

**OF MICROBES AND MEN: DETERMINING SOURCES OF NITRATE IN A HIGH  
ALPINE CATCHMENT IN THE FRONT RANGE OF COLORADO AND SCIENCE  
OUTREACH ON ALPINE HYDROLOGY**

**By KATYA A. HAFICH**

B.S. Environmental Science and B.A. Latin American Studies, University of New Mexico, 2010

A Thesis submitted to the  
Faculty of the Graduate School of the  
University of Colorado in partial fulfillment  
of the requirement for the degree of  
Master of Arts  
Department of Geography 2014

This thesis entitled:

**OF MICROBES AND MEN: DETERMINING SOURCES OF NITRATE IN A HIGH  
ALPINE CATCHMENT IN THE FRONT RANGE OF COLORADO AND SCIENCE  
OUTREACH ON ALPINE HYDROLOGY**

Written by  
Katya A. Hafich  
has been approved for the  
Department of Geography

---

Mark W. Williams, Chair

---

Noah P. Molotch

---

Natalie Mladenov

Date \_\_\_\_\_

The final copy of this thesis has been examined by the signatories, and we  
Find that both the content and the form meet acceptable presentation standards  
Of scholarly work in the above mentioned discipline.

## ABSTRACT

Hafich, Katya (M.A., Geography)

### **Of microbes and men: Determining sources of nitrate in a high alpine catchment in the Front Range of Colorado, and science outreach on alpine hydrology**

Thesis directed by Professor Mark W. Williams

High elevation ecosystems throughout the Colorado Front Range are undergoing a shift from nitrogen-limited systems to nitrogen-saturated systems, resulting in changes in alpine biota and water quality. Nitrate concentrations are increasing in surface water of the Green Lakes Valley (GLV) by  $0.27 \mu\text{mol L}^{-1}$  per year, but atmospheric deposition of dissolved inorganic nitrogen ( $\text{DIN} = \text{NH}_4^+ + \text{NO}_3^-$ ) has recently curtailed due to drought, leaving a gap in our understanding of the source of the increased export of nitrate. Current research suggests multiple theories to explain increased N suggested; increasing nitrogen deposition in precipitation, changing climate, melting cryosphere, and changing microbial communities. Research from GLV points to microbial hotspots of nitrification in barren soils, talus and rock glaciers—not atmospheric deposition—as the primary source of nitrate in surface waters. Increased nitrate levels could be also attributed to melting ice features (permafrost, Arikaree glacier, and a rock glacier) in GLV, which increases hydrologic connectivity that transports nitrate to surface waters in late summer. In this study, we aim to address this gap in understanding by employing a novel triple isotope method for the first time in an alpine catchment to quantify the terrestrial and atmospheric contribution of nitrate to numerous water types in GLV. The  $\Delta^{17}\text{O}—\text{NO}_3^-$  measurement retains an atmospheric signature through microbial processing, enabling us to directly measure atmospheric nitrate in the system. Results show that nitrate in surface waters, including talus, soil water and rock glacier melt, is more than 75% terrestrial, with the strongest atmospheric signals present during snowmelt. These results suggest that efforts to curtail

nitrogen emissions may be too little too late, as alpine catchment biogeochemistry has transitioned to a net nitrification system that is compromising water quality at high elevations. Still, a decrease in nitrogen emissions could have positive effect, hence we address the public awareness of the changes occurring in alpine hydrology with ScienceLIVE curriculum for K-12 students. The unit on Alpine Hydrology utilizes videos, social media, and lesson plans to educate students about the nitrogen cycle, glaciers, and hydrologic flowpaths.

## **DEDICATION**

I would like to dedicate this thesis to my brother-in-law, Patrick Mullen, who passed away at the end of the first year of graduate school. Patrick inspired me to work hard and play hard, without him I would never have entered the world of snow hydrology and backcountry skiing. As he taught through example in his own life, the limit to your accomplishments is your own ambition.

## ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Mark Williams, for supporting me and guiding me through my Master's research. I would also like to thank Dr. Natalie Mladenov and Dr. Noah Molotch for their help as committee members. I would like to thank Dr. Joseph Erbland and Dr. Joel Savarino for hosting me and teaching me to measure  $\Delta^{17}\text{O}\text{---NO}_3^-$  isotopes at the Laboratoire de Glaciologie et Géophysique de l-Environnement, at the Université Joseph Fourier, in Grenoble, France. I'd also like to thank those who have spent countless hours on Niwot Ridge, collecting data that I used in this thesis work: Dr. Nel Cain, Sandor Coscia, Jen Morse, Jeff Lipton, Morgan Zeliff, Jimmy Howe, John Knowles, Hillary Buchanan, and Rory Cowie. Thank you to Holly Hughes, Christine Seibold, Holly Schuss, Hope Humphries, Hanna Ding, Michael Brunetti, Jennah Shein and the rest of the staff of the Kiowa Lab for organizing, processing, and running my water samples. Thanks to Dr. Julie Graf, Dr. Kristin Swihard, Dr. Tammy Maldonado, Heidi Jo Freiburger, and Peter and Liesl Erb for their help with ScienceLIVE and outreach. Thanks to Dr. Elizabeth Root for her help with statistical analysis, and a big thanks to Laura Nash at the Graduate Writing Center for her help with writing style and organization. Thanks to the Semeria family for hosting me during my lab work in Grenoble. A big thanks to all of my close friends and family for their support through the ups and downs of my Master's career. And special thanks to my sister, Willa, and Patty and Davis Glasgow for their unending support and encouragement. And thanks to my parents, Michael and Michelle Hafich for their passion for education and the outdoors, which they have given me.

## TABLE OF CONTENTS

Abstract	iii
Dedication	v
Acknowledgements	vi

### **Chapter 1: The Science of the Alpine Nitrogen Cycle: Determining Sources of Nitrate in an Alpine Catchment Using Triple Oxygen Isotopes of Nitrate**

#### Abstract

1.1 Introduction.....	2
1.2 Site location.....	6
1.3 Methods.....	10
1.3.1 Sample collection.....	10
1.3.2 Laboratory analysis.....	11
1.3.3 Statistical methods.....	12
1.4 Results.....	14
1.4.1 Climate.....	14
1.4.2 Dissolved inorganic nitrogen in wet deposition.....	16
1.4.3 Dissolved inorganic nitrogen in surface and subsurface waters.....	21
1.4.4 Mixing model.....	29
1.4.5 Residence time of atmospheric nitrate.....	33
1.4.6 Geochemical weathering and nitrate production.....	35
1.5 Discussion.....	44
1.5.1 Sites with cryospheric features.....	48
1.5.2 Downstream sites: GLV stream, soil water, groundwater, and Martinelli.....	54
1.5.3 Atmospheric nitrate and the role of hydrologic connectivity.....	57
1.6 Conclusion.....	58

### **Chapter 2: Connecting Alpine Hydrology Research to the Classroom: ScienceLIVE Curriculum**

#### Abstract

2.1 Introduction.....	63
2.2 The history of ScienceLIVE.....	64
2.3 Curriculum description.....	65
2.3.1 The black box of alpine hydrology.....	65
2.3.2 The alpine nitrogen cycle.....	73
2.3.3 Glaciers on the move.....	76
2.4 Conclusion.....	80

References	81
------------	----

## LIST OF TABLES

Table 1	N concentrations and isotopes for all water types.....	18
Table 2	Seasonal DIN deposition in wetfall.....	20



## LIST OF FIGURES

1. Site location map of Green Lakes Valley.....	7
2. Annual mean snow depth at Green Lakes Valley 2005-2012.....	15
3. 2012 Climate and atmospheric deposition in Green Lakes Valley.....	17
4. Boxplots of N concentrations and isotopes for all water sources.....	22
5. Timeseries of N concentrations and isotopes for surface waters in Green Lakes Valley.....	23
6. Timeseries of N concentrations and isotopes for subtalus waters in Green Lakes Valley.....	25
7. Scatterplot of $\Delta^{17}\text{O—NO}_3^-$ and $\delta^{18}\text{O—NO}_3^-$ results.....	31
8. Decay curves fit to $\Delta^{17}\text{O—NO}_3^-$ for residence time analysis.....	34
9. Timeseries of geochemical weathering products in Green Lakes Valley water types.....	36
10. Boxplots of solutes used for PCA in all water types in Green Lakes Valley.....	37
11. Rock glacier PCA biplot.....	39
12. Arikaree glacier PCA biplot.....	41
13. Subtalus water PCA biplot.....	42
14. Green Lakes Valley stream PCA biplot.....	43
15. Martinelli PCA biplot.....	45
16. Scatterplot of $\delta^{18}\text{O—NO}_3^-$ and $\delta^{15}\text{N—NO}_3^-$ results.....	47
17. ScienceLIVE Alpine Hydrology research homepage.....	66
18. Black box of hydrology schematic.....	68
19. Alpine nitrogen cycle game placards.....	75
20. Picture of glacier chute setup.....	78

## CHAPTER 1

### Determining Sources of Nitrate in an Alpine Catchment Using Triple Oxygen Isotopes of Nitrate

#### Abstract

High elevation ecosystems throughout the Colorado Front Range are undergoing a shift from nitrogen-limited systems to nitrogen-saturated systems, resulting in changes in alpine biota and water quality. Nitrate concentrations are increasing in surface water of the Green Lakes Valley (GLV) by  $0.27 \mu\text{mol L}^{-1}$  per year, but atmospheric deposition of dissolved inorganic nitrogen ( $\text{DIN} = \text{NH}_4^+ + \text{NO}_3^-$ ) has recently curtailed due to drought, leaving a gap in our understanding of the source of the increased export of nitrate. Current research suggests multiple theories to explain increased N suggested; increasing nitrogen deposition in precipitation, changing climate, melting cryosphere, and changing microbial communities. Research from GLV points to microbial hotspots of nitrification in barren soils, talus and rock glaciers—not atmospheric deposition—as the primary source of nitrate in surface waters. Increased nitrate levels could be also attributed to melting ice features (permafrost, Arikaree glacier, and a rock glacier) in GLV, which increases hydrologic connectivity that transports nitrate to surface waters in late summer. In this study, we aim to address this gap in understanding by employing a novel triple isotope method for the first time in an alpine catchment to quantify the terrestrial and atmospheric contribution of nitrate to numerous water types in GLV. The  $\Delta^{17}\text{O}—\text{NO}_3^-$  measurement retains an atmospheric signature through microbial processing, enabling us to directly measure atmospheric nitrate in the system. Results show that nitrate in surface waters, including talus, soil water and rock glacier melt, is more than 75% terrestrial, with the strongest atmospheric signals present during snowmelt. Abundant terrestrial nitrate from GLV is

consistent with carbon limitation in barren soil areas in microbially dominated landscape types—talus, rock glaciers, and permafrost—that export nitrate to streams draining alpine watersheds. These results suggest that efforts to curtail nitrogen emissions may be too little too late, as alpine catchment biogeochemistry has transitioned to a net nitrification system that is compromising water quality at high elevations.

## **1.1 Introduction**

The highest elevations of a mountain catchment are a source of water, nutrients, and particulates; all elements of water quality that have cascading effects on downstream ecology (Vannote et al. 1980, Seastedt et al. 2004). In the Colorado Front Range of the USA, high alpine catchments are currently in transition from nitrogen (N) limitation to N saturation (Williams and Tonnessen 2000; Elser et al. 2009). This transition to an N-saturated system, in part, is due to short growing seasons, sparse vegetation, thin soils, and harsh climate that make high-elevation catchments especially susceptible to environmental change (Williams and Tonnessen 2000).

This transition to an N-saturated system is illustrated by the increase in nitrate concentrations in surface waters draining the Green Lake (GL4) catchment, part of the Niwot Ridge Long Term Ecological Research site (NWT LTER), located in the Front Range of Colorado. At the outlet of GL4 from 1985 to 2009, annual volume weighted-mean nitrate concentrations have increased at a rate of  $0.27 \mu\text{mol N year}^{-1}$  (Barnes et al. 2013). In turn, this increase in the concentration of nitrate in surface waters has led to a significant increase in annual nitrate export from the outlet of GL4 (Barnes et al. 2013). This phenomenon of increasing nitrate export in surface waters in high elevation catchments has been observed across the world; in Rocky Mountain National Park in Colorado (Baron et al. 2009), the Alps of northern Italy (Rogora 2007), and southern Norway (de Wit et al. 2007).

The increase in anthropogenic deposition of inorganic N ( $\text{DIN} = \text{NH}_4^+ + \text{NO}_3^-$ ) in wetfall is widely accepted as a driver of increased nitrate export from catchments (Slemmons et al. 2013, Williams et al. 1996). In the southern Rockies, high elevation and proximity to growing urban populations correlates with increasing levels of DIN deposition in wet fall (Nanus et al. 2008). Niwot Ridge, located just west of the highly populated Denver metro area, had the highest loading of inorganic N measured at National Atmospheric Deposition Program (NADP) sites across Colorado and Wyoming, at  $4.6 \text{ kg ha}^{-1} \text{ year}^{-1}$  from 1995-1999 (Burns 2004). On Niwot Ridge, annual volume-weighted mean (VWM) concentrations of nitrate at NADP site CO02 more than doubled from  $< 10 \mu\text{eq L}^{-1}$  in 1985 to over  $20 \mu\text{eq L}^{-1}$  in 2000 and ammonium concentrations demonstrated a fivefold increase, from  $< 3 \mu\text{eq L}^{-1}$  in 1985 to over  $15 \mu\text{eq L}^{-1}$  in 2004 (NADP 2013). Yet, while annual deposition of DIN decreased from 2000-2009 at Niwot Ridge due to drought conditions, nitrate yield in surface waters continued to rise (Barnes et al. 2013), suggesting that increased deposition of DIN in wetfall alone does not sufficiently explain increased nitrate export from the GLV catchment.

In addition to increasing concentrations of DIN in wet deposition, a concurrent change in climate confounds changes in nutrient cycling (Baron et al. 2009). Long-term climate records from Niwot Ridge show trends towards a warmer, drier climate. From 1983 to 2007, average annual air temperatures increased by  $1.08 \text{ }^\circ\text{C decade}^{-1}$  (Clow 2010). Precipitation has decreased at high elevations by  $2.32 \text{ mm yr}^{-1}$  at D1 (on Niwot Ridge, just north of GL4), in large part driven by a regional drought from 2000-2007 (Barnes et al. 2013). Warmer, drier climates drive glacier and permafrost melt in high elevation areas of the Colorado Front Range, as seen by an increase in geochemical weathering products during late summer and early fall (Barnes et al. 2013, Baron et al. 2009). Similarly, rock glacier melt in the GLV had the highest concentrations

of solutes in late fall during drought years 2000-2003 compared to wetter years (Williams et al. 2007). Research suggests that ice melt in late summer and early autumn increases hydrologic connectivity that flushes out excess nitrate built up by microbial activity in talus, blockfields, and the rock glacier (Barnes et al. 2013, Williams et al. 2007, Ley et al. 2004, Brooks et al. 1998, Williams et al. 1997).

Microbial activity also plays a substantial role in determining nitrogen concentrations in alpine catchments throughout the year (Slemmons et al. 2013, Ley et al. 2004). Studies conducted by the NWT LTER program have shown that microbial communities are active throughout the winter as microbial N content along with pools of inorganic N in alpine soils and in so-called “barren soils” increases through winter and spikes during snowmelt (Ley et al. 2004, Schadt et al. 2003, Brooks and Williams 1999, Brooks et al. 1998, 1997, 1996). Moreover, in summer months, Mladenov et al. (2012) observed aeolian deposition of large amounts of organic matter, and hypothesizes that organic matter in dust may serve as an energy source for heterotrophic microbial communities in the alpine that produce ammonium as a byproduct that is then nitrified by autotrophic microbes. Bieber et al. (1998) showed that both N mineralization and nitrification occur in talus fields, however we have not been able to quantify how much of the nitrate produced in talus fields actually reaches the stream at the hydrologic axis of GLV.

There are competing theories on the source of nitrate in streams draining high-elevation catchments. One theory is that the increased nitrate in wet deposition (and perhaps also in dry deposition) flows directly into surface waters. For example, Saros et al. (2010) demonstrated that the presence of glaciers within alpine watersheds in the Rocky Mountains more strongly influenced nitrate concentrations in high-elevation lake ecosystems than any other geomorphic or biogeographic characteristic, hypothesizing that relatively high sublimation and evaporation rates

on glaciers concentrates N, resulting in high nitrate concentration in glacial meltwaters that then flow to the high-elevation lakes with little or no contact with soils or the subsurface. An alternative theory is that increased amounts of DIN deposition in wetfall cause an increase in net nitrification of high-elevation catchments, and that this terrestrial nitrate is then transported to streams by infiltrating snowmelt (Williams et al. 2011). More recent theories suggest that a combination of changes in biogeochemical cycling initiated by N saturation and cryospheric melt due to a warming climate are causing increased nitrate concentrations (Barnes et al. 2013, Baron et al. 2009, Petrone et al. 2006, Jones et al. 2005). Each of these theories has been inferred using measurements of nitrate and geochemical weathering products in surface and subsurface waters, but research has yet to provide a widely accepted explanation of increased nitrate export from high elevation catchments.

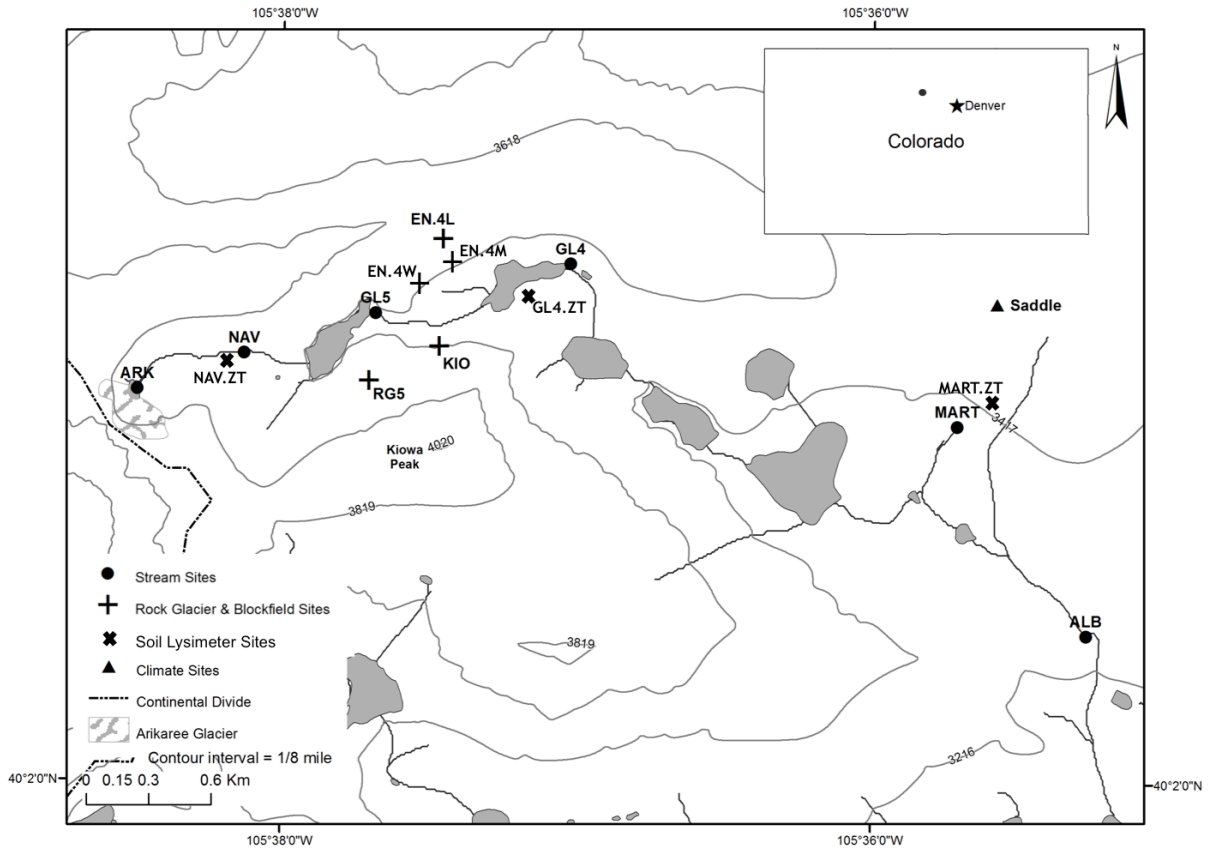
Further work is needed on the process-level controls to fill the gap in our understanding of the contribution of atmospheric deposition versus terrestrial nitrate production. We aim to address the question: is increased nitrate in surface waters of high-elevation catchments from atmospheric nitrate deposition directly transported to surface waters, is it a result of exported nitrate from net nitrification in microbial communities? Or is it some combination of these two sources? And do these sources differ by landscape type, by elevation, and by time? By understanding the inputs of DIN and the resulting controls on biogeochemical cycling in high elevation catchments, we can better understand current trends in nitrate export and how these may change in response to both changes in DIN deposition and climate.

To answer our questions, we collected water samples from numerous sources in GLV in the spring and summer of 2012 to analyze for triple isotopes of nitrate. The isotopes  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate have been used to identify sources of nitrate in alpine catchments (Nanus et al. 2008,

Sickman et al. 2003, Campbell et al. 2002), but  $\Delta^{17}\text{O}$  is difficult to measure and has yet to be used in a high alpine system.  $\Delta^{17}\text{O}$  has been used in a subalpine, N-limited catchment on Niwot Ridge adjacent to GLV. Darrouzet-Nardi and others (2011) found that atmospheric nitrate accounted for ~17% of nitrate in stream water in Como Creek, and had a residence time of about 6.6 days. As Darrouzet-Nardi and others (2011) demonstrated,  $\Delta^{17}\text{O}$  in nitrate is especially useful as oxygen bearing species that are produced terrestrially typically follow the mass-dependent *terrestrial fractionation line* in which  $\delta^{17}\text{O} \approx 0.52 * \delta^{18}\text{O}$ . Nitrate produced in the atmosphere through oxidation by ozone ( $\text{O}_3$ ) of  $\text{NO}_x$  ( $\text{NO}_x = \text{NO}$  and  $\text{NO}_2$ ) shows a significant positive deviation from the terrestrial fractionation line due to mass-independent fractionation (Alexander et al. 2009). To capture this deviation,  $\Delta^{17}\text{O}$  is annotated as  $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 * \delta^{18}\text{O}$  (Thiemens et al. 2006). Non-polar atmospheric  $\Delta^{17}\text{O}-\text{NO}_3^-$  values range from 20 – 35 ‰, whereas microbial  $\Delta^{17}\text{O}-\text{NO}_3^-$  always have a value of 0 (Michalski et al. 2004). Using concurrent measurements of  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ , and  $\Delta^{17}\text{O}$  in the nitrate molecule, along with measurements of concentrations of DIN, we aim to determine whether sources of nitrate in waters of the Green Lakes Valley and Niwot Ridge are atmospheric or microbial (terrestrial) in origin, and how those sources may change spatially and temporally.

## **1.2 Site location**

Green Lakes Valley is an east-facing glaciated valley headed on the Continental Divide about 30 miles west of the Boulder-Denver-Fort Collins metro area (Fig. 1). It is the headwaters of North Boulder Creek within the City of Boulder Watershed, which has been closed to the public access since the 1950's. Green Lakes Valley (GLV) is also part of the NWT LTER program, where climate has been recorded continuously at the D1 (3,700 m) and subalpine C1



**Figure 1.** Site location map of Green Lakes Valley adapted from Barnes et. al (2013). Temperature and precipitation are measured a climate station Saddle. Weekly water samples were collected at the Arikaree Glacier (ARK), Navajo bench (NAV), Green Lake 5 (GL5), Rock Glacier (RG5), Green Lake 4 (GL4), and Martinelli (MART). Stream flow gauging stations are located at GL4 and MART. Soil water samples were collected weekly or as water was available at Navajo Bench (NAV.ZT), Green Lake 4 (GL4.ZT), and Martinelli (MART.ZT). Talus runoff was collected weekly at KIO and EN.4L, EN.4M, and EN.4W.



(3,021 m) meteorological stations since the early 1950's. Mean annual temperature at D1 is  $-3.7^{\circ}\text{C}$  (Williams et al., 1996). Average annual precipitation is approximately 1000 mm, about 80% of which falls as snow (Caine 1995).

The 225-ha GL4 watershed within the GLV is defined by steep slopes, glacial cirques, semi-permanent snowfields, exposed bedrock, talus outcrops, sparse vegetation, and undeveloped soils (Erickson et al. 2005). Ridges defining the valley have bedrock composed of Precambrian schists and gneisses, the Silver Plume quartz monzonite, and Audubon-Albion stock (Williams et al. 2006). Consistent with Williams et al. (1997), we adopt the term talus to include blockfields, felsenmeers, talus cones and talus sheets below cliffs.

