



Reach-Scale Cation Exchange Controls on Major Ion Chemistry of an Antarctic Glacial Meltwater Stream

MICHAEL N. GOOSEFF^{1,*}, DIANE M. MCKNIGHT² and ROBERT L. RUNKEL³

¹*Department of Aquatic, Watershed and Earth Resources, Utah State University, Logan, Utah, USA;* ²*Institute of Arctic and Alpine Research, University of Colorado, Boulder, Colorado, USA;* ³*United States Geologic Survey, Lakewood, Colorado, USA*

Abstract. The McMurdo dry valleys of Antarctica represent the largest of the ice-free areas on the Antarctic continent, containing glaciers, meltwater streams, and closed basin lakes. Previous geochemical studies of dry valley streams and lakes have addressed chemical weathering reactions of hyporheic substrate and geochemical evolution of dry valley surface waters. We examine cation transport and exchange reactions during a stream tracer experiment in a dry valley glacial meltwater stream. The injection solution was composed of dissolved Li^+ , Na^+ , K^+ , and Cl^- . Chloride behaved conservatively in this stream, but Li^+ , Na^+ , and K^+ were reactive to varying degrees. Mass balance analysis indicates that relative to Cl^- , Li^+ and K^+ were taken up in downstream transport and Na^+ was released. Simulations of conservative and reactive (first-order uptake or generation) solute transport were made with the OTIS (one-dimensional solute transport with inflow and storage) model. Among the four experimental reaches of Green Creek, solute transport simulations reveal that Li^+ was removed from stream water in all four reaches, K^+ was released in two reaches, taken up in one reach, and Na^+ was released in all four reaches. Hyporheic sediments appear to be variable with uptake of Li^+ in two reaches, uptake of K^+ in one reach, release of K^+ in two reaches, and uptake of Na^+ in one reach. Mass balances of the conservative and reactive simulations show that from 1.05 to 2.19 moles of Li^+ was adsorbed per reach, but less than 0.3 moles of K^+ and less than 0.9 moles of Na^+ were released per reach. This suggests that either (1) exchange of another ion which was not analyzed in this experiment or (2) that both ion exchange and sorption control inorganic solute transport. The elevated cation concentrations introduced during the experiment are typical of initial flows in each flow season, which flush accumulated dry salts from the streambed. We propose that the bed sediments (which compose the hyporheic zone) modulate the flushing of these salts during initial flows each season, due to ion exchange and sorption reactions.

Key words: ion exchange, major ion chemistry, McMurdo dry valleys, reactive solute transport, stream tracer experiment

* Author for correspondence. E-mail: michael.gooseff@usu.edu

1. Introduction

The McMurdo dry valleys is a polar desert that constitutes the largest ice-free area of Antarctica. Stream waters within the dry valleys are derived from dilute glacial melt and take on increased dissolved solid loads due to interactions in streambed sediment, which makes up the hyporheic zone of these streams. As a result of these upstream processes, closed-basin lakes receive stream waters that are enriched in solutes compared to meltwater originating at the glaciers. Previous studies of chemical weathering in the dry valleys have shown that denudation rates are higher than expected for such a cold, dry climate (Lyons et al., 1997; Nezat et al., 2001; Gooseff et al., 2002; Maurice et al., 2002). Hyporheic exchange in dry valley streams controls the transport of water through storage and evaporation (Gooseff et al., 2003), and controls stream water dissolved solute loads through in-hyporheic chemical weathering and dissolution of marine aerosols and calcium carbonate (Gooseff et al., 2002). Dissolved nutrients are retained and/or transformed by benthic and hyporheic microbial communities (Gooseff et al. in press; McKnight et al., 1999; McKnight et al., 2004). We propose that in addition to primary weathering reactions, ion exchange processes on streambed sediment surfaces influence inorganic stream chemistry and solute loads in dry valley streams. Lemmens and Roger (1978) showed that cation exchange was an important control on the dissolved ion concentration of meltwater streams in the foreland of Swiss glaciers, and we believe that this may be important in dry valley meltwater streams too.

Previous studies have shown that stream sorption processes (one-way loss of stream solutes on to streambed sediments) and ion exchange processes (replacement of ions on sediment surfaces by stream solutes) control stream solute concentrations. Several studies have assessed the transport and fate of introduced reactive inorganic and radioactive solutes in temperate streams (Bencala, 1984; Bencala et al., 1984; Cerling et al., 1990; Forsman et al., 2002). Specific reach-scale studies by Kuwabara et al. (1984) demonstrated that dissolved Cu^{2+} was taken up by stream algae and sorbed to bed sediments over a 700 m reach of Convict Creek, California. Bencala (1983) showed that dissolved Sr^{2+} sorbed on to streambed sediments in Uvas Creek, California. Each of these studies focused on sorption processes, rather than ion exchange processes, though ion exchange processes have been found to be an important control on dissolved cation transport in several stream systems (Nakagawa and Iwatsubo, 2000; Hodson et al., 2002). Freeman et al. (1995) investigated the transport of dissolved K^+ in a temperate stream and found that it was subject to ion exchange reactions, as its downstream progression was retarded, compared to co-injected Br^- . On a much smaller scale, ion exchange dynamics of sediments have been studied in slurry or microcosm experiments, with respect to implications in larger natural systems (e.g., Shih and Gloyna,

1969). Given the dilute nature of dry valley stream water, we expected that cation exchange reactions would be significant at the stream-reach scale.

