

Geochemistry of Small Canadian Arctic Rivers with Diverse Geological and Hydrological Settings

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S1: Sampling and Analytical Methods

S1.1 River and Lake Water Sample Collection

To ensure sampling methods were easily transferrable between samplers and expeditions, and to maintain consistency with the broader pan-Arctic river geochemical data set, we followed the general sampling methods outlined by the Arctic Great Rivers Observatory (Arctic-GRO; <http://www.arcticgreatrivers.org/>) and used Arctic-GRO-developed geochemical sampling kits. All sample handling was carried out wearing nitrile gloves (Fisher Scientific) and Arctic-GRO kit sample bottles were stored in plastic Ziploc bags until analyses. At most sites, hydrographic measurements were collected using either an RBR-CTD (Ruskin Scientific) or a CastAway-CTD (SonTek).

River sites were accessed using a variety of platforms in different years, as detailed in Table S1. When river sites were accessed by land or by helicopter, river water was collected from within the main flow, accessed from the river bank, with the sampler facing up-stream. When river sites were accessed by aluminum boat or by float plane, river water was collected from mid-channel wherever possible, or from the side of the river if the float plane could not safely maintain its position. Lake sites were accessed by float plane or helicopter, landing in deeper waters away from the shore as near to the center of the lake as possible. At each site, water was collected using pre-rinsed 60 mL syringes (Fisher Scientific) directly from just below the surface, or by first pumping water through a 0.45 μm cartridge filter (Farrwest Environmental Supply) using a peristaltic pump (Pegasus Athena). Water collected for geochemical analyses of dissolved constituents was filtered through 0.22 μm Sterivex cartridges (Millipore) into triply-rinsed 4 mL amber glass vials (Wheaton) for stable water isotope analyses and 125 mL HDPE bottles (Fisher Scientific) for determination of dissolved major and minor element concentrations. Dissolved ion and stable water isotope samples were stored in the dark at room temperature or refrigerated until analyses.

Logistics for the collection and immediate preservation of inorganic carbon samples proved challenging for a multi-platform, multi-partner sampling program. While the best of care was taken to ensure the highest integrity samples were collected, sampling logistics prohibited collecting samples using the same methodology as typical for a routine oceanographic cruise. In 2014, when sampling was completed by float plane or using community partner aluminum boats, samples for the determination of Dissolved Inorganic Carbon (DIC) and Total Alkalinity (TA) were collected either by submerging pre-rinsed 250 mL borosilicate glass bottles (Pyrex) below the water surface

or using a Niskin sampling bottle fixed to a line and closed with a messenger-weight from the side of the vessel. After collection, the headspace was adjusted to ~1% of the sample volume and bottles were stoppered with greased (silicon-free high vacuum grease, Apiezon Type-M) ground glass stoppers, held in place with elastic bands or vinyl electrical tape (3M). Samples were then stored in an cool, dark, insulated box. Because of the sampling conditions, carbonate system samples were preserved with 200 μ L saturated HgCl₂ solution once back on land. This meant that samples sat for a maximum of 5-8 hrs in the aircraft or boat before processing. In 2015, when sampling was carried out by helicopter, DIC and TA samples were collected by pumping river water through a 0.45 μ m cartridge filter (Farrwest Environmental Supply) using a peristaltic pump (Pegasus Athena) into 250 mL borosilicate glass reagent bottles (Pyrex). Bottles were allowed to overflow at least one full bottle volume, and headspace was adjusted to ~1% of the sample volume before being preserved and stored as described above.

Samples for the determination of salinity were collected in parallel with carbonate system samples, either by filling bottles below the water surface (2014) or by pumping water through a 0.45 μ m cartridge filter (2015). Glass bottles (200 mL) and caps were rinsed three times before filling, then capped with a plastic insert followed by a screw on cap (after McLaughlin et al., 2012).

