Trace Metal Geochemistry of Remote Rivers in the Canadian Arctic Archipelago

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Abstract

Trace metals are essential micronutrients for phytoplankton, as well as useful tracers of biogeochemical processes in aquatic systems. The largest Arctic rivers are known to play an important role in the cycling of trace metals in the Arctic Ocean; however, these systems account for little more than half of Arctic freshwater discharge, leaving a major gap in our understanding of the trace metal geochemistry from smaller river systems. This is especially problematic for rivers draining the Arctic coastal margins, as these continuous permafrost systems are anticipated to be particularly sensitive to climate change. This study presents the first observations of dissolved and particulate trace metal concentrations and lead isotopes in 14 rivers in the Canadian Arctic Archipelago (CAA). Dissolved concentrations of aluminum, iron, manganese, nickel, copper, zinc, cadmium, and lead display clear spatial variability in their distributions. Small rivers located in the central islands of the CAA have remarkably low concentrations of these trace metals, while the rivers draining the southern continental landmass have higher values. This geographic variability in dissolved metal concentrations reflects both differences in bedrock geology and the South-North environmental gradients in the Archipelago. We extrapolate these findings to estimate the dissolved trace metal concentrations for other rivers draining the CAA based on their geographic location. Elemental ratios measured in the suspended particulate matter in

several rivers indicates a significant enrichment of nickel, copper, zinc, and lead over the crustal composition. In particular, lead isotope composition shows an extremely large range, varying from the highly radiogenic Tree River ($^{206}Pb/^{207}Pb$: 1.5121) in the south, to the relatively unradiogenic Glacier River ($^{206}Pb/^{207}Pb$: 1.0153) in the central CAA. Lack of correlation between the Pb isotopic composition and Pb enrichment, suggests Pb is derived from within the watershed. This work presents the first observations of dissolved and particulate trace metal concentrations in small coastal draining rivers from the CAA, an important first step in developing a baseline against which to evaluate future change in the high Arctic.

Keywords: Trace metals, Lead isotopes, Arctic rivers, Freshwater systems, Geochemistry, Canadian Arctic Archipelago

1 Introduction

The study of trace elements in aquatic environments has increased since 1970's due to the advancement of analytical and sampling techniques, bringing about a better understanding of their key roles in nutrient dynamics and carbon cycling (Morel et al., 2013). For instance, manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), and cadmium (Cd) are involved in virtually all important physiological pathways of planktonic organisms (Morel and Price, 2003). Deficits of these biologically essential metals can limit phytoplankton growth, while at high levels certain metals can be toxic, especially lead (Pb), Cd, and Cu (Bruland et al., 1991). Furthermore, trace elements, such as barium (Ba), Pb, aluminum (Al), and gallium (Ga), are useful tracers of biogeochemical and physical processes as well as anthropogenic perturbations in aquatic environments (Anderson et al., 2014). The isotopic compositions of some of these trace elements can also provide useful geochemical information. For example, differences in lead isotopic signatures are extensively used to "fingerprint" anthropogenic and natural sources of lead-containing particulates to the environment (Bollhöfer and Rosman, 2002; Cheyne et al., 2018; Komárek et al., 2008).

Arctic rivers play an important role in the biogeochemical cycles of organic carbon, nutrients, major ions, and trace metals in the Arctic ocean, where approximately 11% of world's river flow is discharged (Bring et al., 2016; Dahlqvist et al., 2007; Guay et al., 2010; Hölemann et al., 2005; Lammers et al., 2001; Millot et al., 2003; Pokrovsky et al., 2010; Rember and Trefry, 2004). Initially, available data describing dissolved and particulate trace metal distributions was limited to the largest Arctic rivers. Trace metal concentrations have been reported for the Yenisey, Lena, and Ob rivers since early 90s (Dai and Martin, 1995; Guay et al., 2010; Guieu et al., 1996; Hölemann et al., 2005; Martin et al., 1993), and since 2002, trace metal data for the Yenisey, Lena, Ob, Mackenzie, Yukon, and Kolyma rivers have been collected through the Pan-Arctic River Transport of Nutrients, Organic Matter, and Suspended Sediments (PARTNERS) and Arctic-Great Rivers Observatory (Arctic-GRO) projects (https://arcticgreatrivers.org/). More recently, the dissolved and particulate trace metal geochemistry of small and medium sized

permafrost dominated Arctic rivers has been investigated along the Alaskan, Russian, and Siberian coasts (Barker et al., 2014; Dahlqvist et al., 2007; Pokrovsky et al., 2010; Rember and Trefry, 2004).

Despite these recent studies, little is known about the trace metal characteristics of small sized rivers draining the continuous permafrost regions of the high Arctic islands of the Canadian Arctic Archipelago (CAA). This region has an important role as a pathway through which Arctic waters of Pacific origin are exported to the North Atlantic (Beszczynska-Möller et al., 2011; Jones, 2003). During its flow from the Arctic Ocean to Baffin Bay and the North Atlantic, the geochemistry of transiting waters is altered due to interactions with extensive continental shelves and riverine inputs (Michel et al., 2015), enhancing the productivity of CAA marine system, which is estimated to support up to 32% of the total primary production of the Arctic shelves (Hill et al., 2013; Michel et al., 2006). Even though the annual mean discharge of individual CAA rivers is small (< 15.2 km^3; Water Survey of Canada, 2017) compared to the average annual discharge of the Mackenzie River (~283 km^3; Water Survey of Canada, 2017), the combined outflow of all CAA rivers (201 to 257 km^3/yr; Alkire et al., 2017; Lammers et al., 2001) could have a considerable influence on the freshwater balance of Arctic Ocean waters transiting the CAA. In the context of climate change, where Arctic river discharge is expected to increase due to the intensification of the global hydrological cycle (Bring et al., 2016; Peterson et al., 2002), characterizing the major and trace element distributions of coastal draining Arctic rivers will be essential in determining the impacts of terrestrial warming on the marine environment.

The aim of this paper is to determine the concentrations and distributions of dissolved and particulate trace metals and lead isotopes in coastal draining rivers across the CAA, and explore the environmental variables affecting trace metal distributions. We also investigate the sources of particulate trace metals in the CAA.

2 Methods

2.1 Sampling

Fourteen coastal draining Arctic rivers in the Canadian Arctic Archipelago (Table 1) were sampled in the summer of 2015 (August) during the Canadian Arctic GEOTRACES program, Fig. 1. This paper details particulate and dissolved trace metal results, whereas observations of river dissolved inorganic (major ions, stable isotopes, inorganic carbon) and organic (dissolved and particulate carbon composition) carbon are presented in Brown et al. (*in review*). Rivers were accessed using the ship's helicopter as the CCGS Amundsen travelled through the CAA. At each site, river water samples (250 mL) were collected by hand using gloves and clean low density polyethylene (LDPE) bottles while standing in the river and facing upstream (salinity measured for all samples was below 0.19, Table S1). The LDPE bottles were opened and closed under water, just below the river surface, to avoid external contamination. River samples were collected into Bel Art LDPE bottles that were thoroughly cleaned by soaking in successive baths at 60 °C of Extran Liquid Detergent (VWR), 6 M environmental grade HCl, and 0.7 M trace metal grade nitric acid (HNO_3, Fisher Scientific, Ontario, Canada) for 1 day, 1 week, and 1 week, respectively, as recommended by the GEOTRACES Protocol (http://www.geotraces.org/).

Once back on the ship, trace metal samples were immediately filtered in a portable trace metal laboratory, equipped with HEPA filters, using an acrylic vacuum chamber with Teflon filter holder and tubing. The filters used were 0.2 µm supor polyethersulfone (PES) membrane filters (VWR) that were previously washed with 1 M trace metal grade hydrochloric acid (HCl; Seastar Chemicals Inc., Sidney, Canada) at 60 °C for 24 h, and then rinsed and stored in Milli-Q water. Between each sample, the filter holder and tubing were rinsed with 1% trace metal grade HCl and Milli-Q water to avoid cross-contamination. The filtered water was acidified to pH ~1.8 by the addition of 6 M HCl and stored in clean LDPE bottles. PES filters containing the particulate load were dried under the laminar hood and stored in cleaned plastic capsules. PES filters were always handled using pre-cleaned plastic forceps and clean gloves.

For ease of comparison, rivers are grouped by their geographic location (Fig. 1). The continental rivers are those that have their watersheds on the North American continent and include the Tree (#15), Ellice (#14), and Simpson (#13) rivers (black circles). The central CAA rivers are the Pasley (#12), Le Feuvre Inlet* (#11), and Creswell (#10) rivers (black squares), and the northern rivers are the Mecham (#9), Cunningham (#7), Garnier (#8), Saaqu (#5), Marcil Creek (#4), Devon Island* (#6), Glacier* (#2) and Akpat Kuunga* (#1) rivers (black diamonds). Rivers with no official name on available charts were named according to distinctive features of the region, denoted by *.

