2+} , Na^+ , Si) decreased exponentially and significantly ($p < 0.05$) with increasing elevation. To illustrate with dissolved silica, a measure of the rate of chemical weathering, there was a statistically strong ($R^2 = 0.74$, $p = 0.002$) inverse relationship with elevation (Figure 2.4), as the concentrations increased by over an order of magnitude from NAV ($15.7 \mu\text{moles L}^{-1}$) to BET ($189 \mu\text{moles L}^{-1}$).

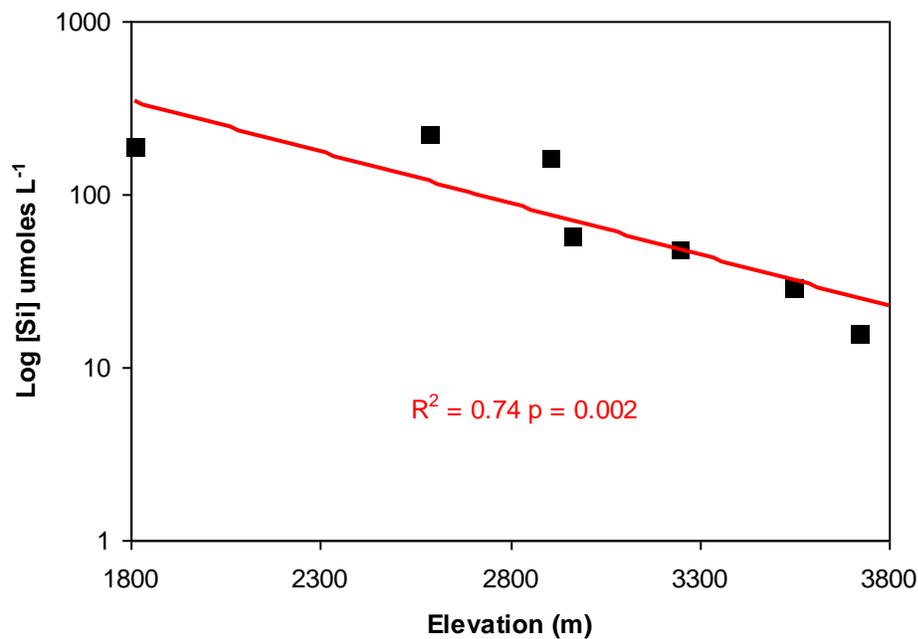


Figure 2.4: Relationship between seasonal VWM dissolved silica concentration (logarithmic scale) and elevation. The regression line is a least-squares best fit. The rate of chemical weathering decreases more or less exponentially with elevation.

If the second hypothesis, that the relative contributions of different primary minerals to the solute load would change systematically with elevation, is correct there should be a change in

the Ca^{2+} to Na^+ ratio in surface waters with elevation. The relative contributions of different primary materials to the solute load does not change systematically with elevation, as evidenced by the lack of an elevational trend in the Ca:Na ratio ($R^2 = .07$, $p = 0.57$) (Figure 2.5). Thus, our data do not support hypothesis 2.

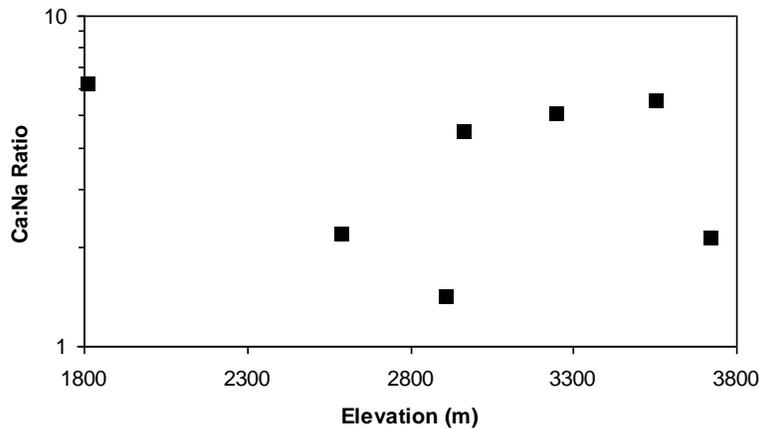


Figure 2.5: Ratio of calcium concentration to sodium concentration as a function of elevation.

Nutrients

The seasonal maximum concentration of nitrate for all the sites was $29 \mu\text{eq L}^{-1}$, which occurred at GL4 on the rising limb of the hydrograph (Figure 2.6). Concentrations of nitrate at GL4 then declined in a consistent pattern to about $3 \mu\text{eq L}^{-1}$ in the late summer. At CC, nitrate concentrations were always near or below detection limits, with a seasonal VWM mean of $0.2 \mu\text{eq L}^{-1}$. In contrast to CC, nitrate concentrations at GG were greater than $10 \mu\text{eq L}^{-1}$ at the initiation of snowmelt and following summer rainfall. Nitrate concentrations in streamflow at BET were also near $10 \mu\text{eq L}^{-1}$ during snowmelt, then decreased towards detection limits the rest of the season. Nitrate export of 1.75 kg ha^{-1} at GL4 was more than an order of magnitude greater than any of the other basins (Table 2.3).

There was a general decreasing trend in DON with increasing elevation, except for at BET (Figure 2.6). The highest mean VWM seasonal concentration was measured at GG (13.3 $\mu\text{moles L}^{-1}$), and the lowest at GL4 (3.33 $\mu\text{moles L}^{-1}$). At GL4 and Como, DON concentrations were highest on the rising limb of the hydrograph, then decreased. In contrast, at GG concentrations remained elevated through most of the summer near 20 $\mu\text{moles L}^{-1}$. Seasonal export of DON was similar for the three higher basins, GL4 was 0.54 kg ha^{-1} , 0.42 kg ha^{-1} at CC and 0.62 kg ha^{-1} at GG, while it was negligible at BET.

