Late season mobilization of trace metals in two small Alaskan arctic watersheds as a proxy for landscape scale permafrost active layer dynamics


1. Introduction

Climate warming in the Arctic has led to increasing air temperatures (Peterson et al., 2002; Arndt et al., 2010), resulting in thawing of permafrost and the downward migration of the seasonally thawed active layer into previously frozen material (Hinzman and Kane, 1992; Osterkamp and Romanovsky, 1997, 1999; Jorgenson et al., 2006; Christiansen et al., 2010; Romanovsky et al., 2010; Smith et al., 2010). This active layer response to climate warming may influence the geochemical composition of rivers in the Arctic via increasing trace element transport, increasing organic carbon mobilization, and evolving biogeochemical cycles, among other factors (Vuceta and Morgan, 1978; Kane et al., 1989; McNamara et al., 1997; Rember and Trefry, 2004; White et al., 2007; Muskett and Romanovsky, 2011; Pokrovsky et al., 2011). This partly reflects the fact that the majority of subsurface flow in permafrost systems occurs in the active layer (McNamara et al., 1997). Consequently, the downward expansion of the active layer may increase the exposure of labile mineral phases to weathering processes and provide an enhanced weathering signal in soil-pore and surface waters.

In the absence of mining or industrial activities, mineral weathering is the major source of trace metals to surface waters in pristine Arctic rivers. Therefore, developing a mechanistic understanding of trace metal behavior and transport in the subsystem of soils and surface waters provides insight into active layer chemical weathering processes. In addition, the redox environment of a given watershed controls trace metal mobility. As a consequence, observations of changes in fluxes of redox sensitive elements can be used to evaluate redox conditions.

Increasing air temperatures in the Arctic have the potential to degrade permafrost and promote the downward migration of the seasonally thawed active layer into previously frozen material. This may expose frozen soils to mineral weathering that could affect the geochemical composition of surface waters. Determining watershed system responses to drivers such as a changing climate relies heavily on understanding seasonal controls on freshwater processes. The majority of studies on elemental concentrations in Arctic river systems have focused on sampling only from spring snowmelt to the summer season. Consequently, there remains a limited understanding of surface water geochemistry, particularly with respect to trace metals, during late fall and early winter.

To examine the variability of metal concentrations as a function of seasonality, we measured trace metal concentrations from spring melt to fall freeze-up in 2010 in two high Arctic watersheds: Imnavait Creek, North Slope, Alaska and Roche Mountanee Creek, Brooks Range, Alaska. We focused on aluminium (Al), barium (Ba), iron (Fe), manganese (Mn), nickel (Ni) and zinc (Zn). Concentrations of ‘dissolved’ (<0.45 μm) Al, Ba, Fe, and Mn in Imnavait Creek waters and Ba in Roche Mountanee waters were highest in late fall/early winter. To link observed surface water concentrations at Imnavait Creek to parent soil material we analyzed the elemental composition of a soil core from the watershed and tracked the soil temperatures as a function of time and depth. The results from this study show a distinct seasonal signature of trace metal concentrations in late fall that correlates with the depth of the thawed active layer.

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Many studies have used biogeochemical tracers such as dissolved organic carbon, radiogenic isotopes, nutrient fluxes and major ion concentrations to investigate watershed dynamics, permafrost degradation, carbon sources, the timing of spring melt, and seasonal controls on elemental export (Cooper et al., 2005; 2008; Petrone et al., 2006; Keller et al., 2007; 2010; McClelland et al., 2007; Townsend-Small et al., 2010; Bagard et al., 2011). However, only a few studies have employed trace metals as a proxy for permafrost dynamics at the watershed scale (Martin et al., 1993; Dai and Martin, 1995; Rember and Trefry, 2004; Bagard et al., 2011). Furthermore, most of these studies only measured concentrations of trace metals in surface water samples without considering the composition of soil and soil pore water, and none have examined dissolved trace metal data in the context of the soil thermal regime (i.e., the timing of thawing and freezing of the active layer). As a result, there is a lack of information linking the trace metal composition of subsurface and surface flow within Arctic watersheds to the geochemistry of underlying soils and seasonal permafrost active layer dynamics.

Trace metal concentrations in surface waters fluctuate on a seasonal basis partly due to variations in precipitation, temperature, the extent of active layer thaw, and the composition of the underlying soils. The degree to which the watershed responds to climate warming can also play a role in trace metal fluctuations, as a whole (Hinzman et al., 1991; Bagard et al., 2011). Due to the strong seasonality of Arctic freshwater processes (Chapin et al., 2005; Bagard et al., 2011), the response of riverine trace metal signatures to increasing active layer depth should be most evident during late fall, when the active layer is at its deepest yearly extent and the base flow component is increasing toward the yearly maximum values, as was observed in two major Russian Arctic rivers for almost 60 years (Peterson et al., 2002; Yang et al., 2002; Hinzman et al., 2005). Any changes to the overall source of major and trace elements to subsurface flow in late fall could potentially be evident as a pulse, different than the signature of a baseflow dominated stream, which is the expected dominant contributor of trace metals to surface waters during this time of the year in the Arctic. Many studies reporting trace and major element concentrations in Arctic river systems have only focused on spring and/or summer flow regimes (Martin et al., 1993; Dai and Martin, 1995; Guieu et al., 1996; Rember and Trefry, 2004). As such, there remains a limited understanding of trace metal transport and behavior in Arctic rivers during late fall and early winter (Bagard et al., 2011) when mineral weathering processes continue to occur deep in the soil column.