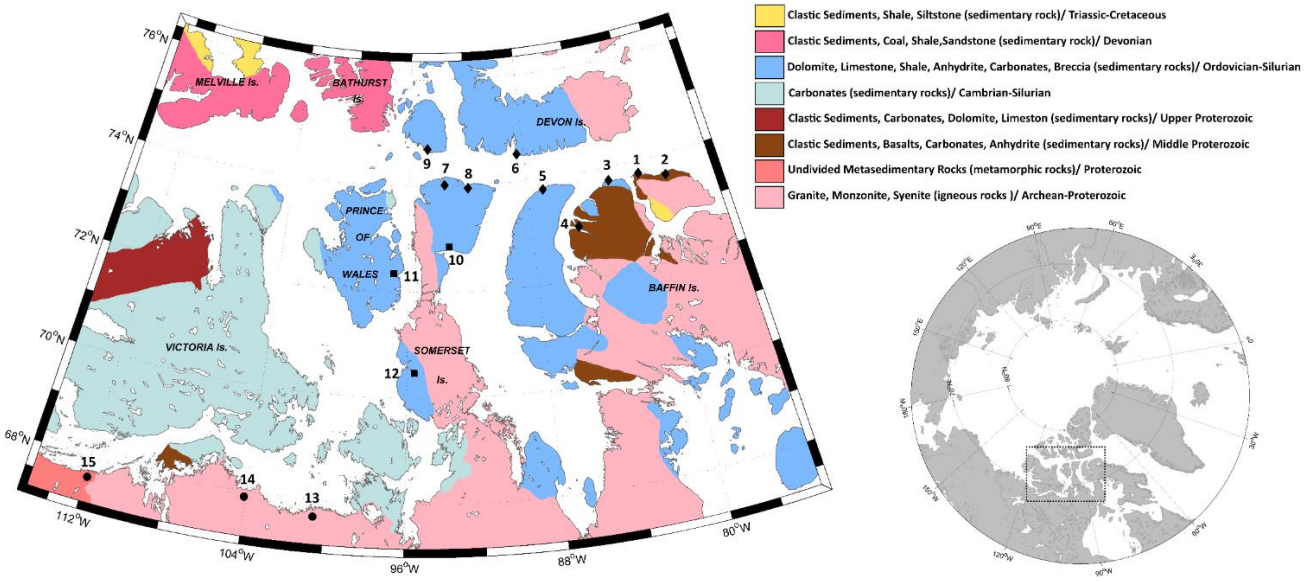

Fig. 1. Rivers sampled during the Canadian Arctic GEOTRACES program in the summer of 2015 (August). Northern rivers are displayed with black diamonds, central rivers with black squares, and continental rivers with black circles. The names of the sampled rivers are presented in Table 1. A simplified bedrock geology map is superimposed in the Figure; geological data was modified from Okulitch (1991) and Nunavut Geoscience (2017).

2.2 Sample processing and analysis

River samples were analyzed for dissolved and particulate trace metals in The Pacific Centre for Isotopic and Geochemical Research (PCIGR), an analytical center at the University of British Columbia (UBC). To prevent contamination, the processing and analyses of the samples were conducted in class 1000 laboratories, maintained in an overpressure environment by HEPA filtered air, and under class 100 laminar flow fume hoods. All the plasticware used during the analysis was cleaned as described in section 2.1.

Dissolved trace metals: In order to remove the organic matrix of the samples, which complicates the analysis by inductively coupled plasma mass spectrometer (ICP-MS), and to pre-concentrate the dissolved trace metals, filtered river water was poured in Teflon flat-bottom Savillex vials, dried down in a PFA-coated heating block (120 °C), and then 400 µL of trace metal grade HNO_3 was added. After acid evaporation the samples were resuspended in 1.5 mL of 1% HNO_3 with trace quantities of indium as an internal standard.

Suspended Particle Matter analysis: Large volume river water samples were collected into pre-cleaned 10 L HDPE cubetainers and filtered through a specially designed filtration unit described in Voss et al. (2015). Waters were filtered through 90 mm PES membrane filters (Millipore, pore size 0.22 µm) and then stored frozen. Once thawed, collected sediments were rinsed from the filters with Millipore purified water, freeze dried, then weighed; following the methods described in Voss et al. (2015). Suspended particulate matter (SPM) is reported as the weight of material recovered divided by the volume of water filtered, in mg/L.

Particulate trace metals: Filters containing the particulate fraction were digested following the protocol described by Ohnemus et al. (2014). Briefly, filters were placed into Teflon flat-bottom Savillex vials containing the piranha solution (trace metal grade sulfuric acid/hydrogen peroxide [3:1]; Fisher Scientific, Ontario, Canada) and heated at 110 °C for 60-120 min to completely dissolve the organic fraction and the PES filters. The mineral matrix was digested by heating the residues of the previous step under reflux using a mixture of trace metal grade mineral acids (HNO_3, HCl and hydrofluoric acid, Fisher Scientific, Ontario, Canada). The residues were heated for 3-4 h at 100-110 °C, and then the sample was taken to dryness at 100-110 °C. Once dry, 2 mL of HNO_3/H_2O_2 was added to each vial, and taken to dryness a second time on the hotplate at 100-110 °C. The final dry residue was resuspended in a small volume (100 µL) of HNO_3/H_2O_2 and then heated at 110 °C. After vigorous bubbling ceased, vials were uncapped and dried at 135 °C. Finally, the residues were re-dissolved in 2 mL of 1% HNO_3 with trace

quantities of indium as an internal standard. Particulate samples were diluted before the analyses, and concentration are expressed as µg of metals per liter of river water filtered.

Trace metals measurement: Dissolved and particulate Fe, Mn, Al, Ba, Cu, Ni, Zn, Pb, Ga, and Cd were analyzed from a ten-point calibration curve prepared in 1% trace metal grade HNO_3 from 1 ppm certified single element standards. The analyses were conducted by a high resolution Thermo Finnigan Element2 ICP-MS at the PCIGR. A medium mass resolution was selected for Fe, Mn, and Ga analysis in order to remove the isobaric interferences caused by $^{40}Ar^{16}O$ and $^{40}Ca^{16}O$ for ^{56}Fe, $^{15}N^{40}Ar$ for ^{55}Mn, and $^{138}Ba^{+2}$ for ^{69}Ga; the rest of the trace metals were analyzed using low mass resolution. Brand new low-flow PFA-Teflon nebulizer (Elemental Scientific Inc., Omaha, USA) and sample and skimmer cones (Fisher Scientific, Ontario, Canada) were used for this study.

During sample analysis, procedural blanks, filter blanks, and quality control spikes were routinely run to ensure quality throughout the measurements. The accuracy was calculated by analyzing SLRS-2 and SLRS-5 (river water, National Research Council of Canada) and JSd-1 (stream sediment, Geological Survey of Japan) certified references materials multiple times (Table S2). As these river water reference materials do not report Ga values, the accuracy for this element was evaluated base on spiked samples. All analyzed elements for both dissolved and particulate phases were in good agreement with certified reference materials. The average and standard deviation values (1SD) for dissolved and particulate trace metals are presented in Table S2. The relative standard deviation (1RSD) of reference material was 3.5% or better for most the dissolved elements, while the values for Zn, a highly contamination prone element, were higher (~14%). The RSDs of most of the particulate analyses ranged between 3-11%, and for Pb and Ba was 16 and 20%, respectively.

Lead isotopic measurement: The measurement of Pb isotopes in the suspended particulate matter (SPM) of CAA rivers was done at the Department of Earth Sciences, University of Toronto, Ontario, Canada, using a Thermo Scientific Neptune Plus Multi-Collector ICP-MS with an APEX inlet system

(Elemental Scientific Inc, Omaha, Ne, USA). Trace metal clean procedures were followed during sample preparation and all reagents and matrix solutions were made using acids that were Optima-gradeTM (Fisher Scientific, Ontario, Canada). The method of sample processing, column purification, and Pb isotope analysis was based on the methods of Cheyne et al. (2018) and Reuer et al. (2003). Sample filter digests were heated and allowed to reflux in a solution of 900 µL HNO_3 and 100 µL HCl for 24 h to reduce any traces of organic matter remaining after sample digestion. The solutions were then dried and the solids redissolved in ~2N HBr prior to column separation in polypropylene microcolumns loaded with AG 1 x 8 anion exchange resin (chloride-form, 200-400 mesh). The resin was cleaned with three 1 mL aliquots of 6 N HCl and multiple aliquots of MQ water, and then conditioned with 4 mL 2N HBr. Sample solutions were loaded to the resin and the matrix washed through with 2 mL 2 N HBr and 2 mL 1.7 N HCl. Finally, Pb was eluted with 4 mL 6 N HCl, dried and redissolved in 2% HNO_3 for isotope analysis. The MC-ICP-MS was run with X and Jet cones to enhance the sensitivity of the instrument to about 0.2V/ppb for Pb 208. This configuration allowed isotope measurements on Pb concentrations as low as ~1ppb with an uncertainty of 1000 ppm (2SD) for $^{206}Pb/^{207}Pb$. Due to persistent blank issues with Tl, the instrumental mass bias was corrected using sample-standard bracketing with the NIST 981 Pb standard as the bracketing standard and no internal Tl correction. Each sample was strictly bracketed by standards. The errors reported are the 2SD of replicate runs, or are the largest 2SD of the run if a sample was only run one time. Two process standards (NIST 981 and USGS basalt BCR-2), which went through the same purification method as the samples, had measured isotope values (presented in Tables S3 and S4) that were in agreement with the published values (Cheyne et al., 2018; Galer, 1998; Weis et al., 2006).