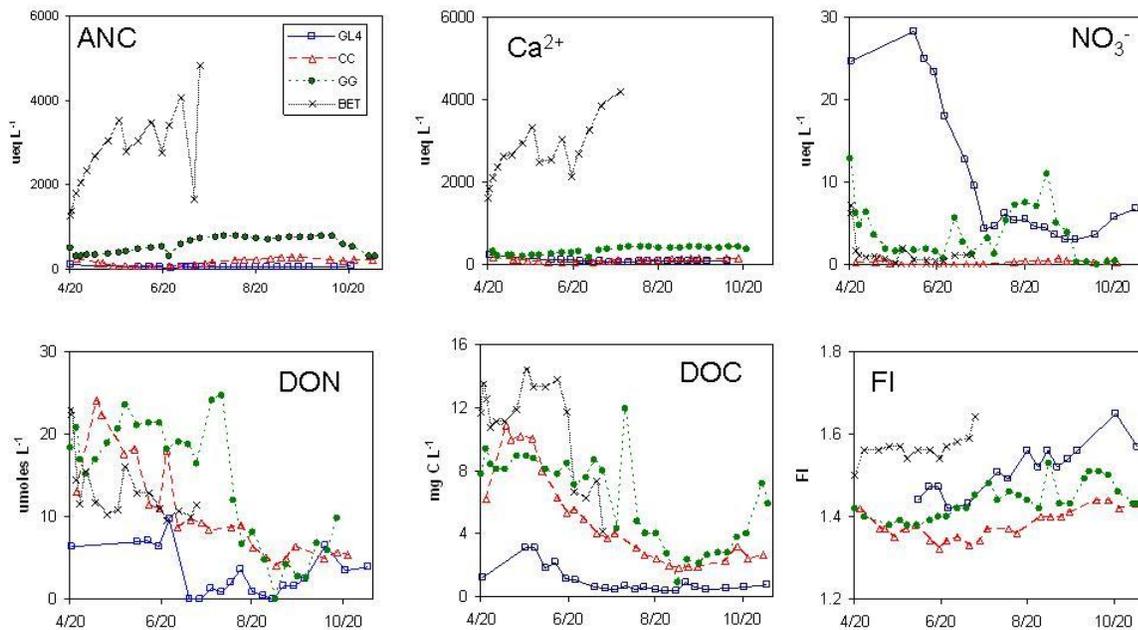


Figure 2.6: Time series of ANC, Ca²⁺, NO₃⁻, DON, DOC concentrations and FI during 2009 sampling season at GL4, CC, GG, and BET.

The concentrations of DOC followed a similar pattern to DON, except that DOC was highest at BET, the lowest elevation site. The maximum seasonal DOC concentration at the highest site, GL4, was only 3.7 mg C L^{-1} , whereas BET had a maximum concentration of 14.4 mg C L^{-1} . The range was small in the two alpine sites and temporal variance increased in the subalpine, montane and foothills sites. The variance was especially high in BET and GG due to high peaks in the early summer associated with rain events. Mass fluxes of DOC increased from 9.9 kg C ha^{-1} at GL4 to $19.0 \text{ kg C ha}^{-1}$ at GG. BET had the smallest export of 0.2 kg C ha^{-1} even though the DOC concentrations were the highest at this site.

Surprisingly, the highest FI values were at the lowest elevation BET site, followed by the alpine GL4 site. At BET the FI values were always near the mean of 1.57, with little variance. In contrast, FI values at the other three sites showed a seasonal pattern of decreasing during snowmelt and then a consistent increase on the recession limb of the hydrograph. For the small subset of samples, we found that the average %HPOA for GL4, GG, and BET were 38.5% (n=4), 49.7% (n=2), and 53% (n=1) respectively (Barnes, *in review*). The samples were all collected between June 11th and June 25th. The Cory and McKnight PARAFAC model reproduced the 3-D EEMs reasonably well, in all cases the residuals were less than 5%. Component 4, indicative of reduced quinones, made up the largest percentage of the fluorescing DOM pool (19-36%) at all sites. Component 2, related to oxidized quinones, was the second largest contributor (13-18%); while components 8 and 13, indicative of protein like molecules, contributed between 3% and 10% to the DOM pool (Barnes, *written communication*). The sum of components identified as microbial in origin by Cory and McKnight (2005) from Antarctic-only DOM samples (components 3,4,6,7, and 9) were 43% at GL4, 48% at GG and 42% at BET (Barnes, *in review*).

We further evaluated how solute concentrations changed with elevation by adding additional sites from Green Lakes Valley, and also sites along the main stem of Boulder Creek. Here we show a box and whisker plot for selected solutes from 3800 m to 1800 m (Figure 2.7).

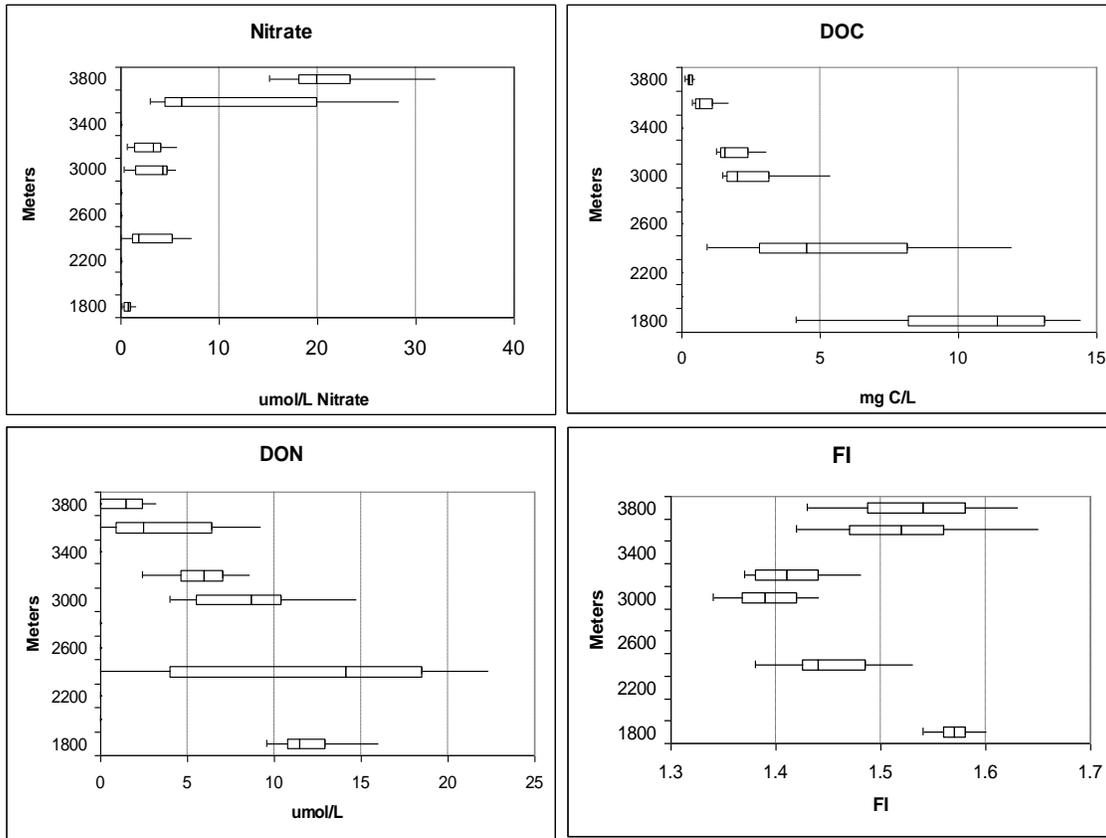


Figure 2.7: Box and whisker plots of nitrate, DOC and DON concentrations and FI along an elevational gradient. The variation represents seasonal variability throughout the sampling season.