Talus slopes in the valley above GL4 are predominantly straight and steep, with angles in excess of  $32^{\circ}$  and a planar form (Rapp, 1960). Soils are relatively undeveloped within talus formations and in nearby colluvium; some areas retain accumulations of fine particles (clays, sands) and organic materials that support vegetation (Bieber et al. 1998, Williams et al. 1997). Soil depths within talus vary from  $<0.05$  m to 1 m with no developed soil horizons (Bieber et al. 1998). Discontinuous permafrost is present above 3,500 m in Niwot Ridge and within the GL4 watershed (Leopold et al. 2013, Janke 2005, Ives and Fahey 1971).

The valley floor is mostly vegetated with willows and grasses on developed soils that comprise about 20% of the basin area above the outlet of GL4. Vegetated sites on talus are composed primarily of the graminoids *Kobresia myosuroides* and *Deschampsia caespitosa* and the forbs *Acomastylis rossii* and *Bistorta bistortoides*. A qualitative increase in vegetation has been observed on talus areas and “barren soils” as plants move higher and higher in the valley (M. Williams, personal communication), possibly due to a warming climate and increased colonization of barren soils by microbial communities (King et al. 2010).

GLV contains a series of paternoster lakes that stretch eastward from the 9-ha Arikaree glacier (ARIK) (Fig. 1). Immediately downstream of ARIK, the North Boulder Creek flows through subsurface paths to the Navajo bench (NAV), where it turns into a braided stream that flows through a series of lakes, including Green Lake 5 (GL5) and Green Lake 4 (GL4). A rock glacier (RG5) is between GL5 and GL4 on the south side of the valley. Several talus sites are sampled in GLV; one at the base of the north-facing side of Kiowa Peak (KIO), and three sites on the south-facing slope beneath D1 (EN.4W, EN.4M and EN.4L) (Fig. 1). The 8-ha Martinelli (3,380 m) catchment is a snowfield-dominated catchment originating on Niwot Ridge northeast of GLV. In contrast to GLV, Martinelli (MART) does not contain any glacial features or permafrost due to its southern aspect and lower elevation.

Niwot Ridge forms the northern boundary of the GLV, and is the site of other experimental areas, including a meteorological station, snow lysimeters, a subnivean laboratory and an Aerometrics wet-chemistry precipitation collector at the Saddle CO02 site (3520m a.s.l.; Fig. 1) operated as part of the National Atmospheric Deposition Program (NADP). A second site at C1 (3015 m a.s.l.; Fig. 1), NADP CO90, is located below treeline to the east of Niwot Ridge. The NWT LTER program operates a third Aerometrics wet-chemistry precipitation collector following NADP protocols at the Soddie site (3345 ma.s.l.). However, this site is not part of the NADP network, which allows the NWT LTER program to analyze wet deposition samples for solutes not analyzed as part of NADP, including dissolved organic carbon (DOC), dissolved organic nitrogen (DON), total dissolved phosphorus (TDP), dissolved organic phosphorus (DOP), and stable water isotopes and the triple isotopes of nitrate.

## 1.3 Methods

### 1.3.1 *Sample collection*

*Snow and snowmelt.* Physical and chemical properties of snow were measured weekly at two sites on Niwot Ridge (Saddle and Soddie) following the protocols presented in Williams et al. (1999; 1996). Snowmelt water was collected in 1-m<sup>2</sup> snow lysimeters before contact with the ground (Williams et al., 1996). Snowmelt water flowed by gravity from the snow lysimeters about 5 m into a subnivian laboratory, where grab samples were collected approximately daily. Annual snow surveys were conducted in GLV between 1996 and 2012 at maximum accumulation following the protocol of Erickson et al. (2005); here, we report values from 2005 to 2012. The number of snow depth measurements ranged from a low of 274 in 2008 to a high of 679 in 2007. Additionally, five or six snow pits are sampled for physical and chemical properties during the snow survey.

*Surface and Talus Waters.* Surface waters were collected as grab samples about weekly during the 2012 ice-free season from ARIK, RG5 outflow, and the outflow of GL5, GL4, and MART. Subtalus water was collected as grab samples when water was available from KIO, EN.4L, EN.4W, and EN.4M. On 22 May 2012, we conducted a synoptic survey of subtalus water during snowmelt. Eleven samples were chosen from the survey to spatially represent GLV. Samples were collected in polyethylene bottles that were soaked with deionized (DI) water overnight and then rinsed with DI water five times; bottles were further rinsed three times with sample water at the time of collection. All water samples were stored at 4° C in the dark and transported to our wet chemistry laboratory within 7 days for analysis.

*Soil water.* Zero-tension soil lysimeters, constructed of halved 400-mm long sections of PVC pipe 250 mm in diameter, capped on one end, and plumbed to drain into a 1-L storage

bottle connected to the surface with tygon tubing, were installed in the mid-1980s (Litaor, 1993). Four zero-tension soil lysimeters were installed on the southeast side of GL4, about 20 m from the lake on a northwestern aspect. Two zero-tension soil lysimeters following the same design were installed on the Navajo Bench in 2009, between ARK and GL5. Sample collection began when soil lysimeters were snow free. After snowmelt, soil lysimeters rarely contained water except after rain events.

*Groundwater.* Piezometers with slots at the bottom 1.5 m were installed in 2005 at the Saddle site at depths of 6.3 m (SAD.D3) and 8.4 m (SAD.D4) in bedrock units of Tertiary quartz monzonite and Precambrian Silver Plume quartz monzonite. Groundwater samples were collected using a teflon bailer weekly using the same bottles used to sample surface waters.

### **1.3.2 Laboratory analysis**

All water and snow samples were initially analyzed at the Kiowa Environmental Wet Chemistry Lab at the University of Colorado Boulder for pH, acid neutralizing capacity (ANC), conductance, major ions, and reactive silicate (Si) following the protocols presented by Williams et al. (2006). Snow samples were stored frozen (-20°C) for 1 to 2 months until analysis. For analysis, snow samples were placed in covered polyethylene buckets and melted overnight at room temperature and then analyzed as for water samples. Upon arrival to the Kiowa Lab, water samples were immediately filtered through pre-rinsed (300 mL), 47-mm Gelmen A/E glass fibre filters with ca. 1- $\mu\text{m}$  pore size. Detection limits for all major solutes were less than 0.2  $\mu\text{eq L}^{-1}$ .

Subsamples for isotopic analysis of nitrate were filtered through 0.2 glass fiber filters, then frozen (-20°C) until analysis in November 2012. Before freezing, nitrite concentrations were measured to ensure that there were not sufficient amounts of nitrite present to interfere with the

analysis of the isotopic content of nitrate. Nitrite in all samples was below  $0.88 \mu\text{mol L}^{-1}$ , and deemed too low to interfere with isotopic analysis of nitrate (Hastings et al. 2004).

All samples analyzed for nitrate isotopes were sent to the Laboratoire de Glaciologie et Géophysique de l'Environnement, Université Joseph Fourier, Grenoble, France in October 2012. For analysis, frozen samples were thawed at room temperature. An on-line bacterial method and mass spectrometry (Morin et al. 2009, Kaiser et al. 2007) were used to determine the isotopic content of nitrate ( $\Delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{15}\text{N}$ ). A minimum of 50 nmol of nitrate was converted to gaseous  $\text{N}_2\text{O}$  under anaerobic conditions by the denitrifying bacteria *Pseudomonas aureofaciens*. The  $\text{N}_2\text{O}$  was then decomposed into a mixture of  $\text{O}_2$  and  $\text{N}_2$  by passing through a gold tube heated to  $900^\circ\text{C}$ . The mixture of  $\text{O}_2$  and  $\text{N}_2$  was then separated by gas chromatography and injected into an Isotope Ratio Mass Spectrometer (IRMS; Thermo Finnigan MAT 253). Isotopic ratios were internally standardized with  $\text{N}_2$  and  $\text{O}_2$  gas standards. International nitrate reference materials (USGS 32, 34, and 35 (Bohlke et al. 2003)) were run as blanks through the entire process for calibration. Raw values were then compared to the reference values for a bulk approach correction for any isotopic effect that may have occurred throughout the analytical procedure. The overall accuracy of the method is calculated following Morin et al. (2009), using  $1.5\sigma$  of the residuals from the linear regression between the measured standards and their expected values. For this analysis, the calculated uncertainty values were 2.5 ‰, 2.7 ‰, and 1.4 ‰ for  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ , and  $\delta^{15}\text{N}$ , respectively.

### **1.3.3 Statistical methods**

A two-member mixing model utilized  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values to quantify the contribution of atmospheric nitrate in wetfall (rain and snow) versus terrestrial nitrate in water samples. The atmospheric end member was the mean  $\Delta^{17}\text{O}$  value of rain and snow samples. The soil end

member is 0 ‰, which is the  $\Delta^{17}\text{O}$  signature of nitrate formed by microbial processes such as nitrification (Michalski et al. 2004). A similar approach was used to determine atmospheric and terrestrial contributions to nitrate in surface waters using  $\delta^{18}\text{O}$  of nitrate. The calculation to determine terrestrial nitrate contribution using  $\Delta^{17}\text{O}$  values was as follows:

$$\text{Terrestrial } \text{NO}_3^- = \text{Total } \text{NO}_3^- \left( \frac{\text{Sample } \Delta^{17}\text{O} - \text{Atmospheric } \Delta^{17}\text{O}}{\text{Terrestrial } \Delta^{17}\text{O} - \text{Atmospheric } \Delta^{17}\text{O}} \right) \quad (1)$$

The same equation was used with  $\delta^{18}\text{O}$  values.

We also calculated the residence time of atmospheric nitrate in the watershed using the approach of Darrouzet-Nardi et al. (2012), by fitting  $\Delta^{17}\text{O}$  values in surface waters to an exponential decay equation and calculating the inverse of the decay constant. The result describes the characteristic turnover time of nitrate at the sample site.

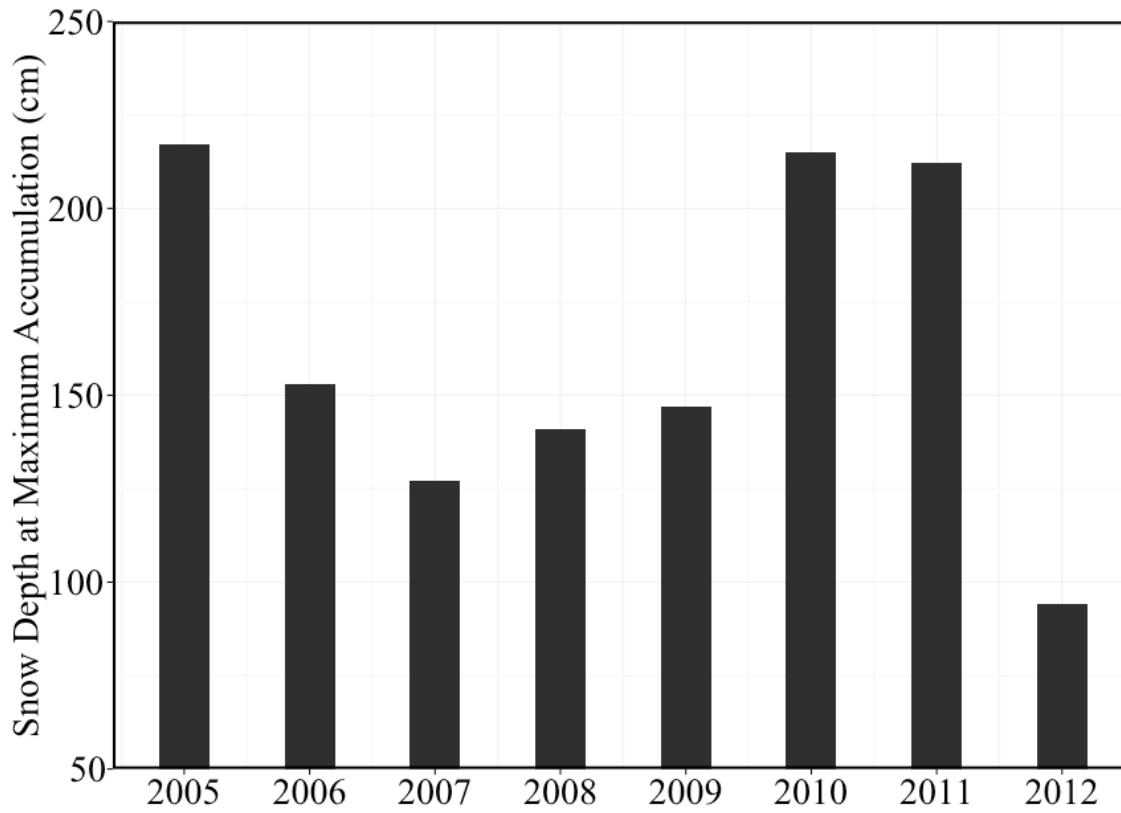
A Principal Components Analysis (PCA) was run on water types following the methods of Christopherson and Hooper (1992) as an independent check on whether terrestrial nitrate identified by the nitrate isotopes is also associated with geochemical weathering products. End-member mixing analysis (EMMA) is based in part on PCA, and has been previously used in the GLV for Martinelli and GL4 by Liu et al. (2004) and for the RG5 rock glacier by Williams et al. (2006). We use the conservative tracers identified by those authors as conservative tracers of geochemical weathering, which are ANC,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ , Si, and  $\delta^{18}\text{O}$ . We plotted PCA results of geochemical weathering products with total nitrate, terrestrial nitrate, and atmospheric nitrate onto biplots to examine associations between the various forms of nitrate and geochemical weathering products. We calculated concentrations of atmospheric and terrestrial nitrate by multiplying the  $\Delta^{17}\text{O}$ — $\text{NO}_3^-$  mixing model results with measurements of total nitrate concentrations. All solute units were in  $\mu\text{eq L}^{-1}$ .

We also ran correlation matrix analysis to compare how concentrations ( $\text{mg L}^{-1}$ ) of total nitrate, absolute atmospheric nitrate, and absolute terrestrial nitrate in water samples responded to forcing by precipitation amount and concentrations. Terrestrial and atmospheric contributions to nitrate in these waters were calculated as in the PCA analysis above. Precipitation was measured as daily precipitation summed over the same week that streams were sampled. Atmospheric inputs of DIN were calculated as weekly precipitation amount multiplied by concentrations of ammonium and nitrate in wetfall that week, providing weekly DIN loading in wetfall ( $\text{mg ha}^{-1} \text{wk}^{-1}$ ). Because discharge was available for GL4 outlet and Martinelli, instead of concentrations we evaluated how weekly specific nitrate yields ( $\text{mg ha}^{-1} \text{wk}^{-1}$ ) responded to atmospheric inputs of DIN. Nitrate yields were estimated as the product of concentrations and the accumulated water discharge, following the protocols presented in Hood et al. (2003) and Barnes et al. (2013). For our analysis, we calculated specific yield for GL4 and MART by dividing the weekly yield of nitrate by the area (ha) of each catchment. For all analyses, we then tested for correlations among the parameters above as well as lag times of 1 and 2 weeks. If all variables were parametric, the Pearson's  $r$  was used. In the case where variables were not parametric, Spearman's  $\rho$  was used.

## **1.4 Results**

### ***1.4.1 Climate***

Compared to the long-term climate record at NWT LTER, 2012 had an anomalously warm and dry winter and spring, and one of the wettest summers. Snow depth measured at maximum accumulation ranged from 0 to 650 cm with an average depth of 94 cm ( $n=495$ ) (Fig.



**Figure 2.** Annual mean snow depth measured at maximum snow accumulation from 2005 to 2012 for the 225-ha Green Lake 4 catchment. The number of snow depth measurements ranges from 274 in 2008 to 679 in 2007.

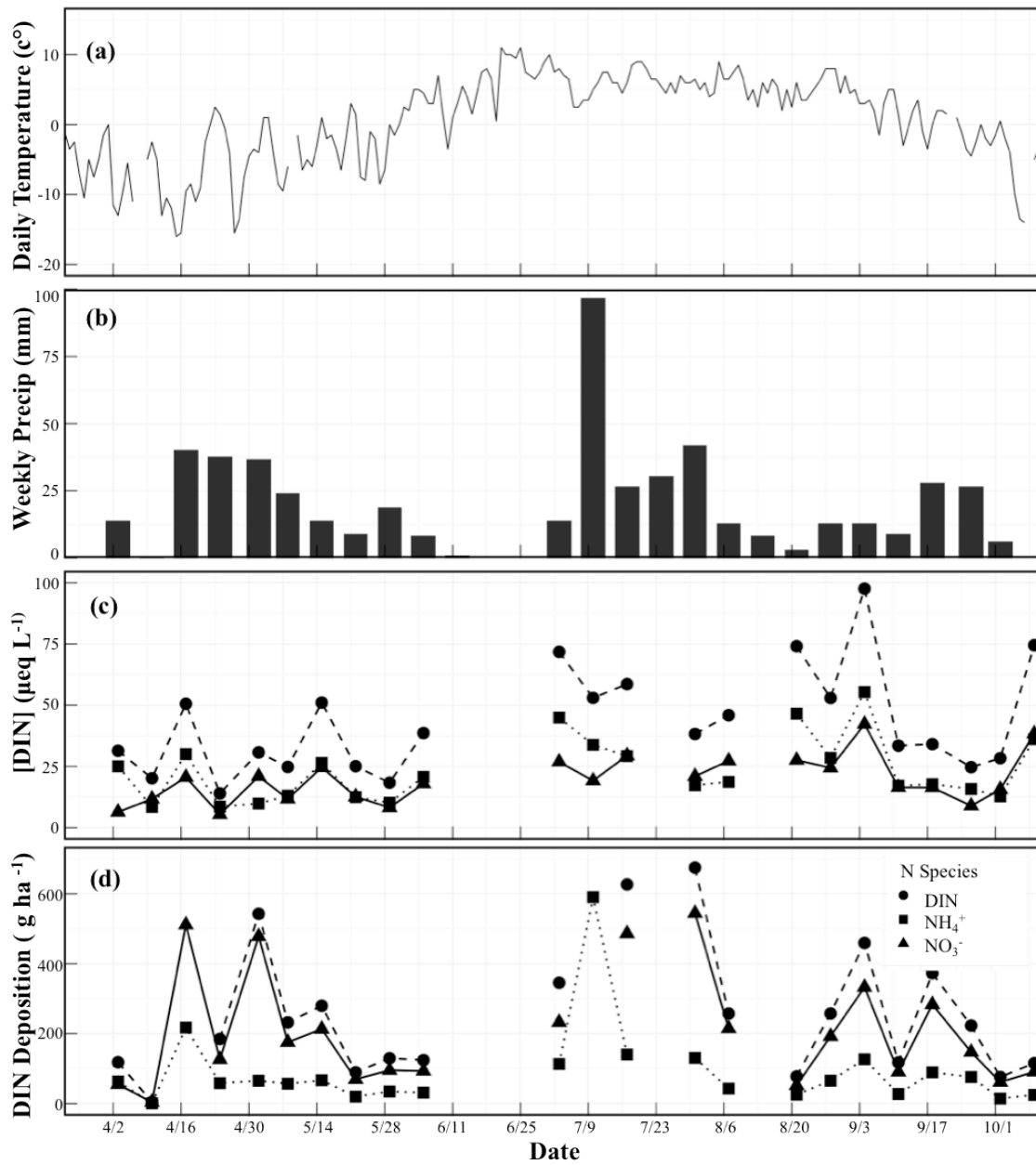


2). The mean snow depth in 2012 of 94 cm was less than the previous low of 123 cm in 2002 (Williams et al. 2006), the largest drought year in Colorado history at that time. Snowmelt started in mid April when daily average air temperatures rose above 0°C, several weeks earlier than normal (Fig. 3a). While the precipitation remained below normal through June 2012, July 2012 was the wettest July of the previous 25 years at the Saddle, with a total of 196 mm recorded at the Saddle CO2 NADP site (Fig 3b). The 2012 climate was anomalous compared to the last 25 years, but exemplifies trends in lower April 1 SWE and increased summer precipitation in Colorado (Clow 2010), and may be indicative of future climate.

#### ***1.4.2 Dissolved inorganic nitrogen in wet deposition***

The primary form of DIN in the snowpack was nitrate (Table 1). The VWM concentration of nitrate at maximum snow accumulation in 2012 was 7.0  $\mu\text{eq L}^{-1}$  and ranged from 5.2 to 11  $\mu\text{eq L}^{-1}$ . Ammonium concentrations in snow were slightly lower with a mean of 6.3  $\mu\text{eq L}^{-1}$  and ranged from 4.1 to 10  $\mu\text{eq L}^{-1}$ . DIN concentrations in snow thus averaged 13  $\mu\text{eq L}^{-1}$ . Snowmelt samples were collected before contact with the ground at the beginning of snowmelt when DIN concentrations are higher during the ionic pulse (Campbell et al. 1995, Williams and Melack 1991); few samples were collected at the tail end of snowmelt in part because the snowpack melted faster than normal in 2012. Average concentrations of nitrate at 18  $\mu\text{eq L}^{-1}$  and ammonium at 11  $\mu\text{eq L}^{-1}$  in snowmelt were two to three times higher than in the snowpack. Nitrate concentrations ranged between 7.4 and 32  $\mu\text{eq L}^{-1}$  and ammonium concentrations ranged between 2.0 and 66  $\mu\text{eq L}^{-1}$  in snowmelt.

The mean  $\pm$  SE value for  $\Delta^{17}\text{O—NO}_3^-$  ( $n = 13$ ) in the seasonal snowpack was  $28.6 \pm 2.9\text{‰}$ . This value was similar to the  $28.6 \pm 0.2\text{‰}$  ( $n = 3$ ) reported for the snowpack at maximum accumulation for the subalpine Como Creek by Darrouzet-Nardi et al. (2012), suggesting a fairly



**Figure 3.** 2012 Climate and atmospheric deposition in Green Lakes Valley. Time series of (a) daily temperature ( $^{\circ}\text{C}$ ) at Saddle, (b) weekly precipitation (mm) at Saddle (c) concentrations ( $\mu\text{eq L}^{-1}$ ) of DIN in wet deposition measured weekly, using Soddie chemistry data, and (d) weekly loads ( $\text{g ha}^{-1}$ ) of DIN deposition using Soddie chemistry and Saddle precipitation measurements.

Water Type	Mean NO <sub>3</sub> <sup>-</sup>	Mean NH <sub>4</sub> <sup>+</sup>	Mean δ <sup>18</sup> O	Mean δ <sup>17</sup> O	Mean δ <sup>15</sup> N
Rain	18.3 ± 6.7 (n=13)	21.9 ± 10.7 (13)	70.7 ± 2.3 (10)	26.3 ± 1.8 (13)	-3.1 ± 2.1 (13)
Snow	7.0 ± 1.9 (13)	6.3 ± 1.8 (13)	–	28.6 ± 2.9 (13)	0.6 ± 1.1 (13)
Snowmelt	18.5 ± 6.8 (14)	11.5 ± 16.4 (14)	71.6 ± 4.6 (4)	27.1 ± 2.9 (14)	0.4 ± 2.3 (14)
Groundwater	8.8 ± 1.3 (14)	0.7 ± 1.1 (14)	-6.2 ± 2.2 (14)	1.4 ± 0.6 (14)	3.6 ± 0.9 (13)
Soil Water	61.7 ± 94.8 (20)	4.0 ± 4.3 (20)	12.7 ± 12.8 (17)	5.7 ± 4.1 (20)	2.0 ± 3.4 (20)
Subtalus Water	35.7 ± 21.8 (37)	0.9 ± 1.3 (37)	14.2 ± 7.1 (33)	6.6 ± 3.0 (37)	-0.6 ± 1.5 (37)
Rock Glacier	80.7 ± 14.9 (8)	0.5 ± 1.2 (8)	13.7 ± 2.5 (8)	5.3 ± 1.4 (8)	0.8 ± 1.7 (8)
Arikaree	22.0 ± 11.6 (8)	9.7 ± 6.7 (8)	20.1 ± 15.4 (7)	8.9 ± 5.8 (7)	0.2 ± 1.7 (8)
GLV Stream	22.7 ± 10.1 (33)	1.2 ± 1.7 (33)	12.0 ± 4.9 (31)	5.6 ± 2.3 (33)	1.3 ± 2.2 (33)
Martinelli	8.5 ± 4.2 (6)	0.8 ± 1.5 (6)	26.2 (1)	9.1 ± 1.9 (6)	0.1 ± 1.2 (6)

**Table 1.** Average DIN concentrations ( $\mu\text{eq L}^{-1}$ ) and isotopic values of nitrate (per mil(‰)) at GLV and Niwot Ridge, 2012 reported with SD and sample size (in parenthesis).

consistent value for  $\Delta^{17}\text{O—NO}_3^-$  in snow at Niwot Ridge sampled at maximum accumulation. The average  $\delta^{15}\text{N—NO}_3^-$  values in snow were slightly positive at  $0.6 \pm 1.1 \text{ ‰}$ . There was little spatial or temporal variation in the isotopic values of nitrate in the seasonal snowpack (data not shown). Snowmelt ( $n = 15$ ) had similar average values compared to snow for both  $\Delta^{17}\text{O—NO}_3^-$  and  $\delta^{15}\text{N—NO}_3^-$ , suggesting little or no isotopic fractionation during snowmelt (Table 1). The  $^{18}\text{O—NO}_3^-$  value in snowmelt ( $n=4$ ) was  $71.6 \pm 4.6\text{‰}$ . We were unable to analyze for  $\delta^{18}\text{O—NO}_3^-$  in snow samples due to insufficient sample quantity.