2.3 Calculations and Statistical Analysis

In this study, the enrichment factors for the studied elements were calculated using the following equation: $EF= [(Me/Al)_{river}]/[(Me/Al)_{crustal}]$, where $(Me/Al)_{river}$ is the metal to Al ratio measured in the rivers and $(Me/Al)_{crustal}$ is the metal to Al ratio reported for the average crustal composition. The average element concentrations from the upper continental crust were obtained from Rudnick and Gao (2013).

The statistical analysis and graphics in this manuscript were developed using MATLAB 9.2 and Python 3.6.0. River discharge data for the Mecham, Ellice, and Tree rivers were obtained from the Water Survey of Canada (Water Survey of Canada, 2017). Multivariate analysis such as factor and principal component analysis (PCA) are widely used in environmental studies to estimate sources of trace and heavy metals and to spatially characterize multiple areas based on geochemical data (Chabukdhara and Nema, 2012; Loska and Wiechuła, 2003). In this work, dissolved trace metal data were used in the PCA to assist in the study of the geographical variability of trace metals distributions in CAA, in concert with bedrock geology data (Nunavut Geoscience, 2017; Okulitch, 1991). Trace metal data were z-score normalized before PCA.

2.4 Data availability

The authors declare that all data generated in this study is available in this article and its Supplementary Information files.

3 Results

3.1 Trace metal distributions in CAA rivers

Concentrations of dissolved and particulate trace metals, and lead isotopic ratios measured in 14 remote rivers in the Canadian Arctic Archipelago (Fig. 1) are reported in Table 1; an extensive review of the published data on trace metals for Arctic freshwater systems is presented in Table S5.

Table 1 Dissolved and particulate trace metal concentrations (dTM and pTM) and lead isotopic ratios measured in CAA rivers. Duplicate samples, when available, are displayed for each river. dTM concentration are expressed in nM for Al, Fe, Mn, Ba, Ni, Cu and Zn, and pM for Cd, Pb and Ga. pTM concentrations are expressed as µg/L.

Rivers	Al		Fe		Mn		Ba		Ni		Cu		Zn		Cd**	Pb		Ga		Pb Isotopes*	
	dTM	pTM	dTM	pTM	dTM	pTM	dTM	pTM	dTM	pTM	dTM	pTM	dTM	pTM	dTM	dTM	pTM	dTM	pTM	206/207	208/206
Akpat Kuunga ***(1)***	205/218	1377	1.23/2.30	688	6.31/6.50	10	170/173	9.81	0.132/0.099	2.58	2.19/2.29	3.59	0.398/1.58	2.51	8.08/11	1.53/3.20	0.779	85/92	0.507	1.1913	2.2383
Glacier ***(2)***	616	19355	212	13980	164	151	44	168	7.31	17	1.60	17	2.42	42	11	35	4.71	381	6.66	1.0153	2.4238
Marcil Creek ***(4)***	116/117	561/670	39/48	307/360	1.11/1.20	6.00/6.70	300/303	2.68/4.85	1.08/1.17	6.70/2.07	11/11	3.89/3.87	0.901/1.16	1.58/2.15	8.24/8.72	3.23/5.22	0.676/0.678	11/12	0.298/0.319	1.2520	2.0612
Saaqu ***(5)***	107/112	78/88	0.592/2.23	60/57	0.632/0.693	0.756/0.760	16/16	0.701/0.663	0.603/0.601	0.091	0.998/1.02	0.10/0.10	0.407/0.653	0.173/0.663	5.12/5.87	1.01/1.26	0.045/0.035	48/48	0.034/0.023	1.3321	1.9030
Devon Isl. ***(6)***	133	79	0.913	51	2.35	0.553	185	0.479	0.117	<LOD	0.657	0.11	1.12	0.861	5.51	1.74	0.027	54	0.020	1.2795	1.9738
Cunningham ***(7)***	87/91	1.81	1.33/1.25	1.85/2.15	0.366/0.356	0.114/0.099	44/44	0.024/0.011	1.07/1.09	<LOD	2.26/2.31	0.07/0.08	0.007/0.005	0.221	3.59/5.25	0.601/0.670	0.010/0.011	56/58	0.003	-	-
Garnier ***(8)***	82	952	1.07	674	0.218	11	95	6.14	0.527	4.44	1.81	3.5	0.402	2.32	4.56	3.53	0.793	62	0.335	1.2177	2.0286
Mecham ***(9)***	63	1.87	0.638	1.66	0.067	0.104	27	0.028	0.777	<LOD	1.88	0.09	0.069	<LOD	9.99	1.49	0.013	36	0.003	-	-
Creswell ***(10)***	49/51	86/171	6.02/5.30	53/104	6.72/7.18	0.787/2.02	241/243	0.601/1.65	1.17/1.21	0.100	3.62/3.63	0.14/0.17	0.908	0.546/0.227	9.28/12	4.48/6.07	0.031/0.059	38/43	0.020/0.044	1.2144	2.0682
Le Feuvre Inlet ***(11)***	66/66	132/37	3.79/3.35	78/19	2.28/4.42	1.92/0.514	241/242	0.372/1.92	0.765/0.850	<LOD	5.80/5.89	0.10/0.09	1.74/3.44	0.274	10/10	1.59/1.78	0.039/0.020	45/46	0.027/0.014	1.1350	2.3648

Pasley ***(12)***	54	1.42	4.67	2.05	0.923	0.115	82	0.042	2.05	<LOD	5.04	0.09	0.258	<LOD	9.17	1.72	0.014	69	0.003	-	-
Simpson ***(13)***	321/ 857	1469/ 1638	258/ 506	765/ 865	51/54	22/23	16/17	11/18	5.59/ 5.69	1.11/ 3.60	9.09/ 9.28	3.58/ 3.43	1.18/ 2.38	2.69/ 3.86	11/14	32/73	0.855/ 0.975	18/41	0.417/ 0.519	1.29 76	2.02 46
Ellice ***(14)***	551/ 631	510/ 530	1142/ 1053	401/ 411	11/11	10/11	25/25	4.98/ 4.87	10/10	2.05	12/13	3.50/ 3.57	4.83/ 5.35	2.93/ 2.29	14/20	60/64	0.715/ 0.705	24/32	0.256/ 0.230	1.28 32	2.04 64
Tree ***(15)***	96/ 209	264/ 287	73/ 133	190/ 202	26/26	5.17/ 5.74	301/ 307	2.94/ 3.09	8.16/ 8.17	2.13	9.19/ 9.33	3.52/ 3.49	6.91/ 7.19	3.03/ 4.51	22/23	12/15	0.638/ 0.641	19/35	0.190/ 0.183	1.51 21	1.66 70

<LOD: concentrations that were below the limit of detection. Ni LOD: 0.086 µg/L and Zn LOD: 0.038 µg/L
*: Pb isotopic ratios were measured in the particulate phase
**: Particulate Cd was not analyzed in this study

Dissolved trace metals: Dissolved trace metal concentrations measured in this study show some general trends (Fig. 2). Rivers with headwaters on the Canadian continent (Fig. 1, black circles) had high values for most of the elements with the exception of Ba and Ga. The geochemistry and flow of these rivers differ from the other rivers in this study, which have their headwaters within the islands of the CAA (discussed in section 4.1). The Glacier River (#2) had high concentrations of Al, Fe, Mn, Ni, Cu, Pb, and Ga; and the northern and central CAA rivers had lower concentrations of trace metals in comparison to rivers in the south and the Glacier River (Fig. 1, black squares and diamonds).

In addition to the general trends highlighted above, Marcil Creek (#4) had concentrations of dissolved Fe and Cu greatly exceeding the values of the other northern rivers. Unlike the distribution of most trace metals analyzed in this study, Ga showed slightly lower values (18-41 pM) in the continental rivers than most of the central and northern rivers (35-92 pM). Dissolved Ba concentrations displayed a large spatial variability across the sampled rivers showing an opposite pattern to the rest of the elements; similar Ba

distributions have been observed by Alkire et al. (2017) in small CAA rivers. Moreover, Ba concentrations spanned the range of values reported for Eurasian rivers (~20-141 nM) and North American rivers (~170-425 nM; Guay et al., 2009).

Compared with available data in the literature, the dissolved concentrations measured in most of the central and northern CAA rivers (excluding the Glacier River) were extremely low, especially for Cunningham (#7), Mecham (#9) and Pasley (#12) rivers. For instance, the concentrations of Al (~2-3 times), Fe (~3-34 times), Mn (~2-100 times), Ni (~2-40 times), Cu (~2-5 times) and Pb were ~3-32 times lower than the lowest reported values for Arctic rivers, including small Alaskan and Russian Arctic rivers and creeks with comparable flow and size (Table S5 and references therein). On the other hand, the concentrations of the former trace metals (Al, Fe, Mn, Ni, Cu, and Pb) measured in continental CAA rivers lie in the lower end of the range reported for other Arctic rivers. The dissolved concentrations of Ba, Zn, and Cd for most of the studied CAA rivers were in the range of values reported for other Arctic rivers, Table S5 and references therein.