It is also possible that major and trace ions mobilized in late fall are stored in the shallow subsurface during freeze up and contribute to the following year’s spring thaw signal. Mobilization of major and trace elements to surface waters during early spring is typically attributed to spring snowmelt when precipitation that has accumulated during winter is released (McNamara et al., 1997; Rember and Trefry, 2004; Petrone et al., 2006). However, elemental transport to surface waters during spring snowmelt potentially encompasses contributions from previously mobilized species stored in the surficial layers as well as input from the snowpack (Bagard et al., 2011). With increasing depth of permafrost thaw and the potential increase in late fall mineral weathering fluxes to watersheds, there are potential ramifications for a change in biogeochemical fluxes from watersheds during the spring and fall seasons. Our goal was to examine whether trace metal concentrations in surface water draining areas of continuous permafrost can provide a signal of permafrost active layer dynamics distinguishable over normal variability at the watershed-scale. Since our data is not part of a multi-year dataset, we primarily aim to identify whether there is a seasonal aspect to river trace metal geochemistry and establish a baseline of measurements for longer-term monitoring in the future.

Surface water samples were collected and analyzed for trace metal analysis from spring melt in mid-May through the initiation of fall freeze-up in mid-October. We mainly focused on Imnavait Creek, a small headwater stream underlain by continuous permafrost and dominated by tussock sedge tundra with organic-rich soils (Osterkamp and Payne, 1981; Walker et al., 1989). In the Imnavait watershed, we excavated a 1 meter deep soil pit to identify and define soil horizons, and we collected a 61 cm soil core to quantify the vertical distribution of trace metals. Thermistors were installed into the active layer to continuously measure soil temperature as a function of depth.

As a relatively small, low gradient stream dominated by organic-rich soils, Imnavait Creek typifies many small watersheds throughout the high Arctic. We also collected samples from Roche Mountanee Creek as an analog for permafrost active layer processes occurring in higher gradient, larger watersheds containing primarily exposed bedrock. As a result, our findings from these end member drainages have utility for extrapolation to broader areas in the Arctic.

To achieve our goals, we: (1) quantified variations in metal concentrations as a function of seasonality in two high Arctic streams, (2) characterized metal concentrations in soil layers within the Imnavait Creek watershed and relate them to freezing and thawing processes, (3) tracked the influence of water sourcing from the snowmelt signal, precipitation and groundwater signal on trace metal fluctuations in surface waters, (4) developed a conceptual model relating trace metal chemical composition in surface waters to permafrost active layer dynamics at Imnavait Creek, and (5) compared the model to the seasonal variability in metal concentrations at a physiographically different watershed to determine if relationships identified in Imnavait Creek are broadly applicable to other Arctic watersheds.

2. Materials and methods

2.1. Field study

Two watersheds located in the northern foothills of the Brooks Range in the Alaskan Arctic were examined in this study: Imnavait Creek (2.2 km²) and Roche Mountanee Creek (89 km²) (Fig. 1). Imnavait Creek is a small headwater stream located in a valley formed on Sagavanirktok glacial till (Hamilton, 1986). A network of water tracks drains the hillslopes of the watershed and the creek is comprised of a chain of small ponds intermittently connected by water tracks that flow into the Kuparuk River (McNamara et al., 1997). The area is dominated by erosional topography (Black, 1976) underlain by continuous permafrost 250 to 300 m deep (Osterkamp and Payne, 1981). Vegetation predominantly consists of tussock sedge tundra (Walker et al., 1989) with organic rich soils and sphagnum moss/ericaceous plants (Kane et al., 1989). This accumulated acidic vegetation, as well as the saturated soil conditions, are primary contributors to the overall low pH values of stream water (approximately 4.5–6.5) throughout the summer (Everett et al., 1989; Walker et al., 2002).

The soils at Imnavait Creek are organic-rich, poorly drained silt loams covered by a peaty layer. They consist of highly weathered clays and silicates under acidic and often waterlogged conditions during the spring and summer (Walker et al., 1989; Kane et al., 2000). There are also embedded mineral layers consisting of silt overlying glacial till (Kane et al., 1989; McNamara et al., 1997, 1998). The soil is weathered to a greater extent than areas south of the North Slope within the Brooks Range (Fig. 1), and the parent material may less effectively neutralize organic and carbonic acids (Ping et al., 1998). Portions of the soil profile have been described as having a high chroma color, indicating the oxidation of iron minerals, whereas adjacent zones are gleyed, pointing to more reducing conditions (Ping et al., 1998).

Roche Mountanee Creek is located approximately 30 km south of Imnavait Creek along the Dalton Highway. The drainage basin has extensive bedrock exposure and is underlain by continuous permafrost. In addition to some tussock sedge tundra along the lower section of the watershed the predominant vegetation is a low-lying alder bush. The area has shrub-covered lowlands and tundra-covered and rocky uplands. Ridgelines reach about 1.5 km above sea level. The pH of this river ranges from circumneutral to slightly basic due to the carbonate-rich terrain and the minimal presence of organic vegetation and soils (Till et al., 2008).

