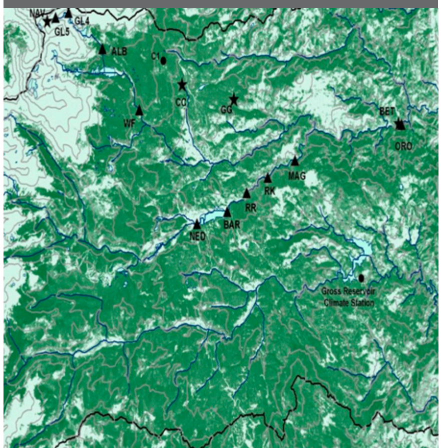
Special Section:
Critical Zone Observatories

Mark W. Williams*
Rebecca T. Barnes
Jordan N. Parman
Michele Freppaz
Eran Hood



Analysis of water draining headwater catchments from the foothills to the Continental Divide of the Colorado Front Range show that the rugged topography drives unique biogeochemical processes, low-elevation basins are closer to N-saturation than previously thought, and that a space-for-time substitution is warranted at the snow/rain transition.

M.W. Williams and J.N. Parman, Dep. of Geography and Institute of Arctic and Alpine Research, Univ. of Colorado, Boulder, CO 80309-0450; R.T. Barnes, Dep. of Geological Sciences, Univ. of Colorado, Boulder, CO 80303 and Dep. of Earth Science, Rice Univ., Houston, TX 77005; M. Freppaz, Univ. degli Studi di Torino, Di.Va.P.R.A.– Chimica Agraria e Pedologia–Laboratorio Neve e Suoli Alpini. 44, Via Leonardo da Vinci, 10095 Grugliasco (TO); E. Hood, Dep. of Natural Sciences, Univ. of Alaska Southeast, Juneau, AK 99801. *Corresponding author (markw@snobear.colorado.edu).

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Stream Water Chemistry along an Elevational Gradient from the Continental Divide to the Foothills of the Rocky Mountains

Small changes in the flux of energy, chemicals, and water to mountain catchments may invoke large changes in the local climate, ecosystem dynamics, and water quantity and quality. The Landscape Continuum Model (LCM) was developed in part to improve our understanding of how high-elevation ecosystems might respond to future perturbations. We sampled water chemistry along the main stem of Boulder Creek in the Colorado Front Range from the foothills to the Continental Divide, along with four headwater catchments, to address two questions: (i) Is there value in extending the LCM concept to lower-elevation headwater catchments? (ii) Is a "space-for-time" substitution along an elevational gradient appropriate when there are changes in ecosystem type? Our results show that the hydrochemistry of headwater catchments along the elevational gradient of Boulder Creek was different when compared to the main stem. Headwater catchments amplified the fluxes of inorganic and organic solutes when compared with sites at similar elevations along the main stem of Boulder Creek, consistent with the LCM. Our results also suggest a space-for-time substitution along an elevational gradient is warranted for at least some biogeochemical processes when there is a switch from the snow to rain transition in annual precipitation. For example, the high concentrations of base cations and dissolved organic carbon in the foothills catchment when compared with higher elevation catchments is consistent with increased rates of biogeochemical cycling with increasing air temperature at lower elevations. However, the low-elevation catchment had a lower specific discharge than other catchments with similar annual precipitation, but higher percentages as snowfall, resulting in decreased fluxes of these products.

Abbreviations: ALB, Albion site; ANC, acid-neutralizing capacity; BAR, Barker Reservoir site; BC-CZO, Boulder Creek Critical Zone Observatory; CC, Como Creek site; BET, Betasso site; DIN, dissolved inorganic nitrogen; DOC, dissolved organic carbon; DOM, dissolved organic matter; DON, dissolved organic nitrogen; EEMs, excitation–emission matrices; FI, fluorescence index; GG, Gordon Gulch site; GL4, Green Lakes 4 site; GL5, Green Lake 5 site; HPOA, hydrophobic organic acids; LCM, Landscape Continuum Model; LTER, Long-Term Ecological Research; MAG, Magnolia site; NADP, National Atmospheric Deposition Program; NAV, Navajo site; NCAR, National Center for Atmospheric Research; NED, Nederland site; NWT LTER, Niwot Ridge Long Term Ecological Research site; ORO, Orodell site; RK, Rocky Knob site; RR, Ridge Road site; SUVA, specific UV absorbance; VWM, volume-weighted mean; WSF, Watershed Flume site.

Human-driven alterations of the global environment—including changes to climate, atmospheric composition, nutrient cycles, hydrologic cycling, and ecosystem structure—are now pervasive throughout the world, and accelerating (e.g., Steffen et al., 2007; IPCC, 2007; Galloway et al., 2008; Röckstrom et al., 2009). While such changes have brought substantial benefits to humanity (e.g., Smil, 2001; Kareiva et al., 2007; Townsend and Howarth, 2010), they are often accompanied by increasingly detrimental outcomes for both people and ecosystems (Galloway et al., 2008; Carpenter et al., 2009), including those in and around mountain ecosystems (Bowman and Steltzer, 1998; Williams and Tonnessen, 2000; Bowman et al., 2006). Indeed, while some remote portions of high-elevation ecosystems manage to avoid direct transformation via land use change (Bourgeron et al., 2009), taken as a whole, alpine tundra and montane forests have been identified as particularly sensitive to, and impacted by, an array of human-induced environmental changes that currently challenge society (IPCC, 2007; Williams et al., 2002).

Small changes in the flux of energy, chemicals, and water to mountain catchments may invoke large changes in climate, ecosystem dynamics, and water quantity and quality (Williams et al., 2002). The presence of a seasonal snowpack in mountain environments may amplify climate signals because of the storage and release of liquid water, solutes, and particulates from the seasonal snowpack (Seastedt et al., 2004). Moreover, meteorological, hydrological, cryospheric, and ecological conditions change greatly over relatively short distances in mountain areas because of their rugged terrain, and thus the boundaries between these systems are sensitive to small environmental changes (e.g., Erickson et al., 2005). The harsh conditions characteristic of these environments suggest that organisms in mountain ecosystems are on the razor's edge of tolerance (Williams et al., 1998). Consequently, organisms—and the biogeochemical processes mediated by them in high-elevation catchments—are notably vulnerable to small changes in climate and other environmental parameters (Williams and Tonnessen, 2000; Bowman et al., 2006). As a result, it is urgent that we improve our understanding of how hydrologic processes and biogeochemical cycling in mountain catchments will respond to a combination of changes in climate and by atmospheric deposition of pollutants such as dissolved inorganic nitrogen (DIN = $NH_4^+ + NO_3^-$).

Climate change will almost certainly reduce the depth, duration, and distribution of the continental snowpack at mid-latitudes, as well as perennial cryosphere features such as glaciers (Vergara et al., 2007) and permafrost. There is good evidence that warming has already modified snowpack, especially at elevations where the snowpack is maintained at a relatively high temperature (Mote, 2006; Nolin and Daly, 2006). In fact, snow cover decreased during the interval from 1966 to 2005 across the entire northern hemisphere, except in November and December (IPCC, 2007). Results from a recent study by Clow (2010) indicate that even the mountains of Colorado, with their high elevations and cold snowpacks, are experiencing substantial shifts in the timing of snowmelt and snowmelt runoff toward earlier in the year.

Moreover, due to their close proximity to the Denver–Boulder metropolitan region and agricultural areas to the east, high-elevation watersheds in the Colorado Front Range are exposed to disproportionately high rates of inorganic N deposition (Baron et al., 2000; Heuer et al., 2000; Williams and Tonnessen, 2000). The aquatic and terrestrial systems in these areas are particularly sensitive to even small changes in N deposition due to relatively sparse vegetation, thin soils, and short growing seasons (Suecker et al., 2000; Kuhn, 2001). As a result, alpine areas are already experiencing shifts in ecosystem structure and function (Seastedt et al., 2004). More specifically, historically N limited high-elevation ecosystems are approaching the initial stages of N saturation, fundamentally transforming the biogeochemical cycles that are integral to ecosystem health (Williams et al., 1996a). It is becoming increasingly important to more fully understand how the hydrological and biogeochemical cycles of these mountain landscapes respond to two major drivers of global change: increased inorganic N deposition and changes in climate.

To gain a better understanding of how mountain ecosystems are potential bellwethers of climate change, it is important to outline a conceptual model of how these high-elevation ecosystems accumulate and redistribute both exogenous material derived from the atmosphere and endogenous material that comes from the mountains themselves. Several studies have proposed such models, recognizing that changes in water and nutrient inputs rarely occur in a uniform fashion across the ecosystem. While some researchers emphasize the spatial heterogeneity in topography (Billings, 1973) and soil development (Burns and Tonkin, 1982) in determining zones of accumulation and redistribution, others more explicitly address physical transport via fluvial networks (Vannote et al., 1980) and material spiraling (Fisher et al., 1998).

