THE GEOCHEMISTRY OF MINOR CATIONS WITHIN ANTARCTICA STREAM WATER:
DETERMINING THE ROLE OF THE HYPORHEIC ZONE

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By

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Approved by

[Signature]

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The McMurdo Dry Valleys, Antarctica, are a polar desert containing ephemeral streams driven by glacial meltwater that flow 4–12 weeks in the austral summer. These streams contain a shallow area of porous sediment known as the hyporheic zone where there is rock-water interaction and water can be temporarily stored. Major cations have been analyzed in these streams every year since 1992, but only one other study has analyzed minor cations (Li, Rb, Sr, Ba) in these waters. This study is the first to examine minor cation concentrations in comparison to changes in discharge and in stream transects. Transect samples were collected at three streams that flow into the ocean: Wales, Commonwealth, and Miers, and diurnal samples were collected at Von Guerard Stream and Anderson Creek. Streams were analyzed for Li, Sr, Rb, and Ba, and their concentrations ranged 0.1–2.3 µM, 0.3–1.1 µM, 5.1–11.7 nM, and 0.03–0.3 µM, respectively. Downstream profiles show increases in Li, Rb, and Sr moving downstream, suggesting chemical weathering or rapid salt dissolution. Chemostatic plots for Von Guerard Stream and Anderson Creek show solute mobilization and production varies in proportion to flow, as previously seen with the major cations (i.e., Na⁺, Ca²⁺, K⁺, Mg²⁺). This suggests that one of two processes control concentrations: rapid dissolution or hyporheic exchange. Hysteresis plots at Anderson Creek show both alkali and alkaline earth metals move in a clockwise rotation, where concentrations are higher on the rising limb than the falling limb. In Von Guerard Stream, alkali metals show clockwise rotation, while alkaline earth metals show an increase in concentration as discharge decreases. These results suggest that the source of alkali metals in stream water is from rapid salt dissolution, while alkaline earth metals originate from weathering in the hyporheic zone. These results help to explain chemical weathering and hyporheic
exchange within the McMurdo Dry Valleys and therefore understand the structure and limitations in this ecosystem better.
ACKNOWLEDGEMENTS

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INTRODUCTION

The McMurdo Dry Valleys are a polar desert located in West Antarctica in the Transantarctic Mountains (Figure 1). They are located at 76–79° south latitude and 158–170° east longitude, spanning a total area of 4800 km², making them the largest ice free area in Antarctica (Levy et al., 2013). The Dry Valleys have a mean annual air temperature of -18°C, however temperature varies greatly with elevation and distance from the coast (Doran et al., 2002). Precipitation is under 3 cm/yr in the form of snow, and is quickly sublimated due to the arid conditions (Fountain et al., 2010). The Dry Valleys landscape is dominated by loose sediment and exposed bedrock. Alpine glaciers form meltwater streams that, during the austral summer, flow into ice-covered, closed basin lakes or the Southern Ocean. While there is no groundwater in the McMurdo Dry Valleys due to the cold temperatures, high sublimation rates, and permafrost at shallow depths, a shallow area of porous sediment is filled with stream water along the stream bed. This area is referred to as the hyporheic zone and is an area of high rock-water interaction. This zone plays an important role in the biogeochemical processes along the streambed. Biological organisms within the Dry Valleys consists of nematodes, rotifers, bacteria, benthic algal mats, and mosses, but does not have orders higher than these organisms. Microorganisms live within the streambed and depend on the hyporheic zone as a source for water and nutrients (Gooseff et al., 2002).

While the sun does not set for 4 months in the summer, flow rates of these streams still show a variance over a 24-hour period due to the angle at which the sun hits the glacier. This causes a filling and flushing of the hyporheic zone every 24 hours. During high flow, water fills the hyporheic zone, where it interacts with the sediment and dissolves salts into solution, a process referred to as hyporheic exchange. Another source of major and minor cations is salt
deposits along the streambed. Water near the surface of the streambed evaporates due to the Dry Valleys’ arid environment. When this evaporation occurs, it leaves salt deposits from mineral weathering in the hyporheic zone. This salt is later dissolved back into the stream when flow increases. These two sources of cation concentrations are distinguished for both major and minor cations in the stream water in this study using c-Q loop analysis outlined by Evans and Davies (1998), who show that c-Q loops can be used to infer mixing processes that create observed hydrochemical responses.