SI.2 Analytical Geochemical Methods

Analytical methods used in this study for the determination of geochemical concentrations are well established. Dissolved cation concentrations (Na, Mg, K, Ca, Rb, Sr, Ba, U) were determined on a Thermo Scientific Element2 single collector, inductively-coupled plasma mass spectrometer (ICP-MS) or a Thermo Scientific iCAP Qc quadrupole ICP-MS, both at WHOI. Molar concentrations of analytes were determined against certified reference materials (CRM) SU1640a, provided by National Institute of Standards and Technology (USA), as well as SLRS-5 and SLRS-6 provided by the National Research Council (Canada). Twenty samples were analyzed on both the E2 and iCAP to compare major cation concentration determination (Na, Mg, K, Ca) on the two systems, with results agreeing within \pm 5% for all four elements, and generally better than \pm 2%. Dissolved anion concentrations (e.g., Cl, SO₄) were determined using a Dionex ion chromatography (IC) system, also at WHOI. IC response was evaluated against serial dilutions of an internal standard as well as IAPSO standard seawater CRM (Batch P160), CRM concentrations were always within \pm 3% of reported values for anions measured (Cl, SO₄). Oxygen and hydrogen isotope composition of water ($\delta^{18}\text{O}$, $\delta^2\text{H}$) were determined using a Picarro L2120-I cavity ringdown spectrometer at Brown University with analytical precision of \pm 0.1‰ and \pm 1‰, respectively, and are reported

relative to V-SMOW. Dissolved Organic Carbon (DOC) concentration was determined at the Woods Hole Research Center using a Shimadzu high-temperature TOC-V analyzer following Holmes et al. (2012; Student Partners Program). Reported DOC concentrations were calculated from the mean of three to five sample injections, where the coefficient of variance was always < 2 %; replicates of external standards yield an overall analytical precision of < 5 % (Mann et al., 2012). Cation, anion, stable water isotope and DOC analyses followed the methods outlined in Voss et al. (2014).

DIC was measured coulometrically following Dickson et al. (2007) using a VINDTA 3D system from Fisheries and Oceans Canada's Institute of Ocean Sciences aboard the *CCGS Louis S. St. Laurent*. TA was determined using an open-cell continuous titration with an automated Dosimat 665 titrator (Metrohm) and Red Rod pH combination electrode (Radiometer Analytical) in 2014, and using open-cell continuous titration method with an automated ATT-05 (KIMOTO electric. co. LTD.) and Red Rod pH combination electrode (Radiometer Analytical) in 2015. Endpoint detection was made using a modified version of Dickson et al. (2007) LabView computer program in both years. Both DIC and TA were calibrated against certified reference materials provided by Andrew Dickson (Batch 133 and 138 for 2014 and 2015, respectively, Scripps Institute of Oceanography). Pooled Standard Deviation (Sp; IUPAC, 1997) of duplicate analyses for DIC (n = 20) and TA (n = 20) were $\pm 4.0 \mu\text{mol kg}^{-1}$ and $\pm 3.0 \mu\text{mol kg}^{-1}$.

Salinity was determined either at the Institute of Ocean Sciences (Sidney, BC) or aboard the *CCGS Louis S. St. Laurent* using a Guildline Autosalinometer (Autosal) Model 8400B (SN: 68572 or 69086, respectively) referenced against IAPSO Standard Seawater (OSIL, batch P156 and P157 for 2014 and 2015, respectively) as described in McLaughlin et al. (2012). Salinity is reported on the Practical Salinity Scale 1978 (PSS78). Observations from all of the rivers sampled are available in Tables S2 and S3.

SI.3 Discharge Data

Historical daily discharge (flow) data were accessed from the Environment Canada (EC) HYDAT Database National Water Data Archive using their EC Data Explorer v2.1 with hydrometric and station information data provided by the WSC, release edition: October 18, 2016 (HYDAT, 2016). Preliminary daily average discharge data for the Coppermine River and Freshwater Creek in 2016 were provided by EC. We note that EC was unable to fill gaps in the data records for these two

rivers over our study period (2014-2016) due to lack of measurements. We chose two different approaches to fill data gaps in these two rivers as described below.

