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Nitrate Content and Potential Microbial Signature of Rock Glacier Outflow, Colorado Front Range

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Abstract

Here we characterize the nutrient content in the outflow of the Green Lake 5 rock glacier, located in the Green Lakes Valley of the Colorado Front Range. Dissolved organic carbon (DOC) was present in all samples with a mean concentration of 0·85 mg L^{-1}. A one-way analysis of variance test shows no statistical difference in DOC amounts among surface waters ($p = 0{\cdot}42$). Average nitrate concentrations were 69 μmoles L^{-1} in the outflow of the rock glacier, compared to 7 μmoles L^{-1} in snow and 25 μmoles L^{-1} in rain. Nitrate concentrations from the rock glacier generally increased with time, with maximum concentrations of 135 μmoles L^{-1} in October, among the highest nitrate concentrations reported for high-elevation surface waters. These high nitrate concentrations appear to be characteristic of rock glacier outflow in the Rocky Mountains, as a paired-difference *t*-test shows that nitrate concentrations from the outflow of 7 additional rock glaciers were significantly greater compared to their reference streams ($p = 0{\cdot}003$). End-member mixing analysis suggest that snow was the dominant source of nitrate in June, 'soil' solution was the dominant nitrate source in July, and base flow was the dominant source in September. Fluoresence index values and PARAFAC analyses of dissolved organic matter (DOM) are also consistent with a switch from terrestrial DOM in the summer time period to an increasing aquatic-like microbial source during the autumn months.

Keywords: rock glacier; nitrate; DOC; microbe; alpine; PARAFAC

Introduction

High-elevation landscapes are extreme environments for life. They are oligotrophic areas with little microbial biomass, similar in this respect to high latitude polar soils (Ley *et al*., 2004). While polar soils have been studied extensively (Mack *et al*., 2004), analogous studies in high altitude areas are rare. These areas are interesting in their own right as one of Earth's most extensive extreme environments: high mountains are present on all seven continents. Recent investigations of alpine talus and blockfields in the Colorado Front Range report surprisingly large amounts of microbial biomass in these environments (Williams *et al*., 1997; Bieber *et al*., 1998; Ley and Schmidt, 2001). There have also been recent reports of microbial activity in subglacial environments (Sharp *et al*., 1999; Skidmore *et al*., 2000, 2005). Rock glaciers are omnipresent features in most high-elevation environments (Barsch, 1996). However, no research has been conducted to date on the presence and amount of nutrients in the outflow of rock glaciers, nor on the presence or absence of microbial life.

Active rock glaciers may be considered an extreme environment for life in that they are permanently dark, oligotrophic, and constantly cold (≈°C). What little research that has been conducted on the chemistry of rock glaciers has focused on the solute content of geochemical weathering products, such as the concentrations of base cations and conductivity in outflow. Giardino *et al*. (1992) noted that rock glaciers physically and chemically influence the water that passes through them and act as a concentrating rather than a filtering mechanism. The lack of information on the geochemistry of outflow from rock glaciers is partly because of the logistical constraints in collecting and analyzing water samples

for chemical content in rugged and isolated environments. Collecting and analyzing samples for nutrient content is even more difficult because organic nutrients are delicate and concentrations can change rapidly without strigent collection and handling techniques.

There is some urgency to understanding the sources, fate, and transport of nutrients to high-elevation areas of the Rocky Mountains. Numerous authors in the last decade have reported on the increasing amounts of inorganic nitrogen in wet deposition to the Rocky Mountains and resulting changes in ecosystem function in these areas (e.g. Baron *et al*., 1994; Williams *et al*., 1996a; Baron and Campbell, 1997; Brooks and Williams, 1999; Campbell *et al*., 2000; Meixner *et al*., 2000; Williams and Tonnessen, 2000; Burns, 2003). Several studies have shown that discharge from talus and blockfields in the Rocky Mountains contain elevated amounts of nitrate (e.g. Williams *et al*., 1997; Bieber *et al*., 1998; Campbell *et al*., 2000; Clow *et al*., 2003). The nitrate in the outflow of talus and blockfields appears to result primarily from microbial activity where the microbes are carbon limited and hence move the nitrogen cycle towards net nitrification (e.g. Ley and Schmidt, 2002; Ley *et al*., 2004). An outstanding question is whether rock glaciers act like blockfields and also have high nitrate in their outflow, or are rock glaciers biologically inert?

Here we characterize the nutrient content in the outflow of the Green Lake 5 rock glacier (RG5) in 2003, located in the Green Lakes Valley of the Colorado Front Range. The primary focus is on nitrate, but we also evaluate ammonium and DOC content. The nutrient content in the outflow of RG5 is compared to that of other surface waters draining landscapes characteristic of alpine environments, including glaciers, blockslopes, late-lying snow patches, and alpine streams. The presence or absence of organic and inorganic nitrogen pools and microbial biomass at the surface of the rock glacier is quantified. We combine this information with a recent report by Williams *et al.* (2006) using three component hydrograph separation and end-member mixing analysis to understand the sources that contribute nutrients to the outflow of RG5. These potentially site-specific results are compared to a regional synoptic sampling campaign to better understand the spatial distribution of nitrate concentrations in the outflow of rock glaciers in the Rocky Mountains. Last, the fluoresence properties of dissolved organic matter (DOM) in the outflow of RG5 are evaluated for a microbial signature using the approach of Cory and McKnight (2005).

Site

The upper Green Lakes Valley is an east-facing glacial valley, headed on the Continental Divide in the Colorado Front Range (40°03′N, 105°35′W). Named for a series of shallow paternoster lakes, the Green Lakes Valley is the headwaters of North Boulder Creek and lies within the City of Boulder Watershed. Green Lakes Valley is a Long-Term Ecological Research (LTER) network site. The upper valley is approximately 225 ha in area, with an elevation range from 4084 m at the Continental Divide to 3515 m at the outlet of Green Lake 4 (Figure 1). Most of the surficial deposits are of Holocene age, accumulated since deglaciation about 12 000 years ago (Harbor, 1984).

The continental, high mountain climate of Green Lakes Valley has been recorded continuously at an elevation of 3700 m at the D-1 meteorological station on Niwot Ridge for over 50 years and for shorter periods on the valley floor (Greenland, 1989). Mean annual temperature at D-1 is −3·7 °C (Williams *et al*., 1996c). Precipitation amounts presented here are from the D-1 meteorological station (Figure 1, http://culter.colorado.edu:1030/). Permafrost appears to be continuous on north-facing slopes and discontinuous on south-facing slopes, with high sensitivity to any increases in air temperature (Janke, 2005b,a). Almost 80 per cent of the approximately 1000 mm of recorded annual precipitation falls as snow (Caine, 1996). The bulk snow pack temperature remains below 0 °C until late spring, introducing a lag in the hydrological cycle by concentrating the release of melt water in a short, intense period of runoff (Caine, 1996). The Green Lakes Valley and much of Colorado experienced drought years from 2000 through 2002 (Williams *et al*., 2006).

RG5 is a lobate rock glacier, located in the talus foot zone on the north-facing side of Kiowa Peak at an elevation of 4000 m (Figure 1), formed during the Holocene (White, 1981; Caine, 2001). It is slow-moving, with a maximum surface velocity of about 2 cm yr^{-1}, an order of magnitude less than flow rates of valley-floor rock glaciers in the Front Range (White, 1981; Benedict *et al*., 1986). The top of RG5 supports patches of alpine tundra, similar to the talus and blockfields of the valley (Williams *et al*., 2006). Nitrogen mineralization studies were located here, with triplicate plots on vegetated sites and triplicate plots on non-vegetated soil-like areas. A deep and late-melting snow patch is located just above RG5 in a depression caused by movement of RG5 away from the cliff face. The outflow stream at the toe of the most active area of the rock glacier drains through boulder debris, which makes measurement of discharge very difficult (Krainer and Mostler, 2002). We collected water samples for chemical, nutrient, and isotopic analyses from the outflow stream, although we were not able to measure discharge, we did record fluctuations in water level.