Three streams were sampled along their flow path for major and minor cations: Commonwealth Stream, Wales Stream, and Miers Stream. Commonwealth Stream is located on the eastern side of Taylor Valley and flows out to the McMurdo Sound (Figure 3). The stream cuts though a portion of buried ice near its delta, which prevents the formation of a hyporheic zone due to lack of sediment for the stream water to interact with. Wales Stream also lies within the eastern side of Taylor Valley and flows into the McMurdo Sound (Figure 4). It is located on the southern side of Taylor Valley, opposite to Commonwealth. Miers Stream is located in Miers Valley and flows through Miers Lake (Figure 5).

Anderson Creek and Von Guerard Stream were sampled to determine diel variations in cation concentrations in relation to discharge (Figure 2). Von Guerard Stream is located is on the south side of Taylor Valley in the Kukri Hills and flows into Lake Fryxell. It is a meandering stream with a low gradient and wide stream width. Anderson Creek lies on the northern side of Taylor Valley within the Asgard Range. Its flowpath cuts along the side of Canada glacier and has a high stream gradient.
Figure 1. The McMurdo Dry Valleys, Antarctica. The Dry Valleys are located in the Trans Antarctic Mountains on the west side of Antarctica.
Figure 2. Stream locations within The McMurdo Dry Valleys. Anderson Creek (AC), Von Guerard (VG), Commonwealth, and Miers Stream are all located within Taylor Valley. Miers Stream is in Miers Valley, south of Taylor Valley.
Figure 3. Sampling sites along Commonwealth Stream. CW7 represents the site of a tributary that feeds into Commonwealth Stream between sampling sites CW6 and CW8. All other points represent samples along the stream that were used in creating stream transect plots. (Figure provided by Polar Geospatial Center)
**Figure 4. Sampling sites along Wales Stream.** All points represent samples that were used in creating stream transect plots, where W1 is the sample closest to the glacier and W8 is the delta of Wales Stream. (Figure provided by Polar Geospatial Center)
Figure 5. Sampling sites along Miers Stream. M1, M2, and M6 represent samples collected along Adams Stream that feeds into Miers Lake. M3, M4, M5, M7, M8, and M9 represent samples collected along Miers Stream that were used in creating Miers Stream transect plots. (Figure provided by Polar Geospatial Center)
METHODS

Cleaning of Bottles
Samples were collected in Nalgene® high-density polyethylene (HDPE) bottles that had been soaked in 1% HCl, rinsed with dilute acid three times, then rinsed with deionized (DI) water three times.

Sample Collection
Major and minor cation samples were collected during the 2015–16 field season. While the sample container was held downstream of the flow, bottles for cations were rinsed with stream water three times while the sample collector wore nitrile gloves to minimize contamination. For stream transects, samples were collected at 3 streams: Wales Stream and Commonwealth Stream in Taylor Valley, and Miers Stream in Miers Valley (Figure 2). From each stream, 4–8 samples were collected, depending on the length of the stream. The average distance between sample collection points was 0.91 km. Diel samples were collected every three hours over a 27-hour period at two streams, Von Guerard Stream and Anderson Creek in Taylor Valley (Figure 2). Diel sampling locations for both Von Guerard Stream and Anderson Creek were close to the stream gauge at locations where the streams enter Lake Fryxell and Lake Hoare, respectively.

Laboratory Analysis
Major and minor cation samples were filtered through 0.4 µm pore size Whatman® Nuclepore™ polycarbonate membrane filter within 24 hours of collection. Filtering apparatus had previously been rinsed profusely with DI water and was rinsed again between the filtration of each sample. Major cations (Na+, K+, Ca2+, and Mg2+) were measured using ion chromatography (IC) on a Dionex DX-120 ion chromatograph. Major cations were measured in McMurdo Station, Antarctica. Precision and accuracy of the major cations analyses can be found
in Table 2 (Welch et al., 2010). Minor cations (Rb+, Sr2+, Ba2+, and Li+) were shipped to The Ohio State University and analyzed using Inductively Coupled Plasma- Mass Spectrometry (ICP-MS) on the Thermo Scientific Element 2™. Sample vials were prepared for minor element analyses by rinsing 10mL Falcon tubes™ three times with DI water and adding 2% HNO3 to each sample. Blanks were prepared by rinsing a low density polyethelene (LDPE) bottle with DI water three times, filling with DI water, and then adding 2% HNO3 to match sample matrix. Samples were calibrated on a weighted linear regression curve and blanks were analyzed periodically throughout the analysis to check for drift and contamination. Precision of measurements can be found in Table 1.