DIN concentrations in summer rain were higher than in the seasonal snowpack by a factor of 3 or so (Table 1). Average values for both nitrate and ammonium in rainfall were about  $20 \mu\text{eq L}^{-1}$ , with nitrate ranging from  $8.2$  to  $29 \mu\text{eq L}^{-1}$  and ammonium ranging from  $9.5$  to  $45 \mu\text{eq L}^{-1}$  (Fig. 3c). Average DIN concentrations summer rain were thus  $38 \mu\text{eq L}^{-1}$ . This pattern of higher concentrations of DIN in summer rain compared to the seasonal snowpack at NWT LTER is consistent over many years (Mladenov et al. 2012).

DIN loads were highest in July concurrent with large rain events (Fig. 3d). The summer (Jun-Aug) of 2012 had the highest recorded DIN deposition of  $2 \text{ kg N ha}^{-1}$  in the 25-year record of NADP site CO02, twice the 25 year average deposition of  $1.1 \text{ kg N ha}^{-1}$  (Table 2, NADP 2013). Winter (Dec-Feb) deposition was average, spring (Mar – May) deposition was below average, and fall (Sep –Nov) deposition was also below average (Table 2). While summer had anomalously high N deposition, the total deposition for the 2012 water year was  $4.2 \text{ kg N ha}^{-1}$ , below the 25-year average of  $6 \text{ kg N ha}^{-1}$ .

The isotopic content of nitrate in summer rain was similar to snow and snowmelt for  $\Delta^{17}\text{O—NO}_3^-$  and  $\delta^{18}\text{O—NO}_3^-$ , but not for  $\delta^{15}\text{N—NO}_3^-$  (Table 1). The average value  $\pm$  SE of  $\Delta^{17}\text{O—NO}_3^-$  was  $26.3 \pm 1.8\text{‰}$  ( $n = 13$ ) and  $\delta^{18}\text{O—NO}_3^-$  was  $70.7 \pm 2.3\text{‰}$  ( $n = 10$ ). In contrast to snow, all

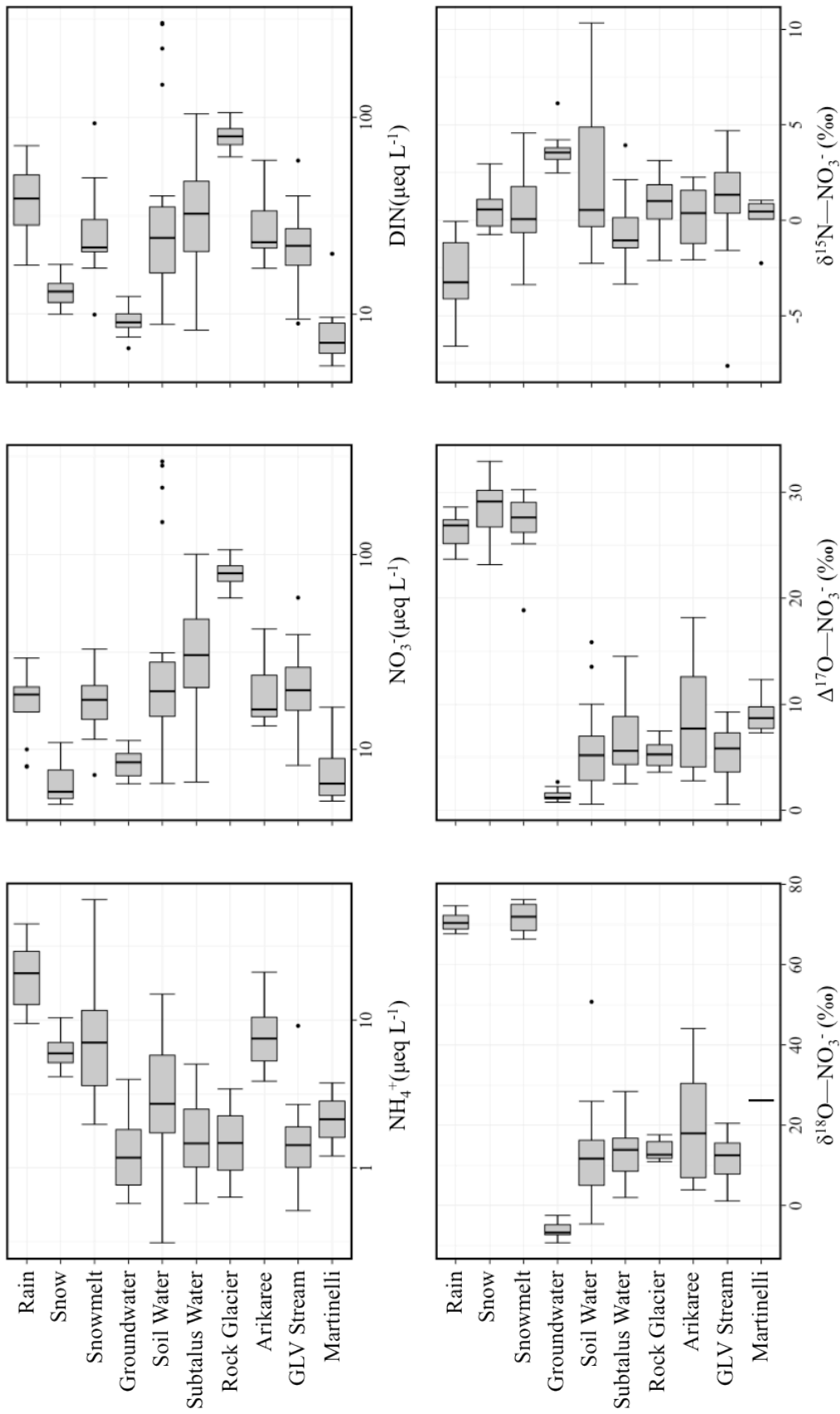
<b>Season</b>	<b>2012 DIN Deposition</b>	<b>1987-2012 Average DIN Deposition</b>
Winter (Dec-Feb)	1.2	1.2
Spring (Mar-May)	1.2	1.4
Summer (Jun-Aug)	2.0	1.1
Fall (Sep-Nov)	1.0	1.2
Water Year Total	4.2	6

**Table 2.** Seasonal DIN deposition in wetfall from NADP (2013). All values are in kg N ha<sup>-1</sup>.

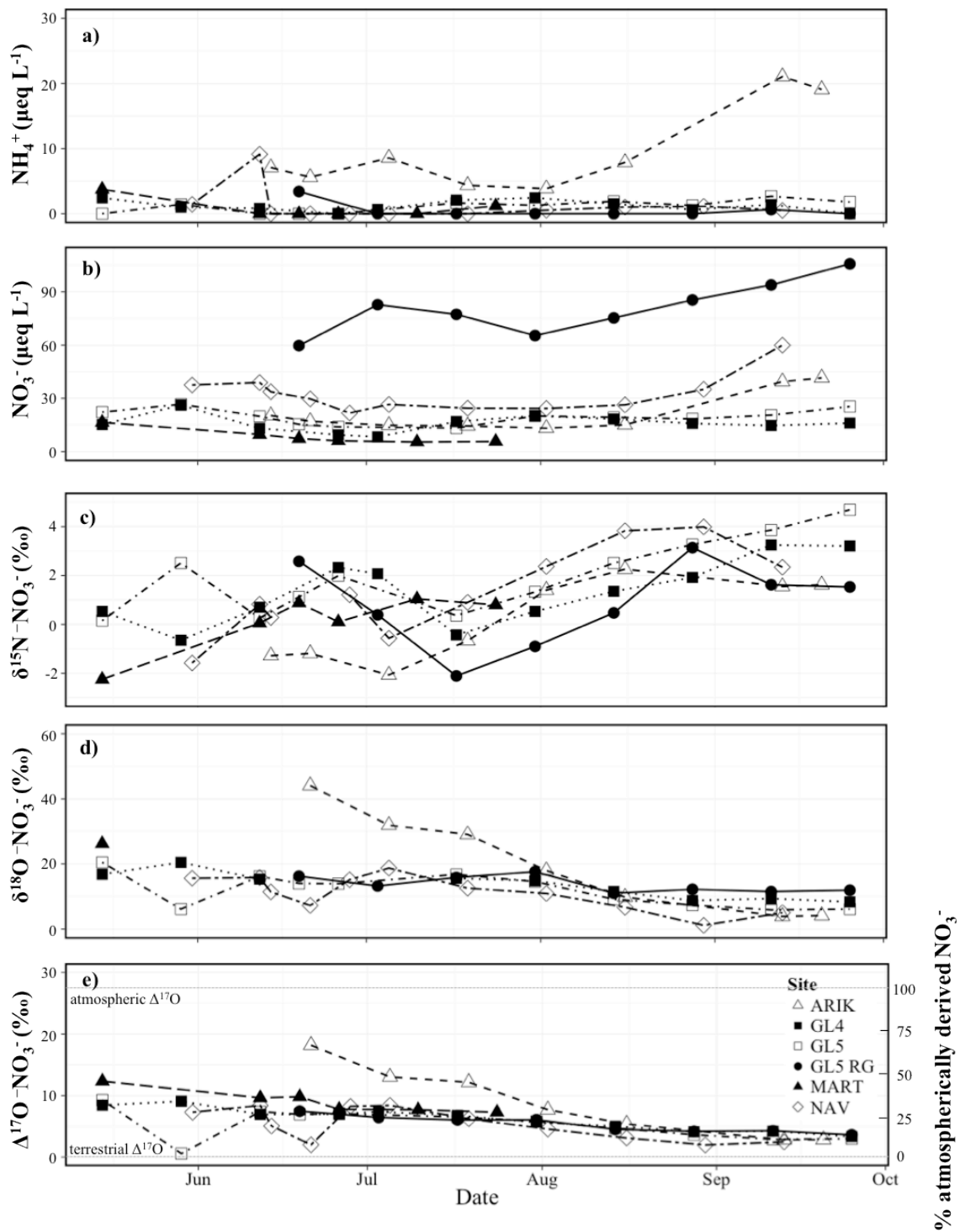
$\delta^{15}\text{N—NO}_3^-$  ( $n = 13$ ) values were negative, ranging between  $-0.1$  and  $-6.6\text{‰}$  with a mean of  $-3.06 \pm 2.1\text{‰}$ . The differences in the  $\delta^{15}\text{N—NO}_3^-$  of rain and snow are consistent with the results of Nanus et al. (2008), which suggests the possibility of a seasonal change in the sources of nitrate in wet deposition to the Rocky Mountains.

### ***1.4.3 Dissolved inorganic nitrogen in surface and subsurface waters***

*GLV Stream.* In contrast to snow and summer rain, the dominant form of DIN in surface waters was nitrate (Fig. 4). The arithmetic mean concentration at Navajo, GL5, and GL4 was  $22 \mu\text{eq L}^{-1}$  for  $\text{NO}_3^-$  and  $1.2 \mu\text{eq L}^{-1}$  for  $\text{NH}_4^+$  ( $n=33$ ), thus a mean DIN of  $23 \mu\text{eq L}^{-1}$ . Nitrate concentrations at GL4, GL5, and Navajo ranged between  $8.3$  and  $60 \mu\text{eq L}^{-1}$ , while ammonium concentrations were much lower and ranged from below detection limits to  $9.1 \mu\text{eq L}^{-1}$ . Nitrate concentrations in surface water generally follow a seasonal pattern with an initial increase on the rising limb of the hydrograph, much lower concentrations at peak flows, then a recovery to higher values on the recession limb of the hydrograph (Liu et al. 2004, Hood et al. 2003). However, the early season increase in nitrate values in 2012 was highly muted compared to most other years, likely due to the very low snowpack and fast snowmelt (Fig. 5). After a small peak in late May/early June, nitrate concentrations were steady at the GL5 and GL4 outlets, but significantly increased in August and September at NAV (Fig. 5). The values of the oxygen isotopes of nitrate in surface waters showed a general tendency to be closer to terrestrial values than atmospheric values (Fig. 4). The mean  $\pm$  SE  $\delta^{18}\text{O—NO}_3^-$  was  $12 \pm 5\text{‰}$  ( $n=31$ ) and the mean  $\pm$  SE  $\Delta^{17}\text{O—NO}_3^-$  was  $5.6 \pm 2.3\text{‰}$  ( $n=33$ ). Oxygen isotope values of nitrate generally decreased through the summer, and converged to a common value of about  $2\text{‰}$  at the end of summer for both  $\Delta^{17}\text{O—NO}_3^-$  and  $\delta^{18}\text{O—NO}_3^-$  (Fig. 5). The mean  $\pm$  SE  $\delta^{15}\text{N—NO}_3^-$  was  $1.3 \pm 2.2\text{‰}$ .  $\delta^{15}\text{N—NO}_3^-$  values increased in August and September at all sites (Fig. 5).



**Figure 4.** Boxplots showing median and quartiles (box for 25% and 75% and whisker for 5% and 95%) for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{DIN}$ ,  $\delta^{18}\text{O}-\text{NO}_3^-$ ,  $\Delta^{17}\text{O}-\text{NO}_3^-$ ,  $\delta^{15}\text{N}-\text{NO}_3^-$  values in Rain, Snow, Snowmelt, Groundwater, Soil Water, Subtalus Waters, Rock Glacier, Arikaree, GLV Stream, and Martinelli. Points indicate outliers within the sample population for a given sample type/location.



**Figure 5.** Time series of a) concentrations of  $\text{NH}_4^+$ , b) concentrations of  $\text{NO}_3^-$ , c) the isotopic signature of nitrogen ( $\delta^{15}\text{N}$ ), d) the isotopic signature of oxygen ( $\delta^{18}\text{O}$ ) and e) oxygen ( $\Delta^{17}\text{O}$ ) throughout the summer of 2012 in surface waters in Green Lakes Valley. Results for the two-member mixing model for the two sources of  $\text{NO}_3^-$  are shown on the right side of the  $\Delta^{17}\text{O}$  panel. The line and point types represent different sampling sites (see legend in *bottom right*).

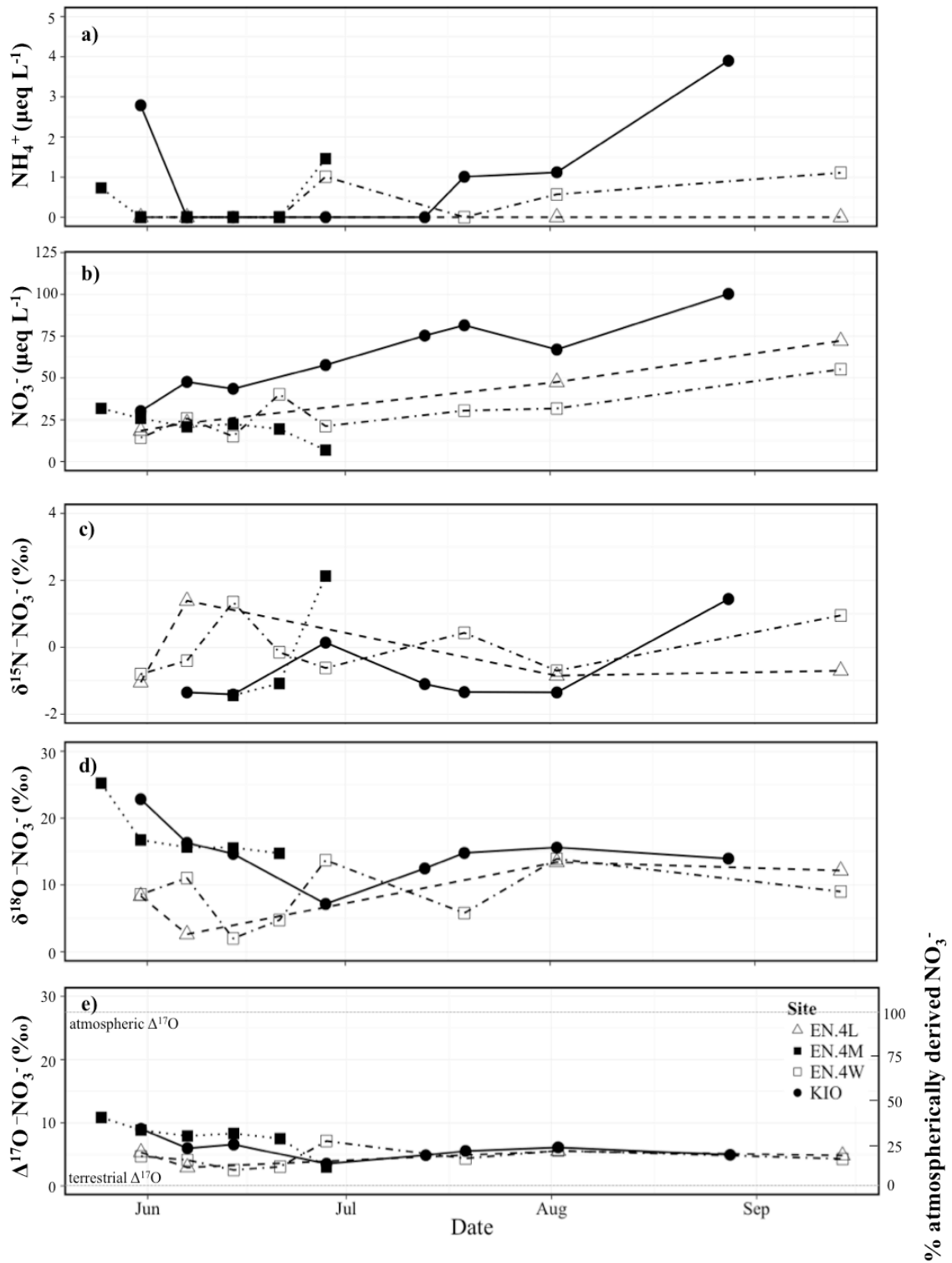


The concentrations of DIN at MART were the lowest of all sites (Fig. 4). The mean nitrate concentration was  $8.5 \mu\text{eq L}^{-1}$  ( $n=6$ ) and the mean ammonium concentration was  $0.83 \mu\text{eq L}^{-1}$  ( $n=6$ ), thus the mean DIN was  $9.3 \mu\text{eq L}^{-1}$ . Nitrate concentration steadily decreased through the season at MART, beginning at  $16.5 \mu\text{eq L}^{-1}$  in May, and ending at  $5.4 \mu\text{eq L}^{-1}$  in July (Fig. 5). The MART stream stopped flowing in August shortly after the Martinelli snowfield melted out.

Oxygen isotopes in nitrate at MART were closer to precipitation values than oxygen isotope values at the other sampling sites for surface waters, with the highest measured value of  $\delta^{18}\text{O—NO}_3^-$  of  $26.2 \text{‰}$  and a mean  $\pm$  SE  $\Delta^{17}\text{O—NO}_3^-$  of  $9.1 \pm 1.9 \text{‰}$  ( $n=6$ ). The initial maximum  $\Delta^{17}\text{O—NO}_3^-$  value of  $12.3 \text{‰}$  in May was higher than all other values for surface water, but  $\Delta^{17}\text{O—NO}_3^-$  values decreased similar to the other surface water sites through the season (Fig. 6). The mean  $\pm$  SE  $\delta^{15}\text{N—NO}_3^-$  was  $0.1 \pm 1.2 \text{‰}$  ( $n=6$ ). Similar to the GLV stream sites,  $\delta^{15}\text{N—NO}_3^-$  values at MART increased through the summer (Fig. 6).

*Groundwater.* Groundwater had low N concentrations and low variability compared to surface water in GLV. Average nitrate concentrations in groundwater of  $8.5 \mu\text{eq L}^{-1}$  were similar to snowmelt and lower than summer rain (Table 1). In contrast, the mean ammonium concentration of  $0.69 \mu\text{eq L}^{-1}$  was much lower than in either the seasonal snowpack or summer rains. The mean DIN concentration of groundwater of  $9.2 \mu\text{eq L}^{-1}$  was similar to the low DIN concentrations at MART (Fig. 4).

The oxygen isotopes of nitrate in groundwater were much lower than in snow or rain (Fig. 4). The mean  $\pm$  SE  $\Delta^{17}\text{O—NO}_3^-$  was  $1.4 \pm 0.6 \text{‰}$  ( $n = 14$ ), very close to the terrestrial end-member of 0. Similarly, the  $\delta^{18}\text{O—NO}_3^-$  value of  $-6.2 \pm 2.2 \text{‰}$  ( $n = 14$ ) was much lower than in either snow or rain. In contrast, the  $\delta^{15}\text{N—NO}_3^-$  ( $n = 13$ ) values were on the high end of the range, with a mean  $\pm$  SE of  $3.6 \pm 0.9 \text{‰}$ . There was no seasonal pattern in either concentrations



**Figure 6.** Time series of a) concentrations of NH<sub>4</sub><sup>+</sup>, b) concentrations of NO<sub>3</sub><sup>-</sup>, c) the isotopic signature of nitrogen (δ<sup>15</sup>N), d) the isotopic signature of oxygen (δ<sup>18</sup>O) and e) oxygen (Δ<sup>17</sup>O) throughout the summer of 2012 in sublatus waters of Green Lakes Valley. Results for the two-member mixing model for the two sources of NO<sub>3</sub><sup>-</sup> are shown on the right side of the Δ<sup>17</sup>O panel. The line and point types represent different sampling sites (see legend in *bottom right*).

or isotopic values of nitrate in groundwater (data not shown).

*Soil water.* DIN concentrations in soil water were much more variable relative to all other water types in GLV (Fig. 4). Nitrate values ranged from 6.7 to 300  $\mu\text{eq L}^{-1}$  with a mean of 62  $\mu\text{eq L}^{-1}$ . Ammonium concentrations ranged from 0 to 15  $\mu\text{eq L}^{-1}$  with a mean of 4.0  $\mu\text{eq L}^{-1}$ . There appeared to be no consistent variation with time, but there was variation with location. The lowest-elevation lysimeters located at Green Lake 4 were more variable compared to soil lysimeters at the higher-elevation sites at Kiowa and Navajo Bench. For example, nitrate values in soil water samples collected near Green Lake 4 on May 31 and July 19 were an order of magnitude higher than the rest of the samples of soil water on those dates, with concentrations of nitrate ranging from 146 to 285  $\mu\text{eq L}^{-1}$ .

Average values of oxygen isotopes of nitrate in soil water were in the range between precipitation and groundwater values (Fig. 4). The mean  $\pm$  SE  $\Delta^{17}\text{O—NO}_3^-$  was  $5.7 \pm 4.1$  ‰ (n = 20) and the  $\delta^{18}\text{O—NO}_3^-$  value was  $12.7 \pm 12.8$ ‰ (n = 17). The  $\delta^{15}\text{N—NO}_3^-$  values were extremely variable, ranging between  $-2.3$  and  $10.3$ ‰.  $\delta^{15}\text{N—NO}_3^-$  values were most variable at the beginning of the season during snowmelt, but hovered closer to zero in August and September (data not shown).

*Subtalus Water.* Concentrations of DIN in subtalus water increased throughout the season, and were in general higher than concentrations of DIN in streams. The mean value of the concentration of nitrate in waters draining talus sites was 35  $\mu\text{eq L}^{-1}$ , well above the mean values in rain and snow, and more similar to soil water (Fig. 4). There was a temporal pattern to nitrate values, which ranged from 6.8 to 100  $\mu\text{eq L}^{-1}$ , with concentrations increasing throughout the season at all sites except one (Fig. 6). At EN.4M, N concentrations decreased at the beginning of the season in June until July when runoff ceased for the remainder of the season. In contrast to

nitrate, the average values of ammonium in water draining talus sites was less than  $1 \mu\text{eq L}^{-1}$ , with no temporal patterns. Ammonium contribution to DIN values was negligible, thus the mean DIN was  $36 \mu\text{eq L}^{-1}$ .