In this paper, we investigate stream-reach scale ion exchange reactions in a glacial meltwater stream, which may exert an important control on stream water chemistry. We present the results of a stream tracer experiment in which stream solute concentrations of Li^+ , K^+ , Na^+ , and Cl^- are elevated for several hours. We used mass balance analysis to identify differences in major cation behavior. Simulations of transport of Cl^- , Li^+ , K^+ , and Na^+ , assuming conservative (no reaction) and first-order decay reactivity (reaction proportional to the solute concentration), are presented and analyzed. We interpret these results as indicating that ion exchange reactions within the streambed sediments preferentially adsorb Li^+ , and release K^+ and Na^+ . We propose that these exchange reactions may be important in these meltwater streams during initial flows each flow season, when elevated concentrations of inorganic solutes are observed in the streams.

2. Study Site

The McMurdo dry valleys are located at roughly 78 °S latitude, on the western coast of McMurdo Sound, Antarctica (Figure 1). Glaciers, open

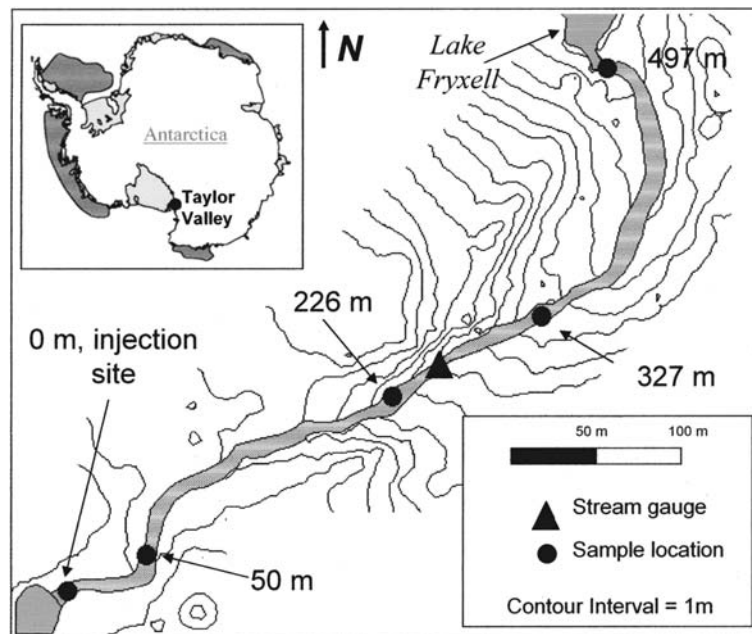


Figure 1. Location map of the Taylor Valley (inset) and Green Creek, which originates at the southeastern corner of the Canada Glacier and terminates in Lake Fryxell. Solute injection and stream water collection sites are noted.

expanses of barren patterned ground, stream channels, and permanently ice-covered, closed basin lakes dominate the landscape. The climate is defined by a mean annual air temperature of $-20\text{ }^{\circ}\text{C}$, less than 10 cm water equivalent of precipitation, as snow, and austral summers with 24 hours of sunlight.

Glacial melt is the main source of streamflow, which generally lasts for 6–12 weeks during the austral summer. Streambeds are composed of porous, unconsolidated alluvium, in which hyporheic zones are established, extending several meters from the edge of the stream (Conovitz et al., 1998). Streams exchange water with different lateral zones of the hyporheic zone over time scales of hours to months (Runkel et al., 1998; Gooseff et al., 2003). In shallow-gradient stream reaches, freeze–thaw cycles have produced a stable stone pavement, which allows for extensive microbial mat coverage (predominantly *Nostoc* and *Phormidium* species) on top of the pavement (McKnight et al., 1998, 1999). We present results from an experiment performed on Green Creek, which originates at the southeastern corner of the Canada Glacier in Taylor Valley, and extends about 1 km from the base of the glacier, terminating in Lake Fryxell (Figure 1). Stream discharge, water temperature and specific conductivity are recorded at a 15-min interval at a stream gauge located roughly half way down the reach. Stream chemistry samples are collected by MCM-LTER (McMurdo Dry Valleys Long Term Ecological Research Project) personnel periodically (during site visits on an irregular schedule) throughout each flow season to monitor major ion concentrations. Early season concentrations of Li^+ , Na^+ , K^+ , and Cl^- average 0, 167, 25, and $183\text{-}\mu\text{M}$ in Green Creek ($n = 6$ first-of-season samples, <http://huey.colorado.edu/LTER>), though flow-season average concentrations are 0, 110, 20.8, and $105\text{ }\mu\text{M}$, respectively (McKnight et al., 2004).