Discharge data for Von Guerard Stream and Anderson Creek used in the calculations are available on the McMurdo Dry Valleys- Long Term Ecological Research (MCM-LTER) website: http://www.mcmlter.org/. Stream discharge measurements are collected every 15 minutes throughout the entire flow season. Steam discharge rates are collected using Campbell CR10 dataloggers and monitored using pressure transducers PSS-1 and PS-2 models from Paroscientific Corporation and Accubars from Sutron Corporation.
**RESULTS**

Minor cations were measured on a total of 5 streams in the McMurdo Dry Valleys. Diel samples collected at Von Guerard and Anderson Creek have concentrations for Li, Sr, Rb, and Ba that ranged 0.1–2.3 µM, 0.3–1.1 µM, 5.1–11.7 nM, and 0.03–0.3 µM, respectively. Stream transect concentrations were collected at Commonwealth Wales and Miers and concentrations ranged 0.06–0.6 µM, 0.4–1.7 µM, 4.7–13.6 nM, and 0.06–2.9 µM for Li, Sr, Rb, and Ba, respectively. Within all streams, measured concentrations for Li, Sr, Rb, and Ba ranged 0.06–2.3 µM, 0.26–1.7 µM, 4.7–13.6 nM, and 0.03–2.9 µM, respectively.

**Diel Samples**

Samples were collected every three hours during a 27-hour period at both Anderson Creek and Von Guerard Stream. During sample collection at Anderson Creek (1/13/2016 11:00 through 1/14/2015 14:00) the discharge rate ranged 28.1–113.5 L/s, while Von Guerard Stream had much lower discharge during sample collection (1/9/2016 15:00 through 1/10/2016 18:00), ranging 3.2–18.7 L/s. Chemostatic plots were created for both streams, where discharge vs cation concentrations are plotted on a log-log scale (Figures 6 and 7). The plots show very little variation in cation concentration, while discharge range over an order of magnitude. This is very typical for Taylor Valley streams, where previous work on major cations have demonstrated little concentration change with discharge (Leslie, 2013)

**ANDERSON CREEK**

Hysteresis plots have been previously utilized to describe the source of the solute to the stream waters (Evans and Davies, 1998). Hysteresis plots for Anderson Creek show clockwise rotation for all major and minor cations, where concentrations are higher on the rising limb of the
hydrograph than on the falling limb (Figure 8 and 9). Ba shows an overall decrease in concentration over the 27-hour period.

**VON GUERARD STREAM**

Hysteresis plots for Von Guerard Stream show differences for the alkali and alkaline earth metals. The alkali metals, Na, K, Li, and Rb, all rotate in a clockwise rotation, where overall concentrations are higher on the rising limb of the hydrograph than on the falling limb (Figure 10). These cations show a decrease in concentration as flow increases, and the concentrations then begin to increase again as flow decreases. For cations Ca, Sr, and Mg, hysteresis plots show that initially, as flow increases, there is little to no change in concentration, followed by an increase in concentration as flow begins to decrease (Figure 11). When the flow remains constant, the concentrations decrease, followed again by an increase in concentration as flow decreases. Ba shows this same pattern as do the other alkaline earth metals, however there is an overall decrease in Ba concentration over the 27-hour sampling period.
Figure 6: Chemostatic plots for major and minor cations within Anderson Creek. Both major and minor cations exhibit little variation in concentration as discharge varies over an order of magnitude, suggesting that solute mobilization and production varies proportionally with discharge.
Figure 7: Chemostatic plots for major and minor cations within Von Guerard Stream. Both major and minor cations exhibit little variation in concentration as discharge varies over an order of magnitude, suggesting that solute mobilization and production varies proportionally with discharge.
Figure 8: Anderson Creek hysteresis plots for alkali metals. Hydrograhps move in a clockwise rotation, where concentrations are higher on the rising limb than the fallig limb. This suggests rapid salt dissolution as the alkali metal source.
Figure 9: Anderson Creek hysteresis plots for alkaline earth metals. Hydrographs move in a clockwise rotation, where concentrations are higher on the rising limb than the falling limb, suggesting rapid salt dissolution.
Figure 10: Von Guerard hysteresis plots for alkali metals. Hydrographs show an overall clockwise rotation, where concentrations are higher as discharge increases. This suggests rapid salt dissolution.
Figure 11: Von Guerard hysteresis plots for alkaline earth metals. The hydrographs show an increase in alkaline earth metal concentration as discharge begins to decrease due to drainage from the hyporheic zone.
Stream Transects

Commonwealth, Wales, and Miers Streams were sampled along their stream length between December 24 through 29, 2015. Along each stream length, all samples were collected within 5 hours starting at the collection point closest to the source glacier to the delta.