A synoptic survey of subtalus water was conducted on May 22 during peak runoff to investigate spatial variation of nitrate concentrations in subtalus water, as subtalus waters have high nitrate concentrations and talus dominates a large area in GLV. The survey enabled us to distinguish if the high nitrate concentrations in talus were terrestrial in origin or the result of the release of atmospheric nitrate held within the snowpack in the form of an ionic pulse. Nitrate concentrations ranged from  $13.4$  to  $46 \mu\text{eq L}^{-1}$  with a mean nitrate concentration of  $26 \mu\text{eq L}^{-1}$ , which was similar to the other talus sites collected in May that had a mean value of  $22 \mu\text{eq L}^{-1}$  on May 31. The ammonium concentration of the subtalus waters in the synoptic survey had a range of  $0$  to  $5.3 \mu\text{eq L}^{-1}$  and a mean of  $1.7 \mu\text{eq L}^{-1}$ , which was slightly higher than the EN and KIO talus site May 31 mean of  $0.7 \mu\text{eq L}^{-1}$ .

The isotopic values of oxygen and nitrogen in the nitrate in water draining talus sites varied widely and showed opposing trends over time. The mean  $\pm$  SE  $\delta^{18}\text{O—NO}_3^-$  was  $14.2 \pm 7.1\text{‰}$  ( $n = 33$ ) and the mean  $\pm$  SE  $\Delta^{17}\text{O—NO}_3^-$  was  $6.6 \pm 3.0\text{‰}$  ( $n = 37$ ). At all sites,  $\Delta^{17}\text{O—NO}_3^-$  and  $\delta^{18}\text{O—NO}_3^-$  values declined sharply at the beginning of the summer until July, when values increased until August (Fig. 5). Oxygen isotope results were notably similar between sites in late summer (August and September) at around  $5\text{‰}$  ( $\Delta^{17}\text{O—NO}_3^-$ ) and  $13\text{‰}$  ( $\delta^{18}\text{O—NO}_3^-$ ). With a mean  $\pm$  SE value of  $-0.6 \pm 1.5\text{‰}$  ( $n = 37$ ),  $\delta^{15}\text{N—NO}_3^-$  results showed an opposite seasonal pattern, sharply increasing at the beginning of the summer (especially at EN.4M), decreasing midsummer, and increasing again at the end of the season (Fig. 6). The synoptic survey of subtalus waters on May 22 had higher oxygen isotope values for nitrate than the talus site

samples on May 31, suggesting a slightly higher portion of atmospheric nitrate throughout the valley in subglacial water during snowmelt. The talus survey mean  $\pm$  SE  $\delta^{18}\text{O}\text{---NO}_3^-$  was  $19.6 \pm 8.9\text{‰}$  (n = 8), whereas the talus site mean  $\delta^{18}\text{O}\text{---NO}_3^-$  was  $14.1 \text{‰}$  (n = 4) on May 31. The talus survey mean  $\pm$  SE  $\Delta^{17}\text{O}\text{---NO}_3^-$  was  $8.8 \pm 3.8 \text{‰}$  (n = 11), compared to the talus site mean  $\Delta^{17}\text{O}\text{---NO}_3^-$  of  $7.0 \text{‰}$  (n = 4).  $\delta^{15}\text{N}\text{---NO}_3^-$  values survey values were also higher than the site values on May 31, the talus survey mean  $\pm$  SE was  $-0.6 \pm 1.9\text{‰}$  (n = 11), and the talus site  $\delta^{15}\text{N}\text{---NO}_3^-$  mean was  $-1.8 \text{‰}$  (n=4).

*Rock Glacier Melt.* Rock glacier melt had the highest DIN concentrations of all sites over the sampling period, and was primarily in the form of nitrate (Fig. 4). Nitrate concentrations ranged from 60 to 106  $\mu\text{eq L}^{-1}$ , with a mean concentration of 80  $\mu\text{eq L}^{-1}$ . Nitrate concentrations remained in the 60-80  $\mu\text{eq L}^{-1}$  range through the summer until concentrations increased to above 100  $\mu\text{eq L}^{-1}$  in September (Fig. 5). Ammonium concentrations were much smaller, with a mean of 0.5  $\mu\text{mol L}^{-1}$ .

The isotopic content of nitrate in rock glacier melt was similar to that of soil water and talus runoff, falling between precipitation and groundwater values (Fig. 4). The mean  $\pm$  SE  $\Delta^{17}\text{O}\text{---NO}_3^-$  value was  $5.3 \pm 1.4\text{‰}$  (n=8), and the mean  $\delta^{18}\text{O}\text{---NO}_3^-$  was  $13.7 \pm 2.5\text{‰}$  (n=8).  $\Delta^{17}\text{O}\text{---NO}_3^-$  values steadily decreased through the summer from 7.5 in June to 3.6 in September (Fig. 5). In contrast,  $\delta^{18}\text{O}\text{---NO}_3^-$  and  $\delta^{15}\text{N}\text{---NO}_3^-$  values had no seasonal pattern.  $\delta^{15}\text{N}\text{---NO}_3^-$  values had a mean  $\pm$  SE of  $0.8 \pm 1.7\text{‰}$  (n=8) and ranged from -2.1 to 3.1  $\text{‰}$ .

*Arikaree Glacier Melt.* The DIN concentration in melt from Arikaree glacier was similar to snowmelt, which is consistent with previous observations that Arikaree runoff behaves chemically similar to snowmelt (Williams et al., 2006). The mean nitrate concentration was 22  $\mu\text{eq L}^{-1}$  (n=8), and ranged from 13 to 41  $\mu\text{eq L}^{-1}$ . Ammonium accounted for roughly a third of

DIN, with a mean concentration of  $9.7 \mu\text{eq L}^{-1}$ . Arikaree typically has high ammonium concentration early in the season, which can be explained by the release of  $\text{NH}_4^+$  in Arikaree melt water that has minimal contact with soil, thus decreasing opportunities for sorption and immobilization (Hood et al. 2003). Ammonium concentrations were actually highest at the end of the season in 2012 (Fig. 6), which may be attributed to the low snow year and wet summer. Seasonally, DIN concentrations decreased from June until August, and sharply increased in late summer to a peak concentration of  $60 \mu\text{eq L}^{-1}$  (Fig. 6).

While Arikaree DIN concentrations were similar to snowmelt, Arikaree  $\text{NO}_3^-$  oxygen isotope values were closer to soil water and talus than precipitation or snowmelt values (Fig. 4). The mean  $\pm$  SE  $\Delta^{17}\text{O—NO}_3^-$  was  $8.9 \pm 5.8\text{‰}$ , and the mean  $\pm$  SE  $\delta^{18}\text{O—NO}_3^-$  was  $20 \pm 15\text{‰}$  (n=7). Arikaree oxygen isotopes of nitrate were the highest measured value of all surface waters, with a maximum of  $18\text{‰}$  ( $\Delta^{17}\text{O—NO}_3^-$ ) and  $20\text{‰}$  ( $\delta^{18}\text{O—NO}_3^-$ ) in June, and steadily decreased throughout the summer to a minimum of  $2.8\text{‰}$  ( $\Delta^{17}\text{O—NO}_3^-$ ) and  $3.9 \text{‰}$  ( $\delta^{18}\text{O—NO}_3^-$ ) in late September (Fig. 6).  $\delta^{15}\text{N—NO}_3^-$  values were similar to surface water, the rock glacier, snow, and snowmelt, with a mean  $\pm$  SE of  $0.2 \pm 1.7\text{‰}$  (n=8).  $\delta^{15}\text{N—NO}_3^-$  values increased through the summer (Fig. 6), from  $-2.1$  to  $2.3 \text{‰}$ , and slightly decreased at the end of the summer.

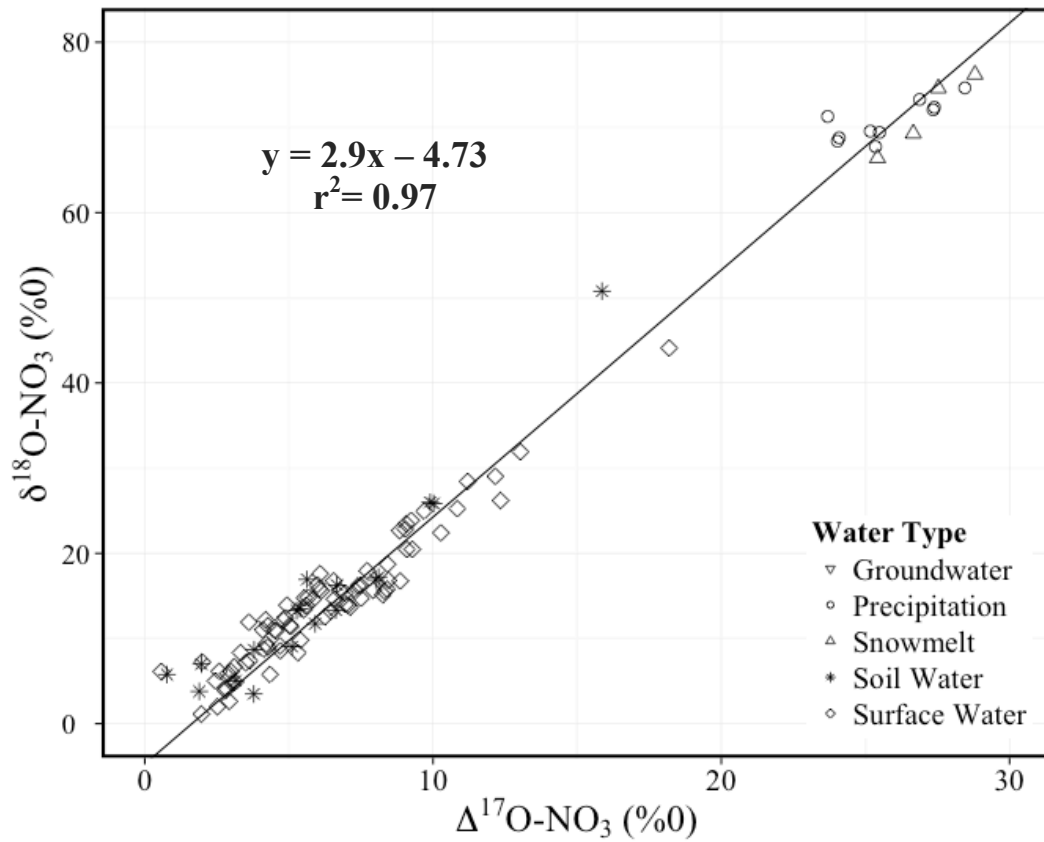
#### **1.4.4 Mixing model**

We used a two-member mixing model to determine the percentage of atmospheric and terrestrial nitrate in waters of the GLV, using  $\Delta^{17}\text{O—NO}_3^-$  and  $\delta^{18}\text{O—NO}_3^-$  values to parameterize each end-member. Atmospheric samples (rain and snow) had a mean  $\pm$  SE  $\Delta^{17}\text{O—NO}_3^-$  of  $27.4 \pm 0.5\text{‰}$  (n=26). These values are well within the documented atmospheric range of  $20\text{--}35\text{‰}$  for  $\Delta^{17}\text{O—NO}_3^-$  (Morin et al. 2009) and suggest that  $27.4\text{‰}$  is a reasonable value of  $\Delta^{17}\text{O—NO}_3^-$  to represent atmospheric nitrate in the mixing model. Similarly, the mean value of

atmospheric nitrate for  $\delta^{18}\text{O}\text{---NO}_3^-$  of  $70.7 \pm 0.7\text{‰}$  ( $n=10$ ) is similar to the range in precipitation from +71 to +78‰ for annual VWM  $\delta^{18}\text{O}\text{---NO}_3^-$  reported by Nanus et al. (2008) from 7 high-elevation NADP sites in the Rocky Mountains, and suggest this value is a reasonable end-member for atmospheric  $\delta^{18}\text{O}\text{---NO}_3^-$  in the mixing models.

The terrestrial end-member for  $\Delta^{17}\text{O}\text{---NO}_3^-$  is simply 0‰, which is the  $\Delta^{17}\text{O}$  signature of nitrate formed by microbial processes such as nitrification (Michalski et al. 2004). However, the terrestrial end-member for  $\delta^{18}\text{O}\text{---NO}_3^-$  is not well constrained (Kendall 1998). To illustrate, Sickman et al. (2003) used a value of 10.5‰ from early season stream waters to parameterize the  $\delta^{18}\text{O}\text{---NO}_3^-$  value for the terrestrial component of a similar two component mixing to quantify the atmospheric and terrestrial contributions to streamflow in the high-elevation and snowmelt-dominated Emerald Lake Watershed in the Sierra Nevada's of California. To estimate the value of  $\delta^{18}\text{O}\text{---NO}_3^-$  for the terrestrial component of our mixing model, we plotted the  $\Delta^{17}\text{O}\text{---NO}_3^-$  and  $\delta^{18}\text{O}\text{---NO}_3^-$  values against each other.  $\Delta^{17}\text{O}\text{---NO}_3^-$  and  $\delta^{18}\text{O}\text{---NO}_3^-$  values are strongly correlated (Fig. 7) with an  $r^2$  of 0.97. Using the known  $\Delta^{17}\text{O}\text{---NO}_3^-$  terrestrial value of 0 and the intercept of the linear regression between the two isotopic ratios, we calculated a microbial  $\delta^{18}\text{O}\text{---NO}_3^-$  signature of -4.7 ‰. This terrestrial value is similar to that calculated by (Darrouzet-Nardi et al. 2011) using the same approach for the subalpine Como Creek catchment on Niwot Ridge.

Mixing model results using  $\Delta^{17}\text{O}\text{---NO}_3^-$  and  $\delta^{18}\text{O}\text{---NO}_3^-$  values indicated that the majority of nitrate in samples collected from all waters were of terrestrial origin, though there was spatial variation among sites. Using  $\Delta^{17}\text{O}\text{---NO}_3^-$ , the mean percentage of terrestrial nitrate in groundwater was 95%, 80% in soil water, 78% in subalpus water, 81% in rock glacier melt, 68% at Arikaree, and 80% in the GLV stream. The snowmelt-fed Martinelli catchment had a



**Figure 7.** Relationship between  $\Delta^{17}\text{O}-\text{NO}_3^-$  and  $\delta^{18}\text{O}-\text{NO}_3^-$ .  $n = 173$ . Linear regression slope, intercept, and correlation coefficient are shown in the *upper left*. Surface water includes GLV Stream, Arikaree glacier, the rock glacier, subtalus waters, and Martinelli.



terrestrial nitrate contribution of 67%, very similar to the 68% released from the Arikaree Glacier. Results using  $\delta^{18}\text{O}\text{---NO}_3^-$  values did not change more than 3%, except for in groundwater and rock glacier melt. Using  $\delta^{18}\text{O}\text{---NO}_3^-$ , groundwater nitrate was 100% terrestrial, and rock glacier melt was 76% terrestrial. The difference between  $\delta^{18}\text{O}\text{---NO}_3^-$  and  $\Delta^{17}\text{O}\text{---NO}_3^-$  mixing model results is likely due to the higher variation of  $\delta^{18}\text{O}$  in water sources that contribute oxygen (Kendall 1998) to terrestrial nitrate in groundwater and the rock glacier.

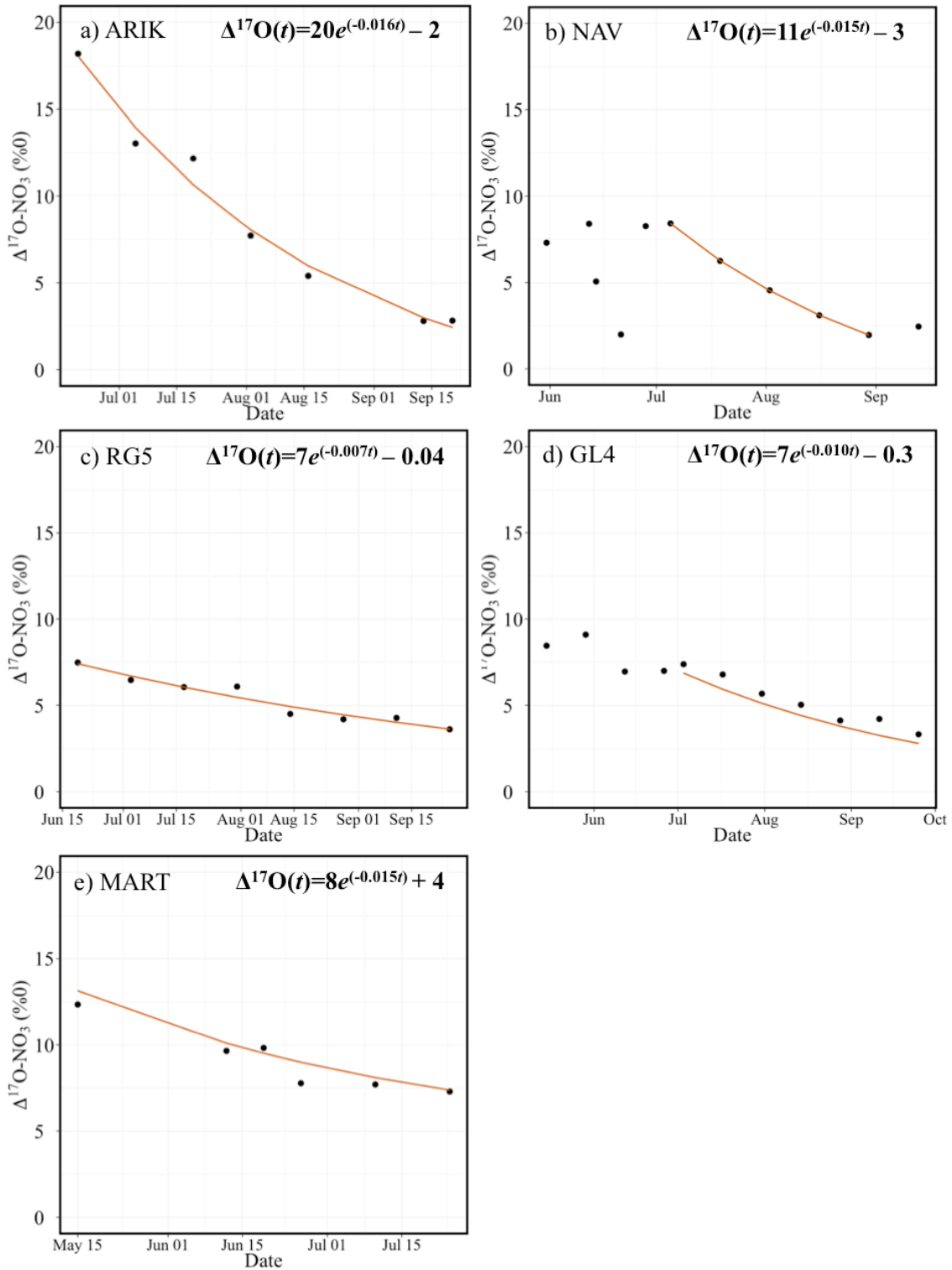
Atmospheric and terrestrial contributions varied with time. The largest contributions of atmospheric nitrate to water samples occurred in early spring during snowmelt. Using  $\Delta^{17}\text{O}\text{---NO}_3^-$  mixing model values, the Arikaree glacier had the highest contribution of atmospheric  $\text{NO}_3^-$  of 66% on June 21, which decreased as the summer progressed to 10% in late summer (Fig. 5). Martinelli had the second highest contributions atmospheric nitrate contributions among all sites, beginning with 44% atmospheric nitrate on May 15 that tapered to 27% on July 24 (Fig. 5). The GLV stream, rock glacier melt, and subtalus water had a similar pattern of decreasing atmospheric contribution and increasing terrestrial contribution with time (Fig. 5; Fig. 6).

Of all surface water sites, the highest elevation site—Arikaree glacier—had the highest concentration of atmospheric nitrate. Below Arikaree, the stream is characterized by subsurface flow through talus and barren soil for several hundred yards to Navajo Bench (Fig. 1). Atmospheric nitrate contributions dropped significantly between Arikaree and Navajo with a mean difference of 20% (ranging from 59% on June 21 to 1% on Sept 31). However, total nitrate concentrations increased significantly between Arikaree and Navajo (fig. 6), suggesting a contribution of terrestrial nitrate between the two sites, thus explaining the proportional decrease of atmospheric nitrate. Downstream of Navajo, t-tests found no statistical difference between Navajo, GL5, and GL4 terrestrial and atmospheric nitrate contributions (Fig. 5).

#### 1.4.5 Residence time of atmospheric nitrate

$\Delta^{17}\text{O—NO}_3^-$  values were fitted with an exponential decay equation at surface water sites when possible, which enabled us to calculate the decay constant that describes the turnover time of atmospheric nitrate (Darrouzet-Nardi et al., 2011). At Arikaree glacier, the equation  $\Delta^{17}\text{O}(t)=20e^{(-0.016t)} - 2$ , and the inverse of the decay constant,  $0.016^{-1}$ , gives a residence time of 62 days (Fig. 8). Following the same method, the residence time of atmospheric nitrate at the rock glacier and Martinelli was 138 and 66 days respectively. These results are about ten times longer than the 6.6-day residence time that Darrouzet-Nardi et al. (2011) report for the subalpine and N-limited Como Creek watershed on Niwot Ridge.

This method assumes one initial input of atmospheric nitrate, and works well for snowmelt dominated sites like Arikaree and Martinelli. In contrast,  $\Delta^{17}\text{O—NO}_3^-$  values at other surface water sites, such as Navajo Bench and GL4, have noise during the early summer and do not follow an exponential curve until July (Fig. 8). The calculated residence time of nitrate at Navajo and GL4 were 68 and 100 days respectively. We attempted to fit decay curves to  $\Delta^{17}\text{O—NO}_3^-$  values at talus sites, but the values were too noisy to fit an exponential decay curve. At one talus site, EN.4L, on the north side of the valley (Fig. 1), atmospheric nitrate actually increased through the season. Atmospheric nitrate contributions decreased through the season at all other subtalus water sites. Sites that have too much noise to calculate a decay rate most likely have additional inputs of atmospheric nitrate from rain events throughout the summer, whereas Arikaree, the rock glacier and Martinelli show a dominant initial input of atmospheric nitrate from snowmelt.



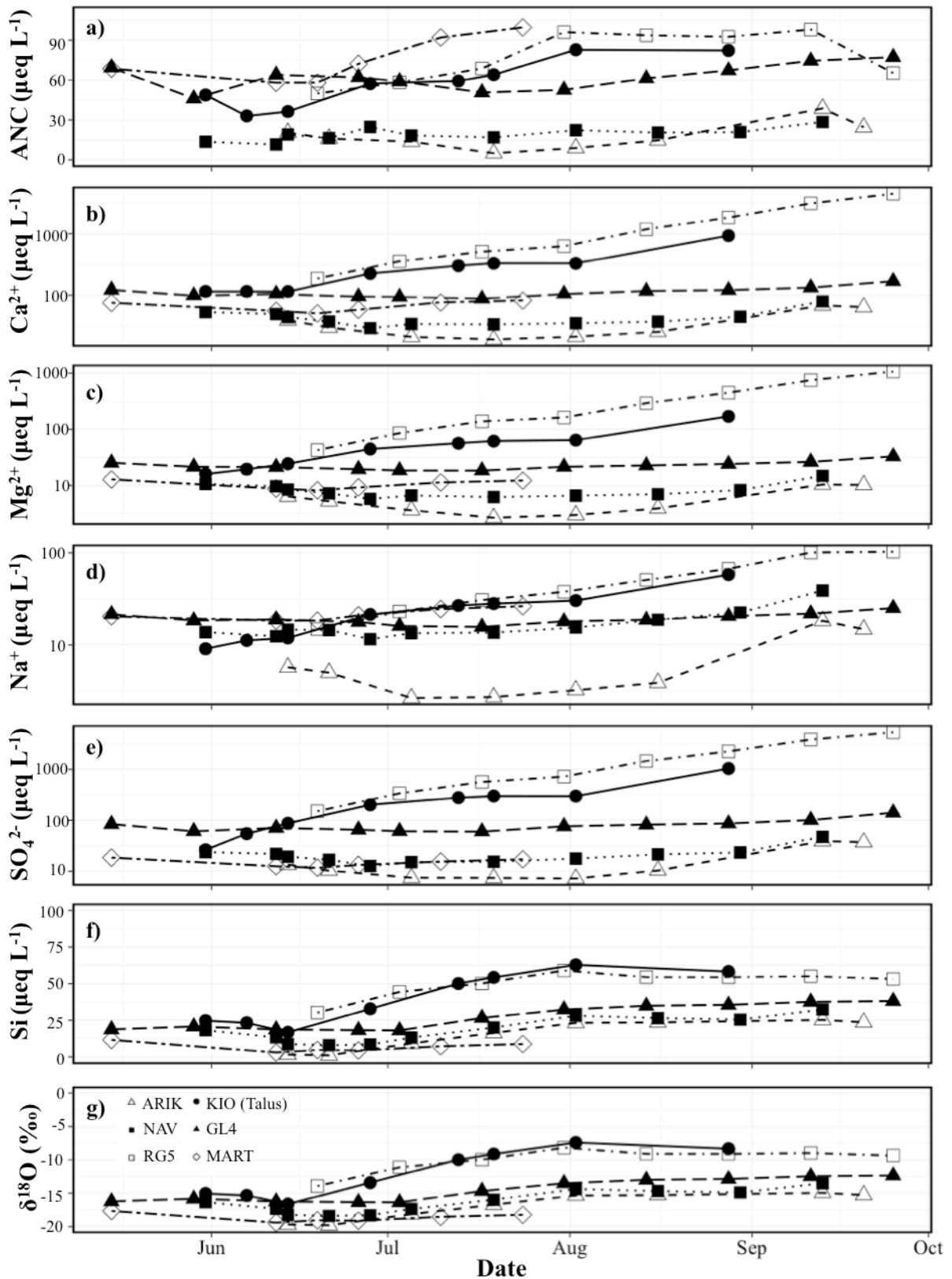
**Figure 8.** Decay curves fit to  $\Delta^{17}\text{O}-\text{NO}_3^-$  values from (a) Arikaree glacier melt, (b) Navajo Bench (c) Rock Glacier melt, (d) Green Lake 4 outlet, and (e) Martinelli. Decay curve equations in top right of each plot.