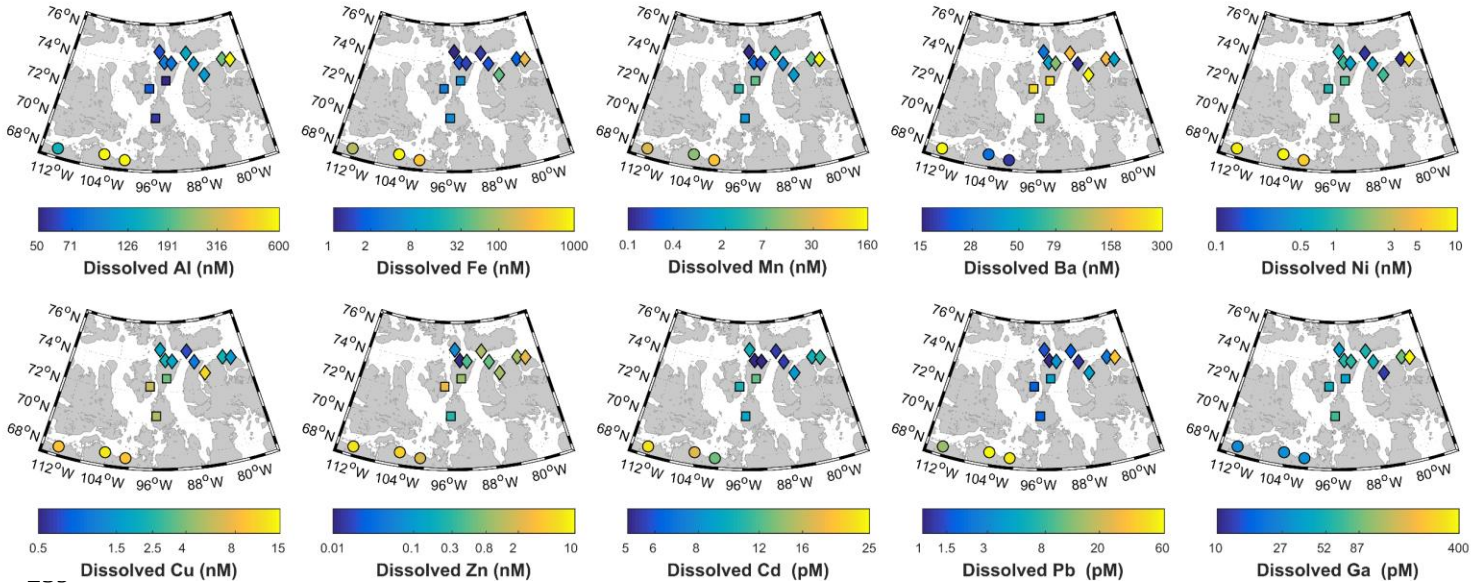

Fig. 2. Dissolved trace metals concentrations measured in 14 CAA rivers; results are expressed in a logarithmic colorbar.

Particulate trace metals: Particulate trace metal concentrations are expressed as µg per liter of water filtered, and, therefore, these values are largely controlled by the SPM concentrations, which varied greatly across the rivers sampled (Table S1). The particulate concentrations of Al and Fe were ~2 to ~3 orders of magnitude higher than Ba, Ni, Cu, Zn, Pb, and Ga, reflecting the relative abundance of these metals in the continental crust (Figs. 3a, 3b and S1, Table 1). Glacier river (#2) had extremely high concentration of all analyzed elements, reflecting its high SPM concentration (Table S1). The remaining rivers can be grouped into 3 different categories based on their concentrations of particulate trace metals (Figs. 3a, 3b and S1). The Akpat Kuunga (#1), Garnier (#8), Simpson (#13), Ellice (#14), and Tree (#15) rivers as well as Marcil Creek (#4) have concentrations ~1 to 2 orders of magnitude higher than the other two groups; the Saaqu (#5), Devon Island (#6), and Creswell (#10) rivers as well as the river in Le Feuvre Inlet (#11) had intermediate concentrations; and the Cunningham (#7), Mecham (#9), and Pasley (#12) rivers, had concentrations ~1 order of magnitude lower than the "intermediate" rivers.

Compared with available data in the literature, Glacier River (#2) exhibited concentrations of particulate trace metals which were ~3 to 94 times greater than those reported for other Arctic rivers, but comparable to those reported for major world rivers (Table S5 and references therein). The particulate trace metal concentrations reported for the Akpat Kuunga, Garnier, Simpson, Ellice, and Tree rivers and for Marcil Creek were similar to or slightly higher than data published for other Arctic rivers (Mn: ~4-14, Cu: ~4 times higher). Particulate concentrations measured in the Saaqu, Devon Island, and Creswell rivers as well as the river in Le Feuvre Inlet were at the same level as values reported for major Arctic rivers, but lower than those reported for major world rivers for Mn, Ba, Ni, Zn, and Pb (Table S5 and references therein). Cunningham, Mecham, and Pasley rivers had the lowest concentrations for most of the analyzed trace metals (excluding Cu), with values that were lower than major Arctic rivers.

3.2 Particulate Trace metals: enrichment factors and lead isotopic analysis

Particulate Ba/Al and Pb/Al ratios measured during this study are displayed in Figs. 3a and 3b, along with the estimated crustal metal/Al ratios, used to evaluate potential contributions of trace metals from

external sources, or sources that differ from upper continental crust. Lead isotopic composition ($^{208}Pb/^{206}Pb$ versus $^{206}Pb/^{207}Pb$) and the relationship between the $^{206}Pb/^{207}Pb$ ratios and Pb/Al ratios are also displayed in Figs. 3c and 3d. Particulate elemental ratios, normalized to Al, for the rest of the elements are presented in Fig. S1.

Fe/Al, Mn/Al, Ba/Al, and Ga/Al ratios (0.538, 0.0078, 0.0087, and 0.0003 respectively) were in agreement to those reported in the literature for crustal ratio (Rudnick and Gao, 2013; Figs. 3a and S1). However, in the Cunningham (#7), Mecham (#9), and Pasley (#12) rivers Mn and Ga ratios were ~ 6 and up to 11 times higher than the average crustal ratios. In contrast, an enrichment of Ni, Cu, Zn, and Pb over the Al fraction compared to upper continental crust was observed for most of the rivers sampled (Figs. 3b and S1). High enrichment factors (EFs, section 2.3) for Ni were observed in Marcil Creek (#4), as well as Garnier (#8), Ellice (#14), and Tree rivers (#15) with values that were 7 to 13 times higher than the average crustal ratios. Similar results were found for Cu and Pb, with EFs ranging from 11 to 37 and 4 to 11 times higher than crustal ratios in the same rivers. The highest values were found in the Cunningham (#7), Mecham (#9), and Pasley rivers (#12) with extremely high EFs for Cu (128-177 times higher) and Pb (29-47 times higher). Zn/Al ratios were remarkably elevated in the Cunningham River (150 times higher) followed by the Devon Island, Saaqu, Ellice, and Tree rivers (6-17 times higher). It is important to mention that the Cunningham (#7), Mecham (#9), and Pasley rivers (#12) had the lowest concentrations of particulate Al, which could have influenced the EF calculations producing artificially high EFs for these rivers.

The Pb isotopic composition of SPM for 11 CAA rivers is presented in Fig. 3c and Table 1. Generally, particulate Pb-isotopic composition was quite heterogeneous across CAA rivers in our study. For example, the Tree River (#15) exhibited the most radiogenic signature for $^{206}Pb/^{207}Pb$ (1.5121) and the lowest value for $^{208}Pb/^{206}Pb$ (1.6670), while the Glacier River (#2) had the most unradiogenic value of $^{206}Pb/^{207}Pb$ (1.0153) and the highest $^{208}Pb/^{206}Pb$ (2.4238). The isotopic composition of the other CAA rivers fell between these two extremes. The wide range in Pb isotopic composition observed in this study

encompasses values reported from multiple studies from different regions and different natural sample types (Fig. 3c). The Pb/Al versus $^{206}Pb/^{207}Pb$ plot revealed that there is no recognizable change in the Pb isotopic composition with increasing Pb enrichment, Fig. 3d.