Minor Cations

Stream transect plots of minor cations were made for three streams: Commonwealth, Wales, and Miers (Figure 12). Commonwealth Stream shows an overall increase in Li and Rb downstream. Ba initially decreases after the first sample collection site and steadily increases after that, but never reaches the concentration at the first site of 0.19 µm. Sr shows an overall increase after the first sample collection site, but decreases at the last collection site, the delta. Wales Stream and Miers Stream show overall increases in Li, Sr, and Rb from the glacial meltwater source downstream, but Ba shows a decrease overall downstream. (Figure 12)

Major Cations

Commonwealth Stream shows an overall increase in Na and K along the stream length, while Ca and Mg show an increase in concentration until the delta, where there is a decrease in concentration. Miers Stream and Wales Stream both show overall increases in Na, K, Ca, and Mg along the stream length (Figure 13). In Miers Stream, there is a sharp decrease in the Ca:Sr ratio after the water moves through Lake Miers (Figure 14).
Figure 12: Stream transects for minor cations. Li and Rb increase overall in all three streams. Sr increases downstream except for the end of Commonwealth due to a dilution via melting of buried ice. Ba fluctuates or decreases downstream due to supersaturation of the mineral barite, BaSO₄.
Figure 13: Stream transects for major cations. Na and K increase downstream in all three streams. Ca and Mg increase downstream in Miers and Wales Stream but decrease in Commonwealth Stream due to a dilution via melting of buried ice.
Figure 14: Miers Stream transect for cation ratios. The Ca: Sr ratio shows a sharp decrease after the water moves through Lake Miers as a result of the precipitation and deposition of CaCO₃ in Lake Miers.
**Discussion**

Dissolved alkali and alkaline earth metals within the McMurdo Dry Valley originate from one of two processes: rapid salt dissolution or weathering from the hyporheic zone. Rapid salt dissolution occurs when previously precipitated salt deposits along the streambed are dissolved into stream water as flow increases. As a result, an increase in concentration due to rapid salt dissolution is detected immediately in stream water concentration. Work over the past 15 years by McMurdo Dry Valleys Long Term Ecological Research site researchers has clearly demonstrated that the locus of both calcium carbonate and alumino-silicate mineral chemical weathering is the hyporheic zones of the Taylor Valleys Streams (Nezat et al., 2001; Maurice et al. 2002; Gooseff et al., 2002; Dowling et al., 2013). Weathering within the hyporheic zone is more complex than the simple dissolution of salt within the flood plains of the streams. Water stored within the hyporheic zone is flushed out every 24 hours, corresponding with the time of peak flow, and filled with “new” glacial meltwater. The water within the hyporheic zone interacts with the sediment and dissolves ions in solution, but this increase in concentration is not detected in stream water measurements until the hyporheic zone is flushed out at the next high flow. This process is referred to as hyporheic exchange (Gooseff et al., 2002).

**Diel Samples**

During the four-month long austral summer, the sun does not set over the McMurdo Dry Valleys. The sun moves in a circular rotation in the sky over a 24-hour period. As a result of that solar rotation, the angle at which the sun hits the glacier determines the discharge rate of the streams where a peak high and low flow rate can be measured every 24 hours. Both Anderson Creek and Von Guerard Stream show this cycle in their discharge data. Major and minor cations
within the streams show chemostaic behavior, wherein cation concentrations show little variation as discharge changes over an order of magnitude. This behavior occurs because an increase in the discharge rate also increases the rates of salt dissolution and hyporheic exchange, thereby increasing dissolved cation concentrations (Wlostowski et al., 2016). When discharge increases, the hyporheic zone expands, allowing for more water-rock interactions. An increase in discharge also causes stream water level to rise, which would extend to salt deposits higher up along the streambed and dissolve them into the stream water.