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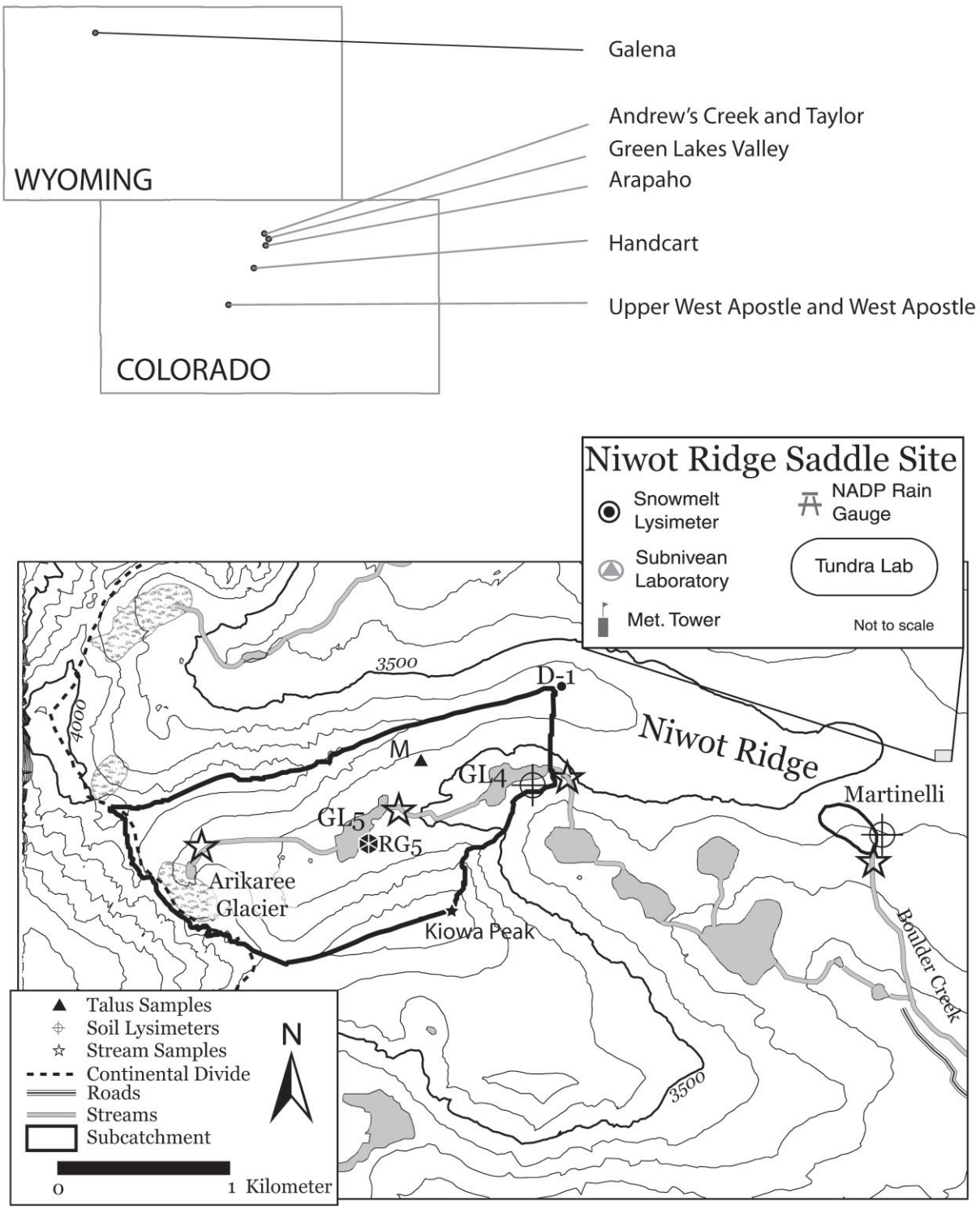

Figure 1. Location map for Green Lakes Valley and synoptic sampling of rock glaciers. Sampling sites from Green Lakes Valley are shown for snow and snowmelt (labeled 'snowmelt'), glacial outflow (Arikaree Glacier), snow field discharge (labeled 'Martinelli'), blockslope/talus flow (labeled 'M for middle blockfield/talus slope'), rock glacier outflow (labeled 'RG5'), discharge from Green Lakes 5 (labeled 'GL5') and soil water collected in zero-tension soil lysimeters. There is a long-term climate station at D-1. Precipitation chemistry is measured weekly at the NADP (National Atmospheric Deposition Program) site (CO02).

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Additional water samples were collected at the following sites (Figure 1): (1) The 9-ha Arikaree glacier at the head of the valley; (2) the outflow of Green Lakes 5 (GL5); (3) a blockfield on the south face of Niwot Ridge, the same location as in Williams *et al*. (1997) and Liu *et al*. (2004) (called 'talus' for shorthand in both those papers), and Williams *et al*. (2006); and (4) the 8-ha Martinelli basin, which represents a snow-field dominated catchment and is located about 400 m from the Saddle site on Niwot Ridge. Soil solution was collected in zero-tension soil lysimeters above Green Lake 4, the same as in Liu *et al*. (2004) and Williams *et al*. (2006). Niwot Ridge, the northern boundary of the Green Lakes Valley, is the site of other experimental areas, including snow lysimeters and a subnivean laboratory, all at the Saddle site (Figure 1). Release of solutes from the snowpack was investigated by collecting snowpack meltwater in 1-m^{-2} snow lysimeters before contact with the ground following the protocol of Williams *et al*. (1996b). Meltwater flowed by gravity from the snow lysimeters about 5-m into the subnivian laboratory. Meltwater discharge was measured continuously in tipping buckets, and grab samples were collected about daily and analyzed for concentrations of major solutes. The Niwot Ridge/Green Lakes Valley LTER site participates in the National Atmospheric Deposition Program (NADP) (Figure 1), which operates about 200 wet precipitation collectors throughout the continental United States. Precipitation samples are collected weekly and analyzed for major solutes using the same protocols, so that precipitation chemistry may be compared among sites, with data available from the Illinois State Water Survey, Urbana, at http://nadp.sws.uiuc.edu. Chemistry of rainfall we report is from this NADP site (CO02). Splits of the precipitation samples from the NADP collector (CO02) are analyzed in our laboratory for organic nutrients.

Synoptic survey

Outflow from seven rock glaciers and nearby reference streams were sampled during the growing season in August 2003. Selection of these sites was based on publications and/or personal communication that noted small streams draining from rock glaciers. Samples were collected directly from the toe of the rock glacier for all seven sites. Reference streams were channelized surface flows in the same watershed and located within 600 meters of the rock glacier outflow. Numerous additional sites were investigated but only these seven sites (all were classic alpine cirques) were characterized by both discharge from a rock glacier and with nearby streams that were not directly connected to the rock glacier. The location of the seven rock glaciers ranged from southern Colorado to northern Wyoming (Figure 1). Arapaho rock glacier is located within the city of Boulder watershed, northwest of Boulder. Upper West Apostle rock glacier and West apostle rock glacier are located in the Sawatch Range between Buena Vista and Leadville, Colorado. Andrew Creek and Taylor rock glaciers are both in the Loch Vale watershed in Rocky Mountain National Park. Handcart rock glacier is located outside the town of Montezuma Colorado. Galena Creek rock glacier is located in the Absaroka Wilderness, northwest of Cody Wyoming.