While not statistically significant, elevation and nitrate concentrations were positively related ($R^2 = 0.51$, $p = 0.07$). In contrast, DON was inversely related with elevation ($R^2 = 0.77$, $p < 0.01$) (Figure 2.8). The percentage of DIN of the total dissolved N (TDN) in the streams decreased with elevation, with DIN (nitrate and ammonium) comprising 90% of TDN at NAV, 79% of TDN at GL4, and only 39% of TDN at ALB. At the CC site, which drains primarily

forested areas, the DIN percentage drops precipitously to 3%. The seasonal mean concentrations of DOC showed a strong inverse relationship with elevation, which explained 97% of the variance in DOC concentrations ($p < 0.001$) (Figure 2.8).

In contrast to the inorganic and organic nutrient concentrations, elevation does not appear to be a strong predictor of DOM character, as assessed by FI. The linear regression analyses demonstrated that only 3% of the variance of FI can be explained by elevation during the 2009 season ($p > 0.05$), most likely due to the high FI values at the two lower elevation sites. However, two components identified by the Cory and McKnight (2005) PARAFAC model had significant relationships with elevation. The protein-like components that resemble tryptophan and tyrosine increase with elevation ($R^2=0.69$, $p<0.05$). In contrast, the C2 component, thought to be indicative of an oxidized quinone, decreases significantly with elevation ($R^2=0.83$, $p<0.05$).

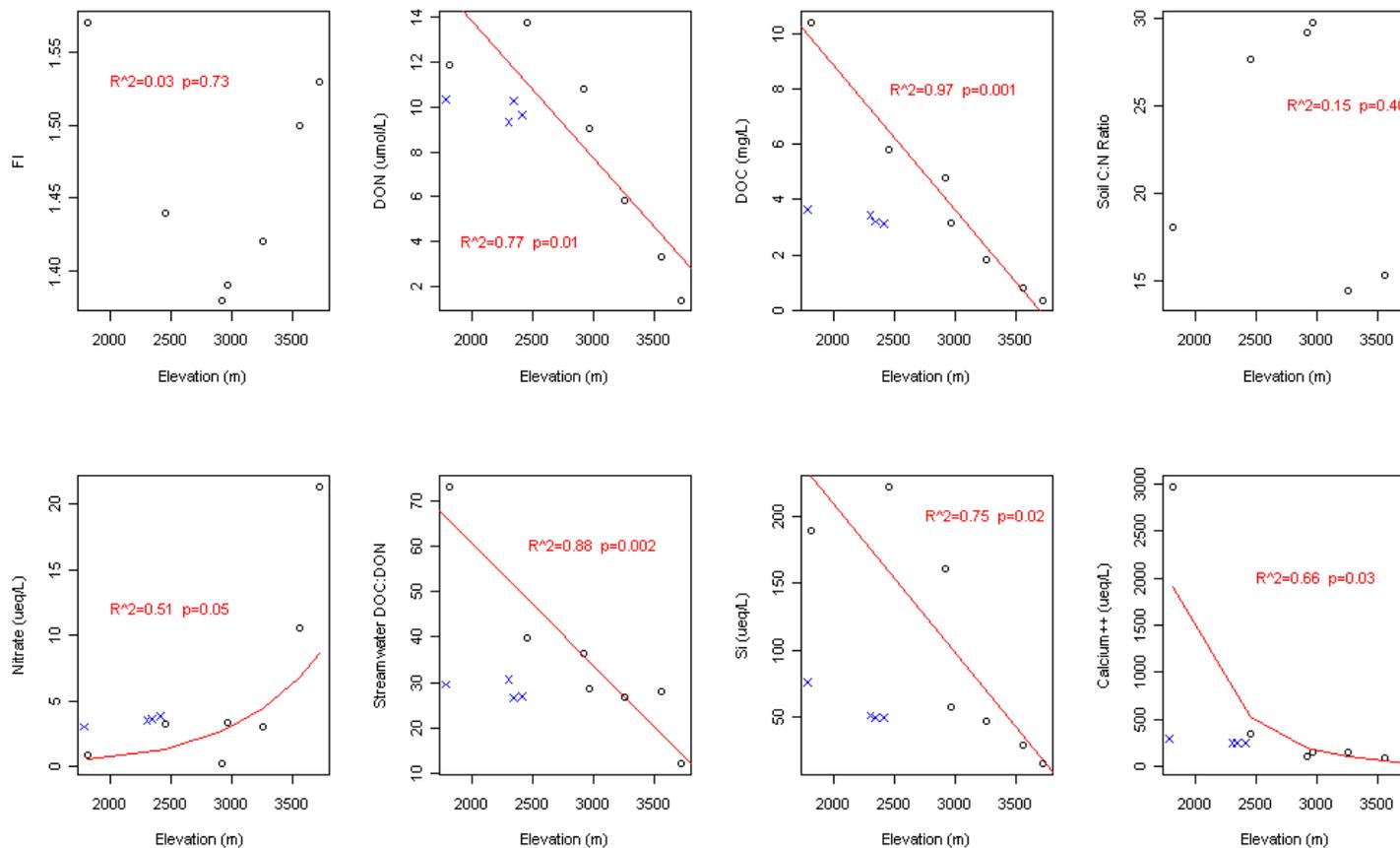


Figure 2.8: Linear regression analyses of FI, DON, DOC, Soil C:N, nitrate, streamwater DOC:DON, silica, and calcium versus elevation. The black circles represent 2009 seasonal volume-weighted mean concentrations (May-October 2009) for the headwater catchment sites in the study area. The blue x's are 2009 seasonal arithmetic mean concentrations for sites along the mainstem of Boulder Creek. These mainstem sites do not follow the same elevational trends as the study sites, indicating that headwater catchments cycle nutrients differently than well-mixed streams, even at similar elevations.