As a result of multiple lithologic sources and dry valley glacial history, the sediment comprising dry valley streambeds has a heterogeneous composition of granite, gneiss, dolerite, Beacon sandstone (Péwé, 1960; Doran et al. 1994), and carbonate deposits (Hendy et al., 1979). The lithology of the Green Creek streambed sediment is varied, dominated by igneous and high-grade metamorphic rocks, and roughly equal amounts of felsic, intermediate and basic compositions (Gooseff et al., 2002). This variability of the sediment lithology is a result of the diverse geology and lacustrine history of the Fryxell basin (Denton et al., 1989; Doran et al., 1994). The few sedimentary minerals that have been reported were probably rafted into the valley bottom during an incursion of sea ice during the Pleistocene (Denton et al., 1989). Gooseff et al. (2002) report a geometric surface area of $3.79 \times 10^{-3}\text{ m}^2\text{ g}^{-1}$ (assuming spherical sediment particle shape) and a BET surface area of $1.23\text{ m}^2\text{ g}^{-1}$ for the bulk sediment. The difference in surface area computation is typical as the geometric surface areas assume an idealized sediment shape, but BET surface areas are computed based on

gas adsorption to sediment surfaces. The $<2\ \mu\text{m}$ fraction from Green Creek contained 35% muscovite/illite/smectite and kaolinite, and roughly 22% primary minerals, and, based on XRD analysis, has mineralogy generally consistent with the lithologies. The courser fraction is mostly primary silicate minerals with some kaolinite and muscovite/illite/smectite. The 2–63 μm fraction has a mineralogy similar to the coarse fraction, except that it is somewhat enriched in amphibole and plagioclase (Gooseff et al., 2002). Low totals for the crystalline material suggest the presence of considerable amorphous weathering products, on the order of 40–65% by weight of the $<2\ \mu\text{m}$ size fraction ($<0.3\ \text{wt}\%$ of the bulk sediment).

Dry valley stream water chemistry is results from both chemical weathering and dissolution of marine aerosols (Green et al., 1988). Lyons and Welch (1997) point out that Li^+ in lakes and streams is generally derived from both of these sources. Gooseff et al. (2002) found that Cl^- and Na^+ also shared these sources, but that dissolved K^+ came primarily from chemical weathering. Angino et al. (1962) suggest that thenardite (Na_2SO_4) dissolution contributes Na^+ to stream water chemistry, and Claridge and Campbell (1977) attributed dissolved K^+ concentrations to dissolution of muscovite micas.

3. Methods

3.1. STREAM TRACER EXPERIMENT

To test our hypothesis that ion exchange reactions in hyporheic sediments (surface and subsurface sediments through which stream water comes into contact) influence stream water cation concentrations, we performed a solute tracer and enrichment experiment in Green Creek on January 13 1996, as part of a nutrient enrichment experiment (see McKnight et al., 2004 for details). The choice of ions and the concentrations in the injection solution were dictated partially by the nutrient concentration enrichment targets, which were to be high enough to observe a definite pulse downstream, but not high enough to enhance stimulation of biotic uptake. The 6.5 L addition solution was composed of 4.13 M Cl^- and Li^+ , 0.12 M K^+ , and 0.24 M Na^+ , corresponding to 26.8 mol Cl^- and Li^+ , 0.8 mol K^+ , and 1.6 mol Na^+ . The enriched solution was added to the stream at a rate of $50\ \text{mL}\ \text{min}^{-1}$ for a period of 3 hours (at the 0 m station in Figure 1).

During the experiment, streamflow decreased from $3.0\ \text{L}\ \text{s}^{-1}$ to $0.3\ \text{L}\ \text{s}^{-1}$ at the stream gauge located just downstream of the 226 m sampling site (Figure 2). To accommodate the large decrease in streamflow, estimates of the flow rate and main channel cross-sectional area at the injection site and sampling sites were obtained using a kinematic wave routing model (see Runkel et al., 1998; McKnight et al., 2004 for details).

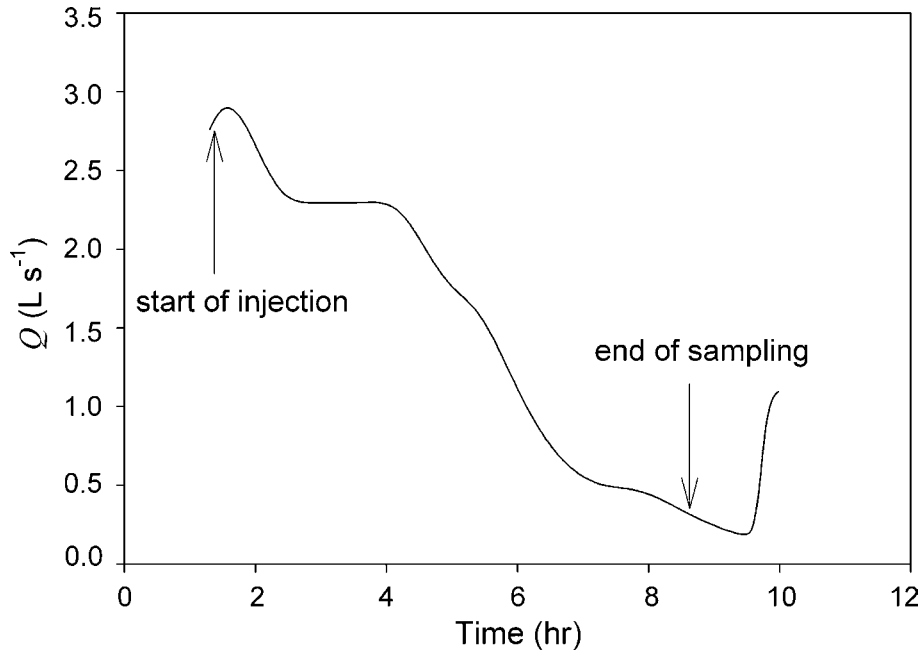


Figure 2. Green Creek hydrograph at sampling station 226 m downstream of injection point, during the tracer experiment. Time 0 is 22:00 hour on 13 January 1996. Diurnal streamflow variation is typical in dry valley streams during the austral summer.