The clockwise rotation for both alkali and alkaline earth metals within Anderson Creek is due to rapid salt dissolution (Nezat et al., 2001). Higher concentrations during increasing discharge can be contributed to salt deposits along the streambed dissolving into stream meltwater as water level increases. When discharge decreases, concentrations are lower due to lack of new salt deposits dissolving into the stream.

Alkali metals within Von Guerard Stream show clockwise rotation due to rapid salt dissolution as described above for Anderson Creek (Figure 10). However, alkaline earth metals show a different hysteresis pattern that is thought to be due to weathering in the hyporheic zone (Figure 11). When the flow begins to decrease, alkaline earth metal concentrations increase due to drainage from the hyporheic zone. After the hyporheic zone drains, concentrations sharply decrease due to input of new glacial meltwater containing low cation concentrations.

It is highly likely that hyporheic exchange occurs in Von Guerard Stream but not in Anderson Creek due to their different stream morphologies. Anderson Creek has a steep streambed gradient, and it cuts into the side of Canada Glacier along its flow path, thereby preventing the formation of a large hyporheic zone. In contrast, Von Guerard Stream has a low
gradient, greater stream width, and follows a meandering flow path, allowing it to form a much larger hyporheic zone (McKnight et al., 1999).

Over the 27-hour sampling period, Ba concentrations show overall decreases in both Anderson Creek and Von Guerard Stream. Mineral saturation calculations show that at low temperatures in these streams Ba is supersaturated with respect to barite. Therefore, Ba concentrations are dependent on temperature related solubility changes. As noted above, Ba could also be influenced by biological uptake and release along the streambed, however more work must be done to understand the role of Ba within these streams better.

Stream Transects

Minor Cations

The increase of Li and Rb in all three streams, and of Sr in Wales and Miers Stream, is due either to rapid salt dissolution or to weathering in the hyporheic zone. However, it is not possible to distinguish between these two solute sources solely from downstream data. The decrease in Sr concentration close to the delta in Commonwealth Stream is probably due to the presence of buried ice in the stream channel. As noted above, Commonwealth Stream cuts into a portion of what is thought to be Last Glacial Maximum buried ice from the advancing West Antarctic Ice Sheet. The diel plots show that the source of alkaline earth metals in stream water is weathering in the hyporheic zone. Since buried ice prevents the formation of a hyporheic zone and probably provides melt water low in ion concentrations, the ice both prevents further input of alkaline earth metals and also dilutes stream water though its melting, causing a decrease in Sr. Ba differs from all the other minor cations because its concentrations either decrease or fluctuate with stream length in all three streams. Ba concentrations are likely to be controlled primarily by
temperature changes affecting its solubility and/or biological uptake and release, as discussed above for the diel sampling. As stream water increases in temperature during the hydrograph, day and/or flow season, BaSO₄ becomes more soluble. The temperature can reach above 0°C, thus greatly affecting the solubility of Ba. More work should be done to understand the dynamics of Ba in these streams better.

**MAJOR CATIONS**

The increase in all major cations in Wales Stream and Miers Stream and alkali metals in Commonwealth Stream is due either to rapid salt dissolution or to hyporheic exchange. Results from Von Guerard Stream and Anderson Creek suggest that Sr²⁺, Ca²⁺, Ba²⁺, and Mg²⁺ are controlled primarily by hyporheic exchange and that Li⁺, Rb⁺, Na⁺, and K⁺ are controlled by salt dissolution. Ca and Mg decrease near the stream delta due to the presence of buried ice inhibiting the formation of the hyporheic zone and/or increasing dilution, as described above.

**CATION RATIOS**

The sharp decrease in the Ca:Sr ratio in Miers Stream after it discharges from Lake Miers is likely due to the deposition of calcium carbonate in Lake Miers (Witherow and Lyons, 2011). Previous calculations show that Lake Miers is supersaturated with respect to calcite at the lake surface causing precipitation of calcium carbonate (Green et al., 1988).
CONCLUSIONS