A total of 60 surface water samples were collected from Imnavait Creek and Roche Mountane Creek between early May and mid-October 2010. We extracted a soil core from the Imnavait drainage and installed a thermistor string within the Imnavait watershed (Onset Computer Corporation, Bourne, MA) to continuously monitor soil temperatures at four depths spanning from the surface to approximately 60 cm depth.

2.2. Soil core collection and analysis and soil pit excavation

A soil core representing the upper 60 cm of the soil column in the Imnavait watershed was extracted using a 10 cm diameter Snow, Ice, and Permafrost Research Establishment (SIPRE) corer. The core was collected from the same location into which the vertical thermistor string was installed (Fig. 1). The core was collected during the winter of 2009, wrapped frozen in freezer paper (Reynolds, Lake Forest, IL), transported and stored frozen in a cold room until analysis. The soil core was collected the winter before collecting surface water samples. The collected core represents approximately 40 cm of material that thaws each year and approximately 20 cm of the permafrost. The collected core was within 20 level meters of the main drainage. A soil pit was excavated in July, 2011 near the coring location that is nearest to the main drainage as shown in Fig. 1.

Excavating a soil pit gave insight to the relative depth of the permafrost-active layer boundary within the watershed. The 1 × 1 meter soil pit was excavated to a depth of 90 cm with shovels and a jackhammer and soil horizons were identified following established soil classification methods (Soil Survey Division Staff, 1993; Ping et al., 2013). In addition, we tested for reducing conditions of a hydric soil system using alpha–alpha-dipyridyl, as outlined in Ping et al. (1998), and alpha-dipyridyl, as outlined in Ping et al. (1998), and established by the U.S. Department of Agriculture, Soil Survey Division Staff, 1993.

The frozen soil core was sectioned into 5 cm long sub-samples using a band saw with a carbon steel blade (93.5 in × 3/8 in. with 6 tpi) in a cold room at the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) facility on Fort Wainwright, AK. The frozen core sections were thawed for 24 h at approximately 22 °C in plastic bags. Pore water was separated from the soil solids by centrifugation (7000 rpm for 20 min). Water samples were decanted, passed through 0.20 µm nylon filters (Whatman, Kent, United Kingdom) fitted to a sterile plastic syringes and acidified with 6 N ultrapure HNO₃. Soil pore water samples were analyzed following the ICP-MS procedures outlined in the next section for surface water samples.

Each 5 cm subsection of the core was dried at 50 °C for approximately 12 h overnight and sieved to <75 µm (≈#200 sieve). Approximately 5–7 gram subsamples were mixed with 5–7 drops of a binder (polyvinyl alcohol) and pressed into a powder pellet using a hydraulic bottle jack at 20,000 psi. Each pellet was analyzed using a PANalytical (Almelo, The Netherlands) Axios four kilowatt wavelength dispersive X-ray fluorescence spectrometer (XRF). The calibration standards for major elements were made using the geologic reference materials BIR-1, PCC-1, JA-2, JB-2, JP-1, JR-1, GXR-3, GXR-1, MRG-1, and SGR-1, as described in Ilgen et al. (2011). Samples and standards were analyzed in triplicate with corresponding errors reported and detection limits calculated based on analysis of the reference standards.

2.3. Surface water collection and analysis

All water sample collection sites were located upstream of the Dalton Highway as depicted in Fig. 1. Nitrile gloves were worn while sampling and water was collected from the main channel of flow using a peristaltic pump outfitted with Masterflex Tygon E-LFL pump tubing (Cole-Parmer, Vernon Hills, Illinois) and precleaned 0.45 µm polycarbonate medium-capacity filter capsules (Geotech Environmental Equipment, Denver, CO). The tubing and filter capsules were flushed for a minimum of 10 s before collecting samples into trace metal grade precleaned acid washed 125 mL HDPE bottles. Samples for trace metal analysis were acidified within 6 h of collection with 6 N ultrapure HNO₃ (Baseline Nitric Acid, Seastar Chemicals, Sidney, BC) in a clean hood at the Toolik Field Station. Samples for chloride analysis were filtered using the same procedure as the trace metal samples, but the chloride samples were not acidified.

Chloride concentrations were quantified on a Dionex ICS-3000 ion chromatograph with an AS–19 anion column (Dionex Corporation Sunnyvale, California) at the CRREL Alaska Geochemistry Laboratory. Each sample had a 10 mL injection volume. A gradient method using potassium hydroxide eluent ranged from 20 mM to 35 mM for anion analyses.
The system flow rate was 1 mL/min and the operating temperature was 30 °C. The ion chromatograph was calibrated through repeat analysis of five calibration standards with concentrations ranging from 0.1 to 120 mg/L. Peaks were identified using Chromel (Dionex, Sunnyvale, California) and were verified visually. Laboratory analytical anion standards with values from 0.1 to 120 mg/L were analyzed repeatedly to verify system calibration and assess analytical precision. Based on these analyses the calculated precision for the analyses is ±5%.

Surface and soil pore water trace metal concentrations were measured using an Agilent 7500ce (Agilent Technologies, Santa Clara, CA) inductively coupled plasma-mass spectrometer (ICP-MS) at the University of Alaska Fairbanks Advanced Instrumentation Laboratory following the general procedure outlined in Creed et al. (1994). To minimize polyatomic interferences from ions having identical mass-to-charge ratios. Percent relative standard deviation (% RSD) values were the mass of the volume delivered was monitored with an analytical balance. Combined error is included in the form of error bars presented in Figs. 6 and 8.