3.2. STREAM WATER ION CONCENTRATION ANALYSIS

Stream water samples were collected at 50, 226, 327, and 497 m downstream, and filtered upon collection using a peristaltic pump with 0.4- μm pore size, 145 mm diameter Gelman membrane filters. Analysis of Cl^- was performed by ion chromatography, and analysis of Na^+ was performed with a Jarrel–Ash model 975 inductively coupled plasma (ICP) spectrometer using standard methods. Li^+ and K^+ analyses were performed with flame atomic absorption spectroscopy on a Perkin Elmer model 5000 spectrometer.

3.3. SOLUTE MASS BALANCE AND CONCENTRATION COMPARISONS

The changes in solute concentration during the experiment were analyzed in two ways at each stream sampling station. A molar mass balance for each solute at each stream sampling site was developed according to the following:

$$M(x) = \int C_{\text{BCT}}(t)Q(t)dt \quad (1)$$

where, $M(x)$ is the molar mass of solute passing a sampling location downstream (moles); $C_{\text{BCT}}(t)$ represents the solute breakthrough curve (rise of stream solute concentration due to the injection experiment) from data collected at that particular location minus background concentrations at each sampling site (M); and $Q(t)$ represents the hydrograph for the particular location (L s^{-1}). To compare reactive solute dynamics utilizing the molar mass changes downstream, ratios of ion concentration (Li^+ , K^+ , and Na^+) to that of Cl^- ($C(t)_{\text{ION}}/C(t)_{\text{Cl}}$), the conservative tracer, are also calculated. The temporal changes in these ratios represent the proportion of change in molar mass relative to the conservative tracer during the observed solute breakthrough curves. An increase in the ratio indicates that the mass of one ion has increased relative to the mass of the conservative tracer Cl^- .

3.4. TRANSIENT STORAGE/ION EXCHANGE SIMULATIONS

Results of the solute enrichment experiment were simulated using a one-dimensional solute transport model that includes inflow, transient storage, and first order uptake of solute (OTIS, Runkel, 1998). Solute concentrations in the main channel (C) and transient storage zone (C_S) are given by:

$$\frac{\partial C}{\partial t} = -\frac{Q}{A} \frac{\partial C}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left(AD \frac{\partial C}{\partial x} \right) + \alpha(C_S - C) + \lambda_{\text{ION}} C \quad (2)$$

$$\frac{dC_S}{dt} = \alpha \frac{A}{A_S} (C - C_S) + \lambda_{S,\text{ION}} C_S \quad (3)$$

where A is the main channel cross-sectional area (m^2), A_S is the storage zone cross-sectional area (m^2), D is the dispersion coefficient ($\text{m}^2 \text{s}^{-1}$), Q is the volumetric flow rate ($\text{m}^3 \text{s}^{-1}$), t is time (s), x is distance (m), α is the exchange coefficient (s^{-1}), λ_{ION} is the first-order rate coefficient for reactive solute loss (< 0) or gain (> 0) in the stream (s^{-1}), and $\lambda_{S,\text{ION}}$ is the first-order rate coefficient for reactive solute loss or gain in the storage zone (s^{-1}). First-order type reactions increase or decrease stream solutes in proportion to the concentration of the solute present in the stream (λ_{ION}) or hyporheic water ($\lambda_{S,\text{ION}}$). The storage zone consists of both the hyporheic zone and open water areas adjacent to the main channel (side pools, etc.). Due to the shallow nature of Green Creek, open water areas are considered negligible and we assume that the storage zone is equivalent to the hyporheic zone. Model simulations were performed for each reach utilizing the upstream sampling station solute observations for the boundary conditions. OTIS takes into account these varying solute boundary conditions as well as the varying hydrograph (Figure 2) computed at each sampling site from kinematic discharge routing (McKnight et al., 2004).

Parameter estimates were obtained in two steps. First, observed Cl^- concentrations were used in conservative ($\lambda = 0$, therefore Cl^- experiences no reaction) OTIS-P (one-dimensional solute transport model with inflow and storage and a parameter estimation package, Runkel, 1998) simulations to estimate the hydrologic parameters describing physical solute transport (A_S , D , α) (McKnight et al., 2004). First-order rate coefficients (λ_{ION} , $\lambda_{\text{S,ION}}$) for Li^+ , K^+ , and Na^+ were then optimized in individual simulations for each ion and each reach utilizing UCODE (a universal computer model parameter optimization code, see Scott et al. (2003) for application to OTIS). Three reaction simulations were considered for each stream reach: stream reactions only, storage zone reactions only, and stream and storage zone reactions combined. The optimal simulation scenario was one that resulted in the best fit to the observations, and, in the case of the stream and/or storage zone reaction scenario, resulted in a model fit without highly correlated parameters (λ_{ION} , $\lambda_{\text{S,ION}}$). UCODE provides information on both agreement between simulated and observed values, and correlations among optimized parameters.

In order to determine the mass increase or decrease downstream, we also integrate the solute breakthrough curves to compute molar masses passing each site for the conservative, observed, and reactive transport simulations. Change in molar mass is computed as the difference between the reactive or observed and conservative integrated molar masses:

$$\Delta M(x)_{\text{ION}} = \int C_{\text{R}}(t)Q(t)dt - \int C_{\text{C}}(t)Q(t)dt \quad (4)$$

where, $C_{\text{R}}(t)$ is the simulated or observed reactive breakthrough curve for a particular solute, and $C_{\text{C}}(t)$ is the simulated conservative breakthrough curve for a particular solute.