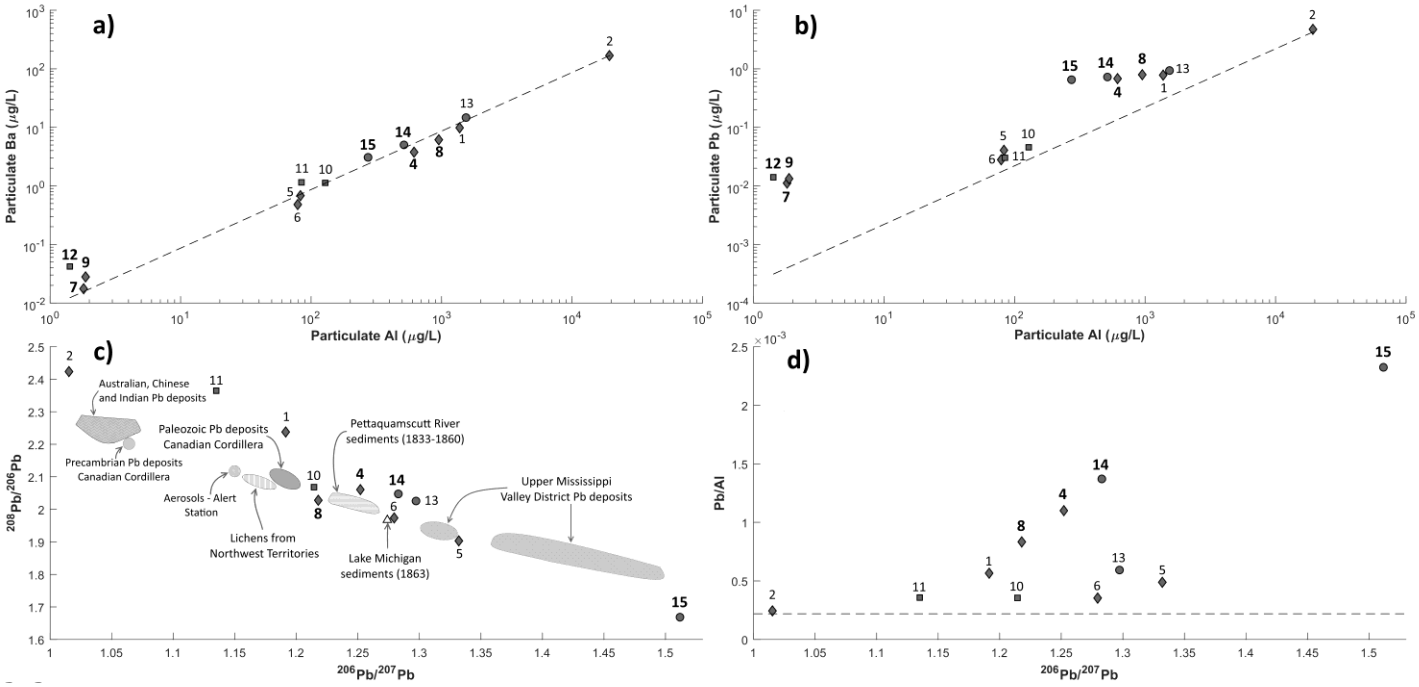

Fig. 3. Particulate Ba/Al and Pb/Al ratios collected from CAA rivers (a and b). Dashed lines indicate the average crustal metal/Al ratio (Rudnick and Gao, 2013) and bolded numbers indicate those rivers which are located in close proximity to mining exploration projects and/or communities. c) Particulate $^{208}Pb/^{206}Pb$ versus $^{206}Pb/^{207}Pb$ composition from CAA rivers and isotopic signatures from selected sources (Godwin and Sinclair, 1982; Graney et al., 1995; Lima et al., 2005; Millen et al., 1995; Sangster et al., 2000; Simonetti et al., 2003). d) Pb/Al versus $^{206}Pb/^{207}Pb$ plot showing the relative enrichment and changing Pb isotopic ratios of CAA rivers. The names of the sampled rivers are presented in Table 1.

4 Discussion

4.1 Spatial variability of dissolved trace metals in CAA rivers: linking trace metal distributions with environmental variables and bedrock geology

All dissolved trace metals, with the exception of Ba, displayed distinctive spatial patterns in their concentrations. For most elements, lower concentrations were measured in the northern and central CAA rivers, whereas high concentrations were observed in the southern continental rivers (Fig. 2); for Ga this pattern is inverted. Marcil Creek (#4) stands out from these trends with noticeably elevated Fe (39/48 nM) and Cu (11 nM) concentrations compared with other northern rivers (1.3±0.6 and 1.7±0.6 nM,

respectively). Marcil Creek has a community nearby (Arctic Bay, ~900 people) and dissolved organic carbon (DOC) concentrations approximately 3 times higher than the other northern rivers (Table S1); both of these distinctive features may help to explain the higher concentrations of Fe and Cu, especially the high DOC concentrations, as the distributions of these elements are strongly controlled by their complexation with organic substances (Dahlqvist et al., 2007; Pokrovsky et al., 2010; Rember and Trefry, 2004).

To further investigate the geographic variability of dissolved trace metals in CAA rivers and understand their drivers, a PCA was applied to the dissolved trace metal data. Three principal components (PC) were selected which accounted for approximately 90% of the total variance (PC1: 52.9%, PC2: 25.2%, PC3: 13.7).

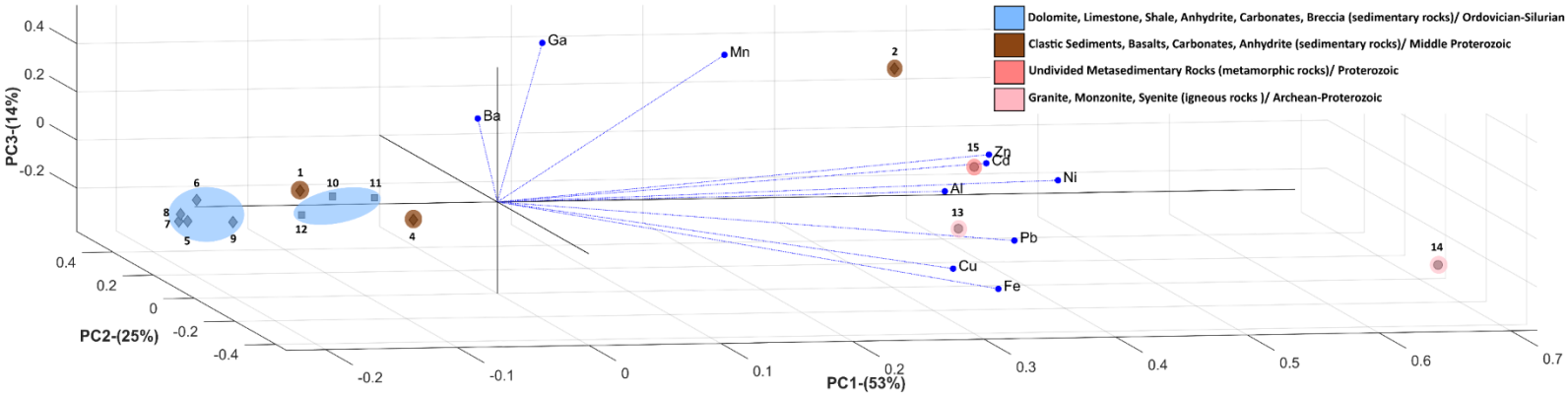

Fig. 4. PCA loadings and score plots for dissolved trace metals. The bedrock geology of each river is superimposed in the figure, with the names of the sampled rivers as presented in Table 1.

PCA results support the contrasting spatial distributions of trace elements observed in CAA rivers (Fig. 4). The northern and central rivers, which share similar trace metal signatures (lower concentrations of most trace metals) are distinctively clustered in the negative PC1 axis, differing from the continental rivers and the Glacier River grouped in the positive PC1 axis. The drainage basins of northern and central rivers generally have similar bedrock geology, characterized by sedimentary rocks such as limestones, siltstones, sandstones, dolomites, and carbonates from the Ordovician to the Silurian periods (Figs. 1 and 4). The bedrock geology of the drainage basins of Akpat Kuunga (#1) and the Glacier (#2) rivers as well

as Marcil Creek (#4) differ from the other northern and central Arctic rivers; the region drained by these rivers is characterized by an older formation of anhydrites, carbonates, basalts, and clastic sediments from the middle Proterozoic (Figs. 1and 4). Despite the difference in the bedrock geology, these rivers are clustered with the rest of the northern and central rivers in the PCA. Glacier River (#2) is the only northern river located in the positive PC1 and PC3 axes. This may be explained by the extremely high particulate concentration of this river (1-4 orders of magnitude higher than all analyzed rivers, Table S1) which may influence the geochemistry of dissolved trace metals. The bedrock geology of the continental rivers is characterized by intrusive rocks (granites, monzonites, and syenites) from the Archean and lower Proterozoic for the Simpson (#13) and Ellice (#14) rivers and Proterozoic metasedimentary rocks for the Tree River (#15), Figs. 1 and 4.

Even though the distribution of trace metals is well correlated with the bedrock geology of CAA, other environmental variables are also expected to play an important role in controlling their spatial distributions. This is also evident in the PCA, where the northern rivers (diamonds) are tightly clustered on the PC1 axis, differentiating from the central rivers (squares) despite sharing similar bedrock geology. The latitudinal gradients of climatic conditions (e.g., solar radiation, precipitation, temperature) across CAA likely accounts for many of the differences between northern and continental CAA watersheds. For example, the development of permafrost soils and vegetation, soil organic carbon content, river discharge, and permafrost active layer thickness, all increase from north to south (e.g., AMAP, 1998; Bring et al., 2016; Hugelius et al., 2014; Tarnocai, 2018; Water Survey of Canada, 2017). These environmental gradients are expected to influence the geochemistry of major and trace elements in downstream freshwater environments, as well as the distribution of DOC, colloids, particulate organic carbon (POC), and SPM, which affect the solubility and partitioning of trace metals (Barker et al., 2014; Dai and Martin, 1995; Holmes et al., 2012; Mann et al., 2012; Rosa et al., 2012; Shiller, 1997). In particular, the S-N gradient in the thickness of the permafrost active layer, an important zone where most geomorphic, hydrological, soil microbial, and biogeochemical activities take place, will have important consequences

for the interaction of river waters with both organic and mineral soils, thus strongly influencing their metal loads (e.g., Bring et al., 2016). Furthermore, unlike the northern CAA, the drainage basins of continental rivers are characterized by the presence of floodplains and wetlands (Millot et al., 2003); interactions of river water with these distinctive ecosystems can alter the fluvial transport of dissolved and colloidal nutrients, DOC, and trace elements (Bring et al., 2016; Millot et al., 2003; Rosa et al., 2012; Shim et al., 2017). Rivers from this study exhibit a clear latitudinal gradient in the distribution of DOC, where continental CAA rivers had notably higher values than northern rivers (360±145 and 37±17 µM C; Table S1). Strong positive correlations ($r > 0.80$) were found for DOC versus dissolved Al, Fe, Ni, and Pb, followed by Cu ($r = 0.77$) and Mn ($r = 0.70$), and moderate correlations ($0.44 < r < 0.57$) were found for Zn, Cd, and Ga, Table 2. The strong association of trace metals with organic complexes has been described for numerous freshwater systems in the Arctic and worldwide (Dahlqvist et al., 2007; Dai and Martin, 1995; Mitchell et al., 2001; Pokrovsky et al., 2010; Rosa et al., 2012; Shim et al., 2017).