The surface waters of Immnavait Creek and Roche Mountain were monitored for in-situ pH measurements during the collection of each sample using a YSI-probe-600XL (YSI, Inc., Yellow Springs, Ohio). The pH probe was calibrated twice per day with pH 4.0 and 7.0 buffer solutions provided by YSI, Inc. The pH probe was located 10 m downstream from the site of sample collection and allowed to equilibrate until the pH measurement stabilized.

2.4. Thermistor installation

A thermistor array was installed in the Immnavait watershed study area in 2009 after the soil core described above was extracted (Fig. 1). The core material was removed and an array of four thermistors, attached to a wooden stake, was lowered into the hole. Temperature probes were set approximately 1, 29, 42 and 53 cm depth. The depth of each thermistor was measured from the ground surface, and a slurry of water mixed with local soil was poured into the hole. The thermistors were connected to a battery powered ONSET-HOBO U12 datalogger (Onset Computer Corporation, Bourne, MA) that recorded temperatures hourly in degrees Celsius.

3. Results

3.1. Soil pit profile and chemical composition of soil column

A photograph of the Immnavait Creek soil pit profile and detailed horizons is shown in Fig. 2. The top portions of the horizons have a high chroma color, whereas the lower portions appear more gleyed, potentially signifying a redox boundary. We further tested the lower portion of the soil (~5 g excavated at roughly 50 cm depth) with 3–5 drops of alpha–alpha-dipyridyl yielded a positive pink color within 30 s, signifying the presence of ferrous iron and reducing conditions. In addition, there was a clear difference in color along the soil horizons and the different redox zones were observed visually upon excavation of the soil pit in Immnavait Creek. The upper 0–20 cm portion exhibited the typical orange-rust color characteristic of Fe(III) during and after excavation. Upon excavation of the lower 25–90 cm, the soil horizons initially screened for any significant errors. Values were then corrected for background using repeated analyses of blanks. Measurement error was assigned to each sample analyzed based on the triplicate measurements, as shown in each data table. Errors associated with dilution are estimated to be within ±5% based on repeat tests of delivery pipettes with an analytical balance. Combined error is included in the form of error bars presented in Figs. 6 and 8.
displayed a dark, lustrous gray-black color but within minutes of being exposed to the atmosphere, orange-rich bands began to appear from 25 to 90 cm. The optical image in Fig. 2 was taken approximately 5 min after excavation of the full soil pit and after the testing with alpha-alpha-dipyridyl. This change in soil chroma as a function of excavation time likely reflects in-situ oxidation of Fe(II) to Fe(III).

Within the watershed and adjacent to the soil pit, we collected a 61 cm soil core. Vertical metal concentrations in mg/kg (ppm) determined by XRF are provided in Table 1 and plotted as a function of soil core depth in Fig. 3. Fe, Mn, and Zn are enriched in the organic layer, likely due to their association with natural organic matter (NOM) (Fig. 2). By comparison, Al, Ba, Cr, Ti, and Zr, as well as Rb, and V (not shown in Fig. 3, but data provided in Table 1) are enhanced in the lower soil horizons. Ni concentrations stay relatively constant throughout the soil core (Table 1). Because Cr and V typically accumulate in reducing zones, their enriched concentrations relative to the upper portions of the soil column can serve as a proxy for more reducing soil conditions (Kimbrough et al., 1999). This clear separation between metals either in soluble species in both the upper (~3–15 cm) and deeper (~20–50 cm) parts of the soil column.

### 3.2. Soil thermal regime

Temperature data from the thermistor installed at Imnavait Creek is shown in Fig. 5. The soil temperature at the surface correlates with fluctuations in the local ambient air temperature. During the Arctic spring, soil predominantly thaws from the top-down. The soil at 0, 29, 42 and 53 cm depth was fully frozen on April 28, 2010 when we initiated measurements. Thawing (temperatures rising above 0 °C) began on May 13 at the surface, on May 23 at 29 cm depth, on June 12 at 42 cm depth and on July 29 at 53 cm depth.

### 3.3. Surface water metal concentrations and pH at Imnavait Creek

Surface water concentrations of Al, Ba, Fe, Mn, Ni, and Zn (in μg/L) are provided in Table 3 and are plotted as a function of sampling date in Fig. 6. The remaining measured metals mentioned in the Materials and methods section were at or below the detection limit of the analytical method. Late fall and early winter yielded the highest stream water concentrations of Al, Ba, Fe, and Mn in Imnavait Creek. Ni concentrations were relatively constant throughout the summer. Zn behaved similarly to Mn except that concentrations did not rise during late fall, consistent with the observation that Zn does not have an enhanced solubility signature deeper in the soil column (Fig. 4). Mn and Zn concentrations peaked during spring snowmelt and late fall. All other metals exhibited a gradual increase in concentrations until the end of September, with peak values in early October. In contrast, Fe, Al, Ba and Ni did not exhibit high, relative concentrations during the spring snowmelt, like Mn and Ni.
Two factors could explain this observation: (1) low, relative solubility of the species present in the top layers of the surface and/or (2) peak values for these specific metals as a result of the snowpack melting and top soil layers thawing occurred before our sampling campaign commenced. Highest measured concentrations of 175.6 μg/L (Al), 15.4 μg/L (Ba), 3383.0 μg/L (Fe), and 165.2 μg/L (Mn), occurred on October 8, 2010. Maximum Zn concentrations of 4.3 and 4.4 μg/L occurred on May 19 (spring freshet) and August 7. Ni concentrations stayed relatively constant between 1.1 and 2.0 μg/L throughout the melt season.