Methods

Sample collection

Precipitation quantity and quality. Physical and chemical properties of snow are routinely measured on a weekly basis at the Saddle site until melt-out using sampling protocols presented in Williams *et al*. (1996b) and Williams *et al*. (1999). The same measurements were conducted on the snow field above RG5 approximately weekly starting on 19 June 2003 until melt out on 14 August. Nutrient values that we report for snow are from these two sites.

Surface waters. Surface waters were collected as grab samples during the 2003 season at the toe of RG5, Arikaree Glacier outflow, GL5 and Martinelli discharge, and blockfield flow, the same sites as in Williams *et al*. (2006) (Figure 1). We also report time series information on the nitrate content of the outflow of RG5 from 1998 to 2004. Polyethylene bottles 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. Stream samples were collected about weekly starting with the initiation of snow melt runoff until freeze-up in the fall. All water samples were transported the same day as collection to our wet chemistry laboratory and treated the same as the snow samples. Surface water samples were also collected from the outflow of the seven rock glaciers and their reference streams in August 2003 (Figure 1). Samples were collected in the same manner as the weekly samples in the Green Lakes Valley and were stored on ice and transported to the Kiowa Laboratory at the Mountain Research Station for analysis.

Soil Nitrogen. Bulk soil pools were sampled and *in situ* incubations of intact soil cores were performed following the procedures of Fisk and Schmidt (1995), Brooks *et al*. (1996), Williams *et al*. (1996c), Williams *et al*. (1997), and Bieber *et al*. (1998), so we could compare our results to their reports of microbial N biomass, inorganic pools of

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nitrogen, and net nitrification rates in the Green Lakes Valley. For each incubation, a 4-cm diameter, 10-cm long thin walled polyvinyl chloride tube was inserted approximately 5 cm into the ground. The tube and its captured soil core were then removed, a soil resin bag was sealed into the bottom of the tube with silicon glue, and the tube was replaced into the ground with its soil core intact (Bieber *et al*., 1998). The resin bags contained 10 grams of Baxter scientific (16–50 mesh) mixed-bed exchange resin and were installed to collect all N leached from the core during the incubation (Brooks *et al*., 1996). The cores were placed on three replicate sites from both vegetated and unvegetated areas on the active, western lobe of the rock glacier on 21 August 2003. The cores were collected after 30 days on September 20. To determine the initial nutrient composition of the soil, an undisturbed 5-cm-deep sample was collected immediately adjacent to each tube on 21 August. Note that these protocols were specifically developed for the high-elevation landscape of Niwot Ridge and the Green Lakes Valley and they have been published in a variety of journals (Fisk and Schmidt, 1995; Brooks *et al*., 1996; Williams *et al*., 1997; Bieber *et al*., 1998).

Laboratory analyses

All water and snow samples were analyzed for pH, acid neutralizing capacity (ANC), conductance, major ions and reactive silicate (Si). Results for these solutes were published in Williams *et al*. (2006). Chemical analyses followed this protocol for all water samples including snow samples. Snow samples were stored frozen (–20 °C) for one to two months until analysis. Blank samples of distilled, DI water stored in sample bags for the same amount of time showed no significant contamination from the bags (Williams *et al*., 1992). Snow samples were placed in covered polyethylene buckets and melted at room temperature. ANC and pH were measured immediately after melting for snow or after return to the laboratory for water samples using the Gran titration technique. Subsamples were immediately filtered through pre-rinsed (300 ml), 47-mm Gelman A/E glass fiber filters with ca. 1-μm pore size. Ammonium was measured immediately on a Lachat QuikChem 4000 Flow Injection Analyzer using a method based on the Berthelot reaction. The detection limit was 0·33 μmoles L^{-1} and precision was 0·91 per cent (Williams *et al*., 2001). Filtered samples were stored in the dark at 4 °C for subsequent analyses within one to four weeks. Nitrate was analyzed using a Dionex DX 500 ion chromatograph with an IonPac AS4A-SC Analytical Column. The detection limit was 0·03 μmoles L^{-1} and precision was 1·1 per cent. Total N (TN), dissolved organic nitrogen (DON), and particulate nitrogen were measured as in Williams *et al*. (2001). Samples for DOC were filtered through pre-combusted glass fiber filters and stored in pre-combusted amber glass bottles. DOC was determined by high-temperature catalytic oxidation using a Shimadzu Organic Carbon Analyzer at the Institute of Arctic and Alpine Research (INSTAAR) in Boulder, CO. Three replicate analyses yielded standard deviations of about 0·06 mg C L^{-1}, with a range of 0·01 to 0·22 mg C L^{-1}. Particulate carbon and total phosphorus were measured as described in Seibold (2001).

Soil Nitrogen. On the same day as collection, soils were sieved to <2 mm and were analyzed for KCl-extractable ammonium, nitrate and microbial biomass following established protocols developed specifically for this and other high-elevation landscapes (Fisk and Schmidt, 1995; Brooks *et al*., 1996; Williams *et al*., 1996c, 1997; Bieber *et al*., 1998). The values for KCl–extractable ammonium and nitrate were determined by adding 50 ml of 2 M KCl to ≈10 grams of the sieved soil. The solution was mixed at 250 rpm for one hour and then incubated for 18 to 24 hours. The samples were filtered through Buchner funnels with Whatman # 1 filter paper. Finally, the extracts were frozen until analyzed using a Lachat flow injection analyzer. The resins were analyzed for ammonium and nitrate in an identical manner. To determine the soil dry weight, ≈5–7 g of soil was dried at 60 °C until it held a constant weight (about 6 days). The bulk density of soil was derived from Ley *et al*. (2004). Net nitrification was calculated as the initial quantity of nitrate measured from cores collected on 21 August and subtracted from the amount of nitrate in the cores collected on 20 September. Net rates of nitrification were converted into g N m^{-2} mo^{-1} so as to be comparable to previous measurements in the Green Lakes Valley.

Microbial biomass N was determined using a chloroform fumigation-direct extraction procedure (Brookes *et al*., 1985), as modified by Fisk and Schmidt (1995), Brooks *et al*. (1996), and Williams *et al*. (1997) for Niwot Ridge and Green Lakes Valley. For each sample, a subsample weighing about 10 g was shaken for 30 min in 100 mL of 0·5 M K_2SO_4 at 150 rpm on a rotary shaker followed by immediate filtration through Whatman # 1 filter paper. A second subsample was fumigated with chloroform for 2d in a vacuum dessicator and then extracted in the same manner. Extracts were digested by persulfate oxidation and analyzed for nitrate as above. The difference in extractable N content of the fumigated and unfumigated soils represented the chloroform-labile N fraction of the soils, and a correction factor of 0·54 (Brookes *et al*., 1985) was applied to estimate microbial N. Note that microbial N concentrations and inorganic N pools should be considered an index of soil N properties rather than absolute values because magnitudes will vary from the same samples depending on holding times, size fraction of soils analyzed, etc. By using the same protocols, we are able to compare our results to Fisk and Schmidt (1995), Brooks *et al*. (1996); Williams *et al*. (1996c); Williams *et al*. (1997), and Bieber *et al*. (1998).

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Fluorescence characteristics of DOM

Three-dimensional excitation-emission matrices (EEMs) were run on filtered whole water samples using a JY-Horiba/Spex Fluoromax-2 spectrofluorometer with DataMax data acquisition software. Collection parameters for the EEMs have been described in detail elsewhere (Cory and McKnight, 2005). The EEMs were corrected for excitation and emission in Matlab following Cory and McKnight (2005). EEM intensities were normalized to the water Raman peak area (excitation wavelength of 350 nm) following Stedmon *et al*. (2003). The fluorescence index (FI) was calculated from each sample EEM as the ratio of intensities of 470 nm over 520 nm at an excitation wavelength of 370 nm. The fluorescence properties of two reference fulvic acids representing terrestrial material (Suwannee River, FI = 1·24) and aquatic microbial material (Lake Fryxell from the McMurdo area of Antartica FI = 1·72) were analyzed as in Klapper *et al*. (2002) and Hood *et al*. (2003). Parallel factor analysis (PARAFAC) was used to characterize the fluorescent fraction of the dissolved organic matter (DOM) in the samples. Stedmon *et al*. (2003) describe PARAFAC as a three-way version of principal component analysis; and when applied to the excitation-emission matrices (EEMs) of samples containing DOM identifies different classes of fluorophores referred to as components. An EEM can be represented as a sum of the components. Our 40 water samples analyzed for EEMs were fit to the thirteen-component PARAFAC model presented in Cory and McKnight (2005).