Minor cations were measured to analyze chemical weathering within the Dry Valleys, Antarctica. Past studies have shown that the hyporheic zone plays an important role in weathering and biogeochemical processes within the Dry Valleys. This study has shown that the hyporheic zone is also important in the weathering of minor cations. Stream transects show that sediment along the streambed is an important source of these cations to stream water, as concentrations increase along stream flowpath. Using c-Q loops (Evans and Davies, 1998) this study was able to distinguish if cations concentrations in stream water originate from rapid salt dissolution or hyporheic exchange. It is found that alkali metals originate from rapid salt dissolution while alkaline earth metals originate from chemical weathering in the hyporheic zone. Anderson Creek does not show weathering in the hyporheic zone because its high stream gradients and undercutting into Canada Glacier prevent the formation of a large hyporheic zone. Von Guerard Stream, however, shows active hyporheic exchange because its low gradient and meandering flowpath allow water to infiltrate and interact with surrounding streambed sediment. This illustrates the importance of stream geomorphology in relation to observed hydrochemical responses. The decrease in Ba concentration along stream flowpaths and during the 27-hour diel sampling period suggests that barite solubility is sensitive to small changes in temperature or possibly to uptake by biological activity along the streambed. This information is useful in understanding chemical weathering and hyporheic exchange within the McMurdo Dry Valleys.
**Recommendations for Future Work**

Collection of samples from both hyporheic pore space and stream water samples will help constrain the observed hydrochemical responses relating to the hyporheic zone. Comparison of the cation concentrations in these different sampling locations to discharge could better describe the chemical weathering process in the hyporheic zone. It would also be beneficial to measure for stable isotopes that have preferential uptake from algal mats or mosses along the streambed. High flow coincides with high nutrient input times and thus biological productivity, which would affect stream cation concentrations. Measurement of stable isotopes would help to determine the amount or significance of biological uptake along the stream flowpath.

Ba was found to be supersaturated within both the stream transects and during the diel sampling. While it is known that barite solubility is controlled though change in temperature and pH conditions, more measurements for barium in regard to fluctuations in temperature and pH could help explain the supersaturation in the streams with respect to barite and if biological uptake might be a factor in the supersaturation of Ba.
REFERENCES CITED


Leslie, D. 2013. The Application of Stable Isotopes, $\delta^{11}$B, $\delta^{18}$O, and $\delta$D, in Geochemical and Hydrological Investigations. (Electronic Thesis or Dissertation).


**Tables**

Table 1: Relative standard deviations for minor elemental concentrations

<table>
<thead>
<tr>
<th></th>
<th>Li⁺</th>
<th>Sr²⁺</th>
<th>Rb⁺</th>
<th>Ba²⁺</th>
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<tbody>
<tr>
<td>Average RSD (%)</td>
<td>3.95</td>
<td>2.17</td>
<td>2.67</td>
<td>2.98</td>
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</table>

Table 2: Relative standard deviations and reporting limit for major cations

<table>
<thead>
<tr>
<th></th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
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<td>RSD (%)</td>
<td>1.6</td>
<td>0.7</td>
<td>1.4</td>
<td>5.6</td>
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<tr>
<td>Reporting Limit (mg/L)</td>
<td>0.2</td>
<td>0.04</td>
<td>0.1</td>
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Table 3. Miers Stream transect cation concentrations.

<table>
<thead>
<tr>
<th>Miers</th>
<th>Li⁺ (µM)</th>
<th>Sr²⁺ (µM)</th>
<th>Rb⁺ (nM)</th>
<th>Ba²⁺ (µM)</th>
<th>Na⁺ (mM)</th>
<th>K⁺ (mM)</th>
<th>Mg²⁺ (mM)</th>
<th>Ca²⁺ (mM)</th>
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<td>M1</td>
<td>0.224</td>
<td>3.54</td>
<td>24.7</td>
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<td>0.47</td>
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<td>0.022</td>
<td>0.02</td>
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<td>M5</td>
<td>0.111</td>
<td>0.749</td>
<td>13.0</td>
<td>0.259</td>
<td>0.10</td>
<td>0.026</td>
<td>0.02</td>
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<tr>
<td>M6</td>
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<td>1.81</td>
<td>19.4</td>
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<td>0.041</td>
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<td>M7</td>
<td>0.120</td>
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<td>12.1</td>
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<td>M8</td>
<td>0.162</td>
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<td>M9</td>
<td>0.362</td>
<td>1.65</td>
<td>13.6</td>
<td>0.143</td>
<td>0.90</td>
<td>0.071</td>
<td>0.10</td>
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</table>

Table 4. Commonwealth Stream transect cation concentrations.