Perhaps the most appropriate conceptual model for high-elevation ecosystems, the Landscape Continuum Model (LCM), was developed by Seastedt et al. (2004) to predict zones of nutrient pooling in both alpine and subalpine areas of a headwater catchment in the Colorado Front Range. The LCM emphasizes the downward transfer of water and nutrients via physical transport vectors such as rivers, wind, rockslides, and avalanches. The unique spatial heterogeneity of landscape cover within the watershed then determines where inorganic and organic matter is likely to accumulate or be exported further downstream. In particular, the LCM predicts that in response to increased N deposition, high-elevation headwater catchments along the Colorado Front Range should exhibit high concentrations of nitrate (NO_3^-) and low concentrations of dissolved organic carbon (DOC).

Past research conducted at the Niwot Ridge Long-Term Ecological Research (LTER) station (Niwot Ridge Long-Term Ecological Research Program, 2009) has validated the LCM conceptual model, finding that stream water yields of NO_3^- decrease moving down an elevational gradient from alpine to subalpine portions of the catchment (Hood et al., 2003a). In contrast, concentrations and yields of DOC are low at higher alpine elevations at Niwot Ridge and consist primarily of autochthonous parent material (Hood et al., 2003b, 2005), also consistent with the LCM. These and other findings (Heuer et al., 1999; Baron et al., 2000; Campbell et al., 2000) have demonstrated the unique manner in which alpine headwater catchments accumulate or export water and nutrients and how increased N deposition alters the biogeochemical cycles of these fragile ecosystems. Additionally, the mechanisms and effects of N saturation in temperate ecosystems have been widely studied in the northeast United States (Aber et al., 1989, 1998; Boxman et al., 1998; Goodale et al., 2000). However, little research has been conducted evaluating stream water nutrient concentrations along a continuous elevational gradient extending from the alpine through the montane zone. Hood et al. (2003a) demonstrated that landscape controls (soil and vegetation characteristics) play an integral role in determining the fate of exogenous and endogenous material, but we do not have a firm understanding of how land cover distribution in different headwater catchments along a altitudinal gradient may impact how nutrient cycles behave.

Often it is taken as a given that climatic change at high-elevation sites will reflect those of lower elevations. The environmental gradients associated with mountain environments suggest that space-for-time substitutions may provide insights on how future changes in climate may affect the local hydrology and ecology. In the space-for-time approach, changes in climatic conditions are simulated by comparing areas that naturally differ in their climatic regimes (Fleischer and Sternberg, 2006). Natural climatic gradients created by altitude, topography, temperature, and rainfall variations can provide a useful framework for studying the effects of climatic changes (Diaz and Cabido, 1997; Kutiel et al., 2000; Dunne et al., 2004).

This study combines two traditional conceptual frameworks: the physical transport controls common in hydrological models and the biogeochemical perspective that emphasizes substrate constraints on reaction potential. By combining these two frameworks, we can gain insight as to how hydrological and biogeochemistry processes interact at the catchment scale. Here we evaluate solute concentrations and fluxes along an elevational gradient in the Boulder Creek Drainage of the Colorado Front Range. Our objectives are twofold: (i) Is there value in extending the LCM concept to lower-elevation headwater catchments? (ii) Is there valuable information in a space-for-time substitution along an elevational gradient when there are changes in ecosystem type? To address these two objectives, we evaluate the following hypotheses:

- Solute concentrations and fluxes in headwater catchments along an elevational gradient are similar to those along the main stem of the watershed.
- Changes in vegetation cover and soil development with elevation prevents a space-for-time substitution of the effects of climatic changes.
- The character of dissolved organic matter changes across an elevational gradient in a predictable fashion from more labile types at high elevation to more recalcitrant types at lower elevations.

Site Description

The Boulder Creek Watershed is about 1160 km^2 in area and drains the Colorado Front Range from the Continental Divide (4120 m) to the eastern plains (1480 m) (Fig. 1). The watershed is located within two physiographic provinces. The upper basin, defined on the west by the Continental Divide, is part of the Southern Rocky Mountain Province and is characterized by steeply sloping valleys. The lower basin, defined on the west by the foothills of the Rocky Mountains, is part of the Colorado Piedmont Section of the Great Plains Province, and slopes gently to the northeast (Worcester, 1960). Here we focus on the mountainous upper basin, which is sparsely populated; the largest community is Nederland, with a year 2000 census population of 1394.

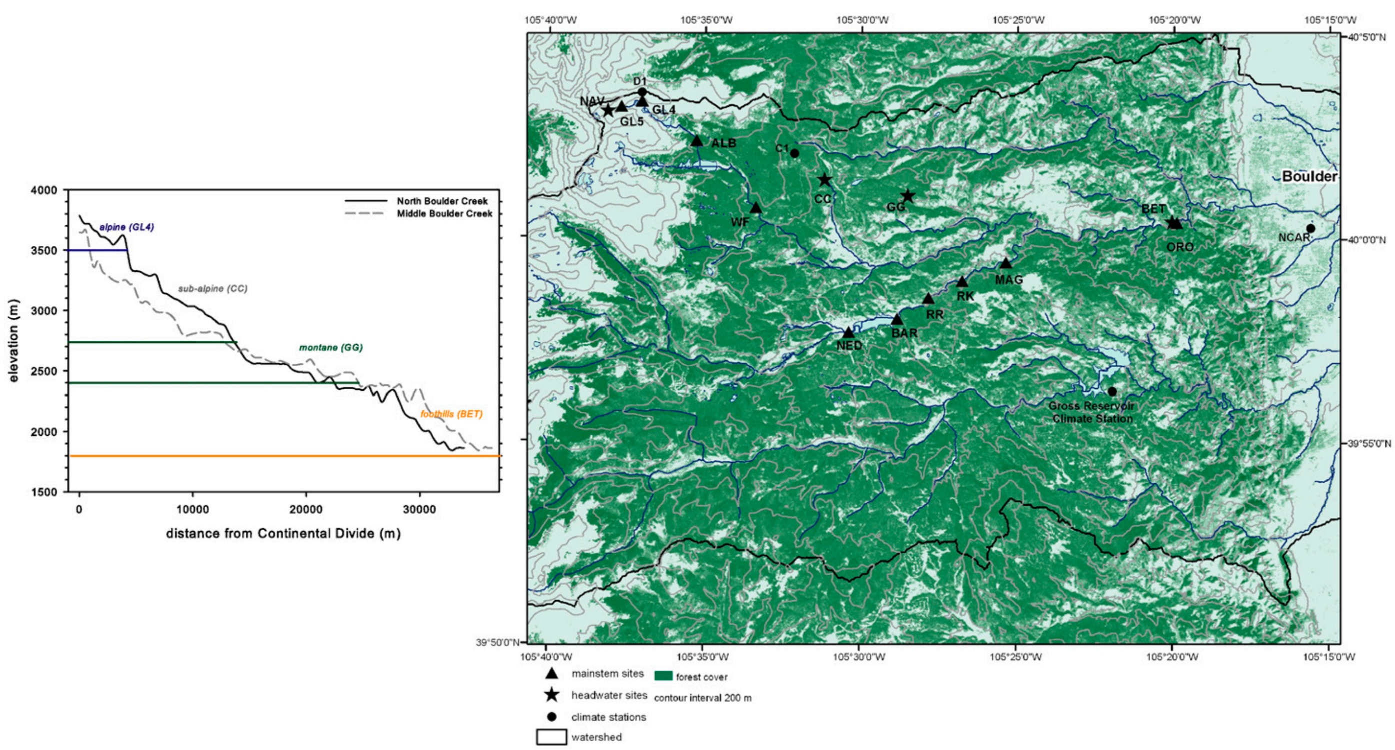

Fig. 1. Map of Boulder Creek watershed with main stem stream sampling locations (triangles), headwater stream sampling locations (stars) and climate station sites (circles). Areas shaded in green are forested. The elevational cross-section of Middle and North Boulder Creeks indicates the location of the four primary climatic zones and the representative headwater stream sampling site.