The pH values for Imnavait Creek as a function of sampling date are presented in Fig. 7. Imnavait Creek exhibits acidic surface water conditions for the entirety of summer. In the spring, pH values are at their lowest for the entire season, dipping below 5 to a value of 4.79 on May 17, 2010. For the majority of late May–June, pH values range from 5.54 to 6.02, with an average of 5.80. Throughout the end of July until mid-August, pH values range from 5.06 to 6.62, with an average value of 5.71. During late fall, pH fluctuates to a greater extent in September than October. Imnavait Creek surface water in September had an average pH of 5.99, ranging from 5.32 to 6.64. For October, the average is 5.65, ranging from 5.24 to 6.00. Overall, Imnavait Creek in late fall/early winter, including both September and October months, exhibits an average pH of 5.84, ranging from 5.24 to 6.64. The lowest pH for the time period occurred in October and the highest pH occurs in September.

3.4. Surface water metal concentrations and pH at Roche Mountanee Creek

Metal concentrations observed in the surface waters of Roche Mountanee Creek in 2010 are provided in Table 4 and plotted as a function of sampling date in Fig. 8. Al, Fe and Mn concentrations increased during the first spring melt flows in mid-May, when flow predominately originates from surface soils and the organic layer. Al and Fe also exhibited increased concentrations during rain events in late July and early August. In the fall, Al, Fe, and Mn concentrations decreased to the lowest values measured, mostly hovering at or below their respective detection limits. The pattern for Ba in Roche Mountanee Creek mimics the patterns for Al, Ba, Fe, and Mn in Imnavait Creek with the highest concentrations occurring in late fall. The highest measured Ba concentration of 70.0 μg/L occurred on October 13. On May 18, Al, Fe

Fig. 3. Vertical metal distributions in soil core collected from Imnavait Creek watershed in late March/early April 2009. Metal distributions show element enhancement associated with (a) the organic layer in an oxidizing zone or (b) in the lower portion of the soil column in a reducing zone.
and Mn concentrations peaked at 107.0, 194.8, and 4.2 μg/L, respectively.

The pH values for Roche Mountanee as a function of sampling date are presented in Fig. 7. For the most part, Roche Mountanee surface water is slightly basic. The pH values range from 6.98 to 8.06. The pH values range from 7.17 to 8.03, with an average pH value of 7.75. During the first half of October, pH values range from 7.17 to 8.06, with an average pH value of 7.52. The lowest observed pH value occurs on May 17 and the highest pH value occurred on May 23 and September 13.

4. Discussion

4.1. Seasonal controls on metal fluctuations in Imnavait Creek surface water

As shown in Fig. 4, pore waters in the oxidizing zone (3–15 cm depth) of the organic layer have relatively high metal concentrations. In comparison, pore waters deeper in the soil column (20–50 cm) also exhibit an enhanced relative mobility of metals, particularly for Fe, Al and Ba and to a lesser extent Mn and Zn. This depth corresponds to the typical maximum vertical extent of seasonal thaw (the active layer) each fall. In the case of Fe, the soluble-rich bands in both the oxidizing and reducing zones are comparable in terms of their bulk aqueous metal concentrations (Fig. 4). However, when compared to the source concentration originally present in the core in solid form (Fig. 3), the difference is substantial. There is approximately 140,000 mg/kg Fe present in the 15–20 cm portion of the organic layer with approximately 0.4 mg/L in soluble form. In comparison, there is approximately 25,000 mg/kg Fe present in the reduced zone lower in the soil column (35–50 cm) and approximately 4 mg/L becomes mobilized upon thawing.

To better visualize the relative metal solubility data presented in Figs. 3 and 4, we plotted the metal partition coefficients (Kd) as a function of depth of the soil core in Fig. 9. Kd values were calculated using the ratio of metal concentrations in the solid fraction of the soil core to the metal concentrations in the pore water extracted from the soil fraction, values shown in Table 5. Therefore, a small, relative partition coefficient indicates high, relative partitioning from the solid to the aqueous phase.

We do not have bulk metal concentrations for the soil column above 10 cm due to the prevalence of moss and plants instead of actual soil. Fe, Al and to some extent Mn, Ba and Zn exhibit a band of high, relative solubility from 10 to 15 cm. We expected to see evidence of this solubility band by high mobilization of Fe and Al to Imnavait Creek during spring snowmelt (Fig. 6), but as stated previously there is potential that these species present above 10 cm soil depth are not as soluble or Fe and Al mobilized before our sampling began on May 19, 2010. Mn and Zn concentrations have a peak in mid-May (Fig. 6), unlike Fe, Al or Ba, indicating that they are potentially mobilized from the organic layer (above 10 cm) to a greater extent than Fe, Al or Ba. In addition, signal dilution

Table 2
Metal concentrations for soil pore water samples extracted from the soil core collected from the Imnavait Creek watershed. (−) indicates below detection limit, (*) indicates qualitative values outside the calibration.