Sources of inorganic N

End Member Mixing Analysis (EMMA) in combination with hydrologic mixing models was used to evaluate potential sources of nitrate and ammonium concentrations in the outflow of RG5. Here we build on the successful use of these hydrologic mixing models by Williams *et al*. (2006) to determine sources waters that contributed to the outflow of RG5 in 2003. The model was created following the procedures in Christophersen and Hooper (1992) and as demonstrated for the Green Lakes Valley by Liu *et al*. (2004). Stream flow samples and end-members were standardized for all conservative tracers following the procedure of Hooper (2003) and Burns *et al*. (2001). The proportion of the selected end-members contributing to streamflow was resolved using the equation:

$$f_i = x_i e_i^{-1} \tag{1}$$

where the subscript i denotes the ith stream sample, and f is the vector of runoff fractions for m components, which sum to 1. The term x is a $1x(p+1)$ vector of stream chemistry where p orthogonal projections are used plus the last element of 1 that represents the constraint of total runoff fraction. The e term represents a $mx(p+1)$ square matrix (Liu *et al*., 2004). Here we evaluate sources of nitrate and ammonium by comparing the modeled results with measured values of nitrate and ammonium in the outflow of RG5.

Results

Nutrient content

Dissolved organic carbon was present in all samples from the outflow of RG5 (Figure 2). The mean concentration of DOC was 0·85 mg L^{-1} and ranged from 0·71 to 1·1 mg L^{-1}. The concentration of DOC in snow averaged 0·29 mg L^{-1} and in rain was 2·37 mg L^{-1}. There was a weak but significant increase in DOC with time ($R^2 = 0·31$, $p < 0·05$) Surprisingly, the DOC concentrations in the outflow of RG5 were similar to those in the outflows of the Arikaree Glacier, Martinelli Catchment, and GL5. A one-way analysis of variance test shows no statistical difference in DOC amounts for these surface waters ($p = 0·42$). Dissolved organic carbon was the major component of DOM, as DON and DOP concentrations were almost always near or below detection limits (data not presented for DON and DOP).

There were significant differences in the concentrations of ammonium among the surface waters ($p < 0·05$). The mean concentration of ammonium in the outflow of RG5 was 1·35 µmoles L^{-1} with a range from below detection limits of 0·33 µmoles L^{-1} to 4·6 µmoles L^{-1}. Ammonium content in snow averaged 5 µmoles L^{-1} and in rain averaged 21 µmoles L^{-1}. There was no seasonal trend in ammonium concentrations except for the Arikaree Glacier. Similar to RG5, ammonium concentrations for the Martinelli catchment, GL5, and blockfield waters were always less than 5 µmoles L^{-1} and often below the detection limits of 0·33 µmoles L^{-1}. In contrast, ammonium in the outflow of the Arikaree Glacier showed a trough-shaped seasonal pattern, with values always greater than 5 µmoles L^{-1}. Concentrations

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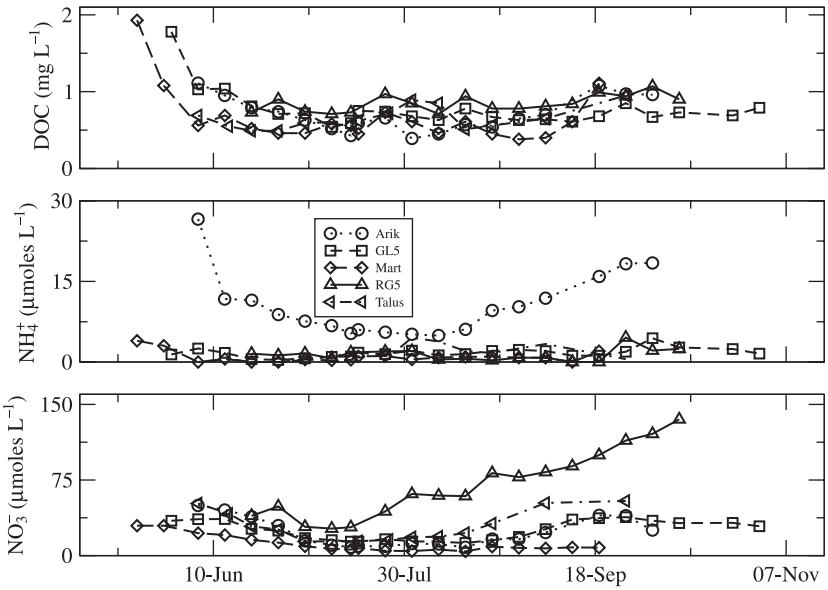

Figure 2. Time series of DOC, ammonium, and nitrate in surface waters of the Green Lakes Valley, for 2003. Note that the scale for the y-axis varies by nutrient. Arik is Arikaree Glacier outflow; GL5 is the outlet of Green Lakes 5; Mart is the outlet of the Martinelli catchment; RG5 is the Green Lake 5 rock glacier outflow; talus is the blockfield site.

of ammonium were greater than 25 μmoles L^{-1} at the initiation of snowmelt, decreased to about 5 μmoles L^{-1} in July, then increased again in the autumn to near 20 μmoles L^{-1}.

For the 2003 field season, the largest difference in nutrient content among the sampling locations was observed for nitrate. The RG5 outflow had average nitrate concentrations of 69 μmoles L^{-1} (Figure 2). In contrast, nitrate averaged 7 μmoles L^{-1} in snow and 25 μmoles L^{-1} in rain. Concentrations of nitrate in the outflow of RG5 at the initiation of snowmelt were about 50 μmoles L^{-1}, similar to the Arikaree Glacier and the blockfield site, and slightly higher than nitrate in the outflow of GL5 and the Martinelli catchment. Nitrate concentrations then decreased at all sites after peak discharge was reached in the Green Lakes Valley. However, nitrate concentrations in the outflow of RG5 began to increase in mid-July, when nitrate concentrations in the other surface waters remained at seasonal lows of less than 15 μmoles L^{-1}. Nitrate concentrations then began to increase in mid-August at all sites except for the Martinelli catchment. Nitrate concentrations from the outflow of the blockfield were about 50 μmoles L^{-1} in the late fall, larger than for outflow from the Arikaree Glacier, GL5, and the Martinelli catchment. However, nitrate concentrations from the outflow of RG5 at the same time were about 100 μmoles L^{-1}, twice that of blockfield discharge. Nitrate concentrations from the outflow of RG5 continued to increase into the late autumn, reaching a maximum value of 135 μmoles L^{-1} on 9 October. A simple linear regression shows that concentrations of nitrate in the outflow of RG5 generally increased with time ($R^2 = 0{\cdot}86$, $p < 0{\cdot}05$).