The upper basin is underlain by primarily Precambrian siliceous metamorphic and granitic rocks (Murphy et al., 2003). These rocks consist of gneisses and schists (1800 million yr old) that were intruded by the Boulder Creek Grandodiorite (1700 million yr old) and the Silver Plume granite (1400 million yr old). Alpine tundra lies above a lower elevation of 3500 m and is sparsely vegetated with perennial forbs and graminoids. The subalpine zone (3500–2700 m) is dominated by Engelmann spruce (*Picea engelmannii* Parry ex Engelm.), subalpine fir [*Abies lasiocarpa* (Hook.) Nutt.], limber pine (*Pinus flexilis* E. James), and lodgepole pine (*Pinus contorta* Douglas ex Loudon), with some aspen (*Populus tremuloides* Michx.), willow carrs, and peat fens. The montane zone (2700–2400 m) is dominated by *Pinus ponderosa* P. Lawson & C. Lawson on south-facing slopes, while the cooler north-facing slopes are a *Pinus ponderosa–Pinus contorta* mix. The foothills zone (2400–1800 m) is composed primarily of *Pinus ponderosa* and *Pinaceae pseudotsuga* Carrière. The headwater region is considered the area upstream of the Peak-to-Peak Highway to the Continental Divide and includes both the alpine and subalpine zones. This area differs from the montane and foothill zones by: (i) having been glaciated during the Pinedale and Bull Lake glaciation events and (ii) having lower amounts of soil organic matter (12–14 kg m^{-2}) than montane and foothill zones (14–16 kg m^{-2}; Kinner, 2003).

Ten sites along North and Middle Boulder Creeks were sampled weekly to biweekly during the ice-free season in 2009. The highest elevation sites Navajo (NAV), Green Lake 5 (GL5), Albion (ALB), and Watershed Flume (WSF) are along North Boulder Creek within the Niwot Ridge Long Term Ecological Research site (NWT LTER). These sites span the alpine and subalpine, ranging in elevation from 3620 m to 2693 m. Five additional sites are located along Middle Boulder Creek; Nederland (NED), Barker Reservoir (BAR), Ridge Road (RR), Rocky Knob (RK), and Magnolia (MAG) and span an altitudinal gradient from 2508 m (NED) to 2229 m (MAG). Orodell (ORO) is located downstream of the confluence of Middle and North Boulder Creeks at an elevation of 1779 m. Importantly, while these sites lie along two adjacent branches of Boulder Creek, the Middle and North Boulder Creek watersheds are very similar in land use and land cover, geology, elevation range, and size (Kinner, 2003). These sites are thus located along the main hydrological axis of Boulder Creek.

We also sampled four headwater catchments of Boulder Creek along this elevational gradient. Waters draining these catchments were sampled for the same parameters as along the main stem, and supplemented with additional analyses of the quality of dissolved organic matter (DOM). The glaciated headwater area consists of two catchments, the alpine Green Lake 4 (GL4) basin and the subalpine Como Creek Basin. GL4 is 225 ha in area (Table 1) and is characterized by a continental climate with a mean annual temperature of −3.8°C and annual precipitation of about 1000 mm (Williams et al., 1996b), 80% of which falls in the form of snow (Caine, 1996). Niwot Ridge forms the northern boundary of the basin, where climate stations and other instruments are operated by the NWT LTER program. The GL4 catchment was glaciated during the Pleistocene and contains glacial and periglacial features such as rock glaciers, along with a string of paternoster-type lakes. Exposed bedrock makes up 29% of the basin area, talus 33%, vegetated soils 29%, the Arikaree glacier 4%, and there are two lakes in the basin (5%) (Erickson et al., 2005). The entire valley is contained within the City of Boulder Watershed, and public access has been restricted for the past 80 yr, resulting in a relatively pristine watershed, protected from recreational disruption. Como Creek (CC) originates on the southeast flank of Niwot Ridge approximately 8 km east of the Continental Divide (Fig. 1). The catchment falls within the Niwot Ridge Biosphere Reserve and ranges in elevation from 2900 to 3560 m, with an area of 664 ha (Table 1). The mean annual temperature is about 4°C, and mean annual precipitation is 800 mm (Monson et al., 2002). In contrast to GL4, a large part of the Como Creek catchment lies atop Pinedale and Bull Lake glacial till, resulting in thin soils on top of the glacial till. A weir is located at the mouth of the basin at an elevation of 2900 m. Importantly, the subalpine Como Creek watershed differs from the nearby alpine Green Lakes Valley in two geomorphic respects: (i) there are no lakes in the catchment, and (ii) there is no talus, exposed bedrock, steep cliffs, or rock glaciers.

The nonglaciated portion of the upper basin of Boulder Creek is now part of the Boulder Creek Critical Zone Observatory (BC-CZO). Gordon Gulch (GG) is a montane ecosystem, 101 ha in area, and lies within the Arapahoe National Forest and joins North Boulder Creek approximately 16 km below Green Lakes Valley (Fig. 1). This site lies within the low relief post-Laramide surface below the glacial limit (Bradley, 1987). Weathered rock profiles

Table 1. Site characteristics of the four headwater catchments, with site abbreviation, elevation at the basin outlet, catchment area, dominant landscape type with percentage of forest cover, mean annual air temperature, mean annual precipitation, and percentage of precipitation that falls as snow. Mean air temperature and precipitation values are 10-yr averages from 1998 to 2008.

Site	Abbreviation	Elevation	Catchment area	Landscape type (Forest cover)	Mean annual air temperature	Mean annual precipitation	Precipitation that falls as snow
		m	ha		°C	mm	%
Green Lake 4	GL4	3550	221	Alpine (0.09%)	−3.7	1000	85
Como Creek	CC	2910	664	Subalpine (81%)	3.9	800	70
Gordon Gulch	GG	2588	101	Montane (68%)	4.0	456	59
Betasso	BET	1810	45	Foothills (55%)	10.7	475	<20

up to 15 m thick are found in this slowly evolving landscape (Isherwood and Street, 1976; Dethier and Lazarus, 2006). The lowest sample site, Betasso (BET) is 45 ha in area and representative of a foothill montane environment with steep forested slopes composed primarily of *Pinus ponderosa* and *Pinaceae pseudotsuga*, drained by an intermittent stream, and with numerous rock outcroppings. These steep slopes were formed over the last ~5 million years by renewed bedrock channel incision progressing headward from the plains, cutting into the post-Laramide surface (Anderson et al., 2006). This area is situated in the lower portion of Boulder Canyon, approximately 10 km west of the city of Boulder (Fig. 1).

The Colorado Front Range and the nearby plains host a number of National Atmospheric Deposition Program (NADP) sites along an elevational gradient. There are three NADP sites in the Boulder Creek Drainage: CO02 at 3520 m, CO90 at 3015 m, and CO94 at 2524 m. About 50 km north are three additional sets of NADP sites: Loch Vale at 3159 m, Beaver Meadows at 2477 m, and Pawnee at 1641 m. These NADP sites allow us to evaluate the relationship between elevation and annual DIN deposition in wetfall.

Methods

Climatology

Climate data has been recorded at the D1 and C1 stations on Niwot Ridge since the early 1950s (Williams et al., 1996b). D1 is located in alpine tundra at an elevation of 3700 m, 2.6 km from the Continental Divide. The C1 climate station is located in a subalpine forest at an elevation of 3005 m, 9.7 km east of the Continental Divide. Climate data for GG is represented by the Gross Reservoir station at an elevation of 2309 m, and compiled from the Western Regional Climate Center (Western Regional Climate Center, 2009). For BET, we used the climate data compiled from the National Center for Atmospheric Research (NCAR) climate station (1670 m), which has continuous measurements since 1893. For all climate station sites, we report the 2009 annual precipitation and mean annual temperatures and compare 2009 to the 10-yr average from 1998 to 2008. As participants in the NADP program (National Atmospheric Deposition Program, 2009), we also partition precipitation into either snow or rain.

Stream Sampling

Within the headwater catchments stream samples were collected weekly during the ice-free season from about 1 May to October in GLV and CC, while at GG and BET samples were collected weekly from April to July 2009 and biweekly during the later summer and fall (August–October 2009). From May to October 2009, samples from Middle Boulder Creek were collected every 2 wk and every week at ORO. Additional samples were taken at ORO throughout the rest of the year on a biweekly basis. Sample collection followed the protocol discussed in Williams et al. (2009). Briefly, samples were collected in cleaned and stream-rinsed high-density polyethylene bottles and were then transported to the Kiowa Environmental Chemistry Laboratory within a few hours of collection, where subsamples were immediately filtered through precombusted glass fiber filters with a nominal pore size of 0.7 μm and stored in the dark at 4°C before analyses. Samples for DOC and DOM characterization were collected in precombusted amber glass bottles with Teflon-lined caps, after filtering through precombusted glass-fiber filters.