2.4.3 Two-Way Repeated Measures ANOVA

The two-way repeated measures analysis of variance tests showed that site was important for all parameters, but not time. For all parameters tested (NO_3^- , DON, DOC, DOC:DON, FI, Si, Ca^{2+} , Na^+), there was a significant difference in response due to the effect of sample location (Table 2.4). Surprisingly, the effect of time was not statistically significant in determining the DOC:DON ratio, nitrate, silica, calcium and sodium concentrations of the samples. However, the analyses demonstrated that the time factor was significant in determining DOM quality and quantity measurements.

Table 2.4: Summary of results of two-way repeated measures analysis of variance tests for concentrations of selected parameters (DOC, nitrate, DON, DOC:DON, FI, silica, calcium, sodium), by site and time. Significant differences ($\alpha = 0.05$) are marked with an asterisk.

DOC	Sum Squares	F Ratio	P	Df
Time	103	7.43	0.0002*	5
Site	233	13.8	0.0001*	6
Nitrate	Sum Squares	F Ratio	P	Df
Time	56.1	0.49	0.7802	5
Site	1540	11.2	0.0001*	6
DON	Sum Squares	F Ratio	P	Df
Time	262	4.93	0.0025*	5
Site	393	6.17	0.0004*	6
DOC:DON	Sum Squares	F Ratio	P	Df
Time	1180	1.62	0.188	5
Site	9380	10.8	0.0001*	6
FI	Sum Squares	F Ratio	P	Df
Time	0.04	13.18	0.0001*	5
Site	0.19	48.3	0.0001*	6
Si	Sum Squares	F Ratio	P	Df
Time	725	0.24	0.9431	5
Site	256000	69.4	0.0001*	6
Ca²⁺	Sum Squares	F Ratio	P	Df
Time	6779	0.76	0.588	5
Site	413569	38.5	.0001*	6
Na⁺	Sum Squares	F Ratio	P	Df
Time	651	1.01	0.429	5
Site	46317	59.9	.0001*	6

2.4.4 Soil Chemistry

The soil sample analyses demonstrated that there is little nitrate present in the soil (Table 2.5). The highest nitrate concentration was 0.03 mg N kg⁻¹. Ammonium concentrations were slightly higher than NO₃⁻, but still low. These concentrations ranged from 0.10 – 2.14 mg N kg⁻¹. Microbial N was generally highest at high elevations (10.45 mg N kg⁻¹ at NAV) and decreased moving down-gradient in elevation (1.97 mg N kg⁻¹ at BET).

Table 2.5: Soil characteristics along an elevational gradient.

Site	Soil C:N	NH ₄ ⁺ (mg N kg ⁻¹)	NO ₃ ⁻ (mg N kg ⁻¹)	Microbial N (mg N kg ⁻¹)
NAV	13.9	2.14	0.02	10.45
GL4	15.3	0.25	0	4.52
ALB	14.5	0.84	0.03	8.35
SLO	17.9	0.17	0	3.10
WSF	29.7	0.12	0	4.25
CC	29.1	0.15	0	3.25
GG	27.7	0.10	0	2.79
BET	18.1	0.19	0.01	1.97

The relatively unvegetated alpine sites have soil C:N ratios that ranged between 13.9 and 15.3. Below treeline, the ratio increased to 29.7 at WSF, 29.1 at CC, and 27.7 at GG. Surprisingly, the C:N ratio decreases to 18.1 at BET, the lowest elevation site.

2.4.5 Soil C:N Ratio vs. Solute Concentration Relationships

The soil C:N ratio showed a strong inverse relationship with VWM nitrate concentrations in streamwaters ($R^2 = 0.46$, $p < 0.005$) and elevation ($R^2 = 0.43$, $p < 0.005$) (Figure 2.9). While it was not a statistically significant relationship, the FI values also decreased at higher soil C:N ratios. Conversely, the soil C:N demonstrated a significant positive relationship with both DOC ($R^2 = 0.25$, $p < 0.05$) and DON ($R^2 = 0.39$, $p < 0.05$). However, the soil C:N ratio was not found to be significant when predicting streamwater DOC:DON ratios.