<table>
<thead>
<tr>
<th>Core 1 (cm)</th>
<th>B (μg/L)</th>
<th>+/-</th>
<th>Al (μg/L)</th>
<th>+/-</th>
<th>Fe (μg/L)</th>
<th>Ti (μg/L)</th>
<th>P (μg/L)</th>
<th>+/-</th>
<th>Sc (μg/L)</th>
<th>+/-</th>
<th>Co (μg/L)</th>
<th>Cu (μg/L)</th>
<th>Cd (μg/L)</th>
<th>Mn (μg/L)</th>
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<tr>
<td>3–5</td>
<td>90.1</td>
<td>0.3</td>
<td>984*</td>
<td>3</td>
<td>3</td>
<td>1.4</td>
<td>3.6</td>
<td>1.4</td>
<td>0.1</td>
<td>4.3</td>
<td>0.1</td>
<td>1.5</td>
<td>0.1</td>
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<tr>
<td>5–10</td>
<td>24.1</td>
<td>0.3</td>
<td>223.9</td>
<td>1.8</td>
<td>1397*</td>
<td>6.6</td>
<td>–</td>
<td>–</td>
<td>3.0</td>
<td>0.1</td>
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<tr>
<td>10–15</td>
<td>–</td>
<td>–</td>
<td>158.3</td>
<td>0.6</td>
<td>405*</td>
<td>5.6</td>
<td>–</td>
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<tr>
<td>15–20</td>
<td>–</td>
<td>–</td>
<td>210.4</td>
<td>4.4</td>
<td>124*</td>
<td>10.0</td>
<td>–</td>
<td>–</td>
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<td>20–25</td>
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<td>–</td>
<td>110.4</td>
<td>2.3</td>
<td>208*</td>
<td>1.5</td>
<td>–</td>
<td>–</td>
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<td>25–30</td>
<td>–</td>
<td>–</td>
<td>13300.0</td>
<td>256.4</td>
<td>572*</td>
<td>11.9</td>
<td>1.2</td>
<td>0.1</td>
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<td>30–35</td>
<td>–</td>
<td>–</td>
<td>10290.0</td>
<td>8.6</td>
<td>136*</td>
<td>1.3</td>
<td>1.9</td>
<td>0.1</td>
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<td>35–40</td>
<td>11.8</td>
<td>0.4</td>
<td>451.5</td>
<td>9.9</td>
<td>89.4</td>
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<td>0.3</td>
<td>237.4</td>
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<th>Sr (μg/L)</th>
<th>+/-</th>
<th>Y (μg/L)</th>
<th>+/-</th>
<th>Ba (μg/L)</th>
<th>+/-</th>
<th>Bi (μg/L)</th>
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<td>–</td>
<td>85.5</td>
<td>1.3</td>
<td>–</td>
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</tr>
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from snowmelt as the sole factor seems unlikely, as we would expect all metals to behave similarly if that were the case.

In the summer months, the soil column continues to thaw and the active layer deepens. This is evident by slightly increasing surface water Fe, Al, Mn, Ni, Zn and Ba concentrations over the course of June, July and August (Fig. 6) correlating with low partition coefficients at soil depths of 20–45 cm (Fig. 9). According to the soil thermal regime (Fig. 5), the soil is thawed for 0, 29 and 42 cm depths at this time, but remains frozen at 53 cm depth.

The soil at 53 cm depth initiated thawing on July 29. All metals exhibit bands of small, relative partition coefficients (high, relative solubility) at depths 45–61 cm. Aluminum follows this pattern at depth 45–50 cm, but at lower depths (50–61 cm) the solubility decreases. The low partition coefficient of these metals in the lower portions of the soil column combined with the subsequent thawing of these layers likely explains the high, relative surface water concentrations in Imnavait Creek in late September and early October. This is evident for Fe, Al, Mn and Ba, but not Zn or Ni. Nickel concentrations stay relatively constant throughout the sampling season, except for in mid-May when they are at the detection limit for the analytical method. Zinc concentrations decrease during late fall, potentially indicative of a limiting Zn source, however, the interpretation of the complex dynamics of Zn mineral weathering during this time of year are beyond the scope of this study. The decrease in Zn concentrations do indicate that discharge is likely not a factor in concentrating the surface water metal signals during this time of year. If that were the case, we would expect all metals to increase late in the season like Fe, Al, Mn and Ba.

### 4.2. Permafrost active layer dynamics inferred at Roche Mountanee Creek

The majority of this project focused on characterizing soil and surface water samples from Imnavait Creek, a small, organic-rich, low gradient tundra stream flowing through glacial till. In an attempt to correlate our findings at Imnavait Creek to a broader area in the Arctic, including to a large watershed with a higher gradient and exposed bedrock, we analyzed surface water from Roche Mountanee Creek (Table 4 and Fig. 8). We did not collect a core, excavate a soil pit, or install thermistors at Roche Mountanee Creek, and no CALM site is present there. Thus, we mainly use the data from Roche Mountanee Creek as an endmember drainage to investigate whether the seasonal dynamics present in Imnavait Creek also occur for a larger, higher gradient stream with different soils, active layer and permafrost composition.