Discharge and Yield Calculations

Water level was measured with a pressure transducer and converted to volumetric discharges by empirical rating curves for all the headwater sites as well as at five main stem sites (NAV, ALB, WF, NED, and ORO). Yields of chemical species were estimated as the product of measured concentrations and the accumulated water discharge for weekly intervals centered on the day of sampling. Seasonal volume-weighted mean (VWM) concentrations for individual species were calculated as seasonal mass flux divided by seasonal discharge, following the approach of Hood et al. (2003b). In this study, seasonal refers to the period between 1 May and 31 October, although it is important to note that in some of the alpine sites, the stream was ice-covered for a portion of this season.

Soil Samples

Soil samples were collected during the growing season in early August 2009 following the approach of Hood et al. (2003b) at the same elevation as the stream sample sites, all within 20 m of the stream, and each site was chosen to represent terrestrial areas that would likely contribute soil water to stream discharge following the variable source area dynamics of Creed and Band (1998). Soil samples were collected as five sets of three replicates for each location. Each set consisted of three soil cores composited in a new polyethylene bag collected using a 20-cm soil corer. The first 20 cm of soil was collected, as this is where the majority of microbial processes and C and N pools occur. Before collecting the soils, the O horizon was removed so that the samples consisted only of the A horizon and underlying horizons when the A horizon was less than 20 cm in thickness. Soils were processed within 12 h for KCl-extractable nitrate and ammonium, microbial biomass N, and total C and N, following the protocol in Hood et al. (2003b).

Laboratory Analyses

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

Dissolved organic matter in a subset of samples was characterized using optical and fractionation methods. All samples from the headwater basins were analyzed for fluorescence index (FI) and specific UV absorbance ($SUVA_{254}$). The determination of fluorescence properties and calculation of FI were as presented in Miller et al. (2006). The FI of these whole water samples were compared with an aquatic reference collected from Lake Fryxell in the McMurdo Dry Valleys of Antarctica and the terrestrial reference was from the Suwannee River that drains the Okeefenokee swamp in Georgia (McKnight et al., 2001). This FI comparison to the two reference fulvic acids serves as a semiquantitative analysis of the precursor organic material (terrestrial vs. aquatic) in the headwater catchments. Filtered stream water was analyzed for UV-Vis absorption using a Hewlett-Packard model 8453 photodiode array spectrophotometer (λ = 200–800 nm) and a 1-cm path length quartz cell. The instrument blank consisted of deionized water, and samples were gravimetrically diluted to be in the range of the instrument. Specific UV absorbance was determined at λ = 254 nm ($SUVA_{254}$), a wavelength associated with aromatic compounds (Chin et al., 1994), and is reported in decadal absorption coefficients (cm^{-1}). $SUVA_{254}$ has been used as a measure of DOC aromaticity (Weishaar et al., 2003) and is determined by dividing the UV-Vis absorbance at λ = 254 nm by DOC concentration (mg C L^{-1}).

To further understand the variability of DOM quality, three-dimensional fluorescence and fractionation methods were used to characterize a small subset of samples. Dissolved organic matter composition was optically characterized using three-dimensional fluorescence, a measure of the fluorescing portion of the DOM pool, using a Fluoromax-3TM fluorometer as described in Wickland et al. (2007). The three-dimensional excitation–emission matrices (EEMs) were subsequently analyzed via comparison to the PARAFAC model developed by Cory and McKnight (2005). This model attempts to predict the EEMs of DOM based on 13 compounds, seven of which have spectra similar to known quinones (Cory and McKnight, 2005).

Following the methods of Aiken et al. (1992), the stream water DOM of this small subset of samples was fractionated using resin columns into three groups: hydrophobic organic acids (HPOA), hydrophilic molecules, and transphilic acids using Amberlite XAD-8 and XAD-4 resins. The amount of organic matter within each fraction was calculated using the DOC concentration and the sample mass of each fraction and are presented as the percentage of total DOC. Stream water samples were fractionated in duplicate, and average values are presented. The standard deviation of these fractions was $\leq$2%. These analyses were not conducted for Como Creek.

Statistical Methods

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

Results

Climate and Hydrology

Mean annual temperatures from 1998 to 2008 increased with decreasing elevation, from 10.7°C at BET to −3.7°C at D1, a lapse rate of 7.0°C per 1000 m. The annual mean 2009 temperature for Green Lakes Valley measured at the D1 climate station was −3.2°C, within 15% of the 10-yr mean of −3.7°C (Table 1). The annual mean temperature at the C1 climate station was 4.3°C, warmer than, but within 15% of, the 10-yr mean of 3.9°C. The mean temperature at the GG site, as measured at Gross Reservoir was 5.1°C, compared to the long-term mean of 4.0°C. The 2009 mean annual temperature at the NCAR climate station was 12.3°C, slightly warmer than the long-term average of 10.7°C.

Annual precipitation from 1998 to 2008 generally decreased with decreasing elevation, ranging from 1000 mm at D1 to 475 mm at BET. The 2009 precipitation at D1 of 1214 mm was 12.1% higher than the long-term average of 1000 mm. At C1, the 804 mm of precipitation in 2009 was similar to the long-term average of 800 mm. Below at Gross Reservoir, there was 511 mm of total precipitation in 2009, compared to the long-term average of 456 mm. At the NCAR climate station, total precipitation in 2009 was 459 mm, within 2 cm of the long-term average of 475 mm. It is worth noting that annual precipitation at both GG and BET was less than 64% of the 804 mm recorded at C1; moving down in elevation from the subalpine forest resulted in a sharp decrease in annual precipitation. Thus, the climate during 2009 was similar to the 10-yr average at all sites along the elevational gradient. Additionally, the proportion of snow in annual precipitation decreased with decreasing elevation (Table 1).

The hydrographs of the high-elevation alpine and subalpine headwater sites, as well as the main stem sites, are characteristic of snowmelt-dominated catchments, with a sharp rising limb followed by a long recession limb after peak discharge (Fig. 2). The lower montane site (GG) exhibited large peaks associated with snowmelt, similar to the higher elevation sites, as well as large increases in discharge in response to summer rain events. BET differs from the other catchments in that it is an intermittent stream characterized by discharge only after precipitation events. The specific discharge measurements show a lag in the timing of peak discharge with increasing elevation, with peak discharge occurring earlier at the lowest elevation sites compared to the higher

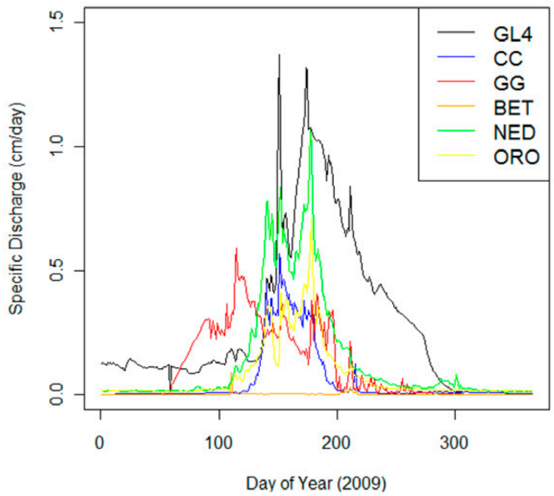

Fig. 2. Specific discharge (cm d^{-1}) at Green Lake 4 (GL4), Como Creek (CC), Gordon Gulch (GG), Betasso (BET), Nederland (NED), and Orodell (ORO) for the 2009 calendar year.

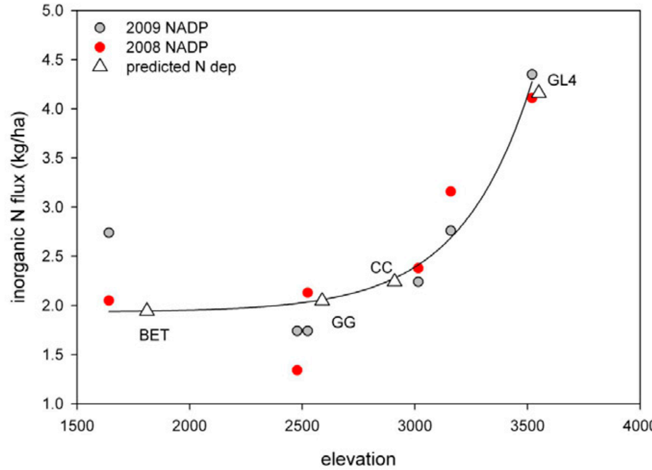

Fig. 3. Flux of inorganic dissolved nitrogen (DIN, kg N ha^{-1}) in annual wetfall along an elevational gradient from the Pawnee NADP site to the Niwot Saddle NADP site. Actual values are included from both 2008 and 2009. The annual flux of DIN at the headwater stream sampling sites are predicted based on the 2008 and 2009 NADP data.

elevation sites. At the lower elevation sites, BET peaked at 0.09 cm d^{-1} on 20 April, and GG peaked at 0.59 cm d^{-1} on 25 April. The CC hydrograph peaked at 0.57 cm d^{-1} more than a month later on 4 June, while peak discharge at the alpine GL4 occurred on 23 June (1.37 cm d^{-1}). Along the main stem, peak discharge occurred following snowmelt in the alpine and was thus later than GL4, on 26 June at NED (70.48 cm d^{-1}) and on 27 June at ORO (70.5 cm d^{-1}). Within the headwater catchments, total seasonal discharge varied by several orders of magnitude, decreasing with decreasing elevation. The total seasonal discharge at GL4 was 1982,000 m^3 compared to 1283,800 m^3 at CC. Discharge at GG was 241,580 m^3, while the smaller and intermittent BET catchment had a total discharge of only 1341 m^3.