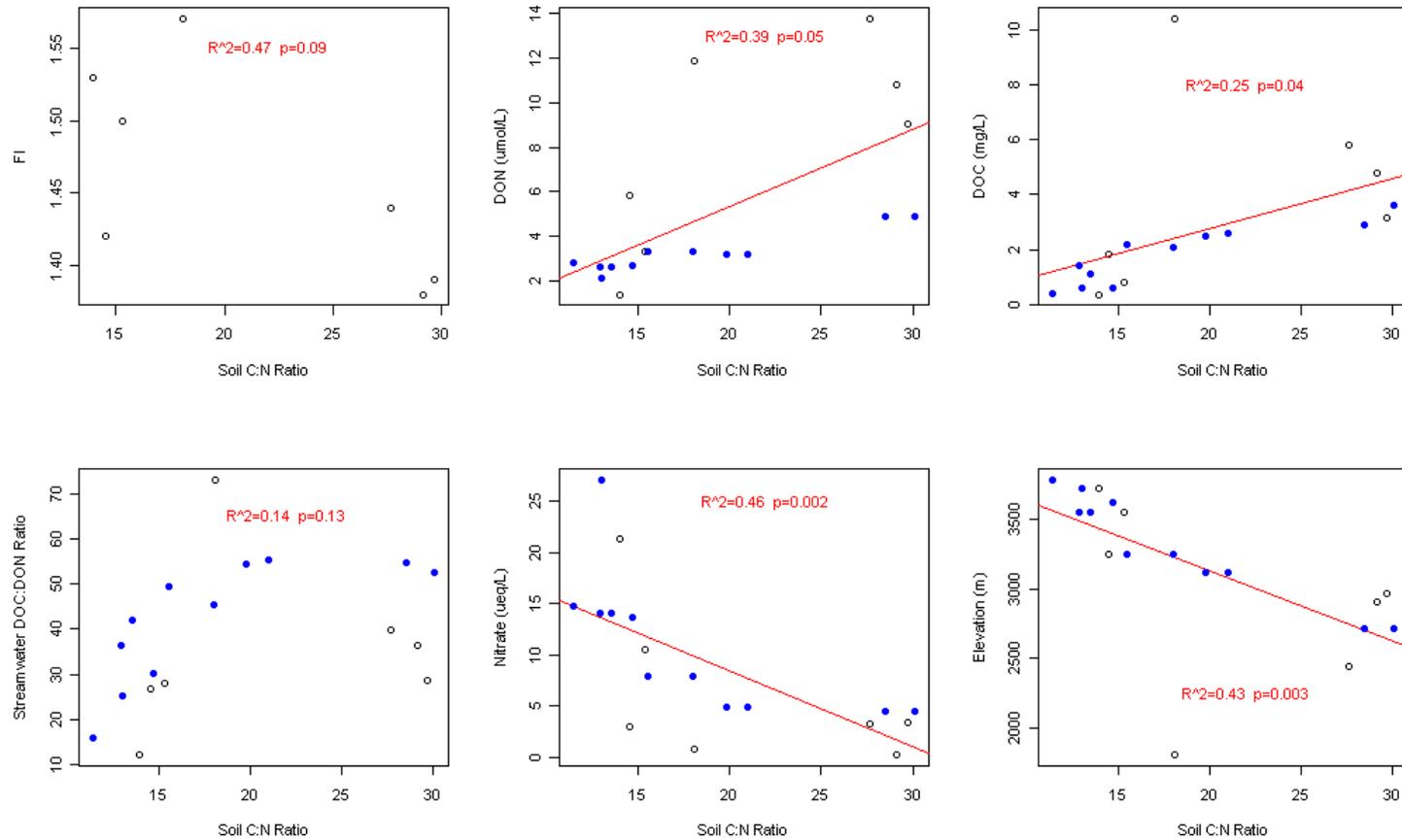


Figure 2.9: Linear regression analyses of FI, DON, DOC, streamwater DOC:DON, NO_3^- , and elevation versus soil C:N ratio. In addition to the 2009 soil data, soil C:N ratios reported from 1998 and 1999 are included as solid blue circles in this figure and regression analyses (Hood et al., 2003).

2.5 DISCUSSION

2.5.1 *Weathering Rates*

The range of seasonal VWM dissolved silica concentrations in the GLV alpine sites (15.7 to 28.7 $\mu\text{moles L}^{-1}$) is lower than the range reported at an alpine site in Loch Vale (34.3 – 43.7 $\mu\text{moles L}^{-1}$) (Clow & Drever, 1996), but the lower elevation climatic zone sites were characterized by higher seasonal VWM silica concentrations (57.0 – 219 $\mu\text{moles L}^{-1}$) that fall within the range reported in a similar elevational study conducted in the Canton of Ticino in southern Switzerland (Drever & Zobrist, 1992). The rate of chemical weathering, as measured by VWM dissolved silica concentrations, decreased more or less exponentially with elevation, supporting our first hypothesis. However, our second hypothesis, that the relative contributions of different primary materials to the solute load would change with elevation, is not supported by the data. Other studies in the Cascade Mountains and Loch Vale watershed (Drever & Hurcomb, 1986; Mast et al., 1990) showed that minor reactive phases such as calcite and amphiboles make a greater relative contribution to the solute load at higher elevations (up to 40% of cations in basin derived from calcite), whereas the less reactive phases such as plagioclase make a greater relative contribution at lower elevation catchments. Here, we find that the Ca/Na ratio in streamwaters does not change systematically with elevation, suggesting that selective weathering is not occurring. These findings could be due to less rapid physical erosion that results in the calcite fraction being depleted from the exposed rocks.

Both air temperature and the concentrations of base cations increased going down the elevational gradient. This is consistent with studies that have shown that greater air temperature

is generally correlated with greater chemical dissolution rates in headwater catchments (Meybeck, 1987; Velbel et al., 1990; Drever & Zobrist, 1992). While there certainly is the potential for high chemical weathering rates in alpine areas that are driven by high rates of physical erosion (Williams et al., 2006), on a broad landscape scale, higher temperatures at lower elevations promote greater concentrations of base cations.

The low base cation concentrations at the highest alpine sites are also consistent with a Riebe et al. (2004) study that showed that the sparsely vegetated, high-altitude terrain of alpine sites in the Santa Rosa Mountains in Nevada are associated with extremely low silicate weathering rates. Another study estimated that the rate of weathering release of calcium and magnesium to streams is 2-5 times higher in vegetated areas than the release to stream in barren areas (Moulton & Berner, 1998). Drever (1994) found that land plants directly affect mineral weathering by generating chelating ligands, modifying pH through organic acid production and altering the physical properties of soil. Again, our base cation concentration results support these trends and we find evidence that landscape controls in the form of vegetation cover result in forested areas having higher base cation concentrations compared to the temperature-limited alpine areas above.

In contrast to the base cation concentrations, export does not demonstrate an inverse relationship with elevation. In fact, the area-weighted flux calculations indicate that the lowest elevation site (BET) exports the least base cations. This finding could be due to differences in geomorphology and precipitation amounts. BET is characterized by deeply incised, steep slopes due to the downcutting of Boulder Canyon. The resulting landscape contains exposed bedrock and a less developed soil profile, possibly resulting in less water storage capacity in soils and minimal groundwater flows. Due to the relatively low precipitation amounts and the absence of

large groundwater inputs compared to the high-elevation sites, BET has a low specific discharge that results in lower base cation fluxes. In comparison, GG receives similar precipitation amounts to BET, but contains deeper soils that have developed over the past 50 million years. These unique geomorphic differences may result in greater groundwater contributions, increased residence times, and greater fluxes in the GG catchment.

2.5.2 Landscape Controls on Carbon and Nitrogen Cycling

The base cation concentration and flux data demonstrate how elevational, climatological, and geomorphic controls influence weathering rates and landcover development. These landscape processes also play a fundamental role in how carbon and nitrogen are transported and accumulated across the different climatic zones. Similar to the base cations, DOC concentrations demonstrated a significant correlation with elevation ($R^2 = 0.97$, $p < 0.001$). This strong relationship appears to be driven by landscape controls. In the alpine, characterized by limited soils, sparse vegetation, and soil C limitation, DOC concentrations are low throughout the season compared to the subalpine and montane stream sites. Our soil C:N data support the concept of progressively carbon-enriched soil coverage moving down elevation. These findings are also consistent with previous work that shows that DOC concentrations in surface waters are strongly correlated with soil organic C pools (Aitkenhead & McDowell, 2000). The sole exception to this trend is the BET site, in which the deeply incised, steep slopes limit soil development and soil organic C pools. While the concentrations of DOC at BET follow the elevational trend, seasonal DOC export was low (0.2 kg C ha^{-1}) due to low specific discharge and limited soil development. The $0.2 - 19.0 \text{ kg C ha}^{-1}$ range of DOC export we report for our catchments is at the low end of

carbon yields reported from 21 forested watersheds in the United States (7-34 kg C ha⁻¹ [Tate & Meyer, 1983]) and from 30 forested catchments in the cool conifer biome (15-74 kg C ha⁻¹ [Aitkenhead & McDowell, 2000]).