Table 2 Pearson's correlation matrix for dissolved trace metals and dissolved organic carbon (DOC) from small CAA rivers (excluding the Glacial river). DOC data is reported in Table S1.

	DOC	Al	Fe	Mn	Ba	Ni	Cu	Zn	Cd	Pb	Ga
DOC	1.00										
Al	0.88*	1.00									
Fe	0.84*	0.86*	1.00								
Mn	0.70*	0.71*	0.37	1.00							
Ba	-0.28	-0.38	-0.34	-0.07	1.00						
Ni	0.81*	0.74*	0.83*	0.59*	-0.09	1.00					
Cu	0.77*	0.62*	0.69*	0.49*	0.22	0.78*	1.00				
Zn	0.51*	0.43**	0.55*	0.45**	0.34	0.84*	0.67*	1.00			
Cd	0.57*	0.44**	0.51*	0.56*	0.30	0.83*	0.69*	0.89*	1.00		
Pb	0.95*	0.97*	0.92*	0.68*	-0.35	0.84*	0.71*	0.52*	0.55*	1.00	
Ga	-0.44**	-0.29	-0.37	-0.35	-0.21	-0.49*	-0.68*	-0.43**	-0.46**	-0.42**	1.00

* Correlation is significant at p-value<0.01 (2-tailed)
** Correlation is significant at p-value<0.05 (2-tailed)

Partition coefficients (K_d) describing how trace metals distribute between aqueous and particulate phases can lend insight to trace metal distributions throughout CAA rivers, including their complexation with organic species and their relative solubility. Higher K_d indicates a greater

tendency for metals to concentrate in the solid phase (particle reactive trace elements), whereas lower K_d indicates a greater affinity to the aqueous phase (Li, 2011). The average K_d from CAA rivers (not including Glacier River; discussed below) increases from Ba>Cu>Ni>Ga>Zn and Mn>AL>Fe to Pb (Table 3) following the general trend expected by their particle reactivity (Ho et al., 2007; Tang et al., 2002). In addition, three rivers stand out as having consistently low K_d values for most trace elements, including the Glacier (#2), Simpson (#13), and Ellice (#14) rivers (Table 3). The estimated K_d coefficients for the Glacier River, which had the largest SPM concentration (Table S1), were notably low compared with other northern CAA rivers. This could be attributed to the particle concentration effect, which results in a decline in the K_d as SPM increases, and is observed in many fresh and estuarine environments (Benoit and Rozan, 1999; Tang et al., 2002). Compared with central and northern CAA rivers, the continental rivers display relatively lower K_d values; these rivers have significantly higher DOC concentrations (Table S1), and therefore, as result of the competitive colloidal-organic complexation, the trace metal solubility is enhanced yielding lower K_d values (Benoit and Rozan, 1999).

Table 3 Partition coefficients (K_d, $\frac{\mu g/g}{\mu g/mL}$) of trace metals in CAA rivers. Kd values were calculated as the ratio of dissolved trace metal concentrations to particulate concentrations. Values are expressed as $\log_{10}$ of K_d.

Rivers	log K_d Al	log K_d Fe	log K_d Mn	log K_d Ba	log K_d Ni	log K_d Cu	log K_d Zn	log K_d Pb	log K_d Ga
Akpat Kuunga ***(1)***	7.5	8.9	6.5	4.7	7.7	6.5	6.7	8.3	7.0
Glacier ***(2)***	6.6	6.7	4.8	5.0	5.2	5.8	6.0	3.4	3.0
Marcil Creek ***(4)***	7.8	7.6	7.5	4.5	7.3	6.2	6.9	8.4	8.1
Saaqu ***(5)***	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Devon Isl. ***(6)***	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Cunningham ***(7)***	5.9	7.5	6.8	3.5	5.7	5.8	8.6	8.0	5.7
Garnier ***(8)***	7.5	8.9	7.8	4.5	7.0	6.4	6.8	7.9	6.8
Mecham ***(9)***	6.9	8.5	8.3	4.7	6.8	6.7	7.7	8.5	6.9
Creswell ***(10)***	7.6	8.0	6.2	4.1	5.8	5.4	6.4	7.3	6.7
Pasley ***(12)***	7.5	8.5	7.9	5.1	6.9	7.0	7.6	9.2	7.4
Simpson ***(13)***	6.7	6.3	5.6	5.5	5.6	5.5	6.2	6.6	7.1
Ellice ***(14)***	6.8	6.1	6.6	5.5	5.8	6.0	6.2	7.1	7.4
Tree ***(15)***	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

N/A: Not available. The K_d from Saaqu (#5), Devon Isl. (#6), Le Feuvre Inlet (#11) and Tree (#15) rivers were not calculated due to the lack of SPM data from these rivers.

4.2 Constraining dissolved trace metal concentrations from coastal draining rivers in the Canadian Arctic Archipelago

The distributions of trace metals in CAA rivers display a clear spatial pattern between northern and central rivers and those rivers draining the Canadian continent. This pattern can be employed to estimate the dissolved concentrations for other small rivers in the archipelago, not sampled in this study, based on their geographic location and bedrock geology. The remote locations of many CAA rivers and their limited access impose significant constraints on sample collection at different periods during the hydrological cycle, precluding the assessment of the seasonal variability of trace metals in this region.

In high latitude rivers, major and trace element as well as DOC, colloids, and SPM, exhibit distinct seasonal variability in their distributions, in particular during the spring snowmelt (Bagard et al., 2011; Barker et al., 2014; Bring et al., 2016; Dahlqvist et al., 2007; Hölemann et al., 2005; Holmes et al., 2012; Mann et al., 2012; Pokrovsky et al., 2010; Rember and Trefry, 2004). During the spring snowmelt period the topsoil layers are intensively flushed, mobilizing organic substances and trace elements from the permafrost active layer interstitial water into freshwater systems (Bagard et al., 2011; Barker et al., 2014; Rember and Trefry, 2004). Insoluble trace elements (e.g., Al, Ba, Co, Cu, Fe, Mn, Ni, and Pb), in contrast with major ions, exhibit a sharp increase in their concentrations during the spring season, with values up to ~25 times higher at spring melt season than during baseline flow in the winter (Bagard et al., 2011; Barker et al., 2014; Hölemann et al., 2005; Peterson et al., 2016; Rember and Trefry, 2004). This spring peak is closely correlated with a concomitant increase in DOC, underscoring the importance of organic and organo-mineral colloids facilitating the mobilization of insoluble elements in Arctic freshwater systems (Bagard et al., 2011; Dahlqvist et al., 2007; Pokrovsky et al., 2010). Additionally, the seasonal variability of trace metals is known to be controlled by the reductive dissolution of Fe-Mn oxyhydroxides and adsorption/desorption reactions (Hölemann et al., 2005; Shiller, 1997).

In this study, CAA rivers were sampled in August during the low flow period (Fig. 5, middle panel). As we were not able to collect samples in different seasons or flow periods, it is difficult to put our

438 observations in context with the annual hydrological cycle. Therefore, we attempt to account for the
439 expected seasonal variability in trace metal concentration by comparing with observations from the
440 PARTNERS and Arctic-GRO data sets that sampled the major Arctic rivers throughout the year (Peterson
441 et al., 2016; Shiklomanov et al., 2018). With the assumption that trace metal concentrations in the small
442 rivers sampled in this study behave like those in the largest Arctic rivers, we can use this comparison to
443 estimate trace metal concentrations from small CAA rivers at the high flow period. First, we applied a
444 linear regression analyses of dissolved trace metal concentrations and DOC versus flow for the Kolyma,
445 Mackenzie, Yenisey, Ob, and Lena rivers to determine the relationship between trace metal
446 concentrations and daily average river discharge (Table S6 and Fig. 5, upper panel). We chose to use a
447 linear regression analysis as it fit the general trends of the data well (Table S6) and, with the limitations
448 on our available CAA data set (one sample from one point in time), we cannot justify the use of a more
449 complex concentration-discharge model to describe our CAA systems. For most of the rivers, the
450 regression analysis showed strong significant relationships between Fe, Cu, Pb, and DOC versus
451 discharge, while Mn and Ni showed strong significant relationships only in the Kolyma and Yenisey
452 rivers (Table S6). When the regression analysis showed a significant relationship (high R^2 and
453 p-value< 0.05), the percentage difference in trace metal concentration between the low and high flow
454 periods was calculated, and this percent value was then used to estimate the trace metal concentrations
455 during the high flow season in the CAA rivers. We chose to apply the percentage difference results from
456 the Kolyma River only to our CAA data set as this river most closely resembles the environmental
457 features of the CAA rivers studied. For instance, the Kolyma River has the smallest and northernmost
458 watershed which is entirely underlain by continuous permafrost (Mann et al., 2012). Moreover, the
459 Kolyma River has the lowest flow (101 km^3/yr), and relatively low values of POC (56±29 µM C), DOC
460 (500±172 µM C), and SPM (42±38 mg/L); features which are similar to the CAA rivers in our study,
461 Table S1 (Alkire et al., 2017). Note that this exercise was not carried out for Ba due to its highly variable
462 distribution, nor was the Glacier River (#2) included in this comparison due its anomalously high trace
463 metal and SPM concentrations, Tables 1 and S1.