4. Results

Chloride was assumed to be conservatively transported downstream, although Cl^- molar masses (Figure 3) and plateau concentrations decrease downstream (Figure 4). With the exception of the Cl^- data collected at 497 m, it appears that the injected pulse was completely sampled at the sampling sites during the experiment (Figure 4). The downstream decreases are due to two potentially competing factors. Firstly, the large size of the hyporheic zone compared to the stream (compare A_S in Table I to A , which was found to decrease from 0.07 to 0.02 m^2) induces a dilution effect downstream. As Cl^- concentrations come to steady state with the hyporheic zone concentrations, much of the Cl^- mass is in storage (see McKnight et al., (2004) for additional information). Secondly, the fact that discharge, and therefore stage,

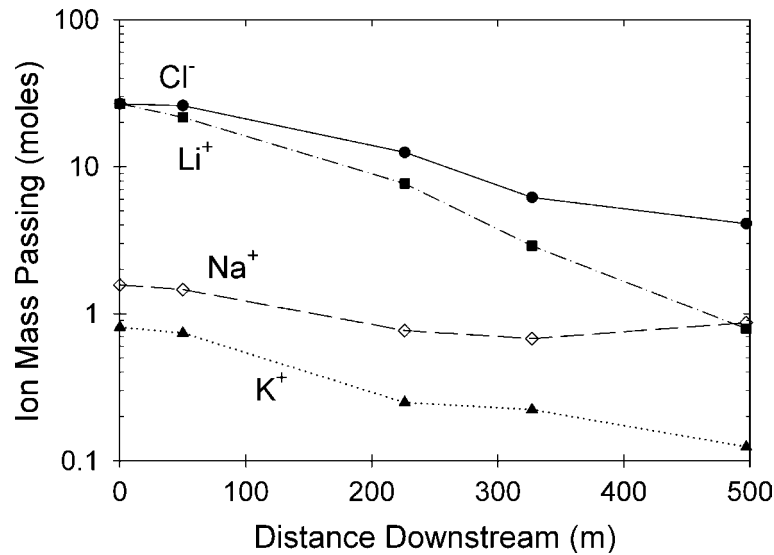


Figure 3. Integrated molar masses of each ion passing each sampling station, as calculated with Equation (1). Values at 0 m represent the amount of solute injected.

decreased substantially during the experiment (Figure 2), indicates that there was likely some abandoned injected solute that had entered the hyporheic zone in sediments that were no longer actively exchanging water with the stream after discharge recession. At each downstream sampling location the rise and decrease of the Cl^- breakthrough curves become broader (Figure 4), evidence of the greater impact of hyporheic exchange on stream solute transport. The increase in solute concentrations after the passing of the injected pulse is most likely due to the strong decrease in stream discharge, resulting in less dilution of stream solute concentrations.

In contrast, clearly Li^+ was lost from the stream water as evidenced by the increased rate of decrease of Li^+ molar mass downstream compared to that of Cl^- (steeper declines for Li^+ in Figure 3). Conservative simulations of downstream Li^+ transport did not fit the observed stream concentrations (Figure 4). Best-fit reactive simulations of Li^+ downstream transport were accomplished with stream uptake of Li^+ in all four reaches and hyporheic uptake in Reaches 2 and 3 (Table I). Ratios of observed Li^+ concentrations to observed Cl^- concentrations decrease downstream, especially during the time of Cl^- plateau concentrations at each site (Figure 5), further evidence of reactive transport compared to Cl^- . For the four reaches, comparisons of reactive and conservative molar masses show that losses of 1.05–2.1 moles of Li^+ per reach occurred within the experimental reaches, but comparisons of observed and conservative molar masses show losses ranging from 1.07 to 4.47 moles of Li^+ per reach (Table II). The conservative simulations take into account the influence of hyporheic exchange on solute transport, but no