Seasonal precipitation type also plays an important role in DOC accumulation and export. Alpine catchments receive a greater percentage of precipitation as snowfall (Table 2.1) and snowpack duration is longer at these elevations compared to lower headwater catchments. As noted earlier, DOC temporal patterns at alpine sites exhibit an early spring spike, followed by a decline to lower levels at baseflow conditions. Previous studies have documented this seasonal signal (McKnight et al., 1997; Hornberger et al., 1994; Hood et al., 2003a), caused by the accumulation of soluble organic material under snowpack while conditions for microbial activity is ideal (Brooks et al., 1999). During the ascending limb of the hydrograph, this accumulated material is flushed out, coinciding with a peak in measured DOC concentrations in streamwaters. After this initial flushing event, concentrations of DOC decline at the alpine sites, as the near-surface pools of soluble organic carbon have been depleted.

This snowmelt pattern is less distinguishable at the lower elevation sites because the snowcover is more intermittent due to warmer temperatures and a greater contribution of rain to precipitation as indicated by field observations using snow poles at GG and BET. Whereas the DOC concentrations at GL4 and CC remain low following snowmelt, the DOC concentrations at GG remain elevated throughout the summer months. This is most likely due to fast flowpaths and shallow soil flushing out organic matter during summer storm events.

Fluorescence index (FI) data provides a useful tool to test the LCM, as it provides a semi-quantitative analysis of sources of DOM (McKnight et al., 2001), an integral component of the conceptual model. In general, DOM production in alpine areas relies more heavily on

autochthonous production, whereas the heavily forested CC site is dominated by terrestrial inputs of DOM. The %HPOA supports these trends, with greater %HPOA observed at lower elevation sites, indicative of terrestrially-derived organic matter rich in fulvic acids. These findings are consistent with the LCM model in which alpine vegetative cover is limited due to low temperatures and longer snowpack duration. In contrast, warmer temperatures promote greater vegetation coverage at lower elevations, resulting in more terrestrially-derived organic matter rich in fulvic acids.

The temporal trends at the alpine sites reveal a late-summer increase in FI, consistent with a Hood et al. (2003b) study in the same watershed. Hood and others attributed these changes to an increase in algal contributions from the Green Lakes to the DOM pool during the summer. However there were not strong seasonal variations in FI at the lower elevation sites. This finding hints at the importance of spatial heterogeneity in evaluating the LCM. Due to the presence of this series of alpine lakes, the character of DOM exported from this drainage is likely to be different (more autochthonous) from a similar alpine catchment that does not contain lakes. The conceptual model also helps put into perspective the potential impact of global change on these alpine lakes. In response to increasing air temperatures, earlier ice-off, and increasing N deposition, phytoplankton communities in the Green Lakes are likely to increase production and export more aquatically-derived labile carbon to the stream (Hood et al., 2005).

The mean seasonal FI values at GG (1.44) and BET (1.57) provide the exceptions to the general elevational trends in DOM character. These relatively high values may best be assessed through the lens of the LCM in the context of climatological controls. The lower elevation CZO sites receive significantly lower precipitation than the Niwot Ridge LTER sites (Table 2.1),

perhaps leading to water limitation in decomposition and production processes. Despite a greater number of growing degree days that would usually promote increased production, water limitation may provide a missing climatic clue to the high FI values at GG and BET.

For example, BET is an intermittent stream characterized by infrequent spikes in its hydrograph that result in stream samples being comprised primarily of “first-flush” events, in which DOM accumulates during dry periods and is rapidly flushed out during precipitation events. Previous work by Miller et al. (2005) shows that rewetting events in chaparral soils enhance carbon and nitrogen release relative to soils that are maintained at a constant soil moisture. They attribute this release to the physical disruption of soil aggregates and extracellular enzyme activity transforming this recalcitrant material into a stress-labile carbon pool primed for release. These enzymes can be active even during long dry periods, thus allowing labile C production during dry periods with low biological demand. McClain et al. (2003) have noted similar findings, showing that water limitation can create “hot spots” and moments in biogeochemical cyclings, with strong signals following episodic rewetting events. While further research is needed to quantify this dry period and “first-flush” hypothesis, it appears that precipitation-limitation overrides general elevational trends when assessing carbon quality at the lower elevation sites.

Sourcewater and flowpaths might offer a possible alternative explanation for elevated FI values at BET. Previous work by McKnight et al. (2001) has demonstrated that Williams Lake, MN groundwater samples have some of the highest FI values (1.9) of all samples included in a survey including Antarctic lakes. The intermittent flow at BET that is sampled could be sustained by a large groundwater input, perhaps contributing to the higher FI values observed (mean = 1.57). Further research is needed to confirm this alternative hypothesis.

In large part, the LCM was originally developed to assess source and sink zones for the accumulation and export of inorganic N in response to the concern over increased N deposition (Seastedt et al., 2004). The original conceptual model helped explain the export and accumulation of nitrate in alpine areas, but extending the analysis to lower elevation catchments can provide insight into how nitrogen cycles differ over a larger climatic range. Again, landscape controls help explain the different concentrations of DIN we find between sites.

Soil C:N ratios serve as an indicator of these landscape controls. A linear regression analysis showed that soil C:N explained approximately 46% of the variation in nitrate concentrations across all seven sites ($p < 0.005$). In comparison, Hood et al. (2003b) found that soil C:N explained 59% of the variation in nitrate concentrations in Green Lakes Valley. The lower R^2 value in this study is likely due to confounding climatological and geomorphic factors at the two CZO sites. The highest nitrate concentrations were observed within the alpine catchments having soil C:N less than 25, a finding consistent with a Gunderson et al. (1998) study that argued that there is a significant increase in net nitrification at soil C:N ratios below 25. The carbon-limitation in the alpine sites is largely a result of a landscape that is dominated by large talus and exposed bedrock areas (Williams et al., 1997; Campbell et al., 2000). These harsh environments with low temperatures and long snowpack duration can not support the developed soil coverage and vegetation communities that are able to retain inorganic N through plant assimilation and uptake. The decrease in nitrate concentrations and export at lower elevations reflects this change in landcover to a vegetated system that is nitrogen-limited instead of carbon-limited. Figure 2.10 demonstrates this carbon limitation at higher elevations (NAV and GL4) that contributes to elevated nitrate concentrations in streamwaters.