#### ***1.4.6 Geochemical weathering and nitrate production***

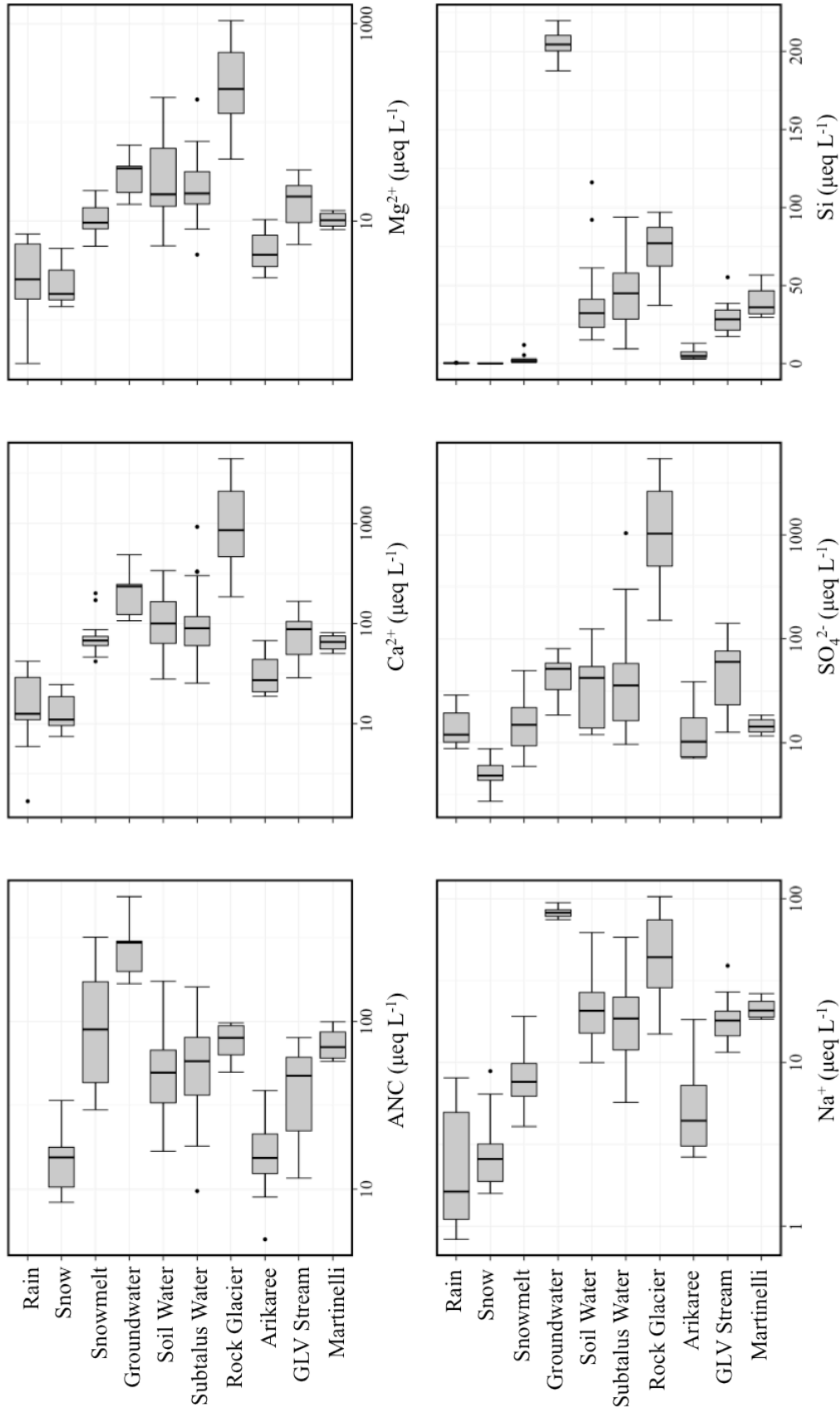
Here, we compare solute concentrations consistent with geochemical weathering products for all water types during the summer of 2012 in order to more fully characterize the terrestrial component of these water bodies. Geochemical weathering products provide an independent evaluation of the terrestrial contribution to the various water bodies. These results, in combination with the isotopic values of nitrate, may help discriminate atmospheric versus terrestrial sources of nitrate in water samples.

Concentrations of solutes in the snowmelt dominated GLV catchment are influenced by discharge volume, which is characterized by the snowmelt hydrograph, defined by a spike in discharge in early summer and a decrease in discharge thereafter. Solute concentrations are high at the beginning of snowmelt due to the combination of the flushing of soils with high ionic concentrations and high solute concentrations from the snowpack itself from the ionic pulse (Caine 1995). After the initial snowmelt pulse, dilution of ground and soil water yield by dilute melting snow results in lower solute concentrations (Fig.9; Caine 1995). Solute concentrations rise in late summer and fall as the volume of discharge reduces after snowmelt ends (ibid). Surface waters in GLV typically follow this temporal pattern of solute concentrations, but in 2012 the initial ionic pulse was muted due to the low snowpack (Fig. 5, 9).

Out of all of the sites in GLV, the rock glacier had the highest concentrations of geochemical weathering products, notably  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  (Fig. 9). The Kiowa talus site showed similar solute concentrations to the rock glacier (Fig. 9) though all of the talus sites together had lower solute concentrations than the rock glacier (Fig. 10). Arikaree often had the lowest concentrations of geochemical weathering products. Martinelli solute concentrations were similar to those at GL4 and Navajo (Fig. 9). Most sites showed an increase in solute



**Figure 9.** Time series of a) concentrations of ANC, b)  $\text{Ca}^{2+}$ , c)  $\text{Mg}^{2+}$ , d)  $\text{Na}^+$  e)  $\text{SO}_4^{2-}$ , f) Si, and g) the isotopic  $\delta^{18}\text{O}$  signature of water types in GLV throughout the summer of 2012. The line and point types represent different sampling sites (see legend in *bottom right*).



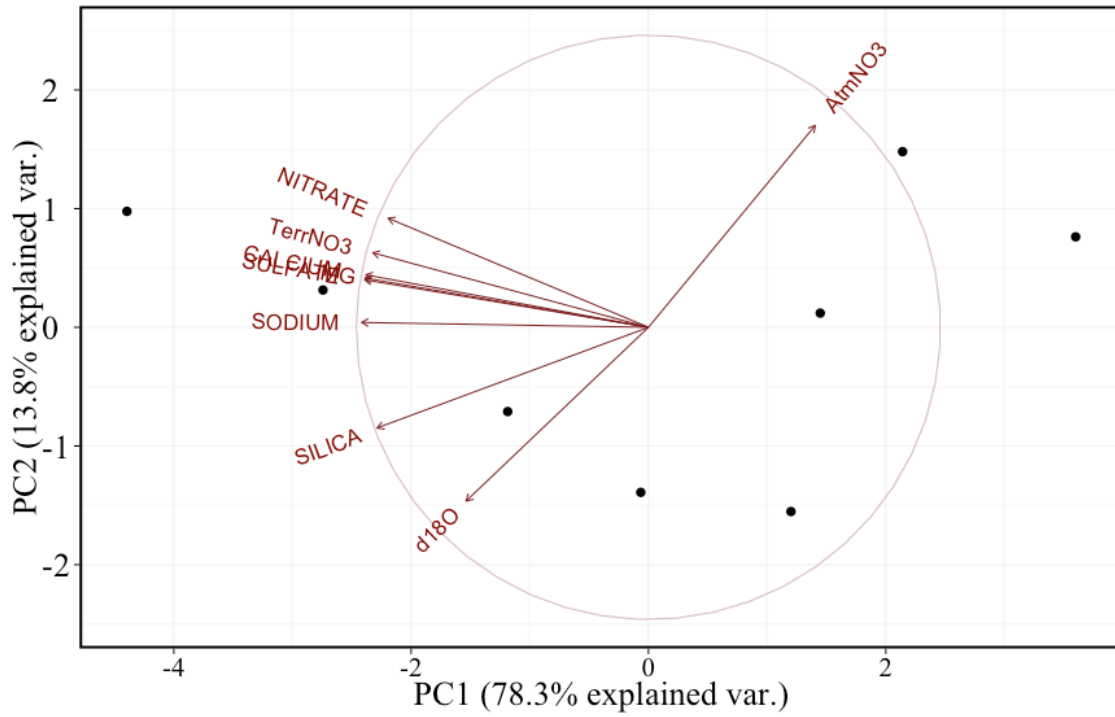
**Figure 10.** Boxplots showing median and quartiles (box for 25% and 75% and whisker for 5% and 95%) for ANC,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ , and Si values in Rain, Snow, Snowmelt, Groundwater, Soil Water, Subtalus water, Rock Glacier, Arikaree, GLV Stream, and Martinelli. Points indicate outliers within the sample population for a given sample type/location.

concentration in late summer and fall, when differences were most pronounced in concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  between the rock glacier/Kiowa talus site, and the stream sites (Fig. 9). Differences were most pronounced in late summer and fall, with the most striking differences in September and October (Fig. 3).

Boxplots showing the median and quartiles of selected solutes and isotopes are presented in Figure 10 to help characterize the terrestrial contributions to different water bodies using Principal Component Analysis (PCA). Solute concentrations in rain, snow, and snowmelt were generally lower than other types of water, whereas the rock glacier generally had the highest solute concentrations. The median value of most solute concentrations in soil water was similar to the talus runoff median values.

We ran a PCA using solute concentrations to evaluate the relationship among total nitrate, terrestrial nitrate, and atmospheric nitrate, and geochemical weathering products. The analysis provides an independent assessment of the association between nitrate and geochemical weathering products, with a focused view of the difference between the behavior of atmospheric and terrestrial nitrate. Results vary between water type and geochemical behavior.

Active near-surface geochemical weathering and microbial activity increase throughout the summer at the rock glacier (Williams et al. 2006), resulting in an increase of geochemical weathering products and nitrate concentrations (Fig. 5; 9). The rock glacier PCA plotted weathering products in a group close to terrestrial nitrate and total nitrate, with atmospheric nitrate plotted separate from the weathering product group (Fig. 11).  $\delta^{18}\text{O}$  plotted on the opposite side of the biplot from atmospheric nitrate, and away from the geochemical solutes group.



**Figure 11.** Rock glacier PCA, including ANC,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Na^+$ ,  $SO_4^{2-}$ , Si,  $NO_3^-$ , atmospheric  $NO_3^-$ , terrestrial  $NO_3^-$ , and  $\delta^{18}O$ . ANC,  $Mg^{2+}$ ,  $Ca^{2+}$ , and  $SO_4^{2-}$  plot on top of one another. All solute units are  $\mu eq L^{-1}$ ,  $\delta^{18}O$  as per mil (‰).

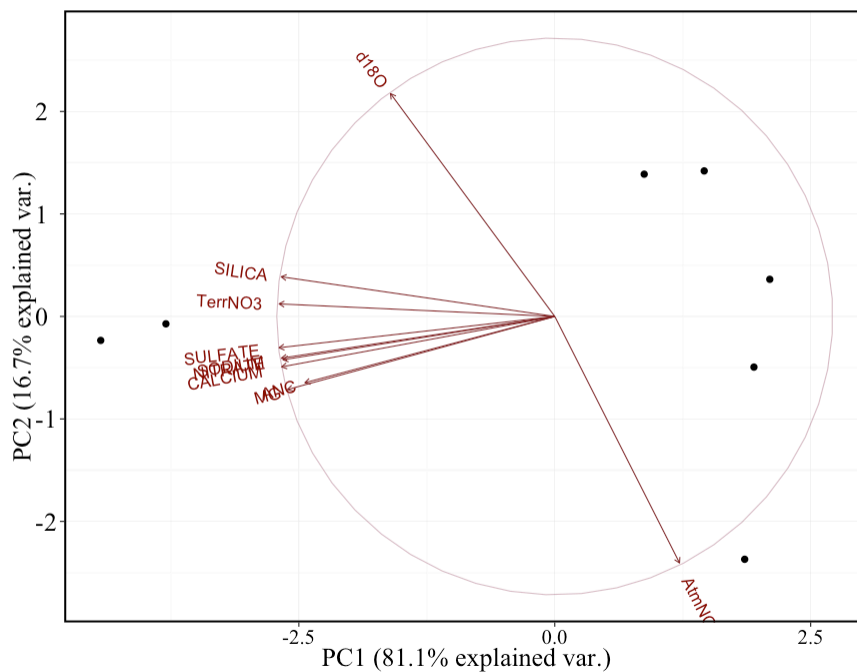


Previous research on Arikaree glacier suggests that near surface weathering processes break down substrate from aeolian deposition take place on the surface of the glacier (Williams et al. 2007). Even though Arikaree runoff has low concentrations of geochemical weathering products (Fig. 9, 10), the Arikaree PCA analysis was similar to the rock glacier analysis, with most geochemical weathering products plotting very close together with terrestrial and total nitrate (Fig. 12). Atmospheric nitrate and  $\delta^{18}\text{O}$  plotted on opposite sides of the geochemical weathering product group (Fig. 12).

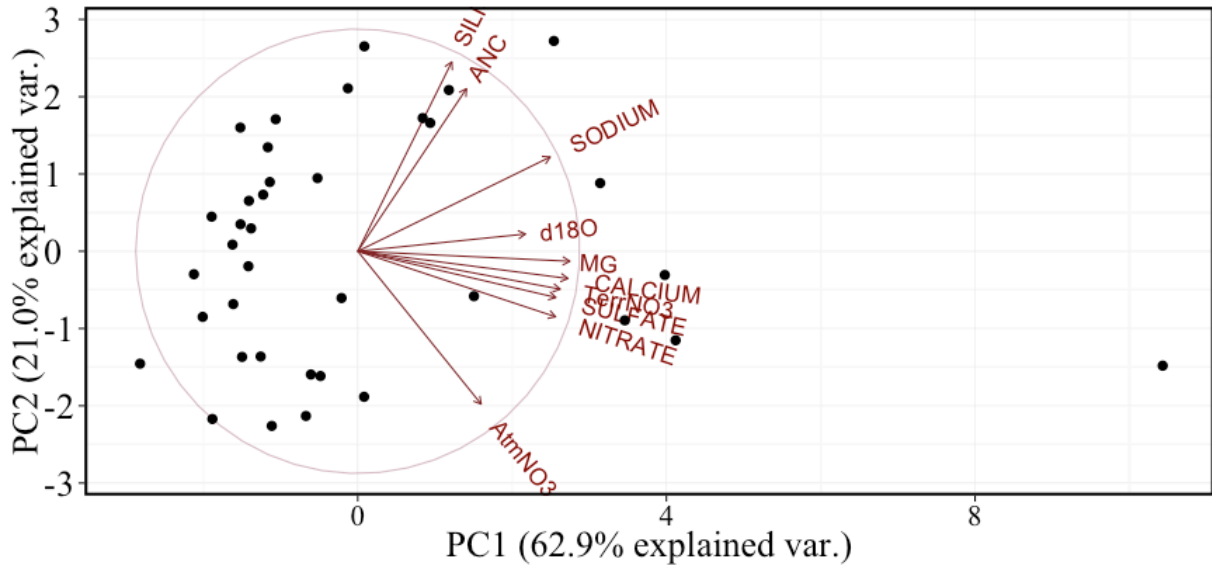
Subtalus waters flush talus areas that are highly active geochemically and biologically (Williams et al. 1997), and show peaks in both geochemical weathering products and nitrate concentrations in late summer (Fig. 6; 9). The subtalus water PCA shows nitrate and terrestrial nitrate plotting close to geochemical weathering products  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{SO}_4^{2-}$  (Fig. 13). Silica and ANC plot together higher on the PC2 axis, and atmospheric nitrate plots lower than the weathering product group on the PC2 axis (Fig. 13).

Interstitial soil water solutes strongly affect the chemistry of small streams, but have significantly less effect as stream size increases (Litaor 1993). Thus, while we can characterize terrestrial solute concentrations at individual sites, the effect of soil water chemistry may be lost by the time water reaches the GLV stream, and so we do not present soil water PCA results.

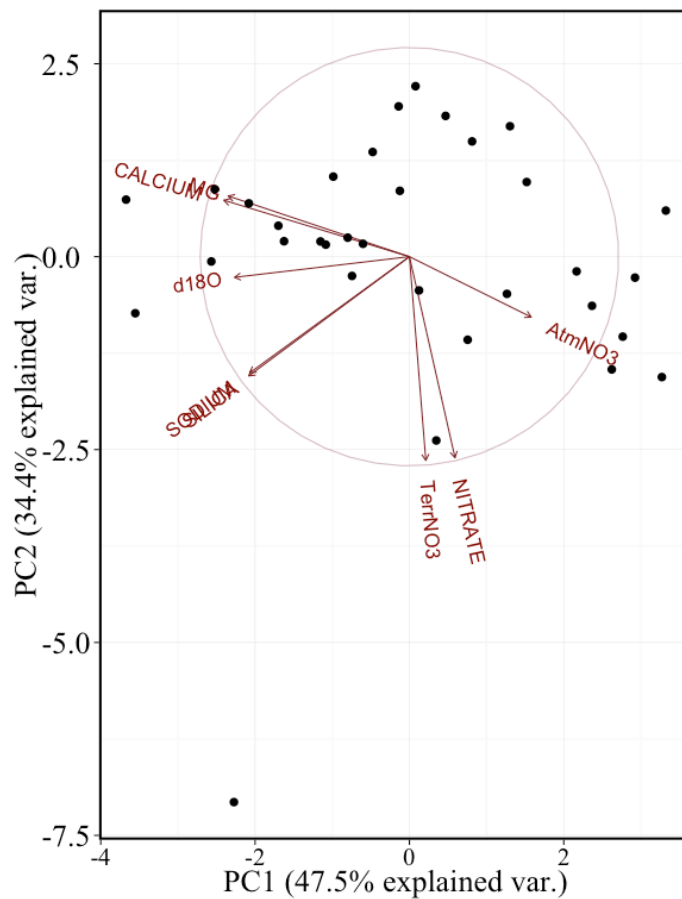
The GLV stream is a mixture of several water sources—snowmelt, talus runoff, and baseflow—that each have a unique geochemical signature and contribute different amounts throughout the year (Liu et al. 2004). The stream PCA, including Navajo, GL5, and GL4, showed weathering products  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Si}$  grouped on one side, with atmospheric nitrate plotted nearly opposite of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (Fig. 14). Total nitrate and terrestrial nitrate are plotted in between geochemical weathering products and atmospheric nitrate on the PC1 axis. While



**Figure 12.** Arikaree PCA, including ANC,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ , Si,  $\text{NO}_3^-$ , atmospheric  $\text{NO}_3^-$ , terrestrial  $\text{NO}_3^-$ , and  $\delta^{18}\text{O}$ . All solute units are  $\mu\text{eq L}^{-1}$ ,  $\delta^{18}\text{O}$  as per mil (‰).  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and total  $\text{NO}_3^-$  plot nearly on top of one another, as do ANC and  $\text{Mg}^{2+}$ .



**Figure 13.** Subtalus water PCA, including ANC, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Si, NO<sub>3</sub><sup>-</sup>, atmospheric NO<sub>3</sub><sup>-</sup>, terrestrial NO<sub>3</sub><sup>-</sup>, and δ<sup>18</sup>O. All solute units are μeq L<sup>-1</sup>, δ<sup>18</sup>O as per mil (‰).



**Figure 14.** GLV stream PCA, including  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , Si,  $\text{NO}_3^-$ , atmospheric  $\text{NO}_3^-$ , terrestrial  $\text{NO}_3^-$ , and  $\delta^{18}\text{O}$ . All solute units are  $\mu\text{eq L}^{-1}$ ,  $\delta^{18}\text{O}$  as per mil (‰).  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  plot nearly on top of one another, as do  $\text{Na}^+$  and Si.

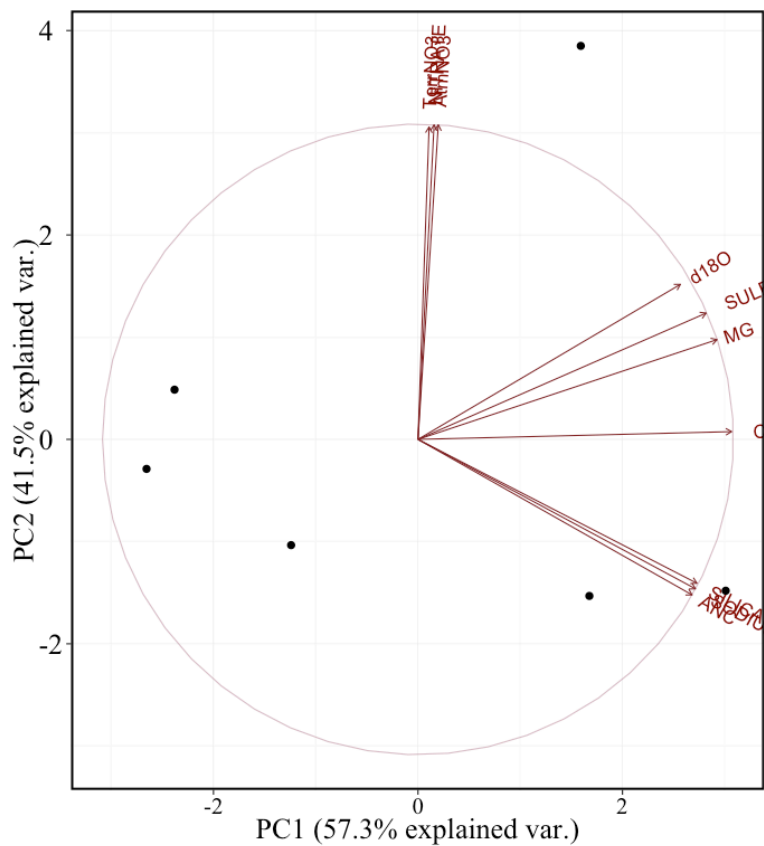
nitrate may be conservative in source waters entering the stream, DIN may not be conservative in the GLV stream system (Hood et al. 2003) This may explain why nitrate plots far away from geochemical weathering products compared to upstream sources such as Arikaree, the rock glacier, and subtalus waters.

At the Martinelli catchment, concentrations of geochemical weathering products and nitrate never came close to concentrations at stream sites in GLV, subtalus waters, or the rock glacier (Fig. 4, 5). The Martinelli PCA shows all nitrate plotting together, apart from geochemical weathering solutes (Fig. 15). When other sites had the highest solute concentrations in late summer, the Martinelli stream had already dried up, suggesting a temporal separation between nitrate export and the season of increased geochemical weathering in summer and fall.

## 1.5 Discussion

Elevated nitrate concentrations in Green Lakes Valley and similar alpine catchments are associated, in part, by increased deposition of DIN in wetfall (Williams et al. 1996). However, growing evidence suggests that a changing climate and microbial N dynamics are contributing to a sustained increase of microbially produced nitrate export in high-elevation areas in many places of the world (Barnes et al. 2013, Baron et al. 2009). The use of  $\delta^{15}\text{N}\text{---NO}_3^-$ ,  $\delta^{18}\text{O}\text{---NO}_3^-$  and the novel application of  $\Delta^{17}\text{O}\text{---NO}_3^-$  enables us to quantify the contribution of atmospheric versus microbial production of nitrate in a high elevation catchment.