Inorganic Nitrogen Deposition in Wetfall

There was a strong relationship between annual deposition of inorganic N in wetfall and elevation ($R^2 = 0.83$, $p = 0.0003$) (Fig. 3). The contribution of nitrate to overall DIN deposition increased significantly with elevation ($R^2 = 0.96$, $p < 0.0001$), contributing 29% at Pawnee (1644 m) and 61% at Niwot Saddle (3520 m). The larger contribution of NH_4^+ at lower elevations is likely due to nearby ranching and agricultural activities. Nitrate deposition increased sharply between 2500 and 3000 m, driven by increasing annual precipitation with elevation (Table 1). According to annual DIN deposition predictions determined by the relationship illustrated by Fig. 3, the alpine portion (4.16 kg ha^{-1}) of Boulder Creek watershed receives more than two times the N load as compared to the foothill region (1.94 kg ha^{-1}).

Stream Chemistry Along an Elevational Gradient

Concentrations of geochemical weathering products generally increased with decreasing elevation along the main drainage of Boulder Creek. To illustrate, VWM seasonal concentrations of acid-neutralizing capacity increased by more than an order of magnitude, from 44.9 μM at GL5 to 293.9 μM at ORO. Similarly, the concentrations of sodium increased from 12.7 μM at GL5 to 90.7 μM at ORO (Fig. 4). Concentrations of calcium also showed a large increase as elevation decreased, from 31.2 μM at GL5 to 129.7 μM at ORO. These decreases in weathering products with elevation were statistically significant in all cases ($p < 0.005$, Fig. 4). There were consistent seasonal variations, with the lowest concentrations during snowmelt runoff and the highest concentrations during low-flow conditions. The Ca/Na ratio increased with elevation as well, from about 2.5 at the low-elevation ORO site to about 5.5 at the high-elevation sites ($R^2 = 0.83$, $p = 0.0002$, Fig. 4). The headwater catchments showed similar negative trends with elevation for the base cations and ANC; however, the concentrations at the headwater basins were generally higher than along the hydrological axis of Boulder Creek (Fig. 4). Interestingly, the Ca/Na ratio for the headwater basins did not fall on the Ca/Na line for Boulder Creek.

In contrast, yields of geochemical weathering product showed a positive relationship with elevation along the main stem of Boulder Creek (Table 2). For example, the seasonal export of calcium showed a statistically significant relationship with elevation ($R^2 = 0.80$, $p = 0.04$), decreasing from NAV (8.4 kg ha^{-1}) to ORO (0.96 kg ha^{-1}). The seasonal export of sodium and silica followed similar patterns and were significantly related to elevation ($p < 0.05$); sodium export was 3.3 kg ha^{-1} at NAV and decreased to 0.40 kg ha^{-1} at ORO, while silica export decreased from 6.7 kg ha^{-1} at NAV to 0.40 kg ha^{-1} at ORO.

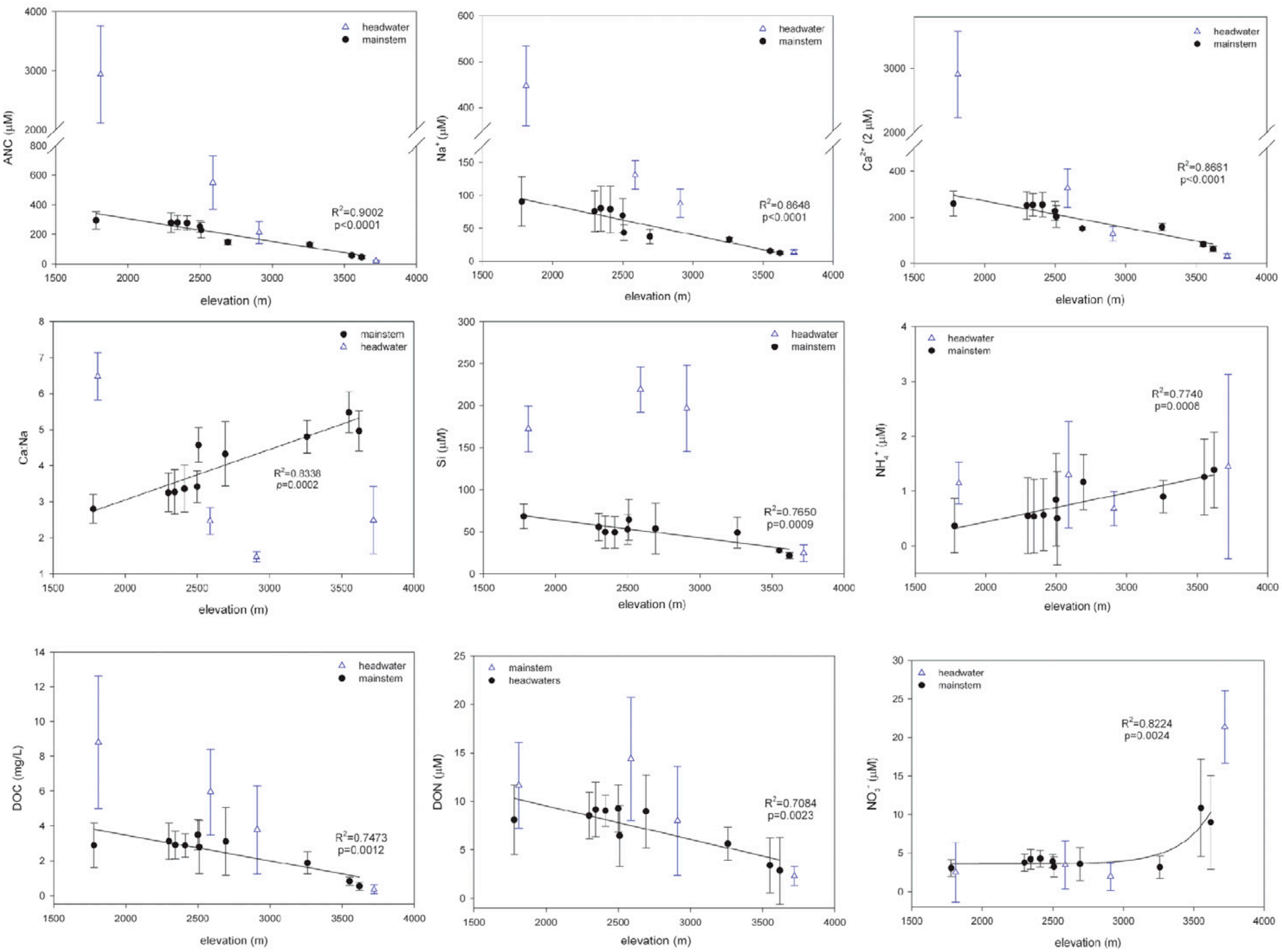

Fig. 4. Regression analyses of ANC, Na^+, Ca^{2+}, Ca/Na, Si, NH_4^+, dissolved organic C (DOC), dissolved organic N (DON), and NO_3^- concentrations versus elevation. The blue triangles represent the headwater sites, and the black circles represent the main stem sites. The regression line is based on the main stem sites, and the R^2 and p values are included if a significant relationship exists.

Table 2. Seasonal export in 2009 for acid-neutralizing capacity (ANC), NH_4^+, Ca^{2+}, Na^+, NO_3^-, dissolved organic N (DON), and dissolved organic C (DOC) for an elevational gradient along main stem and versus headwater catchments (at bottom of table).