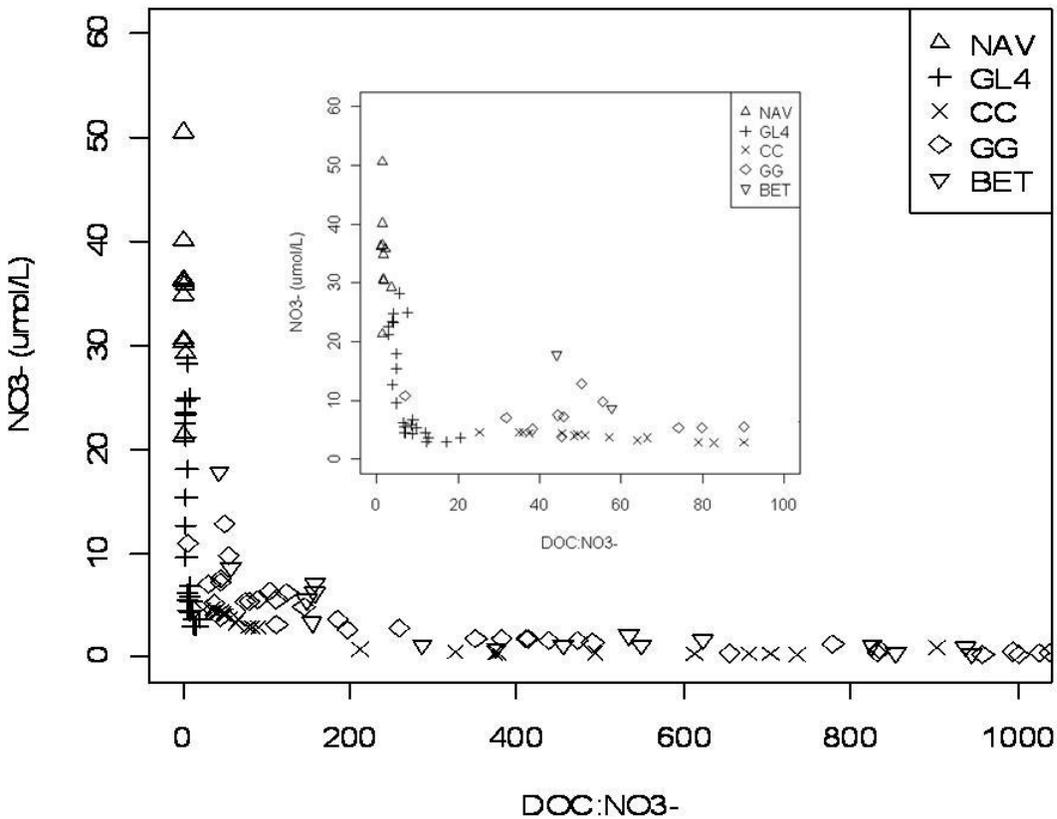


Figure 2.10: Scatterplot of nitrate concentrations ($\mu\text{mol L}^{-1}$) versus DOC: NO_3^- ratio for 2009 streamwater samples at NAV, GL4, CC, GG, and BET. The inset figure is an enlarged scatterplot with a DOC: NO_3^- ratio range from 0-100. When the DOC: NO_3^- ratio falls below the resource stoichiometry threshold of 3.5, the system becomes carbon limited, resulting in nitrate accrual (Taylor & Townsend, 2010).

The ratio of DIN to DON provides a method to assess ecosystem N-status and determine where along the elevational gradient the watershed shifts from being a source to a sink of inorganic nitrogen. Typically, entirely forested catchments (Campbell et al., 2000) and pristine high elevation catchments (Williams et al., 1995) have greater organic N concentrations than DIN concentrations in surface waters. As demonstrated earlier, the ratio of DIN to DON in our study watershed decreases immediately at the alpine/subalpine ecotone (ALB). These findings are consistent with the Hood et al. (2003b) study that found that catchment retention of DIN increases with the extent of soil and vegetative landcover and a Heuer et al. (1999) study that

showed that alpine areas act as a source of inorganic N and subalpine zones serve as a sink for this nitrate leached from above. For comparison, high-elevation catchments at Lake Tahoe (Coats & Goldman, 2001) and the southern Sierra Nevada (Williams et al., 2005) show that organic N concentrations in streamwaters are 1.5 – 5 times higher than DIN concentrations. Here, we find that that percentage of DIN of the total dissolved N is 90% at NAV and 79% at GL4, indicating that the Green Lakes Valley is responding to the increased atmospheric deposition of inorganic N.

The actual process of N assimilation is less understood, though Peterson et al. (2001) have shown that up to 50% of inorganic N in forested headwater catchments is transformed within the stream channel, especially when the stream has a high surface to volume ratio that promotes rapid uptake of N through biological assimilation and denitrification. Certainly, North Boulder Creek has in-stream N processing potential (Barnes et al., *in review*) and much of the nitrate in the stream is removed before the ALB site, but further research is needed to quantify inorganic nitrogen retention rates throughout the entire watershed.

Although we found a marked shift from DIN dominance to DON dominance right at treeline (ALB), consistent with the original LCM model, the nitrate concentrations remained relatively elevated well into the subalpine areas. Even at the WSF site, the mean seasonal concentration of nitrate was $3.9 \mu\text{eq L}^{-1}$, indicating that the upstream alpine portion of the North Boulder Creek catchment may be affecting the downstream chemistry within subalpine reaches. The CC site offers a useful comparison to WSF, as it is located at approximately the same elevation and has a similar aspect, yet is almost entirely forested area as opposed to WSF, which drains the alpine headwaters of North Boulder Creek. At the CC site, the mean seasonal concentration of nitrate was only $0.24 \mu\text{eqL}^{-1}$. A paired t-test ($p < 0.001$) shows that the nitrate

concentrations at WSF are significantly higher than at CC, indicating that DIN concentrations at WSF are subsidized by nitrate export from the alpine areas.

This evidence of nitrate subsidization is of particular concern in the Colorado Front Range, as studies have shown that alpine areas are becoming increasingly N-saturated due to N deposition (Baron et al., 1994; Williams et al., 1996a; Campbell et al., 2000). Given the results from this study, nitrogen saturation within alpine areas could potentially lead to increased downstream export of nitrate, causing periodic acidification and threatening essential aquatic ecosystem services even in vegetated reaches at lower elevations. While traditional indicators of landcover such as soil C:N ratios might predict that subalpine stream reaches would be N-limited, streamwaters that drain unvegetated areas may still be vulnerable to N deposition. In this case, the fluvial transport mechanisms integral to the LCM appear to partially override landscape controls on N status, with potentially negative ecosystem effects.

