



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



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## ABSTRACT

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 aluminum (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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## 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 can provide 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.

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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 km<sup>2</sup>) and Roche Mountanee Creek (89 km<sup>2</sup>) (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 silty loams covered by a peaty layer. They consist of highly weathered clays and silicates under acidic and often water-logged 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).

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