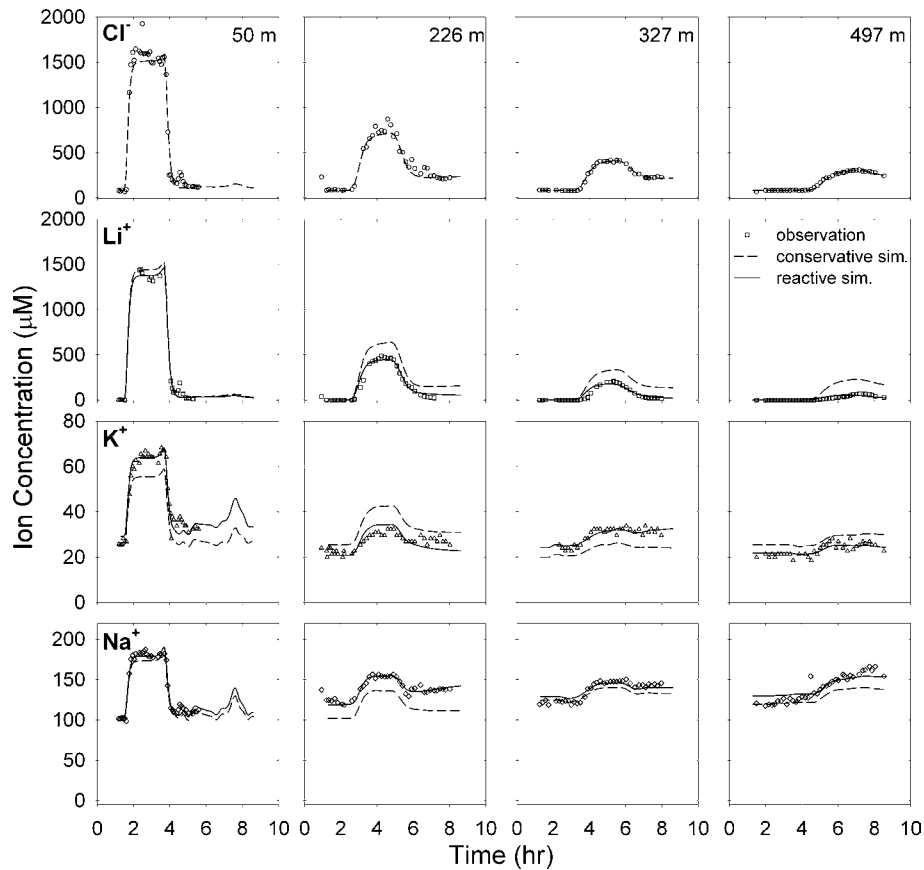


Figure 4. Observed, simulated reactive and simulated conservative solute breakthrough curves from Green Creek stream tracer injection. Cl^- is the conservative tracer; Li^+ , K^+ , and Na^+ were not transported conservatively.

reactions. Thus the conservative simulations represent the potential mass passing each sample collection point.

Stream K^+ concentrations were simulated with reactive transport (Figure 4), with release of K^+ in Reaches 1 and 3, and uptake of K^+ in Reaches 2 and 4 (Table II). The optimized simulations of reactive transport of K^+ were best-fit by stream reactions only in Reaches 2–4, but combined stream and hyporheic reactions in Reach 1 (Table I). Comparison of K^+ concentrations to Cl^- concentrations also point to this inter-reach variability with minor changes of $\text{K}^+:\text{Cl}^-$ ratios during plateau concentrations between Reaches 1 and 2 and Reaches 3 and 4, but an evident increase between Reaches 2 and 3 (Figure 5), indicating the increase of K^+ concentrations in Reach 3.

Conservative Na^+ transport resulted in underestimates of stream Na^+ concentrations in all reaches (Figure 4). For site 226 m, the conservative simulations underestimated Na^+ concentrations for the entire sampling

Table I. Solute transport model optimized parameters, where A_S is the cross-sectional area of the storage zone, α is the exchange rate coefficient, and λ_{ION} is the first order reaction coefficient for each particular ion

Parameter	Stream Reach			
	0–50 m	50–225 m	225–327 m	327–497 m
A_S (m ²)	4.77×10^{-2}	0.398	0.385	6.97×10^{-2}
α (s ⁻¹)	3.46×10^{-5}	1.89×10^{-4}	2.72×10^{-4}	1.14×10^{-4}
Stream Ion Exchange Coefficients				
λ_{Li} (s ⁻¹)	-3.05×10^{-5}	-3.87×10^{-5}	-6.98×10^{-5}	-1.56×10^{-4}
λ_{K} (s ⁻¹)	1.05×10^{-4}	-4.39×10^{-4}	7.29×10^{-5}	3.32×10^{-5}
λ_{Na} (s ⁻¹)	2.47×10^{-5}	0	1.37×10^{-5}	1.72×10^{-5}
Storage Zone Ion Exchange Coefficients				
$\lambda_{\text{S,Li}}$ (s ⁻¹)	0	-7.25×10^{-5}	-2.31×10^{-4}	0
$\lambda_{\text{S,K}}$ (s ⁻¹)	3.14×10^{-6}	0	0	0
$\lambda_{\text{S,Na}}$ (s ⁻¹)	0	5.17×10^{-6}	0	0

Values of $\lambda > 0$ represent a loss of ion within a reach, values of $\lambda < 0$ represent a net gain of that ion within a reach.

period. However, at the 327 m and 497 m sites, the conservative simulation matched the observations for the leading edge of the experiment before the arrival of the injected pulse. Stream Na^+ concentrations were best-fit simulating Na^+ release from bed surface sediments in Reaches 1, 3, and 4, and hyporheic release of Na^+ in Reach 2 (Table I). Increasing $\text{Na}^+:\text{Cl}^+$ ratios downstream also point to the increase of Na^+ (Figure 5). Computed molar mass passing values decrease downstream (Figure 3), but have less decrease downstream than Cl^- , the conservative tracer. Comparison of integrated observed and conservative breakthrough curves shows that from 0.41 to 1.53 moles of Na^+ are released from a given reach, while comparison of simulated reactive to conservative molar masses shows that reaches release from 0.24 to 0.81 moles of Na^+ (Table II).

Mass loss rates per meter stream length indicate the greatest loss of Li^+ in Reach 1, the highest rate of K^+ reactivity (gain or loss) in Reach 1 (Table II). Na^+ reactivity was mixed between the observed versus conservative, which suggests that Reach 1 has the highest activity rates, and reactive versus conservative differences, which suggests that Reach 2 has the highest activity rates (Table II).