2.5.3 Landscape Continuum Model Revisited

The LCM, as developed by Seastedt et al. (2004), provides a useful framework for explaining the nutrient concentrations observed here in the alpine sites. In particular, we found that in response to increased inputs of N via atmospheric deposition, mean seasonal VWM concentrations of nitrate at GL4 ($10.5 \mu\text{eq L}^{-1}$) were significantly greater than concentrations found at lower sites ($0.8 \mu\text{eq L}^{-1}$ at BET). This finding is consistent with the LCM concept of the combination of aeolian, fluvial, and surface transport processes creating zones of nutrient accumulation and export. Specifically, the LCM predicts the elevated nitrate concentrations at GL4, the result of the amplification of the downward movement of nutrients from wind-scoured and unvegetated areas above. The conceptual model also predicts that redeposition of

inorganic N will occur at the alpine/subalpine interface, where treeline acts as a windbreak and collects downward moving nutrients. However, we did not observe these elevated nitrate concentrations ($3.00 \mu\text{eq L}^{-1}$) at the ALB treeline site. In addition, the LCM does not appear to apply to headwater catchments at lower elevations in the montane and foothills climatic zones, as neither GG or BET demonstrated elevated nitrate concentrations.

In order to expand the scale of the LCM and develop a conceptual model for how nutrient dynamics respond to global change across multiple climatic zones, it is useful to more explicitly incorporate elevational and geomorphic controls. The results of simple linear regression analyses indicate that nutrient concentrations (silica, calcium, DOC, DON) can be significantly correlated with elevation. In determining why elevation matters, we assessed how geomorphology characteristics and climate factors interact to control landcover characteristics of headwater catchments.

It is known that, in general, precipitation increases with elevation (Barry, 1973) and temperature decreases moving up gradient. At a broad scale, these two parameters can limit or promote the development of soil and vegetation characteristics. For example, low air temperatures and long-lasting snowpack can inhibit the establishment of plant communities. Soil development is also controlled by temperature at a broad scale, as warmer temperatures are conducive to greater geochemical weathering rates that contributes to pedogenesis. However, geomorphology also plays an important role in shaping landcover characteristics. Within the Boulder Creek watershed, soil development and local relief is shaped by glacial rejuvenation in the upper alpine reaches, slow erosion in the montane portion and fluvial rejuvenation within the foothills climatic zone.

These climatatic and geomorphic large-scale processes will, in turn, affect biogeochemical cycling throughout a wide range of climatic zones. Drawing these processes together, we can revisit the LCM and broaden the analytical scope of the model by assessing how climate and geomorphology, as a function of elevation, drive the accumulation or export of inorganic and organic nutrients (Figure 2.11). Due to climatological limitations and geomorphic conditions that vary by elevation, unique landcover zones develop that drive the creation of source and sink zones for transported nutrients.

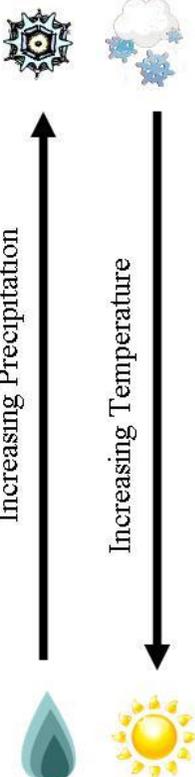
Zone	Geomorphology	Landscape	Biogeochemistry	Climate
 Alpine	Recent glacial scouring	Sparse vegetation, limited soil development	Limited weathering, high DIN, low DOC concentrations	 Increasing Precipitation ↑ ↓ Increasing Temperature
 Subalpine	Recent glacial deposits	Forested, deep layer of fresh sediment	Increased weathering, low DIN, high DOC concentrations	
 Montane	Slow erosion	Forested, deep soil profiles	Increased weathering, low DIN, high DOC concentrations	
 Foothills	Fluvial base level lowering	Forested, steep slopes, thin soils at base of catchment	Low DIN, high DOC concentrations, comparatively low seasonal export	

Figure 2.11: Conceptual model of geomorphic, landscape, and climatological controls on biogeochemical cycles along an elevational gradient that includes alpine, subalpine, montane and foothills landcover zones.

2.5.4 *Future Implications*

Looking to the future, three drivers of global change are likely to alter the biogeochemical cycles along the Colorado Front Range; (1) N deposition; (2) increasing air temperature; (3) mountain pine beetle outbreaks. The expanded LCM provides a useful framework from which to view these potential changes in nutrient dynamics. In large part, the landscape characteristics that are a function of elevation, geomorphology and climate will guide the degree to which these disturbances will effect surface water quality.

Increasing N deposition has resulted in zones of accumulation of nitrate in alpine lakes and streams, while export is limited in forested headwater catchments due to greater assimilation and plant uptake. However, the prospect of increasing air temperatures raises interesting questions as to how alpine system will respond. In some studies, increasing air temperature has been linked to greater nitrate export in alpine catchments due to increased net nitrification rates (Murdoch et al., 1998; Hong et al., 2005) and/or cryosphere melt (Williams et al., 2006; Baron et al., 2009). However, increasing temperatures have also been linked to treeline moving to higher elevations (Malanson et al., 2007). If the area of vegetated landcover increases with warmer temperatures, the alpine area that subsidizes nitrate will decrease, potentially providing a counterbalance against the effects of increased N-deposition.

The future nutrient cycle dynamics are further complicated by the widespread and fast-moving mountain pine beetle epidemic that is occurring in coniferous forests throughout the entire western United States. Following high tree mortality due to pine beetle kill, multiple aspects of terrestrial and aquatic chemistry are likely to change, both in the short-term as organic matter inputs and nutrient uptake change, and in the long-term as new plant communities

assemble in affected sites. Specifically, decaying wood and foliage after tree death could result in the release of carbon and other nutrients that could be exported to surface waters. The cycling of nutrients between soils and the trees will be interrupted as tree uptake ceases, making some fraction of those nutrients available for export (Romme et al., 2006). In a sense, pine beetle outbreak could potentially cause forested catchments to behave like alpine site in terms of N retention and export. While the catchments in this study remain largely unaffected to date, they are literally surrounded to the north, south, and west by regions that have experienced large outbreaks and can offer useful baseline data for biogeochemical and hydrological conditions prior to outbreaks.

2.6 Conclusions

While the LCM, as developed by Seastedt et al. (2004), provides a useful conceptual model for predicting source and sink areas as they relate to inorganic and organic nutrient transport processes in alpine catchments, the framework can be further extended to apply to multiple climatic zones by more explicitly incorporating elevational, geomorphic and climatological controls that drive landcover characteristics. The broadened scope of the revisited LCM helps extend the analytical power of the model to lower elevation headwater catchments and adds predictive insights into how these watersheds could potentially be altered in the face of global change.

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