<table>
<thead>
<tr>
<th>Commonwealth</th>
<th>Li⁺ (µM)</th>
<th>Sr²⁺ (µM)</th>
<th>Rb⁺ (nM)</th>
<th>Ba²⁺ (µM)</th>
<th>Na⁺ (mM)</th>
<th>K⁺ (mM)</th>
<th>Mg²⁺ (mM)</th>
<th>Ca²⁺ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CW1</td>
<td>0.112</td>
<td>0.572</td>
<td>7.00</td>
<td>0.191</td>
<td>0.28</td>
<td>0.025</td>
<td>0.08</td>
<td>0.21</td>
</tr>
<tr>
<td>CW2</td>
<td>0.106</td>
<td>0.456</td>
<td>6.88</td>
<td>0.0804</td>
<td>0.25</td>
<td>0.024</td>
<td>0.07</td>
<td>0.17</td>
</tr>
<tr>
<td>CW3</td>
<td>0.102</td>
<td>0.452</td>
<td>6.67</td>
<td>0.0740</td>
<td>0.23</td>
<td>0.023</td>
<td>0.07</td>
<td>0.17</td>
</tr>
<tr>
<td>CW4</td>
<td>0.109</td>
<td>0.531</td>
<td>7.18</td>
<td>0.0622</td>
<td>0.27</td>
<td>0.027</td>
<td>0.08</td>
<td>0.21</td>
</tr>
<tr>
<td>CW5</td>
<td>0.131</td>
<td>0.528</td>
<td>6.10</td>
<td>0.0732</td>
<td>0.34</td>
<td>0.030</td>
<td>0.09</td>
<td>0.22</td>
</tr>
<tr>
<td>CW6</td>
<td>0.161</td>
<td>0.575</td>
<td>6.11</td>
<td>0.0583</td>
<td>0.43</td>
<td>0.036</td>
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<td>0.24</td>
</tr>
<tr>
<td>CW7</td>
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<td>2.18</td>
<td>19.1</td>
<td>0.204</td>
<td>4.31</td>
<td>0.203</td>
<td>0.90</td>
<td>0.57</td>
</tr>
<tr>
<td>CW8</td>
<td>0.303</td>
<td>0.356</td>
<td>9.44</td>
<td>0.183</td>
<td>1.40</td>
<td>0.078</td>
<td>0.09</td>
<td>0.12</td>
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### Table 5. Wales Stream transect cation concentrations.

<table>
<thead>
<tr>
<th>Wales</th>
<th>Li⁺ (µM)</th>
<th>Sr²⁺ (µM)</th>
<th>Rb⁺ (nM)</th>
<th>Ba²⁺ (µM)</th>
<th>Na⁺ (mM)</th>
<th>K⁺ (mM)</th>
<th>Mg²⁺ (mM)</th>
<th>Ca²⁺ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1</td>
<td>0.129</td>
<td>0.704</td>
<td>4.70</td>
<td>2.88</td>
<td>0.32</td>
<td>0.025</td>
<td>0.06</td>
<td>0.29</td>
</tr>
<tr>
<td>W2</td>
<td>0.0562</td>
<td>0.465</td>
<td>5.99</td>
<td>0.456</td>
<td>0.13</td>
<td>0.020</td>
<td>0.04</td>
<td>0.18</td>
</tr>
<tr>
<td>W3</td>
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<td>0.547</td>
<td>5.79</td>
<td>0.366</td>
<td>0.14</td>
<td>0.024</td>
<td>0.04</td>
<td>0.22</td>
</tr>
<tr>
<td>W4</td>
<td>0.143</td>
<td>0.655</td>
<td>6.31</td>
<td>0.297</td>
<td>0.21</td>
<td>0.036</td>
<td>0.05</td>
<td>0.27</td>
</tr>
<tr>
<td>W5</td>
<td>0.290</td>
<td>0.706</td>
<td>7.40</td>
<td>0.277</td>
<td>0.41</td>
<td>0.064</td>
<td>0.09</td>
<td>0.35</td>
</tr>
<tr>
<td>W6</td>
<td>0.434</td>
<td>0.866</td>
<td>9.58</td>
<td>0.284</td>
<td>0.66</td>
<td>0.086</td>
<td>0.14</td>
<td>0.40</td>
</tr>
<tr>
<td>W7</td>
<td>0.514</td>
<td>0.903</td>
<td>10.9</td>
<td>0.153</td>
<td>0.76</td>
<td>0.099</td>
<td>0.16</td>
<td>0.43</td>
</tr>
<tr>
<td>W8</td>
<td>0.602</td>
<td>0.975</td>
<td>12.2</td>
<td>0.117</td>
<td>0.92</td>
<td>0.113</td>
<td>0.19</td>
<td>0.44</td>
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### Table 6. Von Guerard Stream diel cation concentrations