5. Discussion

5.1. REACH-SCALE EXPERIMENTAL APPROACH

Hydrologists and stream ecologists widely use conservative solute tracer techniques to determine hyporheic exchange parameters. Less conservative

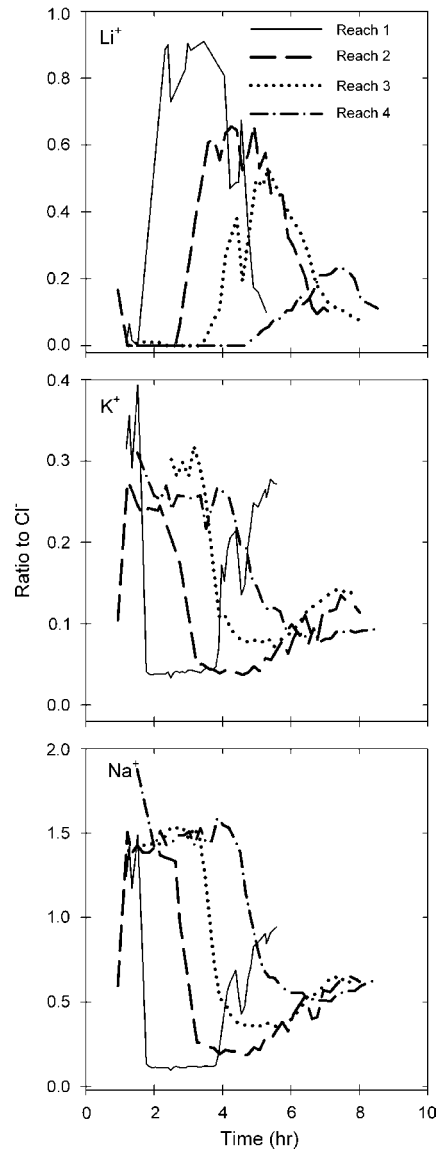


Figure 5. Ratios of observed stream water ion concentrations to observed Cl^- concentrations during stream solute enrichment experiment on Green Creek. Increases in these ratios (relative to Cl^-) suggest a mass increase in the ion of interest along the specified sub-reach.

inorganic cations, such as Li^+ , Na^+ , and K^+ , compared to more conservative anions Cl^- and Br^- have generally been avoided, depending on specifics of a stream system (pH, stream chemistry, etc.). This work shows that the reactive nature of these alternative ions may in and of itself provide a compelling

Table II. Gains and losses of observed and simulated ion molar masses based on the difference between integrated observed and conservative breakthrough curves, and reactive and conservative simulated solute breakthrough curves, for Green Creek solute enrichment experiment, January 1996

Reach	Li ⁺ Mass (mol)	Li ⁺ Rate (mol m ⁻¹)	K ⁺ Mass (mol)	K ⁺ Rate (mol m ⁻¹)	Na ⁺ Mass (mol)	Na ⁺ Rate (mol m ⁻¹)	Net Mass Change (mol)
Observed difference in molar masses							
0–50 m	-4.47	-0.089	0.38	0.008	0.71	0.014	-3.38
50–225 m	-3.44	-0.020	-0.18	-0.001	1.53	0.009	-2.09
225–327 m	-1.28	-0.013	0.30	0.003	0.41	0.004	-0.57
327–497 m	-1.07	-0.006	-0.15	-0.001	0.95	0.006	-0.27
Simulated difference in molar masses							
0–50 m	-1.18	-0.024	0.24	0.005	0.17	0.003	-0.77
50–225 m	-2.19	-0.012	-0.28	-0.002	0.81	0.005	-1.66
225–327 m	-1.10	-0.011	0.25	0.002	0.24	0.002	-0.61
327–497 m	-1.05	-0.006	-0.22	-0.001	0.60	0.004	-0.67

Total mass gained or lost is presented as well as the reach-averaged mass per unit length gained (>0) or lost (<0). Net mass change is a sum of ion mass changes for each reach.

geochemical story, with respect to streambed sediments controlling the transport of such ions. One important benefit of the approach taken in this study is the acceptance and integration of the range of heterogeneity within the experimental reach. Laboratory experimental results are inherently biased by the size of the sample collected, and therefore reflect information about single points in space. The stream reach scale experiment presented here incorporates 497 m of stream reach and over 410 m³ of sediment (computed as $A_s * \text{reach length}/\text{porosity}$ of 0.3), yielding a more integrated result of stream reach controls on inorganic stream water cation dynamics.

5.2. REACTIVE SIMULATIONS

The reactive transport model used in this study is not well suited to an analysis of ion exchange at the reach scale because solute reactions are simulated occurring independent of one another. The fact that the model contains this limitation and probably limits the match of the fit of the reactive solute breakthrough curves suggests that there is indeed an interaction between the arrival of elevated Li⁺ concentrations and changes in K⁺ and Na⁺ concentrations. The model is fairly well-suited for reactive Li⁺ transport; because background concentrations are so low in this stream, the reaction terms in Equations 2 and 3 do not influence stream concentrations prior to the arrival of the injected pulse (Figure 4). On the other hand, because of the

first-order reaction approach incorporated by OTIS, the model simulates elevated background concentrations of K^+ and Na^+ prior to the arrival of the injected pulse during reactive transport simulations; this is particularly evident in the Na^+ reactive simulations in Reaches 3 and 4 (Figure 4).