Measurements of nitrate concentrations in the outflow of RG5 from 1998 to 2004 show a pattern similar to 2003 (Figure 3). Concentrations of nitrate were generally around 50 μmoles L^{-1} at the initiation of snowmelt, decreased to around 30 μmoles L^{-1} in early July, then steadily increased to around 80 μmoles L^{-1} in September. However, there are interesting year-to-year variations. Concentrations of nitrate during the first week of September (which is common to all years) of about 90 μmoles L^{-1} during the drought years from 2000–2001 were about 20 μmoles L^{-1} higher than the 70 μeq L^{-1} for the pre-drought years of 1998 and 1999. Moreover, in the major drought year of 2002, concentrations of nitrate in the outflow of RG5 where on the order of 30–50 μmoles L^{-1} more than the other years on most sampling dates. Nitrate concentrations in the first week of September from 1998 to 2004 increased with time ($r = 0{\cdot}72$) and decreased with annual precipitation ($r = -0{\cdot}73$) ($0{\cdot}10 > p > 0{\cdot}05$ for both). Annual precipitation values are from the D1 precipitation collector.

Synoptic survey

A paired-difference *t*-test shows that that nitrate concentrations from rock glacier outflow in the synoptic survey were significantly different from their reference streams ($p = 0{\cdot}003$, $n = 7$) (Figure 4). For example, water sampled from the tongue-shaped Arapahoe rock glacier had a nitrate concentration of 95 μmoles L^{-1}, about three-times the nitrate concentration

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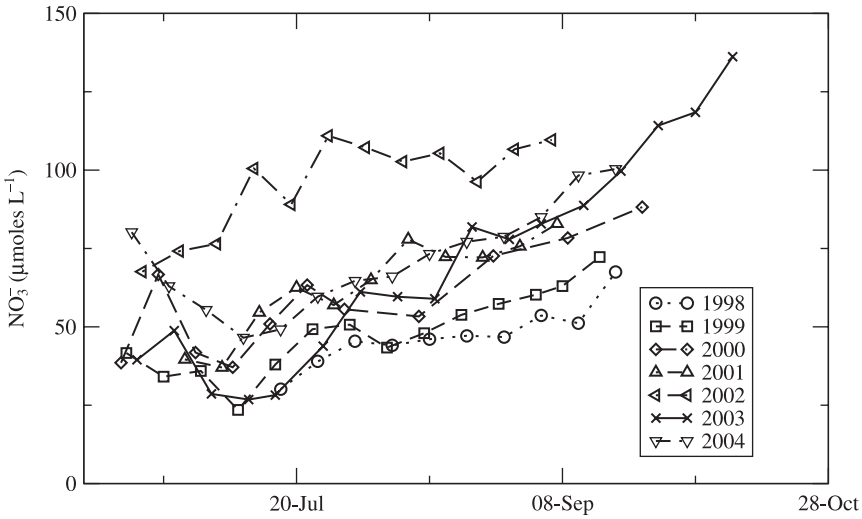

Figure 3. Time series of nitrate concentrations in the outflow of RG5 during the snow-free season from 1998 to 2004.

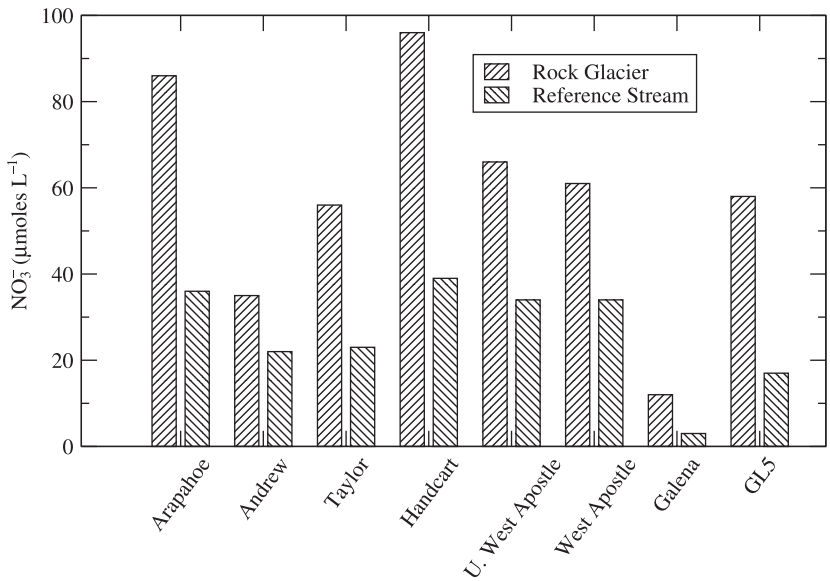

Figure 4. Comparison of nitrate concentrations from the outflow of 7 rock glaciers and co-located surface waters, August 2003.

of 36 μmoles L^{-1} in streamflow below the nearby Arapahoe Glacier. Similarly, the lobate Upper West Apostle and West Apostle rock glaciers had nitrate concentrations of 65 and 61 μmoles L^{-1}, about twice that of the 34 μmoles L^{-1} in the co-located reference streams. To place these nitrate values in perspective, the outflow of RG5 had a nitrate value of 59 μmoles L^{-1} in mid-August. The high nitrate values we report from the outflow of RG5 compared to nearby surface waters appear to be characteristic of the outflow of rock glaciers from the Rocky Mountain region of Colorado and Wyoming.

Source waters

Three component hydrograph separation using EMMA was previously used by Williams *et al*. (2006) at RG5 in 2003 and showed that melted snow comprised an average of 30 per cent of RG5 outflow, soil water 32 per cent, and base flow 38 per cent (Figure 5). Snow was the dominant source water in June, soil water was the dominant water source in July, and base flow was the dominant source in September. Nitrate and ammonium concentrations in the outflow of RG5 for each

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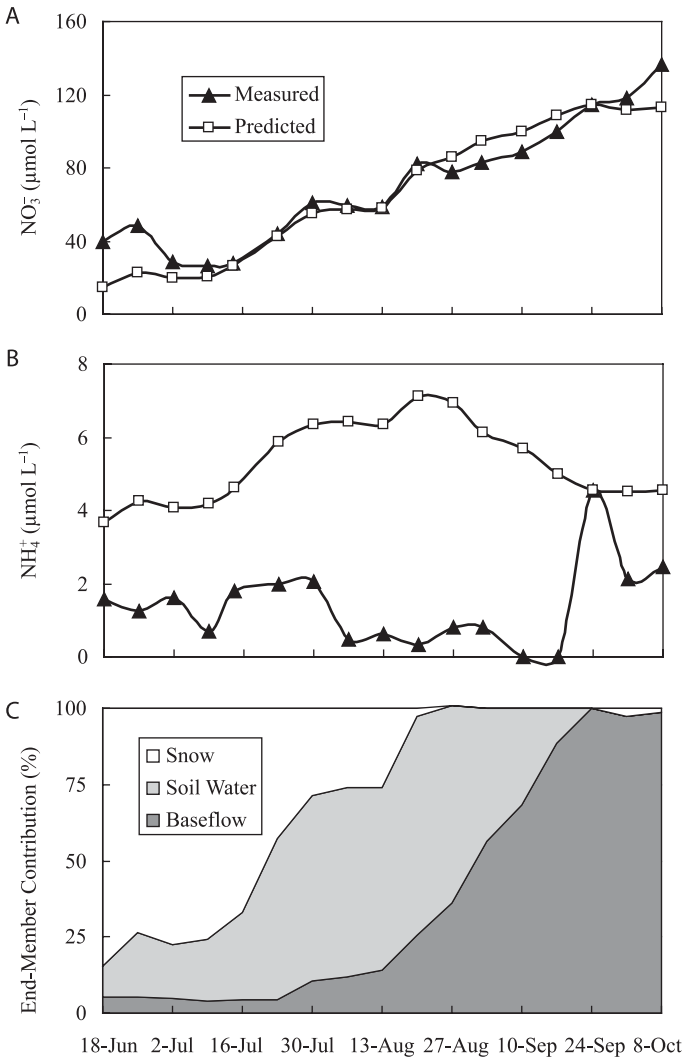