<table>
<thead>
<tr>
<th>Von Guerard</th>
<th>Li⁺ (µM)</th>
<th>Sr²⁺ (µM)</th>
<th>Rb⁺ (nM)</th>
<th>Ba²⁺ (µM)</th>
<th>Na⁺ (mM)</th>
<th>K⁺ (mM)</th>
<th>Mg²⁺ (mM)</th>
<th>Ca²⁺ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VG1-D</td>
<td>2.13</td>
<td>0.964</td>
<td>10.8</td>
<td>0.102</td>
<td>0.22</td>
<td>0.058</td>
<td>0.07</td>
<td>0.39</td>
</tr>
<tr>
<td>VG2-D</td>
<td>2.29</td>
<td>1.01</td>
<td>11.7</td>
<td>0.0872</td>
<td>0.24</td>
<td>0.062</td>
<td>0.07</td>
<td>0.41</td>
</tr>
<tr>
<td>VG3-D</td>
<td>2.27</td>
<td>1.01</td>
<td>9.55</td>
<td>0.0726</td>
<td>0.23</td>
<td>0.057</td>
<td>0.08</td>
<td>0.42</td>
</tr>
<tr>
<td>VG4-D</td>
<td>0.717</td>
<td>1.07</td>
<td>8.66</td>
<td>0.0699</td>
<td>0.20</td>
<td>0.052</td>
<td>0.08</td>
<td>0.42</td>
</tr>
<tr>
<td>VG5-D</td>
<td>0.850</td>
<td>1.08</td>
<td>8.55</td>
<td>0.0625</td>
<td>0.21</td>
<td>0.053</td>
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</tr>
<tr>
<td>VG6-D</td>
<td>1.16</td>
<td>1.12</td>
<td>8.80</td>
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<td>0.054</td>
<td>0.09</td>
<td>0.47</td>
</tr>
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<td>VG7-D</td>
<td>1.10</td>
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<td>8.26</td>
<td>0.0289</td>
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<td>0.050</td>
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</tr>
<tr>
<td>VG8-D</td>
<td>1.00</td>
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<td>8.95</td>
<td>0.0431</td>
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<td>0.051</td>
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<td>VG9-D</td>
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<tr>
<td>VG10-D</td>
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<td>0.057</td>
<td>0.08</td>
<td>0.42</td>
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</table>
Table 7. Anderson Creek diel cation concentrations.

<table>
<thead>
<tr>
<th>Anderson Creek</th>
<th>Li⁺ (µM)</th>
<th>Sr²⁺ (µM)</th>
<th>Rb⁺ (nM)</th>
<th>Ba²⁺ (µM)</th>
<th>Na⁺ (mM)</th>
<th>K⁺ (mM)</th>
<th>Mg²⁺ (mM)</th>
<th>Ca²⁺ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC1</td>
<td>0.219</td>
<td>0.328</td>
<td>7.14</td>
<td>0.301</td>
<td>0.10</td>
<td>0.022</td>
<td>0.03</td>
<td>0.11</td>
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<tr>
<td>AC2</td>
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<td>0.346</td>
<td>5.75</td>
<td>0.199</td>
<td>0.10</td>
<td>0.022</td>
<td>0.03</td>
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</tr>
<tr>
<td>AC3</td>
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<td>0.341</td>
<td>5.14</td>
<td>0.120</td>
<td>0.09</td>
<td>0.019</td>
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</tr>
<tr>
<td>AC4</td>
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<td>0.266</td>
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<td>0.020</td>
<td>0.02</td>
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<td>0.017</td>
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<td>0.08</td>
</tr>
<tr>
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<td>0.303</td>
<td>6.61</td>
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<td>0.10</td>
<td>0.021</td>
<td>0.02</td>
<td>0.10</td>
</tr>
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<td>0.025</td>
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<td>0.12</td>
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<td>8.45</td>
<td>0.132</td>
<td>0.14</td>
<td>0.030</td>
<td>0.03</td>
<td>0.14</td>
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<td>0.11</td>
<td>0.026</td>
<td>0.03</td>
<td>0.12</td>
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</table>