It is surprising that there were so few reactive simulations in which the hyporheic zone reactions contributed to an optimal simulation. This is likely because the changes in stream concentrations of ions (gains and losses) occur on a faster time scale than hyporheic exchange. Gooseff et al. (in press) also found this to be the case in a study of incomplete dissimilatory nitrate reduction to nitrite, though they attributed their observed nutrient dynamics to the benthic microbial mats that cover the streambed of Green Creek. In the case of the rapid losses of Li^+ and K^+ , and gains in K^+ and Na^+ , it is likely that the reactions are occurring within a thin surficial layer of streambed sediments. The chemistry of the water in the pore space of these near-surface sediments is likely to be very similar to stream water, compared to deeper interstitial waters, which tend to be more enriched in dissolved solids, and probably less likely to be involved in ion exchange reactions (Gooseff et al., 2003).

5.3. EVIDENCE OF ION EXCHANGE

Our interpretation that Li^+ exchanges with Na^+ is consistent with a study of Arctic proglacial watersheds, which concluded that Na^+ transport is controlled by ion exchange reactions (Hodson et al., 2002). Our interpretation is also consistent with a stream acidification study (Norton et al., 2000), in which ion exchange was found to control dissolved Na^+ transport. We expected that balanced ion exchange reactions would explain the downstream loss of Li^+ and increase of K^+ and Na^+ . Because the first-order reactive rate coefficients invoke proportional losses or gains to simulated solute concentrations (Equations 2 and 3), none of the λ_{ION} or $\lambda_{S,ION}$ values were expected to balance. That is, we did not expect to compute the same value of λ for Li^+ loss in one reach, matched by a λ for K^+ or Na^+ within the same reach, because Li^+ , K^+ , and Na^+ concentrations were not the same in each reach. Rather, we expected that the mass of lost Li^+ and gained K^+ and/or Na^+ would be balanced. Conservative transport of all three cations in all four reaches did not agree well with observed concentrations (Figure 4). The analysis of our integrated simulation and observed breakthrough curves show that more Li^+ was taken up by the sediments than K^+ and/or Na^+ was released for all reaches (Table II). Further, because the reactive simulations influence the Na^+ and K^+ concentrations prior to the arrival of the injected solutes, the comparison of observed versus simulated conservative molar masses is the most accurate estimate of ion mass gains and losses within Table II. The imbalance indicates that our hypothesis is partially confirmed.

We propose two potential reasons for the discrepancy in mass balances: (1) that Li^+ (and K^+ in reach 2) exchanged with ions for which we did not analyze stream water samples (e.g., Ca^{2+} , Mg^{2+} , etc.), or (2) that a combination of ion exchange and adsorption reactions were occurring in the streambed sediments. The latter explanation is more likely as it is thermodynamically less efficient for Li^+ to exchange with divalent ions, which are preferentially held on sediment exchange complexes, though physically, because Li^+ has such a small ionic radius, Li^+ ions should be able to replace most exchangeable ions, regardless of charge. Alternatively, a combination of these two explanations could be occurring, such that the Na^+ that was released may have been exchanged with either Ca^{2+} or Mg^{2+} , which is more likely than Li^+ exchange with divalent ions. The results presented here do not allow us to differentiate potential ion exchange controls on stream cation transport versus potential biological influences. Given the likelihood that these cations are micronutrients and generally in good supply in these streams, it is unlikely that the biota would respond to such short-term elevated concentrations.

A comparison of the four experimental reaches indicates that there is appreciable hydrologic and geochemical heterogeneity. Reach 2 appears to be unique compared to Reaches 1, 3, and 4 with the largest storage zone, a rapid hydrologic exchange rate (α), and a greater sensitivity to hyporheic Na^+ release than stream Na^+ release (Table I). Reach 2 releases the most Na^+ mass, and has the greatest Na^+ release rate per meter stream length in simulated difference of molar masses (Table II). Alternatively, Reach 1 is evidently a very reactive reach with the highest Li^+ uptake and K^+ release in total mass and the highest rates of Li^+ uptake and K^+ release per meter stream length (Table II), but not the greatest magnitude in first-order uptake rates (Table I). This heterogeneity suggests that future studies of reactive transport in dry valley streams should consider spatial gradients of biogeochemical processes so that an accurate assessment of stream function can be obtained.

6. Conclusions

We present the results of conservative and reactive solute transport simulations for four solutes in Green Creek, Antarctica. Lithium is consistently removed from the water column along all four reaches of the stream, K^+ is both taken up by and released from the bed sediments, and Na^+ is consistently released to the water column. The quantity of lost Li^+ is not balanced by release of K^+ and/or Na^+ , indicating that either liberation of another solute from the sediments is occurring, or that both Li^+ exchange and sorption are occurring. The latter is more likely as it is thermodynamically unlikely that divalent cations are being removed by a monovalent

cation. At the dry valley landscape scale, the buffering of Li^+ concentrations (and to some degree K^+ concentrations also) downstream may be an important process when solute-rich waters move downstream during streamflow initiation each flow season.

Dry valley streams control the quantity and solute load of glacial melt water to closed basin lakes. McKnight et al. (1999, 2004) and Gooseff et al. (in press) show that the microbial communities of dry valley meltwater streambeds and hyporheic zones control inorganic nutrient fluxes to dry valley lakes, particularly fluxes of nitrate. Our results show that dry valley streambed sediments also modulate fluxes of Li^+ and to some degree K^+ to dry valley lakes. In the context of the dry valleys landscape, cation exchange and adsorption reactions are potentially important controls on the geochemical evolution of surface waters.

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