Figure 5. Sources of nitrate (A) and ammounium (B) in the outflow of RG5 were evaluated by plotting observed versus predicted concentrations based on end-member mixing analysis. The lower panel (C) are source waters in the outflow of RG5 for 2003 presented in Williams *et al.* (2006).

sampling date were modeled by weighting their measured value in each of the source waters on that date by the percent contribution of that source water identified by EMMA to the outflow of RG5 (Figure 5). The model successfully predicted the concentrations of nitrate over time in the RG5 outflow ($y = 1{\cdot}05x - 8$, $R^2 = 0{\cdot}90$, $n = 21$, $p << 0{\cdot}001$). The y-intercept was not significantly different than 0 and the slope was not significantly different than 1 ($p > 0{\cdot}05$). This high correlation for predicted and observed values of nitrate concentration indicates that the sources of nitrate were consistent with the source waters for RG5 outflow. However, the model did a poor job of predicting ammonium concentrations ($R^2 = 0{\cdot}16$, $n = 21$, $p > 0{\cdot}05$). These results indicate that ammonium is reactive and is assimilated through some combination of inorganic (e.g. ion exchange reactions) and organic processes after release from snowmelt and soils and before water contributes to the outflow of RG5. In contrast, nitrate appears to behave conservatively as it flows through RG5.

Fluorescence properties of DOM

The FI index for DOM collected from the outflow of RG5 had a mean value of 1·42 and a standard deviation of 0·17. The FI index varied over time and can be classified into three distinct periods (Figure 6). At the beginning of the

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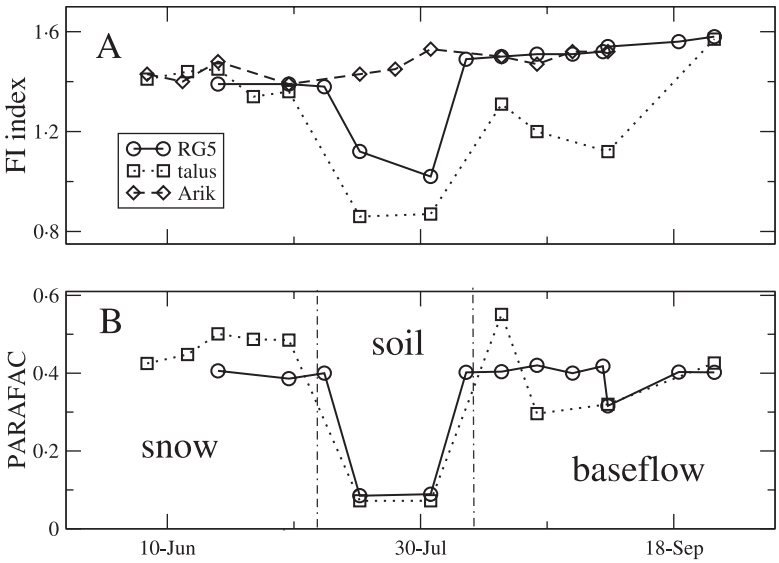

Figure 6. Time series of the fluorescence properties of DOM: (A) Fluorescence index (FI) (B) Selected components of DOM, identified using PARAFAC analysis. We present the sum of components identified as microbial in origin by Cory and McKnight (2005) from an Antarctic-only DOM sample (components 3, 4, 6, 7, 8, 9). Snow, soil, and baseflow refer to source waters for the outflow of RG5 identified by EMMA from figure 5.

sampling season the FI was about 1·4. During mid–season the FI decreased to 1·02. However, the FI began to increase in mid-August and peaked in October at the end of the sampling season with an FI of about 1·6. The FI index for RG5 and the blockfield were similar to the Arikaree Glacier at the start and end of the sampling season, but much lower during mid-summer (Figure 6). PARAFAC analysis of the EEM's for DOM in the outflow of RG5 and the blockfield show a similar pattern over time to the FI index (we did not conduct PARAFAC analysis for the Arikaree samples). We present the sum of components identified as microbial in origin by Cory and McKnight (2005) from Antarctic-only DOM samples (components 3, 4, 6, 7, and 9; note that we did not use components 2 and 12 because these only partially contributed to the Antarctic-only samples). The FI index and PARAFAC components of RG5 were significantly related, with an R^2 of 0·82 ($p << 0{\cdot}01$, $n = 13$). These changes in FI and fluorescence components over time for RG5 and the blockfield suggest that the sources and chemical content of DOM changed over time.

Soil nitrogen

Inorganic nitrogen in soil pools and microbial biomass N were present on the surface of the rock glacier. The mean microbial biomass N in vegetated soils on the surface of RG5 was 114 mg N kg^{-1} (Table I). In contrast, bare soils indicated a much lower amount of microbial biomass (14 mg N kg^{-1}). Pool sizes of inorganic N quantify the amount of nitrate and ammonium available in the soil for assimilation by microbes and plants. The mean inorganic N for

Table I. A comparison of microbial biomass N, inorganic N pools, and net nitrification for the surface of RG5, blockfields, and alpine tundra

Location	Microbial N (mg N kg^{-1})	Ammonium (mg N kg^{-1})	Nitrate (mg N kg^{-1})	Net Nitrification (g N m^{-2} mo^{-1})
RG5 Vegetated	114	4·65	0·80	0·14
RG5 Bare	14	0·33	0·04	0·01
Blockfield Vegetated*	82	5·93	0·63	0·26
Blockfield Bare*	5·4	1·53	0·42	0·09
Tundra**	110	4·10	1·30	0–0·30

* from Bieber *et al.*, 1998. ** inorganic pools from Williams *et al.* (1996); net nitrification from Fisk and Schmidt (1995).

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vegetated sites was $5{\cdot}7 \pm 0{\cdot}9$ mg N kg^{-1}, while bare soils had much less available inorganic N ($0{\cdot}37$ mg N kg^{-1}). Most of the inorganic N was as ammonium, with $4{\cdot}65$ mg N kg^{-1} of ammonium in vegetated soils compared to $0{\cdot}80$ mg N kg^{-1} of nitrate and $0{\cdot}33$ mg N kg^{-1} for ammonium in bare soils compared to $0{\cdot}04$ mg N kg^{-1} for nitrate. The rate of net nitrification was $0{\cdot}14$ g N m^{-2} mo^{-1} for vegetated areas and $0{\cdot}01$ g N m^{-2} mo^{-1} for unvegetated areas.

Discussion

The mean concentration of DOC of $0{\cdot}85$ mg L^{-1} in the outflow of RG5 appears to be similar to those reported for glaciated environments; for example $0{\cdot}14$ to $0{\cdot}77$ mg L^{-1} ($n = 61$) over three summers for the Bow Glacier outflow (Lafreniere and Sharp, 2004). Skidmore *et al*. (2005) report DOC concentrations from a large valley glacier on Ellesmere Island, Canada, of $1{\cdot}2$ mg L^{-1} in basal ice and a range of $0{\cdot}11$ to $0{\cdot}47$ mg L^{-1} ($n = 54$) in supraglacial streams and $0{\cdot}12$ to $0{\cdot}43$ mg L^{-1} ($n = 47$) in subglacial streams. Thus, DOC in the range of $0{\cdot}5$ to $1{\cdot}5$ mg L^{-1} appears to be common in surface waters draining alpine environments, including glaciers, rock glaciers, blockfields, late–lying snow patches, and alpine streams.