Site	ANC	NH_4^+	Ca^{2+}	Na^+	NO_3^-	DON	DOC	Si
	kg ha^{-1}	kg N ha^{-1}	kg Ca ha^{-1}	kg NA ha^{-1}	kg N ha^{-1}	kg N ha^{-1}	kg C ha^{-1}	kg Si ha^{-1}
NAV	16	0.31	8.4	3.3	3.7	0.25	5.89	6.7
ALB	40	0.05	15.4	3.8	0.23	0.41	9.6	7.4
WSF	38	0.06	12.8	3.5	0.19	0.55	12.9	6
NED	4.6	0.01	1.43	0.37	0.09	0.04	1.35	0.77
ORO	3.2	<0.01	0.96	0.4	0.03	0.03	0.73	0.4
GL4	34	0.15	17.3	3.5	1.75	0.54	10	7.2
CC	11	0.01	3.1	2.4	0.01	0.42	14.4	6.4
GG	73	0.03	13.5	6.1	0.1	0.62	19	14.7
BET	1.9	<0.01	2.2	0.1	<0.01	0.01	0.2	0.2

In contrast to the main stem sites, weathering product yields within headwater sites do not follow a simple altitudinal pattern. For example, GG has ANC, Na^+, and Si fluxes that were double that of any of the other headwater sites sampled (Table 2). The foothills headwater catchment (BET) had significantly lower yields than the other headwater sites, for all measured constituents, due to its low and intermittent discharge (Table 2). In addition, ANC, Na^+, and Si fluxes from GG are greater than any of the down-gradient main stem sites (NED and ORO, Table 2). Interestingly, all the headwater sites, with the exception of BET, have ANC, Na^+, Ca^{2+}, Si, NO_3^-, DOC, and DON yields that are an order of magnitude more than the yields of main stem sites NED and ORO.

Concentrations of DON and DOC generally increased with decreasing elevation, while inorganic N showed the opposite trend. To illustrate, VWM seasonal concentrations of DOC significantly increased from 0.35 mg L^{-1} at NAV to 2.89 mg L^{-1} at ORO (Fig. 4) with decreasing elevation ($R^2 = 0.7473$, $p = 0.001$, Fig. 4). Similarly, the concentrations of DON decreased significantly with elevation ($R^2 = 0.70$, $p = 0.002$, Fig. 4) from 2.32 mg L^{-1} at NAV to 8.10 mg L^{-1} at ORO. In contrast, VWM concentrations of nitrate increased significantly ($R^2 = 0.82$, $p = 0.002$, Fig. 4) as elevation increased, from 3.06 μM at ORO to 21.36 μM at NAV. Ammonium concentrations were generally near detection limits at all sites, but did show a statistical increase with an increase in elevation. Thus, the contribution of DIN to the total dissolved N in the main stem increased with elevation, with DIN (nitrate and ammonium) comprising greater than 80% of total dissolved N at GL5 and GL4, 39% at ALB and 31% of total dissolved N at ORO.

Yields of nitrate, DON, and DOC generally increased with elevation along the main stem, but the relationship was only statistically significant in the case of nitrate ($R^2 = 0.98$, $p = 0.001$). The subalpine (CC) and montane (GG) headwater catchments had greater yields of organic matter (DON and DOC) than alpine or foothills headwater systems. In addition, CC and GG had greater DON and DOC yields as compared to main stem sites at similar elevations (Table 2). For example, DOC yields from CC and GG were 14.4 and 19 kg C ha^{-1}, respectively, as compared to yields ranging from 0.02 to 0.04 kg C ha^{-1} at NED and ORO. Similar to the weathering fluxes, BET had lower DOC, DON, and NO_3^- yields as compared to the other headwater catchments, due to its lower annual discharge.

Finally, it is often useful to look at the stoichiometry of nitrogen and carbon within a stream system. Recently, Taylor and Townsend (2010) showed that the relationship of nitrate to the ratio of DOC and nitrate is remarkably consistent across a wide range of Earth's major ecosystems. The DOC/NO_3^- at our sites ranged from a low of 0.41 to more than 1000 (Fig. 5). A scatterplot of nitrate concentration versus the DOC/NO_3^- for 2009 stream water samples at NAV, GL4, CC, GG, and BET shows that high nitrate concentrations were associated with DOC/NO_3^- less than 5 (inset, Fig. 5). The high nitrate, low DOC/NO_3^- ratios were anchored by the high-elevation sites GL4 and NAV. The low nitrate, high DOC/NO_3^- were anchored by the three lower elevation sites. However, it is worth noting that the DOC/NO_3^- for GG and BET ranged widely, from about 5 to more than 1000.

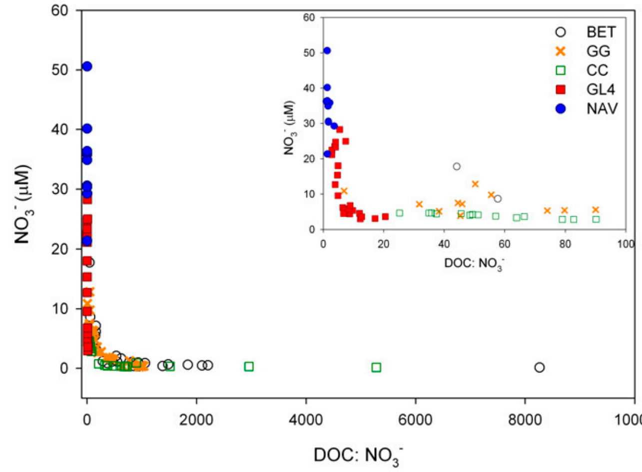

Fig. 5. Scatterplot of nitrate concentrations (μmol L^{-1}) versus the dissolved organic C (DOC)/NO_3^- ratio for 2009 stream water samples at NAV, GL4, CC, GG, and BET sites. The inset figure is an enlarged scatterplot with a DOC/NO_3^- ratio range from 0 to 100.

Dissolved Organic Matter Quality in Stream Water

We evaluated the chemical characteristics of DOM in the headwater catchments using spectral measurements. The highest FI values were at the lowest elevational site (BET), followed by the alpine GL4 site (Fig. 6). At BET and GG the FI values varied little around the mean of 1.57 and 1.44, respectively (Fig. 6). In contrast, FI values at CC and GL5 showed a seasonal pattern: decreasing during snowmelt with a consistent increase on the recession limb of the hydrograph. The volume-weighted SUVA values ranged

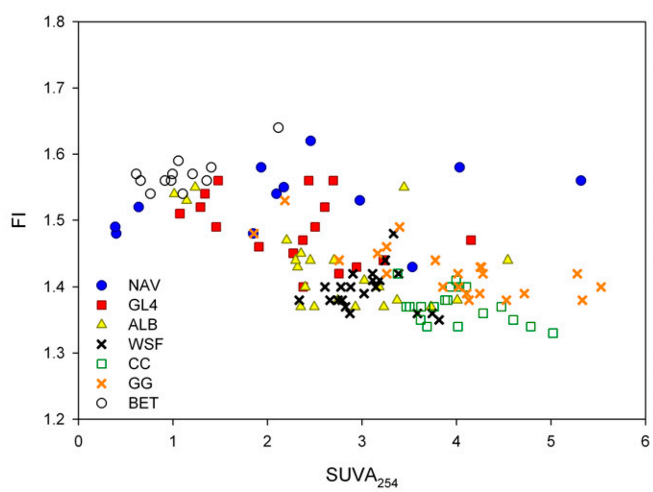

Fig. 6. Crossplot between the dissolved organic matter (DOM) quality parameters specific UV absorbance (SUVA) and fluorescence index (FI) for all samples from the study.

from 1.0 at BET to 4.1 at CC. The SUVA values were highest during snowmelt and then generally decreased with time at GL4 and GG, whereas there was little change in SUVA with time at CC and BET. The higher FI values were generally associated with lower SUVA values, with BET having a FI of 1.57 and a SUVA value of 1.0, while CC had the lowest FI (1.38) and the highest SUVA (4.1). There was not a significant relationship between DOC concentration and either of the primary DOM quality parameters measured, FI ($p = 0.22$) and SUVA ($p = 0.89$). In contrast, SUVA and FI were negatively related ($R^2 = 0.40$, $p < 0.01$, Fig. 6). For the small subset of headwater and main stem samples ($n = 13$), the percentage of hydrophobic organic acids (consisting mostly of fulvic and humic acids) were measured. On average HPOA made up 53, 52, 46, 45, 43, and 39% of the DOM pool at BET, GG, ORO, WSF, ALB, and GL4, respectively, between May and August 2009. For this same set of samples, the Cory and McKnight (2005) PARAFAC model reproduced the three-dimensional EEMs reasonably well, with residuals less than 5% in all cases. Component 4, indicative of reduced quinones, made up the largest percentage of the fluorescing DOM pool (19–36%) at all sites. Component 2, related to oxidized quinones, was the second largest contributor (13–18%), while components 8 and 13, indicative of protein-like molecules, contributed between 3% and 10% to the DOM pool. The sum of components identified as microbial or algal in origin by Cory and McKnight (2005), due to their inclusion in the Antarctic-only sample set (components 3, 4, 6, 7, 8, and 9), contributed between 40 and 55% to the fluorescing DOM pool. The composition of DOM as defined by the HPOA percentage and two components identified by the Cory and McKnight (2005) PARAFAC model were significantly related to elevation. There was a significant negative relationship between elevation and the average HPOA percentage ($R^2 = 0.87$, $p = 0.02$) and C2 component, thought to be indicative of an oxidized quinone ($R^2 = 0.83$, $p = 0.007$). While not significant, there was a positive relationship between protein-like fluorophores, identified by model components C8 and C13, and elevation ($R^2 = 0.69$, $p = 0.07$). For the upper elevation (WSF, ALB, and GL4) main stem sites the fraction of DOM comprised of HPOA decreased from June to August.