Past research has utilized  $\delta^{15}\text{N}\text{---NO}_3^-$  and  $\delta^{18}\text{O}\text{---NO}_3^-$  isotopes to determine sources of nitrate (Ohte et al. 2004, Sickman et al. 2003, Campbell et al. 2002, Burns and Kendall 2002, Kendall 1998). Kendall (1998) explains that  $\delta^{18}\text{O}\text{---NO}_3^-$  helps discriminate between nitrate fertilizer and atmospheric sources where  $\delta^{15}\text{N}\text{---NO}_3^-$  values overlap. On the other hand,  $\delta^{15}\text{N}\text{---NO}_3^-$  values help discriminate between nitrate derived from ammonium in rain, soil organic

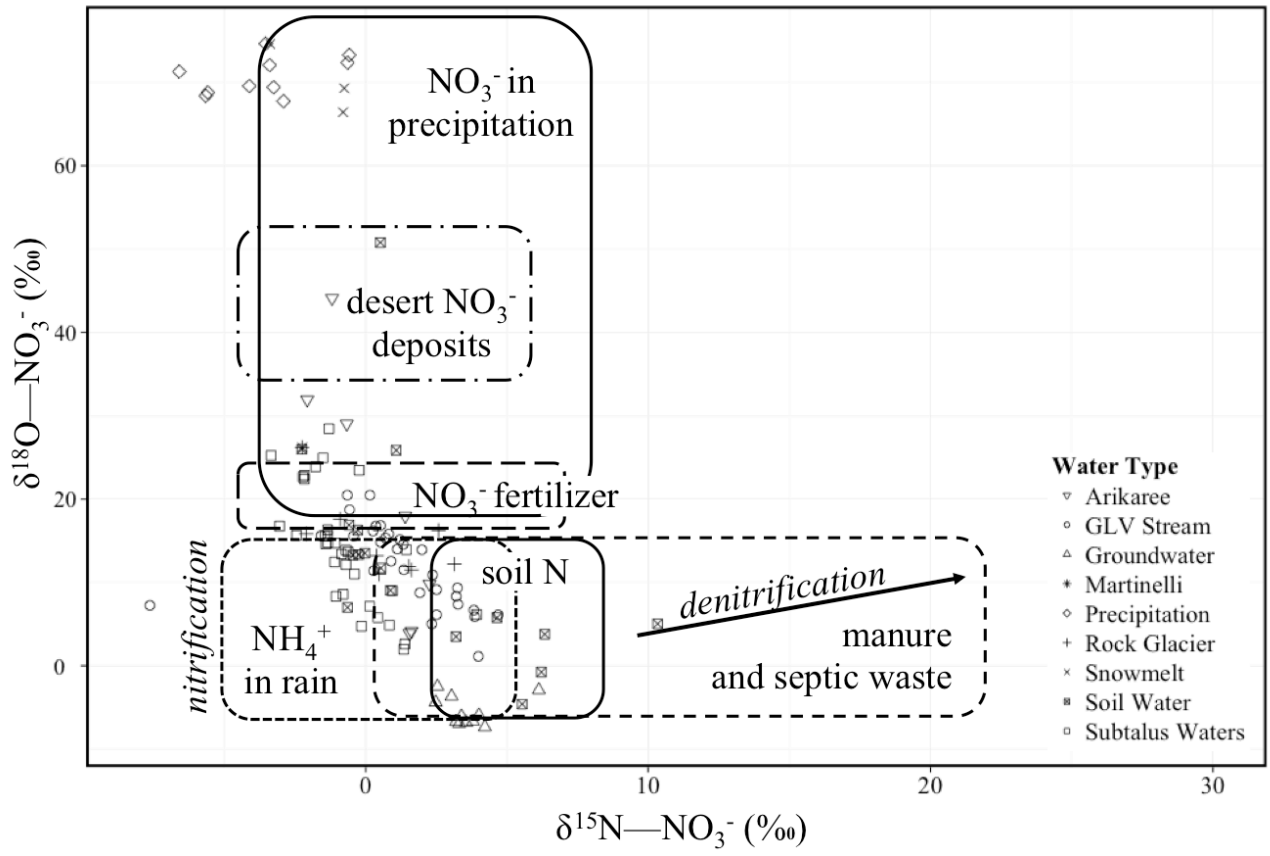


**Figure 15.** Martinelli PCA, including ANC,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Na^+$ ,  $SO_4^{2-}$ , Si,  $NO_3^-$ , atmospheric  $NO_3^-$ , terrestrial  $NO_3^-$ , and  $\delta^{18}O$ . All solute units are  $\mu eq L^{-1}$ ,  $\delta^{18}O$  as per mil (‰). All nitrate plots nearly on top of one another, as do ANC, Si, and  $Na^+$ .

matter, and animal manure where  $\delta^{18}\text{O—NO}_3^-$  values overlap (ibid.). In general, products of biologically mediated reactions—assimilation, nitrification, and denitrification—in the soil have more depleted  $\delta^{15}\text{N—NO}_3^-$  values than the reactants, explaining why products of nitrification plot low on the  $\delta^{15}\text{N—NO}_3^-$  axis (Fig. 16, Kendall 1998).

Campbell et al. (2002) found that stream and talus spring samples in Loch Vale plotted along a mixing line between two clusters on the  $\delta^{18}\text{O—NO}_3^-$  versus  $\delta^{15}\text{N—NO}_3^-$  plot. The first cluster had high  $\delta^{18}\text{O—NO}_3^-$  values and low  $\delta^{15}\text{N—NO}_3^-$  values, representative of bulk precipitation samples collected in spring and summer (ibid.). The second cluster had low  $\delta^{18}\text{O—NO}_3^-$  values, caused by microbial nitrification, and high  $\delta^{15}\text{N—NO}_3^-$  values, which could come from nitrate in snow or ammonium in rain and/or snow (ibid.). We plotted our values on a similar plot (Fig. 16) and found a similar mixing line, with precipitation values plotting as the first cluster, and the rest of the samples plotting along a mixing line towards the second cluster, composed mainly of groundwater and soil water samples. Subtalus waters and the rock glacier samples plotted closely together on the center of the mixing line, and GL4 stream samples and soil water samples plotted along the entire mixing line. We suggest that this figure accurately represents the mixture of sources through the year and would not change substantially if we were to use  $\Delta^{17}\text{O—NO}_3^-$  values, since  $\Delta^{17}\text{O—NO}_3^-$  and  $\delta^{18}\text{O—NO}_3^-$  values correlate nearly 1:1 (Fig. 7). The use of  $\Delta^{17}\text{O—NO}_3^-$  in conjunction with  $\delta^{15}\text{N—NO}_3^-$ ,  $\delta^{18}\text{O—NO}_3^-$  values increases our confidence that the primary source of nitrate exported from alpine catchments is terrestrial in origin. We build on these results by assessing the characteristics of each water type to deepen our understanding of the sources of terrestrial nitrate in GLV.

Isotope results and nitrate concentrations paired with a mixing model, residence time, and PCA analysis suggest that water types divide broadly into two groups. The first group is made up



**Figure 16.**  $\delta^{18}\text{O}-\text{NO}_3^-$  and  $\delta^{15}\text{N}-\text{NO}_3^-$  values from water types in GLV in 2012. Schematic boxes taken from Kendall (1998) show typical ranges of  $\delta^{18}\text{O}-\text{NO}_3^-$  and  $\delta^{15}\text{N}-\text{NO}_3^-$  values from various sources.



of sites with cryospheric features that export terrestrial nitrate, including the rock glacier, subtalus waters, Arikaree glacier. Near-surface geochemical weathering processes that are most active in late summer and fall occur at these sites. The PCA analysis for this group showed geochemical weathering products,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$ , plotting closely to terrestrial nitrate and nitrate. The second group has sites with lower nitrate concentrations that may receive and transport nitrate from upstream sources. This group includes groundwater (not shown), soil water (not shown), the GLV stream and Martinelli. At each of these sites, nitrification is decoupled from geochemical weathering processes, either spatially, as in groundwater and the GLV stream, or temporally, as at Martinelli. Therefore, PCA results show nitrate plotting separate from geochemical products. This grouping is consistent with research that suggests connections between increased geochemical weathering products and nitrate export from cryospheric features in alpine catchments (Barnes et al. 2013, Baron et al. 2009).

### ***1.5.1 Sites with cryospheric features***

The first group is made up of sites with cryospheric features: the rock glacier, talus, and Arikaree. Geochemical weathering and active microbial communities exist near the surface at all of these sites, which are most geochemically active in late summer and fall when ice melt is highest. Looking at trends in the recent 12 years, geochemical weathering product concentrations increased at GLV and the nearby Loch Vale catchment during 2000 to 2006, concurrent with increases in nitrate concentration (Barnes et al. 2013, Baron et al. 2009). Precipitation was below average and summer and fall temperatures were above average during this period. Both Barnes et al. (2013) and Baron et al. (2009) suggest that melting cryospheric features in the alpine—glaciers, rock glaciers, and permafrost—caused by a warming climate explain the increase in geochemical weathering products. Cryosphere melt may directly contribute  $\text{NO}_3^-$  to alpine

catchments, but a more likely explanation suggests that increased melt increases exposure of fresh mineral surfaces that may promote increased microbial activity and nitrification (Barnes et al. 2013, Baron et al. 2009). While these sites are a source of terrestrial nitrate, each site still exports a small percentage of atmospheric nitrate, primarily during snowmelt.

*The rock glacier.* In a survey of rock glaciers across the central Rocky Mountains, Williams et al. (2007) found that rock glaciers have elevated nitrate concentrations compared to nearby streams. Using an EMMA model, Williams et al. (2007) found that seasonal nitrate concentration trends mirrored trends in geochemical weathering products in outflow from RG5 in GLV, suggesting that nitrate moves conservatively from source waters to outflow through the rock glacier as do geochemical weathering products. The source water of rock glacier outflow was primarily snowmelt in June, soil water in July, and base flow in September. High soil water nitrate concentrations in July suggest that soils at the surface of rock glaciers behave similarly to soils in talus with respect to nitrogen cycling, producing pools of inorganic N and microbial biomass N (Williams et al. 2007). Base flow in September is likely a result of internal ice melt, which may provide a larger percentage of outflow in dry years (Williams et al. 2006). It is unknown whether nitrate in baseflow from RG5 is directly from the ice melt, or whether ice melt containing ammonium stimulates nitrification, resulting in increased nitrate in outflow. Research on microbial communities that survive extreme conditions in talus fields suggests that some microbial communities in GLV are adapted to cold, dark, oligotrophic conditions similar to those in the interior of RG5 (William et al. 2007, Ley et al. 2004).

Our results affirm the hypotheses from Williams et al. (2007), showing that the majority of nitrate in outflow from RG5 is produced by terrestrial nitrification. Nitrate concentrations in RG5 outflow were nearly twice the concentrations in the nearby creek (Fig. 4) throughout the

season. Mixing model results showed that nitrate in rock glacier runoff were 81% terrestrial, with the highest percentage of atmospheric nitrate at the beginning of the sampling season at 27% on June 19 (Fig. 5). This is consistent with Williams et al. (2007), who showed that the major source of water in RG5 outflow in June was snowmelt. A residence time of atmospheric nitrate of 138 days suggests that water moves slowly through GLV, allowing for increased geochemical weathering and resulting increased terrestrial nitrification, as indicated by the correspondence of terrestrial nitrate and geochemical weathering products in the PCA analysis (Fig. 13). High geochemical weathering product concentrations and high terrestrial nitrate output in outflow from RG5 affirms that the rock glacier is a source of nitrate in GLV, produce by near-surface weathering that supports microbial nitrification.

*Subtalus waters.* Williams et al. (1997) proposed that elevated nitrate concentrations and reduced ammonium concentrations in subtalus waters were the result of a viable organic system in barren areas with little or no vegetation. Furthermore, they showed that nitrate concentrations in subtalus water were significantly correlated with concentrations of geochemical weathering products such as calcium and silica. They argued that the correlation of nitrate in subtalus water with geochemical weathering products suggests that nitrate concentrations in subtalus water increase with increased residence time, consistent with a biological source for this subtalus water nitrate. Bieber et al. (1998) conducted the first direct measurements of mineralization rates for barren talus areas that were comparable to mineralization and nitrification rates reported for well-developed tundra soils on nearby Niwot Ridge and which were capable of explaining the elevated nitrate amounts measured in subtalus waters.

Our results using triple isotopes of nitrate are consistent with the indirect methods used by Williams et al. (1997) and Bieber et al. (1998) to infer that the majority of nitrate in subtalus

waters was terrestrial in origin rather than atmospheric in origin. We see the same temporal trend of increasing nitrate concentrations in subtalus waters with time as reported in Williams et al. (1997), reaching a maximum concentration of  $100 \mu\text{eq L}^{-1}$  at the Kiowa site in late August (Fig. 6). The Kiowa site consistently had the highest nitrate concentrations of all talus sites (Fig. 6), and the highest geochemical weathering product concentrations (data not shown). The Kiowa talus site is the only site on the north facing side of the valley, and is more likely to have permafrost features beneath (Janke et al. 2005). Permafrost may act similar to the RG5 ice core described in Williams et al. (2006), that melts in late summer and fall, resulting in increased hydrologic connectivity thus flushing out pools of nitrate. And as in Williams et al. (1997), ammonium concentrations in subtalus waters were always near detection limits, consistent with nitrification of atmospheric ammonium in wetfall to terrestrial nitrate (Fig. 6). PCA results also showed terrestrial nitrate and geochemical weathering products plotting close together, suggesting that nitrification occurs at sites with increased residence time in near-surface weathering systems.

*Arikaree glacier.* Williams et al. (2007) argue that sampling the Arikaree Glacier is analogous to sampling a large snowmelt lysimeter. They suggest that high values of ammonium in the outflow of the Arikaree glacier at the initiation of snowmelt are likely the result of solutes released from the supraglacial snowpack in the form of an ionic pulse. Ammonium values of about  $25 \mu\text{mol L}^{-1}$  at this time compared to bulk snow values of about  $5 \mu\text{mol L}^{-1}$  are similar to the concentrations in snowpack meltwater before contact with the ground at Niwot Ridge, which ranged from 5 to 15 times bulk snowpack values (Williams et al., 2001). Similarly, Williams et al. (2007) attributed nitrate values of about  $50 \mu\text{eq L}^{-1}$  in the initial meltwater from the Arikaree

Glacier to atmospheric sources of nitrate stored in the seasonal snowpack and that were released in the form of an ionic pulse.

Our results for the outflow of the ionic pulse in 2012 are not consistent with nitrate from the Arikaree Glacier being atmospheric in origin. The DIN concentrations in melt from Arikaree glacier were similar to snowmelt, with a mean nitrate concentration of  $22 \mu\text{eq L}^{-1}$ , and ranging from 13 to  $41 \mu\text{eq L}^{-1}$ . While Arikaree DIN concentrations were similar to snowmelt, Arikaree nitrate oxygen isotope values were closer to soil water and talus than precipitation or snowmelt values (Fig. 4). Based on  $\Delta^{17}\text{O—NO}_3^-$  mixing model values, the Arikaree glacier had the highest contribution of atmospheric  $\text{NO}_3^-$  of 66% on June 21, which decreased as the summer progressed to 10% in September. And in late summer to early fall, nitrate concentrations increased in the outflow of the Arikaree glacier (Fig. 5), as the percent of atmospheric nitrate decreased and the percent contribution of terrestrial nitrate increased in total nitrate in the outflow of the glacier.

A possible explanation for this increase in the terrestrial contribution of nitrate in the glacier outflow, and the higher concentrations of nitrate in the outflow, is active mineralization processes on and near the surface of the glacier/snow system. Mladenov et al. (2012) showed that wet and dry deposition are important sources of both dissolved organic matter (DOM) and DIN to high-elevation snowpacks in the GLV. Mineralization of organic matter and ammonium from wetfall and dryfall onto the glacier surface during the summer may account for the observed increase in terrestrial nitrate in the outflow of the Arikaree Glacier. Naff et al. (2013) have demonstrated the presence of active microbial populations in the spring and summer snowpack in the GLV, suggesting the possibility of mineralization processes that could produce ammonium as a byproduct, which is nitrified by microbes on or near the surface of glacier snow and ice. If in fact biogeochemical cycling of aeolian deposition is important, we would expect to

see the increase in nitrate concentrations—and the terrestrial contribution of nitrate—reflected in an increase in the amount of calcium over time in the outflow of the glacier. Clow et al. (1997) showed that aeolian deposition is an important source of calcium to high elevation catchments in the Colorado Front Range, with calcite a major component of the mineralogy of the aeolian deposition. And in fact we do see an increase in calcium in the outflow of the Arikaree Glacier from a low of  $19 \mu\text{eq L}^{-1}$  on 19 July to a high of  $68 \mu\text{eq L}^{-1}$  on 13 September.

Though the 2012 climate was anomalous, the increased terrestrial nitrate contribution in Arikaree Glacier outflow is consistent with the snowmelt geochemical signature description. Due to a low snow year, and high summer precipitation (Fig. 2, 3), Arikaree outflow behaved more like a late season snowpack in 2012. Williams et al. (2001) found that late season snowpacks tend to accumulate aeolian deposition in summer, when the presence of liquid water in the snowpack increases the “stickiness” of the snowpack. Late season snowmelt had increased amounts of DOC, DON, and DOP, which Williams et al. (2001) attributed to increased particulate matter on the snow surface being mineralized into these various forms of DOM.

The Arikaree glacier, expectedly, had one of the largest atmospheric nitrate contributions at the beginning of the season, of 66%. This signal did not continue through the season, in fact, total nitrate export actually increased through the summer, as the atmospheric contribution fell and the terrestrial contribution increased (Fig. 5). Residence time of atmospheric nitrate at Arikaree was 62 days, suggesting that throughout the summer atmospheric nitrate does not simply runoff directly from the glacier into the outflow. Residence time of nitrate on the glacier surface is consistent with PCA results that plotted terrestrial nitrate close to geochemical weathering products. While Arikaree does have a large atmospheric nitrate component early in

the summer with snowmelt, it's clear that Arikaree behaves more like the rock glacier and talus late in the summer, and is a source of terrestrial nitrate in GLV.

### ***1.5.2 Downstream sites: GLV stream, soil water, groundwater, and Martinelli***

The second group of sites includes sites that are either downstream of cryospheric features, or spatially disconnected from areas with near-surface weathering and active microbial communities. These sites are GLV stream sites, soil water, groundwater, and Martinelli.

*Soilwater.* Liu et al. (2004) showed that soil water did not contribute a significant amount of discharge in the GL4 catchment; instead subtalus waters contributed a large portion of discharge. In contrast, soil water contributed a small percentage of discharge to the Martinelli stream. While nitrification definitely occurs in soil waters, the contribution of soil water to streams in GL4 and Martinelli is so small that soil water is likely not a prominent source of terrestrial nitrate export. Nitrate concentrations and isotope results were highly variable in soil water samples, suggesting that soil water solute chemistry responds rapidly to rain and deposition events, and flushes water out quickly. Campbell et al. (2002) suggested that soil nitrate  $\delta^{15}\text{N}\text{---NO}_3^-$  values reflect the atmospheric deposition from which the nitrate was derived, and  $\delta^{18}\text{O}\text{---NO}_3^-$  values were characteristic of microbial nitrification. This would suggest that the high variability of  $\delta^{15}\text{N}\text{---NO}_3^-$  values (Fig. 4) reflects the high variability of sources of nitrate in soil water.

*Groundwater.* Groundwater contributes as much as a third of discharge in the GL4 and Martinelli streams as baseflow. Clow (2003) found that talus slopes were the primary groundwater reservoir in the Loch Vale catchment, suggesting that deeper flow paths within talus fields allow for slow discharge of water through fall and winter. Our results show that the deep groundwater in GLV does not have the same nutrient concentrations evident in near

surface subtalus waters. We hypothesize that the majority of nitrate is leached or assimilated before water infiltrates deeper into the groundwater system, as groundwater had low nitrate concentrations compared to other water sources in GLV (Fig. 4). Nitrate was not conservative in the PCA analysis, and plotted far away from geochemical weathering products, suggesting that geochemical weathering processes in groundwater occur in a different place or time than terrestrial nitrification.

*GLV Stream.* We suggest that the GLV stream, for the most part, is not a primary source of terrestrial nitrate, rather it receives and transports nitrate exported from upstream sources; Arikaree glacier, RG5, and talus runoff. The GLV stream is a mixture of several different water sources that contribute different amounts throughout the season. Liu et al. (2004) used an EMMA model to show that stream flow in GLV is comprised of surface flow, talus runoff, and baseflow. Surface flow accounts for nearly 40% of streamflow in June to mid July, and is mainly comprised of saturated overland flow produced by snowmelt. Liu et al. (2004) showed that subtalus water is a major contributor to streamflow beginning in July and throughout the summer and fall. Subtalus water makes up more than half of streamflow in August, after which the baseflow contribution increases in September, when baseflow contributes as much as 80% of flow.

In contrast to the majority of the GLV stream, the highest elevation stretch of stream between Arikaree and Navajo Bench may be both a primary source of terrestrial nitrate and a conduit for upstream sources of nitrate. The short stretch of subsurface flow between ARIK and NAV appears to be a hotspot of microbial activity in GLV where high ammonium loads from glacial melt water are rapidly nitrified. Barnes and others (2013) used a mass balance model to explain that much of the additional nitrate between ARK and NAV is a result of 1:1 N



processing such that one mole of ammonium is nitrified to one mole of nitrate. The flow to the NAV site is perhaps supplemented by additions of nitrate from lateral sources, including subtalus waters and groundwater, and other periglacial features that enter the stream between ARIK and NAV. The 2012 concentrations of nitrate and  $\Delta^{17}\text{O}—\text{NO}_3^-$  results support this hypothesis, showing a jump in nitrate concentrations from ARK to NAV and an increase in terrestrial nitrate (Fig. 5), most likely produced from nitrification of ammonium. Ammonium concentrations decrease substantially between Arikaree and Navajo on any given sampling day (Fig. 5). This suggests that nitrification is happening within the stream, suggesting a slightly different system than at the other sites in this group. The subsurface stretch is similar to talus fields with barren soil patches, so may be a site conducive to microbial activity and geochemical weathering like the sites in the first group.

Downstream of Navajo, nitrate concentrations decrease at GL5 and GL4 (Fig. 5), which is consistent with the findings of Hood et al. (2003) that suggest some assimilation does occur within the aquatic system on the hydrologic axis of GLV. PCA results for the stream sites show that geochemical weathering products do not plot right next to terrestrial nitrate (Fig. 14), as multiple sources entering the stream throughout the year have different contributions of weathering products and nitrate. Contributions of atmospheric and terrestrial nitrate do not vary much among the three sampling sites along the stream, showing that a change in nitrate source within the stream system or between stream sites is unlikely (Fig. 5).

*Martinelli.* Barnes et al. (2013) showed that the Martinelli stream chemistry has been unaffected by changes in climate, due to the lack of cryospheric features. In contrast to GLV, nitrate export did not increase at Martinelli from 1985-2009 (ibid.). Nitrate concentrations at MART were low compared to nitrate concentrations in GLV, and the stream dried up before fall

when nitrate concentrations were highest in GLV. PCA results showed nitrate plotting far away from geochemical products. Atmospheric nitrate had a residence time of about 66 days, similar to the residence time at Navajo Bench, suggesting that nitrate does not directly enter surface waters upon deposition.

### ***1.5.3 Atmospheric nitrate and the role of hydrologic connectivity***

While it is clear that terrestrial sources are the dominant source of nitrate exported in surface waters, atmospheric nitrate is undoubtedly deposited to GLV in wet and dry deposition throughout the year. The question remains; what happens to atmospheric nitrate deposited in GLV?

First, we examine the role of N deposition held within the snowpack from the winter.  $\Delta^{17}\text{O}-\text{NO}_3^-$  mixing model results show that the major contribution of atmospheric nitrate in GLV was in the spring, concurrent with snowmelt (Figs. 5,6). During snowmelt in spring, runoff saturates soil, resulting in saturation-excess overland flow that mainly occurs near the stream channel (Williams et al. 1993). Overland flow is a new, unreacted source of water (Liu et al. 2004), and carries atmospheric nitrate directly to surface water. As soils become unsaturated after snowmelt is over, flow paths that directly transport atmospheric nitrate to surface waters may disappear, resulting in the assimilation of atmospheric nitrate from deposition *in situ*.

To check whether we see a direct response of systems to N deposition events in summer, we evaluated whether export of nitrate in surface waters is correlated with DIN loading and amounts of summer wetfall, or independent of them. We ran correlation tests for each water type in GLV, comparing how concentrations ( $\text{mg L}^{-1}$ ) of total nitrate, absolute atmospheric nitrate, and absolute terrestrial nitrate in water samples responded to forcing by precipitation amount and

concentrations. We added one and two week lag times to account for lag times in infiltration of rain events.