For the Coppermine River time series, 2014 had a complete discharge data record whereas both 2015 and 2016 had incomplete records. Unfortunately, the observational gaps in these two years were large (45 days in the spring, April 14 – June 6, 2015, and 78 days at the end of 2015, followed by the first 158 days of 2016) and, for the days where observations were available, the discharge between years was quite different. Recorded data for 2015 suggested that it was a relatively low-flow year (maximum measured discharge at peak was 55 % of the 27-year average), whereas 2016 was closer to average peak discharge (89 % of the 27-year average). This made it difficult to fill gaps through linear interpolation, as inflection points in the seasonal transition from winter to spring were missing in both years. To mitigate this issue, we chose an arbitrary date during the winter-spring transition (May 12) as our “inflection point” based on the 2014 data set and used this as a point of reference to interpolate the missing data in both years. Specifically, gaps for the low flow period were linearly interpolated from the lowest measured value in winter to the defined inflection point and gaps from this point until the first measurement during freshet were likewise linearly interpolated. We determined the proportional contribution of these data gaps to our annual flux calculations and calculated that discharge observations recorded in 2015 represent 73 % of the annual discharge, whereas the 2016 observations represent 78 % of the annual discharge. From these analyses we concluded that sufficient data were available to estimate reasonable annual fluxes.

The Freshwater Creek discharge time series were complete for 2015 and 2016, however 2014 had a data gap of 24 days (from June 1 – 24) at the start of freshet, representing 8 % of the predicted annual discharge for that year. Unlike the Coppermine River, Freshwater Creek freezes completely through the winter, linking the date of ice break up with the start of seasonal river flow. There was so much uncertainty in choosing the date of ice break up for 2014 that interpolating linearly from a selected “start” date could have overestimated discharge by as much as 100-fold relative to the average value for that same date in the historical record. Instead, we filled the 2014 data gap with average daily discharge values from the 1970 – 2013 data set (HYDAT, 2016), this increased discharge from break-up towards the peak along a shallower slope than interpolating linearly. Difficulties in characterizing the freeze-up and melt periods with LOADEST meant that we only report annual average geochemical fluxes (see manuscript section 2.6).

S2: The CAA Drainage Region

Since most of the rivers of the CAA are ungauged, determining the total discharge for the combined drainage area is difficult. Prowse & Flegg (2000) describe a general relationship between annual discharge (linear inflow) and drainage basin area for different geographical “regions” contributing freshwater to the Arctic Ocean, with groupings based on hydrographic regimes related to run-off yield. If we consider the CAA drainage area as a geographically similar region, we can take the same approach. Using average annual discharge data and drainage basin area for the 18 marine-terminating rivers with historical Water Survey of Canada flow gauges (Fig. 1) we determine a relationship with a slope $1.7 \times 10^{-4} \text{ km}^3 \text{ yr}^{-1} \text{ km}^{-2}$ (Fig. S1). The difference in slope between our estimate and Prowse & Flegg (2000, their figure 2) is likely caused by the difference in the size of drainage “regions” used in the comparison. Our individual drainage basins are smaller than $0.1 \times 10^6 \text{ km}^2$, whereas Prowse & Flegg (2000) include major geographic regions up to $24 \times 10^6 \text{ km}^2$. From this relationship we compute an approximate freshwater discharge of $250 \text{ km}^3 \text{ yr}^{-1}$ for the CAA drainage region, similar to other works using slightly different areas ($\approx 210 \text{ km}^3 \text{ yr}^{-1}$ to $260 \text{ km}^3 \text{ yr}^{-1}$; Alkire et al., 2017; Lammers et al., 2001; Vuglinsky, 1997; Walker, 1977), and comparable to the average annual discharge from the Mackenzie ($316 \text{ km}^3 \text{ yr}^{-1}$) and Yukon rivers ($208 \text{ km}^3 \text{ yr}^{-1}$; Holmes et al., 2012).