Soil Chemistry Along an Elevational Gradient

The soil sample analyses indicated little nitrate present in the soil; the highest nitrate concentration was 0.03 mg N kg^{-1} at ALB (Table 3). Ammonium concentrations were slightly higher than NO_3^-, ranging from 0.10 to 2.14 mg N kg^{-1}. Microbial N was generally greatest at high elevations (10.45 mg N kg^{-1} at NAV) and decreased moving down-gradient (1.97 mg N kg^{-1} at BET). The relatively unvegetated alpine sites have relatively low soil C/N ratios, ranging between 13.9 and 15.3. Below the treeline, the ratio increased to 29.7 at WSF, 29.1 at CC and 27.7 at GG. Surprisingly, the C/N ratio decreased to 18.1 at BET, the lowest elevation site.

The soil C/N ratio decreased significantly with elevation ($R^2 = 0.43$, $p = 0.003$) (Fig. 7), with the exception of BET. The low soil C/N ratio for BET is consistent with the high FI and low SUVA of the DOM at that site. The soil C/N ratio also showed a strong inverse relationship with VWM nitrate concentrations in stream waters ($R^2 = 0.46$, $p = 0.002$). While not statistically significant, the FI values generally decreased at higher soil C/N ratios ($p = 0.09$). Conversely, the soil C/N demonstrated a significant but weak positive relationship with both DOC ($R^2 = 0.25$, $p = 0.04$) and DON ($R^2 = 0.39$, $p = 0.05$). However, the soil C/N ratio was not found to be significant when predicting stream water DOC/DON ratios ($p = 0.14$).

Discussion

Our sampling of water quality in the Boulder Creek watershed encompassed almost 2000 m of elevational change, from ORO (1779 m) to NAV (3785 m). Precipitation increased with elevation, a common occurrence in the Rocky Mountains (Barry, 1973; Körner, 2007). However, specific discharge did not: CC and GG have similar water yields (1933 and 2391 m^3 ha^{-1}, respectively), despite CC receiving 75% more annual precipitation (Table 1). Similarly, GG and BET receive similar amounts of precipitation (Table 1) but have very different water yields.

Both air temperature and the concentrations of base cations increase going down the elevational gradient within the headwaters and main stem stream sites (Table 1, Fig. 4). This is consistent with studies that have shown that greater air temperature is generally correlated with greater chemical dissolution rates in headwater catchments (Meybeck, 1987;Velbel et al., 1990; Drever and Zobrist, 1992). While there is the potential for high chemical weathering rates in alpine areas due to high rates of physical erosion (Williams et al., 2006), on a broad landscape scale, higher temperatures at lower elevations promote greater concentrations of base cations.

The Ca/Na ratio in the main stem stream waters systematically increased with elevation (Fig. 4), suggesting that selective weathering could be occurring. Other studies in the Cascade Mountains and Loch Vale watershed of the Colorado Front Range (Drever and Hurcomb, 1986; Mast et al., 1990) showed that minor reactive phases such as calcite and amphiboles make a greater relative

Table 3. Soil characteristics along an elevational gradient.

Site	Soil C/N	NH_4^+	NO_3^-	Microbial N
		mg N kg^{-1}		
NAV	13.9	2.14	0.02	10.45
GL4	15.3	0.25	0	4.52
ALB	14.5	0.84	0.03	8.35
SLO	17.9	0.17	0	3.10
WSF	29.7	0.12	0	4.25
CC	29.1	0.15	0	3.25
GG	27.7	0.10	0	2.79
BET	18.1	0.19	0.01	1.97

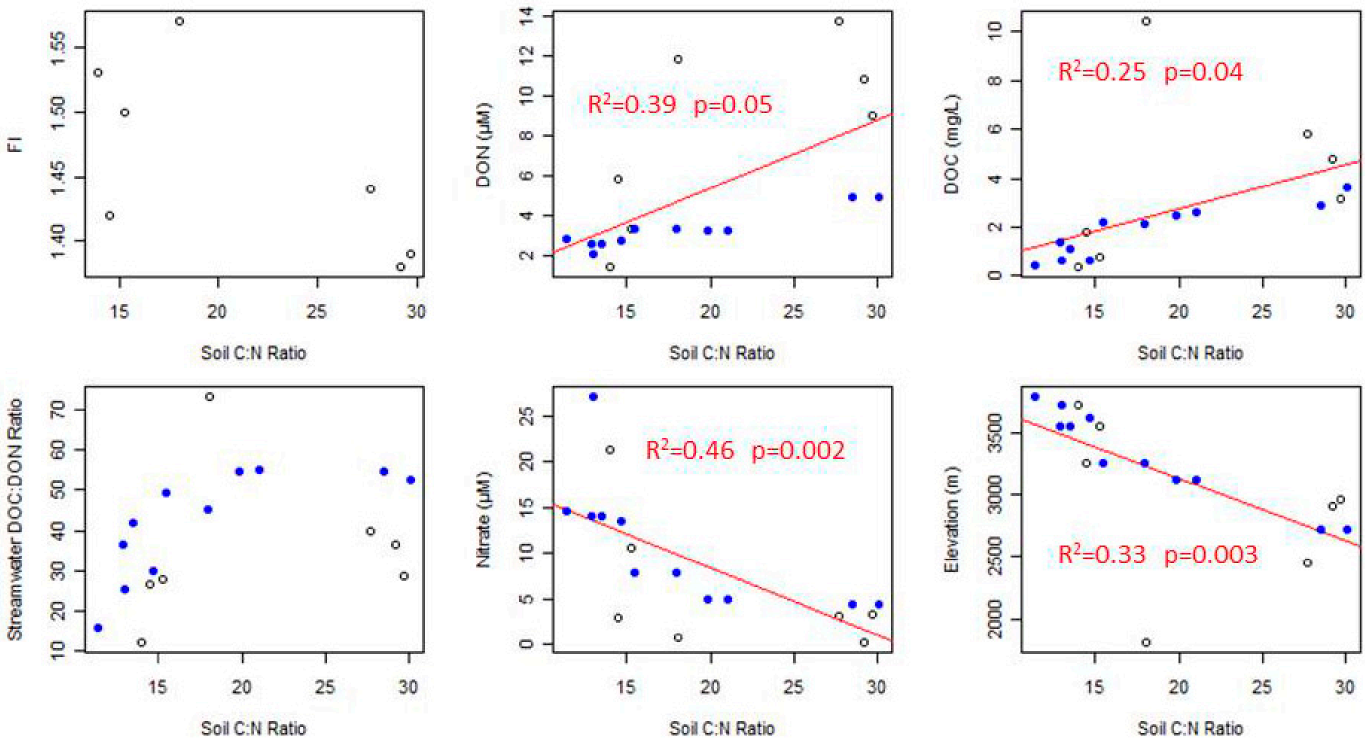

Fig. 7. Regression analyses of fluorescence index (FI), dissolved organic N (DON), dissolved organic C (DOC), stream water DOC/DON, NO_3^- and elevation versus soil C/N ratio. In addition to the 2009 soil data, soil C/N ratios reported from 1998 and 1999 in Hood et al. (2003b) are included as solid blue circles in this figure and regression analysis.

contribution to the solute load at higher elevations (up to 40% of cations in basin derived from calcite), whereas the less reactive phases such as plagioclase make a greater relative contribution at lower elevation catchments. Selective chemical weathering at higher elevations is consistent with increased physical weathering at higher elevations due to freeze–thaw and other processes (Williams et al., 2006).

However, the headwater sites show an almost inverse pattern with the greatest Ca/Na values at the lowest elevation site (BET) and lowest Ca/Na values at the subalpine site (CC). Similarly, the headwater sites do not follow the general trend toward increasing fluxes of weathering products with elevation along the main stem sites. In particular, GG had Ca^{2+}, ANC, and Si fluxes that are an order of magnitude larger any of the other headwater sites. In addition to greater weathering product fluxes, GG has the greatest DON and DOC fluxes of any of the headwater sites (Table 2). Thus, the hydrochemistry of headwater catchments along the elevational gradient of Boulder Creek was different when compared to the hydrochemistry of the main stem.