Subtalus waters were the only water type that showed an immediate response in nitrate concentrations to loading events in summer wetfall. Both total ( $p = 0.008$ ) and terrestrial ( $p = 0.005$ ) nitrate in talus runoff were significantly correlated with DIN in weekly wetfall. Total nitrate concentrations in talus runoff were correlated with loading of DIN, nitrate and ammonium in weekly wetfall, each with a rho value of 0.45. Terrestrial nitrate in talus runoff was also significantly correlated with DIN, nitrate, and ammonium loads in weekly wetfall; the rho value was the same for all parameters at 0.47. In contrast, atmospheric nitrate in talus runoff was not significantly correlated with DIN,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  precipitation loads.

In contrast to atmospheric deposition of DIN in weekly wetfall, atmospheric and terrestrial nitrate in subtalus waters responded differently to weekly precipitation amounts. Atmospheric nitrate in talus runoff was significantly ( $p=0.02$ ) correlated with precipitation amount, with a rho value of 0.37. When one and two week lag times were added, the correlation continued with the same p and rho values. In contrast, total and terrestrial nitrate were not significantly correlated with precipitation. In subtalus waters, rain events may result in a periodic increase in hydrologic connectivity, flushing any labile nitrate (both atmospheric and terrestrial) into water draining talus.

We also saw a response to precipitation events in soil water. Atmospheric nitrate and precipitation significantly ( $p=0.01$ ) correlated with a rho value of 0.53. The correlation was consistent with a one and two week lag time added. This result may be explained by the periodic increase in hydrologic connectivity with precipitation events that are also evident in subtalus

waters, which increased export of atmospheric nitrate held within soil water. There were no significant correlations between nitrate concentrations and precipitation elsewhere in GLV.

Results of the analysis showed that most water systems in GLV do not respond to atmospheric N loading events, indicating that atmospheric nitrate is not directly exported upon deposition but retained within the system. Several studies using  $\delta^{18}\text{O}\text{---NO}_3^-$  and  $\delta^{15}\text{N}\text{---NO}_3^-$  isotopes confirm that most atmospherically-derived nitrate exported from headwater catchments undergoes substantial biogeochemical cycling before being released from the system (Sickman et al. 2003, Campbell et al. 2002, Burns and Kendall 2002). Though atmospheric nitrate concentrations did not respond to N deposition events in GLV, total and terrestrial nitrate in subtalus waters did, suggesting that N deposition and precipitation may stimulate terrestrial nitrification in subtalus waters in two possible ways, by providing a source of  $\text{NH}_4^+$  and/or by increasing soil moisture. Hong et al. (2005) successfully modeled nitrate mineralization and nitrification rates using soil moisture and temperature, and found that warm and wet periods accelerated nitrate loss to surface waters due to increased mineralization rates. Typically, the primary connectivity between terrestrial soils and surface waters in high-elevation catchments is thought to occur during the spring snowmelt season. In summer, warmer air temperatures and reduced precipitation restrict soil moisture, reducing the likelihood of N export in surface waters after snowmelt (Monson et al. 2002). However, sites with cryospheric melt in late summer and fall are able to maintain hydrologic connectivity, and pools of inorganic N can be flushed out of soils at these times (Barnes et al. 2013).

$\delta^{15}\text{N}\text{---NO}_3^-$  results may provide some insight into the fate of nitrate in GLV. As explained earlier, biologically mediated reactions—assimilation, mineralization, nitrification, and denitrification—result in depleted  $\delta^{15}\text{N}\text{---NO}_3^-$  values in reaction products. The amount of

available N for reactions controls the extent of fractionation in biological processes; fractionation in N-limited systems is minimal compared to fractionation in N-saturated systems (Kendall 1998).  $\delta^{15}\text{N—NO}_3^-$  values in the GLV stream, Arikaree, and the rock glacier were most depleted at the beginning of the summer (Fig. 5), lower than the mean snowpack  $\delta^{15}\text{N—NO}_3^-$  value of 0.65‰. Assuming snowpack N as the main source of available N in spring (Williams et al. 1996), the large difference between the snowpack  $\delta^{15}\text{N—NO}_3^-$  and surface water  $\delta^{15}\text{N—NO}_3^-$  indicates large fractionation from biological processing. The majority of biological processing occurring at this time is most likely nitrification, when a large pool of available atmospheric N is available for nitrification (Ley et al. 2004), but assimilation has yet to play a major role at the beginning of the growing season. Throughout the summer,  $\delta^{15}\text{N—NO}_3^-$  values increased in stream water and glacier melt, indicating an alternate fractionation process of  $\delta^{15}\text{N—NO}_3^-$ . Nitrate concentrations were consistently lower at the GL5 and GL4 outlets, downstream of Navajo Bench and Arikaree (Fig. 5), indicating biological assimilation and/or denitrification within the stream, consistent with findings of Hood et al. (2003).  $\delta^{15}\text{N—NO}_3^-$  and  $\delta^{18}\text{O—NO}_3^-$  results suggest that denitrification does not play a major role in the GLV stream (Fig 16), as samples did not plot along Kendall's (1998) denitrification line. Therefore, the primary process leading to decreasing nitrate concentrations with decreasing elevation is assimilation. Biota preferentially assimilate nitrate with depleted  $\delta^{15}\text{N—NO}_3^-$  (Kendall 1998), resulting in enriched  $\delta^{15}\text{N—NO}_3^-$  signatures in nitrate that is not assimilated. As stated before, when larger pools of N are available, greater fractionation occurs. The increase in  $\delta^{15}\text{N—NO}_3^-$  values in stream sites indicates that biota in GL4, GL5, and the GLV stream are able to discriminate between  $^{14}\text{N}$  and  $^{15}\text{N}$  uptake, and as a result we see enrichment of  $\delta^{15}\text{N—NO}_3^-$  in nitrate that is exported. Thus, the increased fractionation as summer progresses is most likely a product of N saturation in GLV.

## 1.6 Conclusion

The combined use of triple oxygen isotopes and  $\delta^{15}\text{N}$  of nitrate show that nitrate in surface waters, including talus, soil water and rock glacier melt, is more than 75% terrestrial, with the strongest atmospheric signals present during snowmelt. The 2012 climate may be a precursor to future climate, with a low snowpack, early snowmelt, and wet summer, resulting in a peak of nitrate export during fall composed mainly of terrestrial nitrate. The primary source of terrestrial nitrate from GLV is from microbially dominated landscape types with active near surface geochemical weathering—talus, rock glaciers, glacier, and permafrost—that export nitrate to streams draining alpine watersheds with increased hydrologic connectivity from melt in late summer and fall. These results suggest that efforts to curtail nitrogen emissions may be too little too late, as alpine catchment biogeochemistry has transitioned to a net nitrification system that is compromising water quality at high elevations.

## CHAPTER 2

### Connecting Alpine Hydrology Research to the Classroom: ScienceLIVE Curriculum

#### Abstract

Graduate students and researchers at Niwot Ridge LTER are working with a newly developed program, ScienceLIVE, to create cutting edge curriculum that utilizes more than 60 years of publicly available climate data and 30 years of hydrologic data. The recently released *Next Generation Science Standards* focus on incorporating the scientific practices of developing and using models, analyzing and interpreting data, and obtaining, evaluating and communicating information. Teachers in Colorado have expressed difficulty in accessing datasets for classroom use, and lack the relationships and connections to university researchers needed to obtain such datasets. The ScienceLIVE Alpine Hydrology unit includes hands-on lessons on glaciers, nutrient cycling, and hydrology. ScienceLIVE ([www.science-live.org](http://www.science-live.org)) serves as a bridge between scientists and the public by offering K-16 students and teachers the ability to interact with active field-science through live research updates, interactive web resources, and the use of lesson plans developed with the scientists, using their actual data. As students work through these exercises, the PIs and their field assistants will directly interact with classrooms via webinars to field questions from students. We believe that creating an accessible platform for public outreach and streamlining researchers involvement will encourage a sustainable education and outreach program for Niwot Ridge LTER and increase public access to valuable long-term climate and hydrologic data.

## 2.1 Introduction

There is a longstanding divide between scientific research, K-12 classrooms, and the public (Strauss 2005). This divide separates “those that do” from “those that teach”, and has resulted with primary and secondary science curricula that is largely based on textbook driven “hands on activities” and “cookbook labs” (Strauss 2005). This approach is largely misleading students in their understanding of the nature of science and exposure to the wide range of possibilities in scientific careers. While all grade school students are not expected to go into scientific careers, the current expectation of science education is that students will leave high school able to understand scientific discourse and relate it to their daily lives (Strauss 2003). In a rapidly changing world faced with several large environmental challenges, it is essential to develop a scientifically and environmentally literate public.

The scientific community of practice often appears too distant and irrelevant to students (Brickhouse et al. 2000), perpetuating the divide between grade school classrooms and scientific researchers. When asked what a scientist looks like, the majority of K-8 students draw a white male working in a white coat in a lab (Barman 1997). Barman (1997) suggests creating videos featuring expeditions and investigations that show scientists outside the lab, and live communications with scientists to change stereotypes of scientists.

In the “Web 2.0” era, younger generations are becoming increasingly active and engaged through technology and the use of social media and digital video, and transitioning from passive activities to more active and creative pursuits (Bull et al. 2008). Participatory media and social networking are transforming the political, commercial, and professional arenas (Gulbrandsen and Just 2011), and provide significant opportunities for increased student engagement in formal learning settings as well as bridging the formal and informal learning arenas (Bull et al. 2008).



ScienceLIVE serves as a bridge between classroom and scientific research by offering K-16 students and teachers the ability to interact with active field-science through live research updates, interactive web resources, and the use of lesson plans developed with the scientists, using their actual data. The online program provides traditional hands-on lessons for classroom that are based on research in Colorado, videos and blogs that follow researchers in the field, and social media that connect the researcher to students and teachers in real time.

The Alpine Hydrology unit was developed to highlight research at Niwot Ridge on the field of hydrology, nutrient cycling, and glacier dynamics. Background information on alpine hydrology explains the science and motivations for research, profiles of researchers give a personal perspective of the scientists, and videos, pictures, and a GoogleMap portal enables students to visit the research site remotely. The nitrogen cycle and glacier lesson were taught in Boulder/Denver public schools during the 2012-2013 school year, and incorporated in teacher professional development workshops hosted by the Biological Sciences Initiative at CU Boulder. The black box of alpine hydrology lesson was created as an introduction to the alpine hydrology unit and to emphasize nature of science principals.

## **2.2 The history of ScienceLIVE**

Peter and Liesl Erb, graduate students in the CU Boulder department of Ecology and Evolutionary Biology, created ScienceLIVE in 2010 in conjunction with the CU based Biological Sciences Initiative (BSI). Liesl taught lessons on pikas in Boulder and Denver area public schools with the Science Squad, and realized that her lessons could reach a broader audience through an online format. She created ScienceLIVE with Peter to distribute her research-based lessons throughout Colorado, and connect students to her research on pikas and climate change. ScienceLIVE has since grown to include units on Bees and Alpine Hydrology.

The ScienceLIVE homepage is created to draw in students, teachers, and the general public, and provide background information in an informal setting to supplement curricula created for the formal classroom setting. Each unit includes an “About” homepage with an introduction to the content of the unit, complete with videos and pictures (Fig. 17). A page entitled “The Question” explains the main research questions of the research group, using text and a short, 5 minute video filmed at the research field site. “The Team” page introduces the researchers in the lab with pictures and a short description of each researcher and their interests. The page entitled “The Data” uses a GoogleMaps portal to show data collected by the research team. For example, the Alpine Hydrology data page includes measurements of nitrate concentrations at different water sampling sites throughout Green Lakes Valley. The “Results” page shows key findings of the research. The “Follow Us” page links to a blog written by the researchers with pictures and videos about their daily research. A link on the blog and ScienceLIVE page connect users to the researcher’s twitter feed. Curriculum for use in formal education can be found on the ScienceLIVE homepage through the “For Teachers” link.

## **2.3 Curriculum description**

The ScienceLIVE Alpine Hydrology unit consists of three lesson plans; the Black Box of Alpine Hydrology, the Alpine Nitrogen Cycle, and Glaciers on the Move. Both the Black Box and Alpine Nitrogen Cycle lessons are for grades 6-12, and Glaciers on the Move is for grades K-8.

### ***2.3.1 The black box of alpine hydrology***

*Lesson summary.* Students observe a “mountain catchment” (a box) that has three flow paths; one that discharges more water than is added to it, one that discharges an equal volume of water that is added, and another that has no discharge (Fig. 18). Students are asked to make

*ScienceLIVE*

## Alpine Hydrology in Colorado

**About Hydrology**


The Questions

The Team

The Data

The Results

Follow Us!



Here in Boulder, the majority of our drinking water comes from Boulder Creek, which originates high up in the Rockies at the Continental Divide. The headwaters of North Boulder Creek are within the City of Boulder watershed, which is closed to the public. Adjacent to the watershed is the Niwot Ridge Long Term Ecological Research site, where students and researchers from CU and across the country study climate, tundra vegetation, pikas and marmots, microbial life, and hydrology (water and snow).

Each year, a few researchers from the University of Colorado are allowed to access the Green Lakes Valley, inside of the City of Boulder watershed, to conduct long-term ecological research.

Alpine hydrologists, like CU graduate student Katya Hafich and professor Dr. Mark Williams, study the amount and quality of water in Green Lakes Valley. A primary concern for hydrologists and city water managers is how much water will be available for use each year. Students from CU monitor and model the snowpack in Green Lakes Valley during the annual snow survey, which occurs when the maximum accumulation of snow is reached. Students and researchers ski into the valley to take 500 snow depth measurements and dig 6 snow pits.

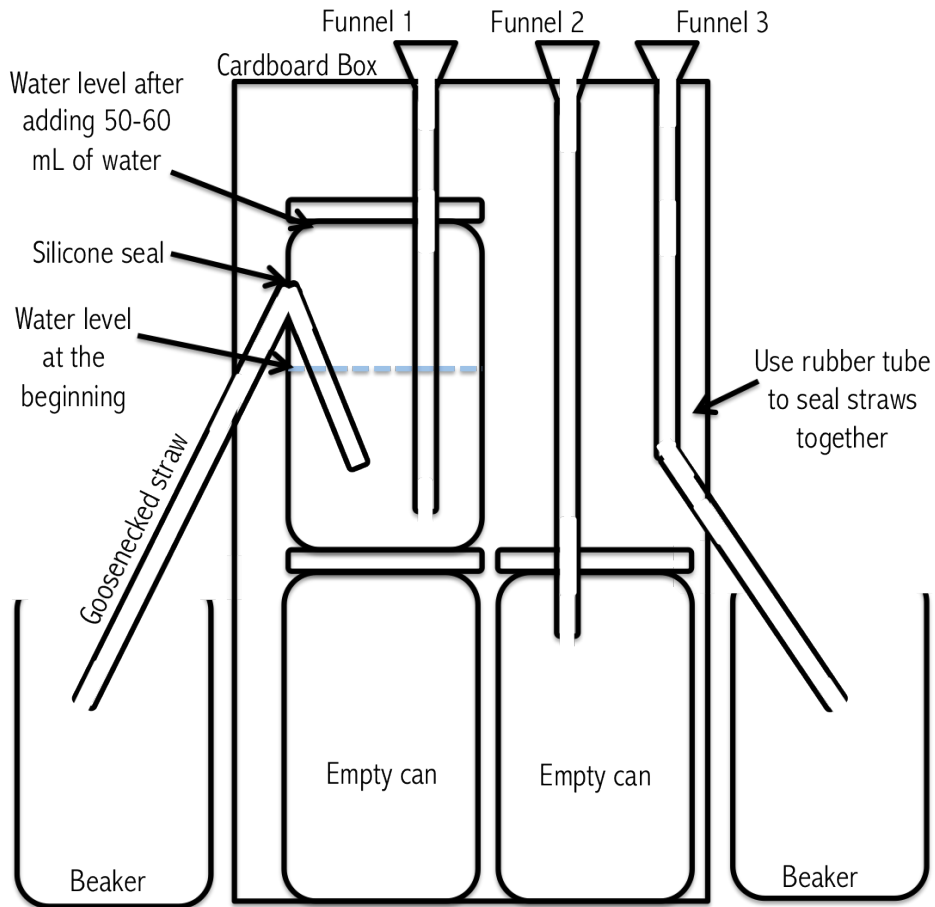
© 2012 ScienceLIVE. All rights reserved.

**Figure 17.** Page describing alpine hydrology research at Niwot Ridge LTER, found at <http://www.science-live.org/hydrology/about/alpinehydrology.html>. The video linked explains the work that snow interns do to collect data on snow hydrology at Niwot Ridge.

observations and inferences about the “catchment”, create and test hypotheses to see how it works, and build a model of the catchment. The box represents different flow paths through mountain catchments; one is through saturated soil water (the path that produces water) and the other is overland flow (the path that doesn’t have extra water), and one that feeds into is groundwater (the path that doesn’t let water out).

*Learning Goals.* The stated content learning goal of the lesson is; “Precipitation can flow through multiple flow paths when it reaches the ground in a catchment. Whether and when it reaches the stream can depend on many factors, including the soil saturation, topography, and geology.” This learning goal directly addresses the Colorado state science standards high school standard 3.6, in the Earth Systems Science section that states “The interaction of Earth’s surface with water, air, gravity, and biological activity causes physical and chemical changes” (p.35, Co Dept. of Ed, 2009). Understanding how water flows through an ecosystem is a foundation of alpine hydrology, and will build upon and deepen students’ knowledge of the water cycle. It will also help students with the Nitrogen Cycle lesson in the Alpine Hydrology unit, but emphasizing flow of matter through an ecosystem.

There are several nature of science (NOS) concepts addressed in the lesson with the overarching concept being the scientific process and the creativity and ingenuity it entails. The black box activity is meant to “provide students with experiences similar to those of scientists” (Lederman 1992). The hydrology “black box” represents the challenges hydrologists face when studying a catchment; they cannot open up the ground beneath to look inside and they are only able to measure the inputs and outputs of a system.



**Figure 18.** The hydrology black box, built from 3 empty soda cans, 3 small funnels, goosenecked straws, rubber tube, silicone, 2 500 mL beakers, and a cardboard box. To use the black box, make sure to pour 270 mL of water into Funnel 1 prior to the demonstration without students knowing. In class, explain that the box is a mountain catchment. The water that we pour into the funnels represents a summer rain storm, and the water that comes out of the box in the straws represents stream flow or discharge. Next, measure out 60 mL three times, and pour 60 mL into each funnel. Measure the water that comes out in each beaker. The demonstration can only be done once (unless you can refill the can through Funnel 1 while the students can't see).

The NOS concepts presented are meant to be explicit in the lesson. As Lederman (1992) argues, students cannot be expected to understand NOS “simply through the performance of scientific inquiry and/or investigations” (p.336), rather students must be explicitly guided in understanding the nature of science. It is up to the teacher to emphasize the aspects of nature of science in the activity explicitly, and there are parts of the lesson built in to explicitly address NOS as well (e.g. observation versus inference discussion).

The first NOS concept addressed is the difference between observations and inferences, stated in the first NOS learning goal. Students are asked to observe the catchment box, and write down their observations. This concept is especially salient in the natural sciences, where most research questions stem from careful observation, and the inferences that are drawn from those observations. Good observation skills are also essential for hypothesis-based learning, which begins with observation (VanDorn 2005). To explicitly address the concept, teachers are asked to have a discussion about observations versus inferences using the students’ own words, explicitly addressing the difference between the two.

The second NOS learning goal is that “scientific knowledge is based on observation but ultimately a product of human inference, imagination, creativity, and collaboration” This concept addresses McComas’ (1998) NOS myth number seven, that “science is procedural more than creative” (p.65). Students are asked to be creative in the process of testing their hypothesis and building models of the catchment box. Students will also work in groups to build models of the catchment box, inspiring creativity and an exchange of ideas. This learning goal also addresses McComas’ (1998) myth number 15, that “science is a solitary pursuit” (p.67).

The third NOS learning goal addresses the definition of a hypothesis. Students are asked to come up with an explanation of how the catchment box works. Following the principles of

hypothesis-based learning, they are then asked to “design a test of their explanation and predict the outcome” (VanDorn 2005). The learning goal emphasizes that the hypothesis is testable, as Galus (2003) emphasizes that a hypothesis is a “testable prediction.” Teachers can emphasize that a prediction would be just a statement explaining where and how much water will come out when water is poured in each funnel, whereas a hypothesis is an explanation of the mechanism or process occurring inside the box that controls how much water comes out where. This learning goal addresses McComas’(1998) myth number three, which states that a hypothesis is an educated guess. The lesson emphasizes that a hypothesis is an explanation, or as Newton used the term, an immature theory (McComas 1998).

The final NOS concept addressed is about scientific models, stating that models are not copies of reality, rather they are a tool that is used to explain and help us better understand natural phenomena. Models are emphasized in the newly released Next Generation Science Standards, as well as in the Colorado state science standards (NGSS 2013, CDE High School Science 2009). This learning goal addresses McComas’ (1998) myth number 13, that states, “science models represent reality” (p.66). The lesson emphasizes the instrumentalist approach that McComas (1998) refers to, using the catchment box to represent scientific ideas, as it doesn’t matter whether it corresponds with reality or not.

These NOS concepts are central to the understanding of the research process in hydrology. The lesson intentionally does not include a procedural diagram of the scientific method, as scientific research in practice does not follow a standard order or process of inquiry (McComas 1998), rather scientists are continually engaging in multiple parts of the scientific process at once. Scientists approach research using a “way of constructing knowledge about the natural world that distinguishes it from other disciplines or ways of knowing” (p.335, Lederman

1992). The four NOS learning goals in the Black Box lesson are central to the scientific process that I've experienced as a researcher, and will help students better understand the nature of science research.

*Lesson Description.* The lesson is designed for 2 50-minute class periods, or one 90-minute lab. To begin the lesson, students are asked to participate in a pre-assessment activity to assess the how much students already know about hydrology. The teacher lays down a rope in the middle of the room (or outside), and put a label on one side that says "Agree", and a label on the other end that reads "Disagree". The teacher then reads three statements; "When it rains in the summer, rain that falls on the ground runs directly into rivers and streams", "The source of water in mountain streams are alpine lakes", and "There is no groundwater in the mountains". For each statement, students are asked stand along the line in a relation to whether they agree or disagree. The teacher can call on students at different parts of the spectrum and ask them to explain why they chose to stand there.

To begin the activity, teachers demonstrate how the box works by pouring water into each funnel. Students are asked to write down their observations. Next, the teacher writes down students' observations on the board, dividing them into observations and inferences, and explains that an observation recognizes or notes a fact or occurrence whereas an inference is a conclusion based on an observation.

The next portion of the lesson introduces students to the scientific process and how to formulate a scientific hypothesis. Teachers explain that hydrology is like working with a black box. Hydrologists are able to measure inputs (rain and snow) and outputs (stream discharge), but unable to see through the earth to see flow paths of water. In hydrology research, scientists begin with observations, create inferences from those observations, and formulate a research question



from those inferences and observations. Students are asked to formulate a research question and a hypothesis about how water flows through the black box. Teachers emphasize that a prediction would be a statement of how much water will come out, whereas a hypothesis is an explanation of the process happening inside the box. Students are then asked to list ideas of how they could test their hypotheses.

To test their hypothesis, students are given a “toolbox” that includes a hydrologic tracer test. Teachers introduce the concept of hydrologic tracer tests that are a tool that hydrologists use to find out where and how fast water flows. Tracers could be a dye or inert chemical that is unlikely to react with other solutes, such as NaCl. For a “tracer test” in the catchment box, the teachers use water colored with food coloring to repeat the demonstration. The 330 mL should come out as a diluted color, whereas the 60 mL should come out the same as it started. Students are asked to write down their observations and inferences in labeled columns for observations and inferences.

Teachers introduce a second tool in the students’ toolbox; model building. Teachers explain that models are a tool that hydrologists use to explain how water travels through a watershed. Models enable scientists to explain a process and better understand it through a process of trial and error. While hydrologists use high level computer models with several inputs (soil type, geology, landcover, topography, etc.), students will attempt to construct a physical model of the catchment box with supplies in class. Students are divided into groups and given an assortment of materials to build a model.

To wrap up the activity, teachers explain that in the environment, water flows through multiple flow paths depending on local characteristics, including soil saturation, geology, ground cover, and topography. There are four ways in which water precipitated onto a catchment can

reach a stream: “(1) direct precipitation (or throughfall) onto an active stream channel; (2) overland flow; (3) shallow subsurface stormflow; and (4) groundwater flow “(Hornberger 205). Water traveling through all flow paths (except direct precipitation onto a stream) could decrease or increase in volume on its way to the stream. The situation in which it increases is when water passes through saturated soil and in effect flushes more water with it out of the soil. It’s very unlikely that volume could increase 5 fold as in the box model, which is a significant exaggeration. Students learn about flowpath hydrology, but are never shown how the box model works, as in the real world hydrologists are never able to look “inside” a mountain catchment.