The soils at Roche Mountanee are sourced predominantly from carbonate bedrock with minimal organics present in the surface and shallow subsurface (Till et al., 2008). The Al, Fe and Mn concentrations measured during the spring are derived from the weathering of the thin, upper portions of the subsurface. Once the mineralogical source of those metals weathers and the soil subsequently freezes (assuming temperature fluctuations behave similarly as recorded at Imnavait, Fig. 5), Al, Fe and Mn concentrations substantially drop during the

### Table 5

Partition coefficients ($K_d$) for the Imnavait Creek soil core. $K_d$ values were calculated using the ratio of metal concentrations (g/kg) in the solid fraction of the soil to the metal concentrations (g/L) in the pore water fraction.

<table>
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<tr>
<th>Core 1 (cm)</th>
<th>Iron partitioning coefficient</th>
<th>Barium partitioning coefficient</th>
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</thead>
<tbody>
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<td>$C_aq$ (g/L)</td>
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<tr>
<td>10–15</td>
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<tr>
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<td>0.000154</td>
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<table>
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<th>Zinc partitioning coefficient</th>
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<td>55–61</td>
<td>72.540</td>
<td>0.0001676</td>
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<table>
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<td>$C_s$ (g/kg)</td>
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<td>6.530</td>
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<td>20.950</td>
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<td>50.480</td>
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<tr>
<td>55–61</td>
<td>72.540</td>
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</table>
summer and are at the detection limit of our analytical method during the fall and early winter. We interpret the late season increase in Roche Mountane surface water Ba concentrations as due to the chemical weathering of carbonate in the active layer.

4.3. Surface water trace metal signatures as a function of snowmelt, surface and base flow influence

Discharge and sources of water play a role in the overall transport of metals to surface waters. However, discharge can be difficult to measure when there are multiple main channels or if ice is present. For this study, we employed surface water chloride concentrations as a tracer for estimating the relative amounts of surface versus base flow to Imnavait and Roche Mountane Creeks. We used chloride because it occurs in the environment primarily as a free ion, rarely complexes or forms ion pairs, and moves through soil conservatively without being significantly transformed (Lockwood et al., 1995; Albek, 1999).

Trace metal–chloride relationships for Roche Mountane and Imnavait Creek surface waters are shown in Fig. 10(a) and (b). Only Ba values are presented for Roche Mountane surface water because concentrations of Fe, Al and Mn were primarily present at or below the detection limit for our method. The snowmelt signature is evident as a transient pulse, characterized by high chloride concentrations, derived from the snowpack, and low relative metal contributions. As the snowpack melts and the surface is exposed, the Roche Mountane ‘summer signature’ in Fig. 10 is characterized by low chloride and metal concentrations, attributed to high discharge during the summer rainy season diluting the signal. This seasonal signature of summer illustrates the dominance of overland surface flow and minimal interactions with the active layer. In the fall, pore waters are forced deeper into the soil column by a freezing surface front and lack of significant precipitation, and as a result the water source becomes dominated by base flow, highlighted in Fig. 10 as the ‘fall signature’. The fall signature shows an increase in water–rock interaction, evident by high Ba concentrations and high chloride concentrations. The Roche Mountane surface water in the fall is dominated by baseflow, however, there is still variability in chloride concentrations late in the season, even in October (Table 4), indicating Ba signal concentration due solely to lack of discharge in the season (Fig. 6) is like in not a factor.

For Imnavait Creek, the high chloride-low metal snowmelt pulse is evident. The pulse is absent for Ni because Ni is at the detection limit of our method during mid-May. For Mn, the snowmelt pulse has higher concentrations of Mn, attributed to the enhanced mobility of Mn species to other metals, comparatively, in the superficial layers of the soil. In contrast to Roche Mountane, the summer and fall signatures at Imnavait Creek do not clearly embody surface water contributions versus baseflow dominated, but rather a mixture of the two with different mixing ratios for each metal. In the fall, the geochemical signature of Roche Mountane Creek is dominated by water–rock interaction, whereas for Imnavait Creek surface water the fall represents surface and baseflow interaction with thawing-frozen soil. For Fe, Mn, Al and Ba at Imnavait Creek there is a linear correlation with chloride toward the very end of our sampling campaign, where metal and chloride concentrations are increasing. This correlation is likely due to an increase in water–soil interaction and a decrease in overland surface flow during this time.

4.4. A conceptual model of permafrost active layer dynamics

A conceptual model for the soil thawing and freezing process and the deepening of the active layer throughout the course of 2010 is schematically illustrated in Fig. 11. As our model suggests, the organic layers and upper portion of the soil column begin to thaw following the snow melt in mid-May and are fully thawed by the end of May. This exposes the surface soil to oxidation and weathering processes, releasing soluble metals from the soil and vegetation surface and flushing them into nearby surface waters. Once the soil below the surface and organic layer begins to thaw and the active layer extends downward, acidic pore water from the surface reaches the reducing front of the subsurface and mobilizes metals.
When the soil begins to freeze in the fall, it does so predominantly from the top-down (Fig. 11). Top-down freezing forces pore water flow paths deeper into the reducing zone of the soil column, where Fe, Al, Ba, and Mn are mobile (Fig. 4), and exhibit low, relative partition coefficients. Acidic conditions, deepening flow paths and greater source concentrations with respect to depth during this time of the year contribute to the overall high, relative metal concentrations shown in Fig. 6. Zinc concentrations decrease, potentially signifying a limiting source of Zn, however, the interpretation of the complex dynamics of Zn mineral weathering in late fall is potentially more complex than the scope of this study can interpret. Ni concentrations stay relatively constant likely due to the partition coefficient being relatively constant with respect to depth. During the time of the season when the active layer is at its deepest annual extent, the surface of the soil column is

Table 3
Trace concentrations (μg/L) of species found in Imnavait Creek surface waters over the course of spring through fall 2010. (−) indicates below detection limit (/) indicates samples not analyzed for chloride.