LCM Revisited: Extending the Model from the Continental Divide to the Plains

The LCM saw the high-elevation system as one strongly influenced by both climatic and topographic drivers. The model explicitly links terrestrial ecosystems to each other and to aquatic ecosystems. The heart of the model is that strong linkages are generated among landscape components as a result of transport processes caused by the rugged topography. These transport agents cause biogeochemical amplification and attenuation of processes not observed in most landscapes.

Our results suggest that there is value in extending the LCM concept to lower-elevation headwater catchments. Concentrations of geochemical weathering products were consistently higher in streams draining headwater catchments when compared to main stem sites at similar elevation. Similarly, fluxes of geochemical weathering products were higher from headwater basins (e.g., GG) than main stem basins at the same elevation (e.g., NED). The Ca/Na ratio increased with decreasing elevation in streams draining headwater catchment, while the opposite trend occurred along the main stem (Fig. 4). These results are consistent with more vigorous chemical weathering in headwater catchments when compared to the main stem. Thus, even in lower-elevation headwater catchments, the rugged topography appears to amplify the transport of geochemical weathering products in surface waters. These results appear to disprove our hypothesis that solute concentrations and fluxes in headwater catchments along an elevational gradient are similar to those along the main stem of the watershed.

Similarly, nutrient cycling appears to differ among headwater basins when compared to main stem sites. While there is a general decrease in nitrate concentrations and export at lower elevations, all forested catchments do not respond the same. Comparing CC and GG, two forested watersheds with similar DOC concentrations and specific water yields, GG exported 10 times more nitrate in 2009 than CC (Table 2). This difference is likely due to the interactions between hydrology and nitrogen biogeochemistry. Gordon Gulch has an intermittent snow pack, receiving more precipitation as rain than CC (Table 1), resulting in the observed nitrate increases during the summer months when the atmospheric deposition flux potentially moves through the system too quickly to be assimilated.

The quality of DOM appears to differ among headwater catchments when compared to the main stem. For example, FI values were relatively high at the lower-elevation catchments, with the average FI of 1.57 at BET similar to and often higher than that of high-elevation sites (Fig. 6). Similarly, there was little difference among headwater catchments in the sum of components identified as microbial in the fluorescing DOM pool. The increasing soil C/N ratios with decreasing elevation support the concept of more progressively carbon-rich soil moving from the alpine to montane ecosystem, consistent with previous work that shows that DOC concentrations in surface waters are strongly correlated with soil organic C pools (Aitkenhead and McDowell, 2000). However, soil C/N within the foothill catchment (BET) was less than any of the other forested sites, likely because the deeply incised, steep slopes limit soil development and hence accumulation of soil organic carbon pools. Thus, the rugged topography of mountain catchments appears to drive unique biogeochemical cycling patterns consistent with the LCM, whether at high-elevation alpine catchments, or lower-elevation montane and foothill basins.

These results do not support our hypothesis that the character of dissolved organic matter changes across an elevational gradient in a predictable fashion from more labile types at high elevation to more recalcitrant types at lower elevation. The stoichiometric results provided by the DOC/NO_3^- ratio shed light on why the quality of DOM changes with elevation in headwater catchments. The carbon limitation and low stream water DOC/NO_3^- ratios (Fig. 5) in the alpine sites are largely a result of a landscape that is dominated by large talus and exposed bedrock areas (Williams et al., 1997; Campbell et al., 2000), with minimal soil development and vegetation coverage. Further, soil C/N ratios less than 25 (Table 3) in the alpine are consistent with a system moving toward net nitrification (Gundersen et al., 1998), resulting in nitrate leaching, decreasing the DOC/NO_3^- ratio in stream water. In particular, the stream water DOC/NO_3^- ratio at NAV falls below the 3.5 threshold identified by Taylor and Townsend (2010) for microbial biomass further inducing the rapid accrual of nitrate in water (Fig. 5).

However, it is worth noting that the DOC/NO_3^- ratio for GG and BET ranged widely, from about 5 to more than 1000. In contrast to CC and GG, BET appears to be carbon limited for most of the year, with a soil C/N less than 25 (Table 3), similar to the highest-elevation sites. These stoichiometric results suggest that headwater catchments at all elevations along the Boulder Creek drainage are at times moving toward net nitrification and the export of both nitrate and labile carbon in surface waters, much different than the patterns reflected by the main stem.

Evidence of nitrate subsidization is of particular concern in the Colorado Front Range, as studies have shown that alpine areas are becoming increasingly N-saturated due to N deposition (Baron et al., 1994; Williams et al., 1996a; Campbell et al., 2000; Williams and Tonnessen, 2000). Given these results, nitrogen saturation within alpine areas could potentially lead to increased downstream export of nitrate, causing periodic acidification and threatening essential aquatic ecosystem services even in vegetated reaches at lower elevations. Using nitrate concentrations in surface flow as an index of N saturation (e.g., Williams et al., 2006; Williams and Tonnessen, 2000), headwater catchments even at low elevation in the Boulder Creek drainage are closer to N saturation than previously thought. This observation is particularly surprising given the lower amounts of DIN in wetfall at BET and GG compared to higher elevation sites (Fig. 3).

Is There Valuable Information in a Space-For-Time Substitution Along an Elevational Gradient When There Are Changes in Ecosystem Type?

Altitudinal gradients are among the most powerful “natural experiments” for testing ecological and evolutionary responses of biota to geophysical influences, such as low air temperature (Körner, 2007). Mountains often have steep environmental gradients given the changes in elevation, providing outdoor laboratories that have stimulated research for centuries (von Humboldt and Bonpland, 1807; Bonnier and Flahault, 1878; Körner, 2003, 2004). These steep gradients in air temperature and precipitation in the Boulder Creek watershed result in stratification of ecosystem types along the altitudinal gradient from Ponderosa pine forests in the foothills to alpine tundra near the Continental Divide (Table 1). These changes in environmental gradients with elevation in the Boulder Creek drainage such as precipitation and soil organic carbon, and resulting changes in ecosystem type, confound using the elevational gradient as a space-for-time substitution to understand how ecosystem processes and biogeochemical cycling may respond to changes in climate or changes in the deposition of DIN in wetfall.

Given these caveats, it does appear that we can use the space-for-time substitution for at least one climate change scenario. The lowest elevation headwater catchment, BET, had the lowest yield for base cations and organic nutrients and the highest concentrations of DOC and geochemical weathering products of all sites sampled (Fig. 4). The unique chemistry and fluxes at BET as compared to the other headwater catchments may be because of differences in precipitation type. The percentage contribution of snowfall to annual precipitation is about 60% or more from GG to the Continental Divide (Table 1). In contrast, the snowfall contribution to annual precipitation at BET is less than 20%. The lower snowfall totals at BET are because it's at a threshold where winter air temperatures are near or above 0°C. Therefore, despite BET and GG having similar amounts of annual precipitation (Table 1), specific discharge is much less at BET than GG (Fig. 2) due to differences in precipitation regime. This suggests that even with no changes in annual precipitation, a transition from predominately snowfall to rainfall in annual precipitation results in a much lower runoff ratio.

In turn, the rain–snow transition has a large bearing on biogeochemical fluxes from headwater catchments. For example, the high concentrations of base cations and DOC in the outflow of BET when compared with higher elevation catchments is consistent with increased rates of biogeochemical cycling with increasing air temperature at lower elevations. However, the low specific discharge in BET results in decreased fluxes of these products. Similarly, the low flushing may be an indication of lower rates of soil and groundwater recharge, resulting in the higher Ca/Na ratios at BET (Fig. 4). Thus, these results suggest a space-for-time substitution is warranted for at least some biogeochemical processes when there is a transition from the snow to rain in annual precipitation.

Summary

In summary, our results suggest that there is value in extending the LCM concept to lower-elevation headwater catchments, as the rugged mountain topography appears to drive unique biogeochemical cycling patterns even in the lower montane and foothill sampling sites. Using nitrate concentrations in surface flow as an indicator of N saturation, even low elevation headwater catchments in the Boulder Creek drainage are closer to N saturation than previously thought. This observation is particularly surprising given the lower amounts of DIN in wetfall at BET and GG compared to higher elevation sites.

Changes in environmental gradients with elevation in the Boulder Creek drainage result in changes in ecosystem type and confound using the elevational gradient as a space-for-time substitution to understand how ecosystem processes and biogeochemical cycling may respond to changes in climate or atmospheric deposition of DIN. However, given these caveats, it does appear that these results suggest a space-for-time substitution is warranted for at least some biogeochemical processes when there is a switch from the snow to rain transition in annual precipitation.

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