For a post assessment, students work on a worksheet than encourages them to reflect on the catchment box model and what the different funnels are meant to represent. Students are asked to also reflect on the ways that the box model successfully represents flow paths in a mountain catchment, and the ways in which it does not.

### **2.3.2 *The alpine nitrogen cycle***

*Lesson Summary.* Students play the role of nitrogen atoms traveling through the nitrogen cycle in an alpine tundra environment. Several placards are set up throughout the room that represent different places that nitrogen is stored, including the atmosphere, soil, and flora and fauna unique to the alpine tundra environment of Niwot Ridge.

*Learning Goals.* This lesson primarily focuses on content goals and less on nature of science. The four learning goals are:

- Nitrogen makes up approximately 80% of the earths atmosphere, and is a vital nutrient to all living things.
- Nitrogen undergoes cycling and transformations so that it can be usable to many different life forms.

- Nitrogen is stored in several different reservoirs such as the atmosphere, living organisms, soils, and surface water.
- Human actions are changing the nitrogen cycle by converting atmospheric nitrogen to more available forms in the cycle through fertilizer production and fossil fuel emissions, resulting in compromised air and water quality that is driving changes in ecosystem and human health.

These learning goals address the Colorado state standards for 6<sup>th</sup> grade life science, 2.2

“Organisms interacts with each other and their environment in various ways that create a flow of energy and cycling of matter in an ecosystem” (p.17) and high school life science 2.1 and 2.1.f, that states that “Matter tends to be cycled within an ecosystem, while energy is transformed and eventually exits and ecosystem; Describe how carbon, nitrogen, phosphorus, and water cycles work” (p.20). NGSS standards MS-LS2-3 and HS-LS2-4 are also addressed.

*Lesson Description.* Teachers begin the class by introducing the importance of nitrogen as an essential nutrient for life. They explain each step of the nitrogen cycle, and emphasize the phase changes and ways in which nitrogen travels through nutrient reservoirs. Next students play the nitrogen cycle game.

To set up the nitrogen cycle game, placards (Fig. 19) are placed at stations around the room, with a stamp and inkpad at each station. Students play the role of a nitrogen atom travelling through nitrogen reservoirs, or stations around the room. Each student is given a “Nitrogen Passport” hand out, and records their journey through the nitrogen cycle using their passport. Students can begin at the station of their choosing. To begin, students stamp in the “Trip #1” box, and write down the name of the station in the same box. Next, students role the die to find out where they will travel to next. Before moving to the next station, students write



**If your die reads:** *Put a stamp on your passport and then roll the die to see where you will travel next!*

<b>1 or 2</b>	You become part of the <b>soil</b> .
<b>3</b>	You are dissolved in water and percolate into the <b>groundwater</b> .
<b>4</b>	You are denitrified by bacteria, and go to the <b>atmosphere</b> .
<b>5 or 6</b>	You are used for growth by a plant, go to <b>Alpine aven</b> .



**If your die reads:** *Put a stamp on your passport and then roll the die to see where you will travel next!*

<b>1 or 2</b>	Spring comes. The snow you are within melts and you trickle into <b>North Boulder Creek</b> .
<b>3 or 4</b>	As temperatures warm, the snow you are within melts and you percolate into the <b>Soil</b> .
<b>5 or 6</b>	As temperatures warm, the snow you are within melts and you percolate deep down to the <b>Groundwater</b> .



**If your die reads:** *Put a stamp on your passport and then roll the die to see where you will travel next!*

<b>An Odd Number: 1, 3, or 5</b>	The pika you are within died. Go to <b>Dead Plants and Animals</b> .
<b>An Even Number: 2, 4, or 6</b>	Congratulations! The pika you are within has excreted and you are in its waste. Go to <b>Scat</b> .



**If your die reads:** *Put a stamp on your passport and then roll the die to see where you will travel next!*

<b>An Odd Number: 1, 3, or 5</b>	You are eaten by a <b>Mayfly nymph</b> .
<b>An Even Number: 2, 4, or 6</b>	You die, and head to <b>Dead Plant and Animals</b> .

Figure 19. Examples of placards for stations in the Alpine Nitrogen Cycle game.

down how they traveled, using vocabulary (if appropriate) or simply writing the mechanism by which they travelled (e.g. fixation versus lightning strike). When playing the game, students may not go to all of the stations, and they may visit some stations more than once. After everyone is finished with the game, students are asked to use the space provided on their passport to draw a diagram or write a short story illustrating their journey through the nitrogen cycle.

At the end of the activity, the class comes back together and discusses their journey through the nitrogen cycle. Students are asked whether the nitrogen cycle ever ends, and if it's possible to visit reservoirs more than once. Students can also be asked to review vocabulary by describing the reservoirs they were traveling to and from as an example of each step of the cycle. For example, students are asked to give an example of assimilation, and could describe a pika eating an alpine avens wildflower.

Teachers can use the game to connect to the Black Box Hydrology lesson and other nutrient cycles by reinforcing the ways in which matter and energy travel through an ecosystem. To connect the nutrient cycle to the water cycle, teachers can ask students if water travels to the same reservoirs that nitrogen does, and if water facilitates the travel of nitrogen through an ecosystem. To connect the lesson to other nutrient cycles, teachers could use the same pictures for each station but have students come up with new rules for the carbon or phosphorus cycle. For example, students would create instructions for the wildflower station for photosynthesis and respiration for a carbon cycle game. Students may have to add or subtract stations.

### ***2.3.3 Glaciers on the move***

*Lesson Summary.* This glacier lesson is created for grades K-8. In an inquiry base activity, students learn about how glaciers move by observing how a "flubber" glacier slides down a tiny mountain valley. While honing their observation skills, they will learn how slope and basal

conditions (roughness of the ground surface) affect glacier movement. Students conclude the activity with a graphing exercise using mass balance data from Arikaree Glacier at Niwot Ridge, to give students an understanding of current glacier dynamics in Colorado.

*Learning Goals.* The lesson learning goals align are content based, and fit within units on landform processes commonly taught in fifth and sixth grade in Colorado.

- A glacier is a large mass of ice that moves.
- Glaciers form from snowfall that accumulates high in the mountains.
- The movement of glaciers has shaped much of the world around us through erosion and deposition, creating U-shaped valleys, hanging valleys, arêtes, horns, and leaving behind glacial erratics.
- Basal conditions and slope affect glacier movement.

The Colorado state standards addressed by the learning goals are the fifth grade Earth Science 3.2, “Earth’s surface changes constantly through a variety of processes and forces” and the sixth grade Earth Systems Science 3.1 “Complex interrelationships exist between Earth’s structure and natural processes that over time are both constructive and destructive” (p. 17; 19, Co Dept. of Ed, 2009).

*Lesson Description.* The lesson utilizes four “glacier chutes”, which are 5 inch diameter PVC split lengthwise, with stands also constructed from PVC to hold up the chutes at an angle (Fig. 20). The four chutes differ by surface (basal condition) and slope. Two chutes are smooth surface, one has a steep slope and the other has a gentler slope. The other two have steep slopes, and one is covered with sandpaper and the other is covered by small rocks.





**Figure 20.** Students using the sandy and steep glacier chute to observe the flubber “glacier” moving downhill. The chute is made out of PVC pipe lined with sandpaper. Picture by Kristin Swihart 2013

Teachers begin the lesson with an introduction to glaciers for students, with pictures of different types of glaciers and the landforms created by glaciers. At the end of the presentation, students are shown a picture of two outlet glaciers side by side that come from the same ice cap. One glacier moves faster than the other, as seen by the heavy crevassing on the surface of the glacier on the left. Students are asked to brainstorm why they think one glacier may be moving fast than the other.

To begin the glacier flubber activity, students are asked to come up with a prediction by answering the question, which glacier will travel the fastest and why? Next, students are divided into four groups, one for each glacier chute. Students prepare for the experiment by placing the flubber at the top of the chute, and measuring the distance between the “terminal wall”, or bottom edge of the flubber, and the top of the chute. Once all students are ready, all groups let the flubber go at once, and observe the flubber as it travels down the chute. Students are asked to make measurements of how far the glacier travelled periodically throughout the experiment. After about 6 measurements and when most “glaciers” have travelled the entire chute, the experiment ends and students calculate the total distance travelled by each glacier. Students compare distance travelled on different chutes, and are asked to write a conclusion that reflects on the results on the experiment and whether their original prediction came true.

*Glacier Follow-Up Activity.* A follow-up workshop uses data from Nel Caine’s research on Arikaree glacier in Green Lakes Valley to show students the effect of warming climate on glaciers at high elevations. Students are asked to make observations of pictures of the glacier, and then are given annual accumulation and ablation values to calculate mass balances (cm WE) for the glacier for 2000-2013. They are then asked to calculate the cumulative mass balance, and



graph their results. The worksheet was created in response to teachers asking for more real data to use in their classrooms.

### **3.4 Conclusions**

Since the launch of the ScienceLIVE Alpine Hydrology unit in fall of 2013, teachers throughout Colorado have expressed excitement about hands on activities that use real data. The Alpine Nitrogen Cycle activity has been most popular, as it gives students a hands on understanding of nutrient cycling, a subject that teachers often don't like to teach (Personal Communication). We hope to continue to develop the ScienceLIVE Alpine Hydrology unit to incorporate more live research updates from snow interns and other members of the Williams lab that work at Niwot Ridge LTER.

## REFERENCES

- Alexander, B., Hastings, M.G., Allman, D.J., Dachs, J., Thornton, J.A., and Kunasek, S.A. (2009). Quantifying atmospheric nitrate formation pathways based on a global model of the oxygen isotopic composition ( $^{17}\text{O}$ ) of atmospheric nitrate. *Atmos. Chem. Phys* 9, 5043-056.
- Barman, Charles R. (1997). Students' views of scientists and science: Results from a national study. *Science and Children* 35(1): 18-23.
- Barnes, R.T., Williams, M.W., Parman, J.N., Hill, K., and Caine, N. (2013). Thawing glacial and permafrost features contribute to nitrogen export from Green Lakes Valley, Colorado Front Range, USA. *Biogeochemistry*
- Baron, J.S., Schmidt, T.M., and Hartman, M.D. (2009). Climate-induced changes in high elevation stream nitrate dynamics. *Global Change Biology* 15, 1777-789.
- Bieber, A.J., Williams, M.W., Johnsson, M.J., and Davinroy, T.C. (1998). Nitrogen transformations in alpine talus fields, Green Lakes Valley, Front Range, Colorado, USA. *Arctic and alpine research*, 266-271.
- Böhlke, J.K., Mroczkowski, S.J., and Coplen, T.B. (2003). Oxygen isotopes in nitrate: new reference materials for  $^{18}\text{O}$ : $^{17}\text{O}$ : $^{16}\text{O}$  measurements and observations on nitrate-water equilibration. *Rapid Commun Mass Spectrom* 17, 1835-846.
- Brickhouse, Nancy W, Lowery, Patricia and Schultz, Katherine. 2000. What kind of girl does science? The construction of school science identities. *Journal of Research in Science Teaching* 37(5):441-458.
- Brooks, P. D., Schmidt, S. K. and Williams, M. W. (1997) Winter production of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  from alpine tundra: environmental controls and relationship to inter-system C and N fluxes. *Oecologia*, 110(3), 403-413.
- Brooks, P.D., Williams, M.W., and Schmidt, S.K. (1998). Inorganic nitrogen and microbial biomass dynamics before and during spring snowmelt. *Biogeochemistry* 43, 1-15.
- Bull, G., Thompson, A., Searson, M., Garogalo, J., Park, J., Young, C., & Lee, J. (2008). Connecting informal and formal learning experiences in the age of participatory media. *Contemporary Issues in Technology and Teacher Education* 4(2): 100-107.
- Burns, D.A. (2004). The effects of atmospheric nitrogen deposition in the Rocky Mountains of Colorado and southern Wyoming, USA—a critical review. *Environ Pollut* 127, 257 - 269.
- Burns, D.A. and C. Kendall. (2002) Analysis of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  to differentiate  $\text{NO}_3^-$  sources in runoff at two watersheds in the Catskill Mountains of New York. *Water Resources Research* 38(5) 10.1029/2001WR00292.
- Caine, N. (1995) Temporal trends in the quality of streamwater in an alpine environment: Green Lakes Valley, Colorado Front Range, USA. *Geografiska Annaler. Series A. Physical Geography*, 207-220.
- Campbell, D.H., Kendall, C., Chang, C.C.Y., Silva, S.R., and Tonnessen, K.A. (2002). Pathways for nitrate release from an alpine watershed: Determination using  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ . *Water Resources Research* 38, 10-1-10-9.

- Christopherson N, Hooper, R.P. 1992. Multivariate analysis of stream water chemical data: The use of principal component analysis for the end-member mixing problem. *Water Resources Research*, 28: 99-107.
- Clow, D. W., Schrott, L., Webb, R., Campbell, D. H., Torizzo, A. and Dornblaser, M. (2003) Ground water occurrence and contributions to streamflow in an alpine catchment, Colorado Front Range. *Groundwater*, 41(7), 937-950.
- Clow, D. W., Mast, M. A., Bullen, T. D. and Turk, J. T. (1997) Strontium 87/strontium 86 as a tracer of mineral weathering reactions and calcium sources in an alpine/subalpine watershed, Loch Vale, Colorado. *Water Resources Research*, 33(6), 1335-1351.
- Clow, D.W. (2010). Changes in the Timing of Snowmelt and Streamflow in Colorado: A Response to Recent Warming. *Journal of Climate* 23, 2293-2306.
- Cobern, W. and Aikenhead, G. (1998). Cultural Aspects of Learning Science. K. G. Tobin and B.J. Fraser (Eds.), *International Handbook of Science Education*, 39-52, Great Britain: Kluwer.
- Colorado Department of Education. CDE: High School Science Standards. 2009.
- Darrouzet-Nardi, A., Erbland, J., Bowman, W.D., Savarino, J., and Williams, M.W. Landscape-level nitrogen import and export in an ecosystem with complex terrain, Colorado Front Range. *Biogeochemistry* , 1-15.
- De Wit, H.A., Hindar, A., and Hole, L. (2008). Winter climate affects long-term trends in stream water nitrate in acid-sensitive catchments in southern Norway. *Hydrology and Earth System Sciences* 12, 393-403.
- Elser, J.J., Andersen, T., Baron, J.S., Bergström, A.K., Jansson, M., Kyle, M., Nydick, K.R., Steger, L., and Hessen, D.O. (2009). Shifts in lake N:P stoichiometry and nutrient limitation driven by atmospheric nitrogen deposition. *Science* 326, 835-37.
- Erickson, T.A., Williams, M.W., and Winstral, A. (2005). Persistence of topographic controls on the spatial distribution of snow in rugged mountain terrain, Colorado, United States. *Water Resources Research* 41, n/a.
- Galus, Pamela J. 2003. A testable prediction. *The Science Teacher* 70(5):10.
- Greenhow, C., Robelia, B. and Hughes, . E. (2009) Learning, Teaching, and Scholarship in a Digital Age: Web 2.0 and Classroom Research: What Path Should We Take Now? *Educational Researcher*, 38(4), 246-259.
- Gulbrandsen, . T. and Just, . N. (2011) The collaborative paradigm: towards an invitational and participatory concept of online communication. *Media, Culture & Society*, 33(7), 1095-1108.
- Hood, E.W., Williams, M.W., and Caine, N. (2003). Landscape controls on organic and inorganic nitrogen leaching across an alpine/subalpine ecotone, Green Lakes Valley, Colorado Front Range. *Ecosystems* 6, 31-45.
- Hong, B., Swaney, D. P., Woodbury, P. B. and Weinstein, D. A. (2005) Long-term nitrate export pattern from Hubbard Brook watershed 6 driven by climatic variation. *Water, Air, and Soil Pollution*, 160, 293-326.

- Hornberger, George M., Raffensperger, Jeffrey P., Wiberg, Patricia L., and Eshleman, Keith N. *Principles of Hydrology*. Baltimore, MD: Johns Hopkins University Press, 1998.
- Ives, J.D., and Fahey, B.D. (1971). Permafrost occurrence in the Front Range, Colorado Rocky Mountains, U.S.A. *Journal of Glaciology* 10, 105-111.
- Janke, J.R. (2005). Modeling past and future alpine permafrost distribution in the Colorado Front Range. *Earth Surface Processes and Landforms* 30, 1495-1508.
- Jones, J. B. (2005) Nitrogen loss from watersheds of interior Alaska underlain with discontinuous permafrost. *Geophysical Research Letters*, 32(2).
- Kaiser, J., Hastings, M.G., Houlton, B.Z., Röckmann, T., and Sigman, D.M. (2007). Triple oxygen isotope analysis of nitrate using the denitrifier method and thermal decomposition of N<sub>2</sub>O. *Analytical Chemistry* 79, 599-607.
- Kendall, C. (1998). Tracing nitrogen sources and cycles in catchments. P.519-576. In C. Kendall and J.J. McDonnell (ed.) *Isotope tracers in catchment hydrology*. Elsevier, Amsterdam, The Netherlands.
- King, A. J., Freeman, K. R., McCormick, K. F., Lynch, R. C., Lozupone, C., Knight, R. and Schmidt, S. K. (2010) Biogeography and habitat modelling of high-alpine bacteria. *Nat Commun*, 1, 53.
- Lederman, Norman G. and Abd-El-Khalick, Fouad. 1992. Avoiding De-Natured Science: Activities that Promote Understandings of the Nature of Science. *Teaching the Nature of Science*.
- Lederman, N. G. (1992). Students' and Teachers' Conceptions of the Nature of Science: A Review of the Research. *Journal of Research in Science Teaching*, 29(4), 331-359.
- Leopold, M., Völkel, J., Dethier, D.P., and Williams, M.W. (2013). Changing mountain permafrost from the 1970s to today; comparing two examples from Niwot Ridge, Colorado Front Range, USA. *Zeitschrift für Geomorphologie, Supplementary Issues*
- Ley, R.E., Williams, M.W., and Schmidt, S.K. (2004). Microbial population dynamics in an extreme environment: controlling factors in unvegetated talus soils at 3750 m in the Colorado Rocky Mountains. *Biogeochemistry* 68, 313-335.
- Litaor, M.I. (1993). The influence of soil interstitial waters on the physicochemistry of major, minor and trace metals in stream waters of the Green Lakes Valley, Front Range, Colorado. *Earth Surface Processes and Landforms* 18, 489-504.
- Liu, F., Williams, M.W., and Caine, N. (2004). Source waters and flow paths in an alpine catchment, Colorado Front Range, United States. *Water Resources Research* 40, n/a.
- Liu, F., Williams, M. W. and Caine, N. (2004) Source waters and flow paths in an alpine catchment, Colorado Front Range, United States. *Water Resources Research*, 40(9).
- McComas, W.F. (ed). *The Nature of Science in Science Education*. Netherlands: Kluwer Academic Publishers, 1998. p. 53-70.
- McComas, W. F. (1997). The Principal Elements of the Nature of Science Dispelling the Myths, Adapted from the chapter in W.F. McComas (ed.) *The Nature of Science in Science Education*, Kluwer: the Netherlands, 53-70.

- Michalski, G., Meixner, T., Fenn, M., Hernandez, L., Sirulnik, A., Allen, E., and Thiemens, M. (2004). Tracing atmospheric nitrate deposition in a complex semiarid ecosystem using  $\delta^{17}\text{O}$ . *Environ Sci Technol* 38, 2175-181.
- Mladenov, N., Williams, M.W., Schmidt, S.K., and Cawley, K. (2012). Atmospheric deposition as a source of carbon and nutrients to barren, alpine soils of the Colorado Rocky Mountains. *Biogeosciences Discussions* 9, 2375-2424.
- Monson, R. K., Turnipseed, A. A., Sparks, J. P., Harley, P. C., Scott-Denton, L. E., Sparks, K., & Huxman, T. E. (2002). Carbon sequestration in a high-elevation, subalpine forest. *Global Change Biology*, 8(5), 459-478.
- Morin, S., Savarino, J., Frey, M.M., Domine, F., Jacobi, H.W., Kaleschke, L., and Martins, J.M.F. (2009). Comprehensive isotopic composition of atmospheric nitrate in the Atlantic Ocean boundary layer from 65 S to 79 N. *Journal of Geophysical Research* 114, D05303.
- Naff, C. S., Darcy, J. L. and Schmidt, S. K. (2013) Phylogeny and biogeography of an uncultured clade of snow chytrids. *Environ Microbiol*, 15(10), 2672-80.
- Nanus, L., Williams, M.W., Campbell, D.H., Elliott, E.M., and Kendall, C. (2008). Evaluating regional patterns in nitrate sources to watersheds in national parks of the Rocky Mountains using nitrate isotopes. *Environ Sci Technol* 42, 6487-493.
- NGSS Lead States. 2013. *Next Generation Science Standards: For States, By States*. Washington, DC: The National Academic Press.
- Ohte, N. (2004) Tracing sources of nitrate in snowmelt runoff using a high-resolution isotopic technique. *Geophysical Research Letters*, 31(21).
- Petrone, K. C., Jones, J. B., Hinzman, L. D. and Boone, R. D. (2006) Seasonal export of carbon, nitrogen, and major solutes from Alaskan catchments with discontinuous permafrost. *Journal of Geophysical Research*, 111(G2).
- Rogora, M. (2007). Synchronous trends in N–NO<sub>3</sub> export from N-saturated river catchments in relation to climate. *Biogeochemistry* 86, 251-268.
- Saros, J. E., Rose, K. C., Clow, D. W., Stephens, V. C., Nurse, A. B., Arnett, H. A., Stone, J. R., Williamson, C. E. and Wolfe, A. P. (2010) Melting Alpine glaciers enrich high-elevation lakes with reactive nitrogen. *Environ Sci Technol*, 44(13), 4891-6.
- Schadt, C. W., Martin, A. P., Lipson, D. A. and Schmidt, S. K. (2003) Seasonal dynamics of previously unknown fungal lineages in tundra soils. *Science*, 301(5638), 1359-1361.
- Seastedt, T.R., Bowman, W.D., Caine, T.N., McKNIGHT, D., Townsend, A., and Williams, M.W. (2004). The landscape continuum: A model for high-elevation ecosystems. *Bioscience* 54, 111-121.
- Sickman, J. O., Leydecker, A. L., Chang, C. C., Kendall, C., Melack, J. M., Lucero, D. M. and Schimel, J. (2003) Mechanisms underlying export of N from high-elevation catchments during seasonal transitions. *Biogeochemistry*, 64(1), 1-24.
- Slemmons, K. E., Saros, J. E. and Simon, K. (2013) The influence of glacial meltwater on alpine aquatic ecosystems: a review. *Environ Sci Process Impacts*, 15(10), 1794-806.
- Thiemens, M.H. (2006). History and applications of mass-independent isotope effects. *Annual*

- Review of Earth and Planetary Sciences 34, 217-262.
- VanDorn, Kristy. 2005. Hypothesis-based learning. *Science Scope* 29(3):57.
- Vannote, R.L., Minshall, G.W., Cummins, K.W., Sedell, J.R., and Cushing, C.E. (1980). The river continuum concept. *Canadian journal of fisheries and aquatic sciences* 37, 130-37.
- Williams, M.W., and Melack, J.M. (1991). Solute chemistry of snowmelt and runoff in an alpine basin, Sierra Nevada. *Water resources research* 27, 1575-588.
- Williams, M.W., Brooks, P.D., Mosier, A., and Tonnessen, K.A. (1996). Mineral nitrogen transformations in and under seasonal snow in a high-elevation catchment in the Rocky Mountains, United States. *Water Resources Research* 32, 3161-171.
- Williams, M.W., Davinroy, T., and Brooks, P.D. (1997). Organic and inorganic nitrogen pools in talus fields and subtalus water, Green Lakes Valley, Colorado Front Range. *Hydrological processes* 11, 1747-760.
- Williams, M.W., and Tonnessen, K.A. (2000). Critical loads for inorganic nitrogen deposition in the Colorado Front Range, USA. *Ecological Applications* 10, 1648-665.
- Williams, M.W., Knauf, M., Caine, N., Liu, F., and Verplanck, P.L. (2006). Geochemistry and source waters of rock glacier outflow, Colorado Front Range. *Permafrost and Periglacial Processes* 17, 13-33.
- Williams, M.W., Knauf, M., Cory, R., Caine, N., and Liu, F. (2007). Nitrate content and potential microbial signature of rock glacier outflow, Colorado Front Range. *Earth Surface Processes and Landforms* 32, 1032-047.
- Williams, M. W., Barnes, R. T., Parman, J. N., Freppaz, M. and Hood, E. (2011) Stream water chemistry along an elevational gradient from the Continental Divide to the foothills of the Rocky Mountains. *Vadose Zone Journal*, 10(3), 900.