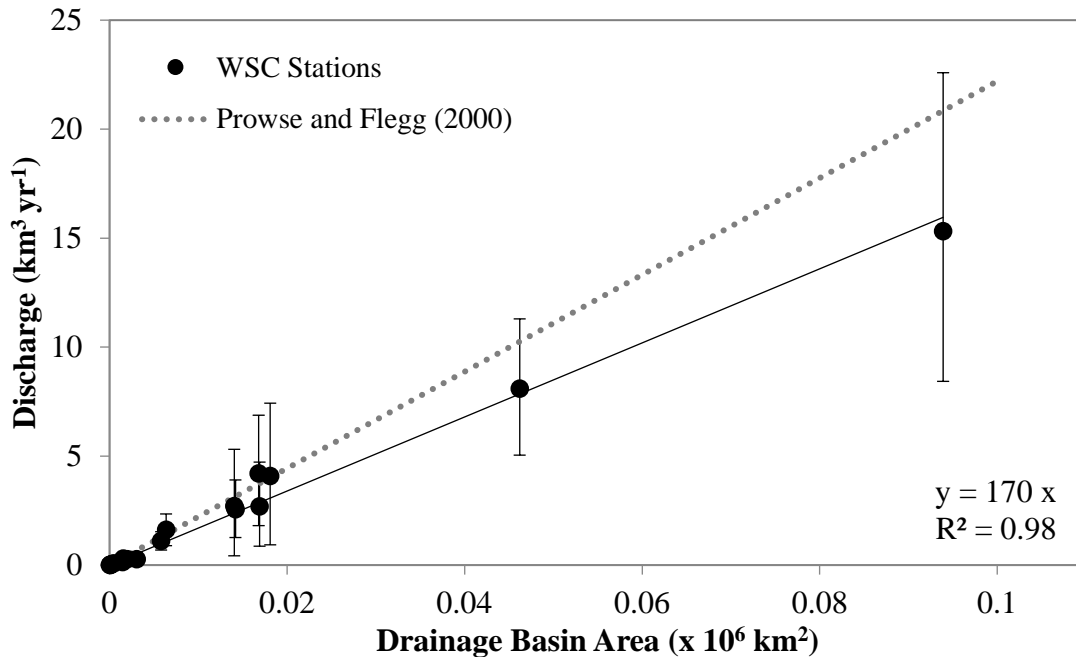


Figure S1. Historical Average River Discharge (\pm High/Low Extremes) recorded at WSC gauge stations positioned in 18 rivers draining into the marine straits of the CAA, including: Allen River, Back River, Burnside River, Coppermine River, Ellice River, Falls River, Freshwater Creek, Gordon River, Hayes River, Hood River, Hornaday River, Inman River, Marcil Creek, Mecham River, Ruggles River, Snowbird Creek, Tree River, and Union River. The WSC data record spans from 1960 to 2014 (HYDAT, 2016), however several rivers have monitoring coverage for a year or less (Li Yung Lung et al., 2018). Average annual discharge plotted against drainage basin area yields a slope of $1.7 \times 10^{-4} \text{ km}^3 \text{ yr}^{-1} \text{ km}^{-2}$, similar to the Pan-Arctic drainage basin relationship reported by Prowse and Flegg (2000: $2.2 \times 10^{-4} \text{ km}^3 \text{ yr}^{-1} \text{ km}^{-2}$; extrapolated into the range of our data set as the dotted line). Here we apply a simple linear regression to the data (i.e., drainage area is presumed to have minimal error) in order to set the intercept at zero. A Type II regression of the same data produces an intercept ($b = 0.2$) which over-estimates the discharge of the smallest WSC rivers (Mecham R., Marcil C.) by as much as an order of magnitude (890 – 1080%), whereas the estimated discharge based on the simple linear regression differs from the WSC measured average for these rivers on the order of -11% to $+28\%$. For rivers without a reported value for drainage basin area in the WSC archive, drainage basin definitions were determined using Canadian Digital Elevation Model data provided by the Natural Resources Canada (<http://geogratis.gc.ca/>), section 2.4.