The low concentrations of ammonium (less than 5 μmoles L^{-1}) in the outflow of rock glaciers, blockfields, late-lying snow patches, and alpine streams compared to snow and rain are consistent with previous reports that ammonium is relatively immobile in these high-elevation environments (Brooks *et al*., 1996; Baron and Campbell, 1997; Williams *et al*., 2001). Ammonium in snowmelt and rain is quickly removed from water moving through the subsurface environment in these high-elevation catchments by biological assimilation and adsorption on ion exchange sites. High ammonium concentrations in the outflow of the Arikaree Glacier are anomalous. At this site, water is sampled before it has been in contact with rock and ground surfaces, and so it is analogous to sampling a large snowmelt lysimeter. The high values of ammonium in the outflow of the Arikaree Glacier at the initiation of snowmelt are thus likely the result of an ionic pulse. Ammonium values of about 25 μmoles L^{-1} at this time compared to bulk snow values of about 5 μmoles 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). Ammonium values in the outflow of the Arikaree Glacier then decreased to seasonal low in mid-July before increasing in the autumn months to about 20 μmoles L^{-1}, similar to ammonium values in rainfall at that time.

Nitrate concentrations of up to 135 μmoles L^{-1} in the outflow of RG5 are among the highest reported for surface waters in high-elevation catchments. In the central European Alps, Psenner (1989) conducted a synoptic survey of 73 high-elevation lakes and reported a mean nitrate concentration of 16 μmoles L^{-1} and a maximum of 32 μmoles L^{-1}. Sommaruga-Wograth *et al*. (1997) reported a maximum value of about 30 μmoles L^{-1} for dissolved inorganic nitrogen ($DIN = NO_3^- + NH_4^+$) from 57 remote alpine lakes of the Alps. For the Sierra Nevada of California, the highest concentrations of nitrate reported are about 40 μmoles L^{-1} at the initiation of snowmelt runoff from the 15-ha High Lake catchment in the Rock Creek drainage (Stoddard, 1995). In the Rocky Mountains, maximum concentrations of nitrate were less than 40 μmoles L^{-1} during synoptic surveys conducted by Musselman and Slauson (2004) for 150 high-elevation lakes and another 44 by Baron *et al*. (2000). Long-term measurements of the solute content of surface waters for Andrews and Icy Brooks streams in Rocky Mountain National Park show maximum concentrations of nitrate of about 40 μmoles L^{-1} during snowmelt runoff (Campbell *et al*., 1995). However, Campbell *et al*. (2002) report a nitrate value of 178 μmoles L^{-1} collected in late April from Spring 19, a talus site at the Loch Vale catchment. Nitrate concentrations in Spring 19 then decreased to about 60 μmoles L^{-1} as snowmelt proceeded.

Elevated nitrate concentrations appear to be characteristic of the outflow of rock glaciers in the central Rocky Mountains. Measurements of nitrate concentrations in the outflow of RG5 during snow-free seasons from 1998 to 2004 show a similar pattern to 2003 (Figure 3), suggesting that the elevated nitrate concentrations we report for 2003 were not specific to that year and are thus characteristic of this rock glacier. Moreover, the results of the synoptic survey conducted with 7 rock glaciers in the Rocky Mountain Region of Colorado and Wyoming during August showed that nitrate concentrations from rock glacier outflow were significantly higher than their reference streams (Figure 4). The type of rock glacier did not appear to be important, as there were no differences in the nitrate concentrations in the outflow of lobate or valley rock glaciers.

Sources of both nitrate and DOC at RG5 appear to change seasonally. Williams *et al*. (2006) evaluated the EMMA solutions for source waters in the outflow of RG5 by reproducing concentrations of all conservative tracers from the EMMA model and comparing them to the measured values. In general, EMMA reproduced the measured concentrations well. For example, the R^2 values for the conservative tracers $\delta^{18}O$, Mg^{2+}, and SO_4^{2-} were all greater than $0{\cdot}95$ with slopes near one (Williams *et al*., 2006). Similarly, EMMA reproduced the concentrations of nitrate in the outflow of RG5 reasonably well, with an R^2 of $0{\cdot}90$ and a slope of $1{\cdot}05$. Thus, nitrate appears to move conservatively from source waters through the rock glacier to its outflow. EMMA results suggest that snow was the dominant source of nitrate in June, 'soil' water was the dominant nitrate source in July, and base flow was the dominant source in September (Figure 5).

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Nitrate concentrations in the outflow of RG5 in June are consistent with the release of nitrate from storage in the seasonal snowpack in the form of an ionic pulse. Williams *et al.* (1996b) have shown that nitrate concentrations in snowpack meltwater before contact with the ground range from 5 to 15 times bulk snowpack concentrations at Niwot Ridge. Bales *et al.* (1990) show a similar ionic pulse for Wyoming snowpacks. The elevated nitrate value of 178 μmoles L^{-1} in April reported by Campbell *et al.* (2002) from Spring 19 was also attributed to an ionic pulse.

Our EMMA results indicates that outflow from RG5 in July was dominated by water and nitrate similar to that collected from zero-tension soil lysimeters in alpine soils (Williams *et al.*, 2006). Our measurements of soil microbial biomass N and inorganic pools of N from the surface of RG5 show that nitrogen is available to support the EMMA results that suggest soils at the top of the rock glacier supply the nitrate found in the outflow of RG5 at this time. Moreover, these values were also similar to those of well-developed alpine soils on Niwot Ridge and to blockfields. Microbial biomass N of 114 mg N kg^{-1} for the vegetated surface of RG5 was similar to the 110 mg N kg^{-1} reported for alpine tundra by Fisk and Schmidt (1995) and more than the 82 mg N kg^{-1} reported by Williams *et al.* (1997) for vegetated talus patches (Table I). The 14 mg N kg^{-1} for bare areas of the surface of RG5 was slightly higher than the 5·4 mg N kg^{-1} for bare areas of the surface of talus patches (Williams *et al.*, 1997). KCL-extractable ammonium values for vegetated surfaces of RG5 of 4·65 mg N kg^{-1} were similar to the 5·93 mg N kg^{-1} of vegetated talus and 4·1 mg N kg^{-1} of alpine tundra (Table I). Net nitrification rates of 0·14 g N m^{-2} mo^{-1} for vegetated surfaces of RG5 were comparable to the 0·26 g N m^{-2} mo^{-1} for vegetated talus and in the middle of the 0 to 0·30 g N m^{-2} mo^{-1} for alpine tundra (Table I). Thus, nitrogen cycling on the surface of RG5 appears to be capable of producing the nitrate in the outflow of RG5 in July identified as soil-like by EMMA. Moreover, the 'soils' at the surface of RG5 appear to behave similarly to the 'soils' of alpine blockfields with respect to nitrogen cycling and resulting pools of inorganic N and microbial biomass N.

Baseflow was the dominant source of water in the outflow of RG5 in September and October and may be the source of nitrate in RG outflow at this time (Figure 5). Williams *et al.* (2006) hypothesized that RG5 has an internal ice core surrounded by interstitial ice intermixed with coarse debris, and that internal ice melt was the source of baseflow. Our EMMA results (Figure 5) are consistent with nitrate in baseflow as the dominate source of nitrate in the outflow of RG5 in September and October. Thus, the source of nitrate in the outflow of RG5 in the autumn months may be from this icy environment. Moreover, nitrate concentrations increase as precipitation decreases, suggesting that internal ice melt with high nitrate concentrations provides a larger percentage of outflow in dry years.

Previous research in the Green Lakes Valley has shown that blockfield 'soil' constitute an extreme environment with ecosystem processes that are often different from those of vegetated systems (Ley *et al.*, 2004). Microbial populations in blockfields of the Green Lakes Valley were active all winter under a deep seasonal snowcover, when light levels were below detection and soil temperatures were 0 °C (Ley *et al.*, 2004). Furthermore, there were strong shifts in microbial communities from cold-adapted micro-organisms that dominated the winter period to warm-adapted microbial assemblages in the summer (Ley *et al.*, 2004). These blockfields appear to be carbon-limited, driving the system towards net nitrification (Williams *et al.*, 1997). Research has shown that there are unique microbial populations in the blockfields of Green Lakes Valley which are adapted for cold, dark, and oligotrophic conditions, the same conditions in the interior of RG5. Taken together, these results suggest that there may be microbial assemblages in both blockfields and the interior of the rock glacier that are active in icy environments and are responsible for the elevated nitrate concentrations in outflow from these two landscape types.