<table>
<thead>
<tr>
<th>Date</th>
<th>Al</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Zn</th>
<th>Ba</th>
<th>Cl</th>
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<td>187.8</td>
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<td>0.1</td>
<td>369.6</td>
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<td>2.9</td>
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<td>3383.0</td>
<td>9.5</td>
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Fig. 5. Imnavait Creek watershed soil temperature (°C) at multiple soil depths as a function of date in 2010. The soil in the Arctic freezes from the top-down forcing pore water flow paths deeper in the soil column.

Fig. 6. Zinc concentrations decrease, potentially signifying a limiting source of Zn, however, the interpretation of the complex dynamics of Zn mineral weathering in late fall is potentially more complex than the scope of this study can interpret. Ni concentrations stay relatively constant likely due to the partition coefficient being relatively constant with respect to depth. During the time of the season when the active layer is at its deepest annual extent, the surface of the soil column is
frozen (late September/October in Fig. 11), and the surface water geochemical composition roughly correlates to the solubility of the metal species in the unfrozen soil layers.

An anticipated increase in active layer thaw depths (Hinzman and Kane, 1992; Osterkamp and Romanovsky, 1997, 1999; Jorgenson et al., 2006; Christiansen et al., 2010; Romanovsky et al., 2010; Smith et al., 2010), or, due to subsidence, a downward movement in the thaw front over time (Belshe et al., 2012; LeBlanc et al., 2012) would liberate previously frozen soils and expose them to mineral weathering processes. This is presented as the downward movement of the top of the “permafrost” layer in Fig. 11 in September and November. The baseline results from the two end members in this study demonstrate that there is likely a strong relationship between the extent of active layer thaw and the trace metal composition of local surface waters. This relationship is complex, driven by soil and mineral weathering sources and trace metal oxidation and reduction characteristics and thus it warrants the attention of multi-year monitoring.

5. Conclusions

Future climate scenarios predict a warmer Arctic, which is expected to cause permafrost degradation and the downward migration of the seasonally thawed active layer, exposing previously frozen soil to mineral weathering processes. This may result in changes to trace metal seasonal signatures in surface waters due to exposing another source of metals in pristine systems. One goal of this study was to discern whether geochemical signatures of trace metals in surface waters

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**Table 4**

Trace concentrations (μg/L) of species found in Roche Mountanee surface waters over the course of spring through fall 2010. (--) indicates below detection limit, (/) indicates samples not analyzed for chloride.

<table>
<thead>
<tr>
<th>Date</th>
<th>Al</th>
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<th>Fe</th>
<th>Ba</th>
<th>Cl</th>
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Fig. 6. Imnavait Creek surface water soluble metal concentrations (μg/L) as a function of date in 2010.

Fig. 7. Imnavait Creek and Roche Mountanee surface water pH values over the course of spring–fall 2010.

Fig. 8. Roche Mountanee Creek surface water soluble metal concentrations (μg/L) as a function of date in 2010.
could provide a landscape or watershed scale proxy for thawing processes in permafrost soils. Our results show a distinct seasonal signature of trace metal concentrations in the end members, Imnavait and Roche Mountanee Creeks. Stream water concentrations of Al, Ba, Fe, and Mn in Imnavait Creek and Ba in Roche Mountanee were highest in the late fall (September and October). This pattern appears to correlate with the depth of the active layer throughout the watershed. The signal for Ba was detectable in both a low gradient tundra stream and a larger high gradient bedrock dominated stream. Other metals (Al, Fe, and Mn) experienced enhanced concentrations in late fall flows in the smaller low gradient stream, but these metals did not exhibit a late fall increase in the higher gradient bedrock dominated stream, likely due to the
difference in the soil composition, pH, organic ligand content and soil water flow rates for the two compared streams. The end member streams can also be characterized by different mixing ratios of surface flow and baseflow during the summer and fall.

Our findings suggest that enhanced weathering at the permafrost-active layer boundary could impact stream water trace metal signatures, but would likely only be observable by comparing late season stream compositions to summer and spring melt measurements. Over time, as permafrost degrades and exposes previously frozen, metal-rich layers, we hypothesize that this late season trace metal signal could potentially be differentiated from the ‘snowmelt’, ‘surface’, and ‘fall’ seasonal signatures established in Fig. 10. However, there are many noteworthy limitations to this hypothesis, particularly differentiating between fluctuating active layer thicknesses due to normal seasonal variability, as opposed to longer-term trends. In order to establish a noteworthy trend relating surface water metal concentrations with increasing active layer depth/degrading permafrost, a watershed likely warrants continuous monitoring of active layer dynamics, with soil and surface water geochemistry.

Presently, this study offers many improvements on previous efforts and provides a baseline of data for future monitoring. Our results capture the seasonality of trace metals in two Arctic watersheds from spring snowmelt until early winter, a measurement that is widely overlooked. We show a correlation between the top-down freezing processes that occur in Arctic soils to metal fluctuations in local surface waters. In addition, our results highlight the complexity of metal transport as a function of seasonality in the presence of permafrost, necessitating the need for longer summer sampling seasons in the Arctic.

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