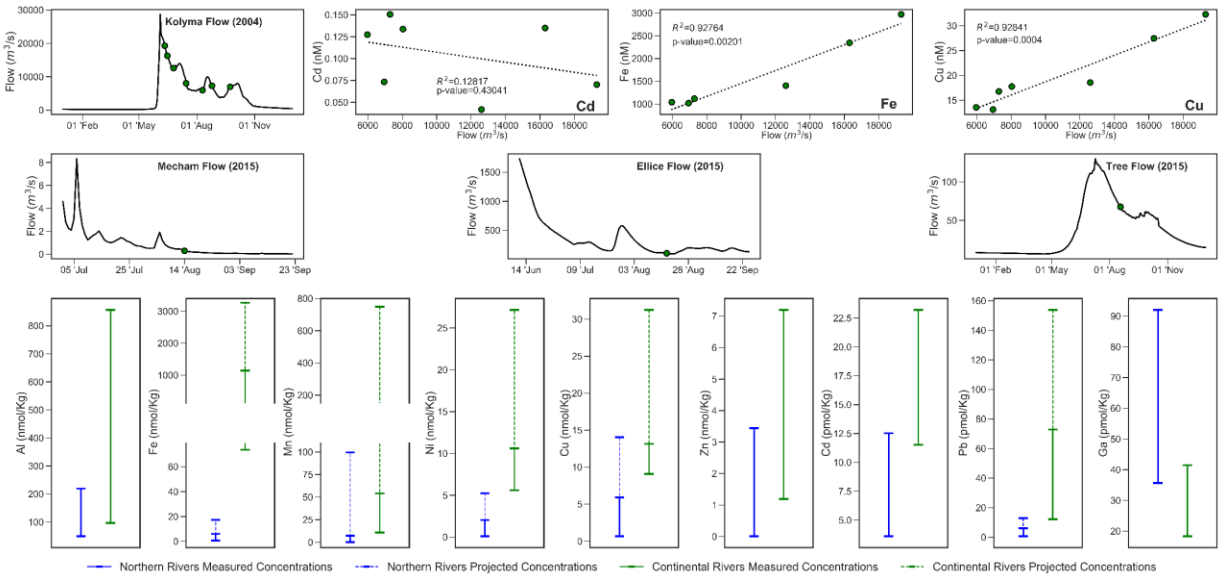

Fig. 5. Upper Panel: average daily discharge of the Kolyma River in 2004, featuring the dates for which trace metal data is available (green dots), and examples of regression analysis of Cd, Fe, and Cu versus flow; data retrieved from Peterson et al. (2016), and Shiklomanov et al. (2018). Full results of the regression analysis are presented in Table S6. Middle Panel: daily discharge of the Mecham, Ellice, and Tree rivers in 2015, featuring the dates when rivers where sampled; data retrieved from the Water Survey of Canada (2017). Lower Panel: ranges of dissolved trace metal concentrations measured for northern and continental CAA rivers and projected concentrations during the high flow season (dashed lines).

The range of dissolved trace metal concentrations measured for northern and continental CAA rivers and the projected concentrations during the high flow season (spring freshet) are presented in Fig. 5, lower panel. Based on the dissolved trace metal concentrations measured in this study, rivers located in northern and central CAA with bedrock characterized by Paleozoic sedimentary rocks (e.g., Melville, Bathurst, Cornwallis, Devon, Somerset, Baffin, Prince of Wales islands; Fig. 1) are predicted to have relatively low values of Al, Fe, Mn, Ni, Cu, Cd, and Pb, as well as high values of Ga (Fig. 5, lower panel). On the other hand, rivers draining from the Canadian continent with bedrock characterized by old Archean intrusive rocks (e.g., continental Nunavut; Fig. 1) are predicted to have relatively high concentrations of Al, Fe, Mn, Ni, Cu, Cd, and Pb, as well as low values of Ga (Fig. 5, lower panel). As CAA rivers were sampled during the low flow season, we anticipate trace element concentrations to differ during the high flow season, as exhibited for many Arctic rivers. Based on the seasonal behavior of Kolyma, we project high flow concentrations to be approximately 190, 1280, 160, 140, and 110 % higher than low flow concentrations for Fe, Mn, Ni, Cu, and Pb, respectively (Table S6 and Fig. 5, lower panel).

Similar increases of dissolved trace metal concentrations (~100% to more than 1300%) during the high flow season have been reported for other small Arctic rivers draining coastal Alaska and Russia (Barker et al., 2014; Guay et al., 2010; Pokrovsky et al., 2010; Rember and Trefry, 2004), and the estimated high flow concentrations for the small CAA rivers in our study are within the ranges of those reported for other small Arctic rivers during the spring freshet period (Table S5 and references therein). It is worth mentioning that the effect of the spring freshet in enhancing the concentrations of insoluble trace metals is expected to be larger in continental CAA rivers than in the northern ones. Watersheds of the small, coastal draining rivers in the southern CAA are characterized by the presence of wetlands, higher soil organic carbon content, as well as increased discharge and DOC concentrations compared to the central and northern CAA rivers, where watersheds are characterized primarily by exposed bedrock (Alkire et al., 2017; AMAP, 1998; Bring et al., 2016; Hugelius et al., 2014; Tarnocai, 2018). These differences are likely to have an influence on the complexation and sources of trace metals (Barker et al., 2014).

In order to provide some context to evaluate the influence of trace metal inputs from small CAA rivers into the marine environment, we compared the concentration measured in this study with those reported for Canada Basin surface waters that would be transiting through the CAA. For most of the CAA rivers, the concentrations of dissolved Al (~20-344 times), Ba (~2-8 times), and Ga (~3-22 times) are higher than those found in the Canada Basin, suggesting that these rivers could act as a potential source for these metals as they mix with Canada Basin derived waters within the CAA coastal system (Giesbrecht et al., 2013; McAlister and Orians, 2015; Thomas et al., 2011). Additionally, the Glacier River and rivers in the southern CAA have higher concentrations of Mn (~3-40 times), Fe (~40-550 times), Cu (~7 times), and Pb (~3-16 times) than those reported in the Canada Basin (Cid et al., 2012; Colombo et al., 2019; Kondo et al., 2016), indicating these rivers could also increase metals loads to ocean waters transiting the CAA, provided these metals make it through the local estuarine zones. Estuaries are highly productive transition environments (Arhonditsis et al., 2007; Fichez et al., 1992) where, in addition to particulate settling, the increase of ionic strength in the river-water interface leads to

complex processes such as flocculation, scavenging, precipitation which affect the distribution and concentration of trace metals (Boyle et al., 1974; Bruland et al., 2013; Tanguy et al., 2011). On the other hand, the concentrations of Ni, Zn, and Cd in Canada Basin surface waters are in the same range or higher than those found in small CAA rivers (Cid et al., 2012; Kondo et al., 2016), suggesting that CAA rivers would serve to dilute these trace metals in transiting waters.

This study reports the first survey of dissolved trace metal concentrations for coastal draining rivers in the Canadian Arctic Archipelago, a necessary step in determining their influence on the distribution of trace elements in CAA marine system. Due to the lack of seasonal observations, we are unable to estimate fluxes of trace metals to the CAA marine system, as any estimates would be highly uncertain. Further research is needed to establish budgets of trace metal fluxes from CAA rivers to the coastal marine environment, including a comprehensive investigation of the seasonal variability of trace metal concentrations and their behavior along the river-ocean mixing-gradients as they are transported into river estuaries.

4.3 Particulate Trace metals: sources, enrichment factors, and lead isotopic analysis

Unlike dissolved trace metals, particulate distributions did not show any spatial trends, as their concentrations are controlled primarily by river SPM. For instance, the anomalously high concentrations of particulate trace metals observed in the Glacier River (#2) can be explained by the high concentration of particles of this river. Glacier River has a high suspended particulate concentration likely composed of glacial flour, and had a SPM concentration of 261.65 mg/L, much higher than values measured for the other rivers (from ~0.03 to ~19 mg/L, Table S1). Trace element concentrations in SPM are largely influenced by grain-size composition, as metals are usually concentrated on fine-grained materials such as clays (Covelli and Fontolan, 1997; Windom et al., 1989). In this study, trace element concentrations were normalized for grain-size and mineralogical variability using Al as a grain-size proxy; this element is one of the most important constituents of aluminosilicates, the main group of minerals found in fine sediment fractions. Al has been extensively used as a proxy in numerous studies because of its high natural

abundance in the earth's crust, the relative constant ratio of metal to aluminum in crustal rocks, and scarce anthropogenic sources (Covelli and Fontolan, 1997; Guieu and Martin, 2002; Windom et al., 1989; Yigiterhan et al., 2011).