The temporal changes in the FI index of DOM in the outflow of RG5 are consistent with these changes in source waters. The FI index has been used to separate terrestrial from aquatic microbial sources of DOM. Hood *et al.* (2003) have shown that the FI index for DOM from high-elevation streams in the Green Lakes Valley is around 1·4 at the initiation of snowmelt, rapidly decreases to about 1·25, and then increases to about 1·5 on the recession limb of the annual hydrograph. To aid in the interpretation of FI values for fulvic acids collected in Green Lakes Valley, they evaluated the fluorescence properties of the two reference fulvic acids representing terrestrial material (Suwannee River) and aquatic microbial material (Lake Fryxell from the McMurdo area of Antartica). The resulting EEMs in these two reference standards were very similar to results reported by McKnight *et al.* (2001). Hood *et al.* (2003) report that six Suwannee River fulvic acid samples ranging in concentration from 1–10 mg L^{-1} had an average FI value of 1·24 with a standard deviation of 0·01. Moreover, the FI values of the Suwannee River fulvic acids were highly consistent with the FI values for fulvic acids collected from soil lysimeters throughout Green Lakes Valley, which had an average value of 1·24 and a range of 1·19 to 1·33 (Table 2 in Hood *et al.* (2003)). For the Lake Fryxell fulvic acids which represent an aquatic microbial end-member, EEMs from six samples ranging in concentration from 1–10 mg L^{-1} were also similar to the results of McKnight *et al.* (2001) and had an average FI value of 1·72 with a standard deviation of 0·02. Hood *et al.* (2003) interpret their FI results as suggesting that that during peak runoff the DOM was derived primarily from terrestrial precursor material and that DOM derived from algal and microbial biomass in lakes and streams was a more important source of DOM during late summer and fall.

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Hood *et al*. (2003) note that the FI values of their reference fulvic acids (1·24 for terrestial DOM and 1·72 for aquatic DOM) were very similar in range, but lower in magnitude, than those described by McKnight *et al*. (2001) (FIs ranging from 1·4 to 2·1), 'suggesting that FI values are somewhat dependent on fluorometer configuration and highlighting the need to calibrate an instrument with fulvic acids of known origin' (Hood *et al*., 2003). Because FI values from the McKnight *et al*. (2001) paper are frequently cited, it is worth pursuing why our FI values and those of Hood *et al*. (2003) differ from McKnight *et al*. (2001), even though the EEMs were similiar in all three studies. McKnight *et al*. (2001) caution on page 47 that fluoresence data should be properly corrected for instrumental biases – otherwise, the values for the fluoresence index may be slightly dependent on fluorometer configuration because of the interference of the emission monochromater grating and the light detector efficiency. Further, they recommend a calibration using fulvic acids of known origin, such as the Suwannee River fulvic acid used in Hood *et al*. (2003) and this study. They stressed the importance of this calibration and the fact that absolute FI values may vary by instrument (McKnight *et al*., 2001). Moreover, McKnight *et al*. (2001) did not normalize their EEM intensities to the water Raman peak area as suggested by Stedmon *et al*. (2003) and implemented by us, Hood *et al*. (2003) and Cory and McKnight (2005). Differences in the spectrofluorometers and the calibration of the instruments explain why this study and Hood *et al*. (2003) obtain similar EEMs but different FI values compared to McKnight *et al*. (2001).

Moreover, Cory and McKnight (2005) measured the EEMs and calculated the FI index for 379 samples using the same Fluoromax-2 spectrofluorometer we used in our study, along with a newer Fluoromax-3 spectrofluorometer cross-calibrated with our Fluoromax-2 spectrofluorometer. They report an average FI index of 1·66 from 73 samples (Table I, supplemental materials) from Lake Fryxell and the larger McMurdo area of Antarctica, very similar to the 1·72 that we report for our Lake Fryxell – only reference standards. Thus, the FI of about 1·6 we report in rock glacier outflow during October appears to be similar to the FI of the McMurdo area of Antarctica, where there are no known vascular plants and where DOM is produced by aquatic microbes (Cory and McKnight, 2005). In contrast, Cory and McKnight (2005) show that DOM in the surface waters around the Toolik Lake Arctic LTER have an FI of 1·31 ($n = 105$), suggesting that DOM pool is dominated by higher plant precursor material. These results suggest that the FI values of less than 1·3 that we measured during mid-summer at both the RG5 outflow and blockfield outflow may have a large component of plant precursor material.

Thus, DOM in the outflow of RG5 at the onset of snowmelt runoff appears to be primarily from release in the seasonal snowpack (Figure 6). During the time period of mid-July to mid-August, the low FI index of DOM in the outflow of RG5 is consistent with DOM produced from decomposition of vegetation on the surface of RG5. The FI values of near 1·6 in the outflow of RG5 in the autumn months suggest a primarily aquatic-like microbial source. Similarly, Lafreniere and Sharp (2004) suggest that elevated FI values from DOM in a glacial stream (when most runoff originates from ice-covered areas) indicate that DOM from glaciated regions was more 'microbial' in character than that derived from ice-free areas which had lower FI values. And FI values for DOM from the outflow of RG5 at both ends of the seasonal hydrograph are similar to those from the Arikaree Glacier (Figure 6), where water is collected before it has a chance to contact the ground surface.

PARAFAC analyses of DOM are also consistent with this switch from terrestrial DOM in the summer time period to an increasing microbial source during the autumn months. Cory and McKnight (2005) analyzed DOM from Antarctica where there is no plant material and where the only source of DOM is of aquatic-microbial origin. They found that DOM components C3, C4, C6, C7, and C9 were associated with organic material of aquatic-microbial origin and these components on average summed to 42 per cent of the PARAFAC model, the same as our samples. In contrast, DOM from plant/terrestrial inputs were found to have decreased amounts of these components. Thus, our PARAFAC analysis suggests that the origin of the DOM in the outflow of RG5 was primarily aquatic-microbial during snowmelt runoff, terrestrial during the mid-summer period, and aquatic-microbial during the autumn months.

Debris-rich layers of a high Arctic glacier have been shown to contain metabolically diverse microbes that could be cultured oligotropically at low temperatures, including aerobic chemoheterotrophs and anaerobic nitrate reducers, sulphate reducers, and methanogens (Skidmore *et al*., 2000). Examination of microbial communities in two subglacial environments using clone libraries and dot blot hybridization techniques showed that microbial activity in these cold, dark, oligotrophic systems was an important contributor to the solute flux from those glaciers (Skidmore *et al*., 2005). Thus, it would not be surprising if there were microbes within the icy interior of RG5.

Conclusions

Here we present the first comprehensive measurements of the nutrient content of the outflow from a rock glacier. Nitrate and DOC were represent in all samples. DOC concentrations were similar to those of other surface waters in this alpine environment. However, nitrate values in the outflow of RG5 were higher than all other surface waters.

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Long-term measurements (1998–2004) show that these elevated nitrate concentrations in the outflow of RG5 occur every year. Moreover, synoptic sampling of seven other rock glaciers also indicated that elevated nitrate concentrations may be characteristic of rock glaciers throughout the Rocky Mountain region. The FI index and PARAFAC analysis of DOM in the outflow of RG5 suggest a microbial source of DOM during the fall months. EMMA analysis suggests that the water source at this time is internal ice melt. The elevated nitrate characteristic of the outflow of RG5 during the fall months may be produced by microbial communities in the interior of the rock glacier. Unique microbial communities adapted to the extreme environment of the interior of rock glaciers – permanently dark, oligotrophic, and constantly cold – may be the source of the elevated nitrate in the autumn months.

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