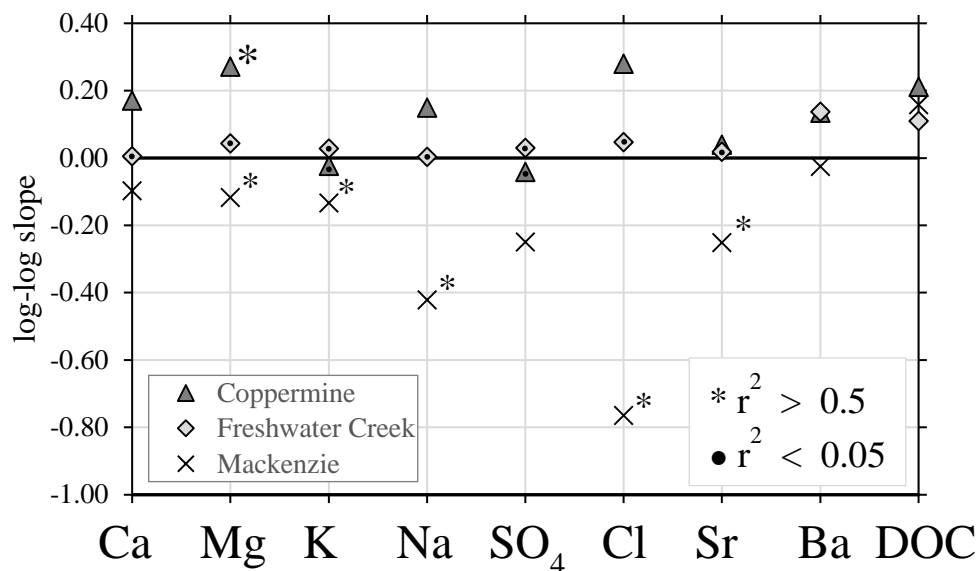


Figure S2. Power-law exponent (slope) from log-log plots of parameter concentration versus runoff yield from time series observations in the Coppermine River (triangles), Freshwater Creek (diamonds), and the Mackenzie River (crosses), as presented in Fig. 5. Plotted on a log-log scale, linear constituent concentration (C) versus discharge (Q) plots indicate a power-law relationship, the exponent (slope) of which can provide insight into the coupling of weathering reactions and hydrology within a drainage basin (e.g., Godsey et al., 2009). To a first order, power-law C-Q relationships reflect the simple dilution of weathering products when the log-log slope approaches -1 (C is inversely proportional to Q), or chemostatic behaviour (C is constant as Q changes; Godsey et al., 2009, their figure 1) with log-log slopes near 0. Dissolved ions in the Mackenzie River trend towards the dilution relationship whereas most of our observations from Freshwater Creek, and some constituents from the Coppermine River, seem to follow the chemostat model more closely. Asterisks beside symbols indicate power-law relationship was strong ($r^2 > 0.5$), whereas dots within symbols indicate an insignificant relationship ($r^2 < 0.05$).

SI: Table Captions

Table S1. Sampling Platforms Utilized for the Canadian Arctic Archipelago Rivers Study 2014-2016.

Table S2. Geochemical Data for the CAA-Rivers Project, collected from 2014 – 2016.

Table S3. Geochemical Time Series Data for the Coppermine River and Freshwater Creek collected from 2014 – 2016.

Table S4. LOADEST model coefficients for inorganic constituent loads and fluxes determined for the Coppermine River and Freshwater Creek, as described in section 2.6. Potassium (K) was determined for the Arctic-GRO rivers to augment the results of Tank et al. (2012). To determine the fit of the time series observational data of each major ion we used the Adjusted Maximum Likelihood Estimate (AMLE) which applies a bias correction by infinite series (Cohn, 1988; Cohn et al., 1992). Following Tank et al. (2012) we only applied models appropriate for short time series (AMLE Models: 1,2,4,6) which were selected according to which model generated the lowest value of the Akaike Information Criterion.