Elemental to Al ratios measured in SPM were compared to average upper continental crustal (UCC) ratios in order to determine if external sources, or sources differing greatly from UCC elemental composition, are important in this region. Particulate ratios show two distinctive patterns. For Fe, Mn, Ba, and Ga, the ratios are in agreement with those reported for the UCC (Figs. 3a and S1), reflecting the crustal composition of the catchment basin. Conversely, the Ni, Cu, Zn, and Pb to Al ratios display an enrichment compared to the UCC for those rivers close to mining exploration projects (Figs. 3b, 6 and S1). Regional differences in the composition of the bedrock being weathered, potentially in combination with anthropogenic sources from mining activities, are proposed to be the main drivers of the high EFs of Ni, Cu, Zn, and Pb observed in the Tree (#15), Ellice (#14), Pasley (#12), Cunningham (#7), Garnier (#8), and Mecham (#9) rivers, as well as in Marcil Creek (#4; Fig. 3b and Fig. S1). Alternative explanations such as errors during sampling and/or sample processing and different particle distribution, characterized by more Fe/Mn oxyhydroxides than aluminosilicates, are not expected to influence the particle ratios. Contamination during sample processing is always a risk when working with trace elements; however, solution and filter blanks were always low and all the samples were corrected by blank subtraction. Some authors reported shifts in the SPM spectrum that can alter the Me/Al values. A commonly studied case is the adsorption of trace metals onto Fe/Mn oxyhydroxide particles, increasing the ratio of these elements over Al (Hölemann et al., 2005; Yigiterhan et al., 2011). The fact that the only elements that show an enrichment over the crustal composition are Ni, Cu, Zn, and Pb, and not Ba or Ga, suggests that oxyhydroxides are not the main factor explaining the distinctive ratios observed in this study.

Although the average crustal composition used to calculate these EFs agree with those reported for the Canadian Precambrian shield (Shaw et al., 2008), regional differences do exist. Sediment-hosted Zn, Cu, Ni, and Pb deposits, metal-bearing volcanogenic massive sulphide (VMS) deposits, and gold deposits

are present in CAA (Bigio et al., 2015; Morrison, 2004; Savard et al., 2000). Owing to the economic importance of these deposits present in Nunavut (Galley et al., 2007; Nassichuk, 1987), this region has been a site of mining exploration and development since the1970's (Morrison, 2004; Nassichuk, 1987). In 2015 alone, more than 40 mining projects were active and 132 prospecting permits were issued in Nunavut (Bigio et al., 2015; Fig. 6). In addition to local point sources, long-range atmospheric transport of metals to the Arctic and Antarctic regions, including Pb, Cu, Zn, Cd, Ni, and Cr, whose anthropogenic emissions have largely surpassed natural emissions (Callender, 2013; Nriagu, 1996), have been widely reported in the literature and studied through the analysis of ice core samples (Boutron et al., 1995, 1994; Callender, 2013; Johansson and Tyler, 2001; Nriagu, 1990).

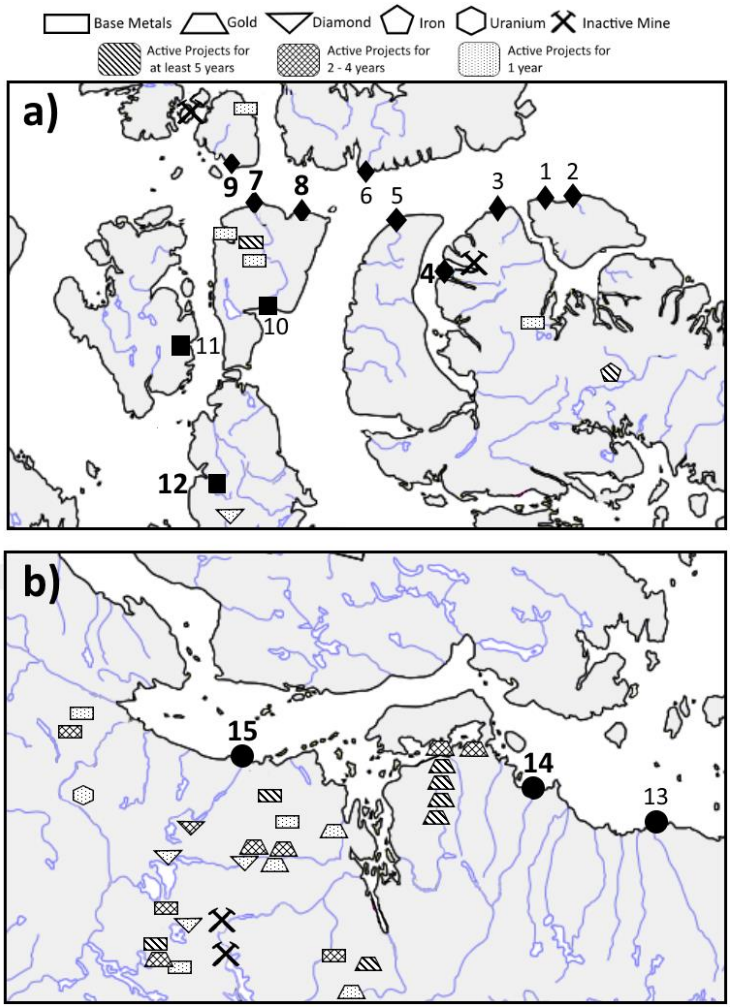

Fig. 6. Mining exploration projects carried out in Nunavut from 2011 to 2016 (Bigio et al., 2015, 2014; Costello et al., 2011; Senkow et al., 2013, 2012). a) northern and central Arctic rivers and b) continental Arctic rivers. The sampled rivers for trace metals are indicated by filled black diamonds, squares and circles; bolded numbers indicate those rivers which are located in close proximity to active mining exploration projects and/or communities. The names of the sampled rivers are presented in Table 1.

In order to assess whether anthropogenic or non-anthropogenic related sources are driving the high EFs observed in some rivers, we further investigate the sources of particulate trace metals in this region analyzing the Pb isotopic composition of SPM from 11 CAA rivers. These rivers were extremely heterogeneous in their Pb isotopic composition (Fig. 3c), displaying a large range from the Tree River ($^{206}Pb/^{207}Pb$: 1.5121 and $^{208}Pb/^{206}Pb$: 1.6670) to the Glacier River ($^{206}Pb/^{207}Pb$: 1.0153 and $^{208}Pb/^{206}Pb$: 2.4238). Most of the remaining rivers have values ranging between 1.1913 and 1.3321 for $^{206}Pb/^{207}Pb$ and between 2.0612 and 1.9030 for $^{208}Pb/^{206}Pb$. The large range of particulate lead isotope data observed may be related to the diversity in composition and age of the bedrock geology across CAA (Fig. 1). Lead isotopes indicate that external sources of metals, coming from long-range atmospheric transport as well as from fossil fuel combustion by heavy machinery operations used in mines and communities, are not the main factors explaining the enrichment of Pb as well as other anthropogenic metals (e.g., Ni, Cu, and Zn) observed in some CAA rivers. If external sources of Pb were the major sources of Pb enrichment, it might be expected that they would have similar Pb isotopic compositions and loadings. This should lead to a correlation between Pb enrichment and Pb isotopes, however, this is not observed in our data (Fig. 3d). In addition, CAA rivers that are closest to mining exploration projects (with the highest EFs) have similar Pb isotopic ratios to those rivers located far away from mines (with the lowest EFs), suggesting that Pb is from natural local sources (Fig. 3d). Lead isotopic data lend an alternative explanation for the extremely high EFs of Pb, Ni, Cu, and Zn observed in CAA rivers located in closest proximity to mining exploration projects. Regional VMS and sediment-hosted mineral deposits are well known to be naturally enriched in base metals and gold (Galley et al., 2007), and hence, may explain the local enrichments of some metals for those rivers located close to mineral deposits. Detailed upstream and downstream sampling around mining areas would be needed to ascertain whether the preferential exploitation of VMS and sediment-

hosted mineral deposits was contributing to local trace metal enrichment, or if the high EFs observed reveal the natural weathering processes of watersheds containing these rocks-types.

5 Conclusions

Dissolved trace metal concentrations measured in 14 small, coastal draining rivers in the CAA are generally lower than values reported for others Arctic and world rivers. This is particularly notable for rivers from the northern CAA, which have some of the lowest trace metal values ever reported for freshwater systems. This study demonstrates that the distribution of dissolved trace metals across the CAA is largely influenced by the South- North environmental gradients (e.g., DOC) and the bedrock geology of the region. Linking the spatial variability of trace elements to the seasonal data available from the Kolyma River, we estimate that spring peak discharge from CAA rivers could have dissolved trace metal concentrations on the order of ~200% of the values we measured during low flow in summer for most metals. Particulate trace metals show an enrichment of Pb, Ni, Cu, and Zn relative to the average crustal composition in rivers located near active mining exploration projects. Nonetheless, as this enrichment is not accompanied by any noticeable trend in Pb isotopic signatures, external sources are not considered responsible for the high EFs, but instead, enrichment of these elements appears to be due to local sources. This study establishes a baseline of dissolved and particulate trace metal data in small rivers across the CAA, and highlights the importance of continued investigations of spatial and temporal distributions of trace metals within Arctic rivers draining coastal permafrost systems, which are sensitive to both climate change and increased anthropogenic activities.

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