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Bryophytes as Heavy Metal Biomonitors in the Canadian High Arctic

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Abstract

Mosses are a major component of the tundra flora in the Canadian Arctic, yet their use in arctic contaminant research is lacking. Biomonitoring of atmospheric heavy metal deposition using mosses has been extensively employed in Europe, providing a higher sampling density than precipitation monitoring. Temporal, spatial, and habitat gradients of concentrations and enrichment factors of As, Cd, Cr, Cu, Ni, Zn, and Pb (and its stable isotopes) in mosses from Ellesmere Island are examined. Anthropogenically influenced concentrations of As, Cr, Cu, Ni, and Zn in samples collected in 2007 were observed. Concentrations of heavy metals in hydric taxa were larger than those observed in xeric or mesic taxa, though non-significant. Generally, heavy metal concentrations decreased from 1983 to 2007 in a single high arctic locality, though non-significant. Pb-isotope ratios were radiogenic and characteristic of the High Arctic Islands. Trends in high arctic moss data corresponded with environmental proxies such as glacial ice cores, lake sediments, and atmospheric aerosols illustrating the usefulness of bryophytes as biomonitors. This paper outlines the utility of using mosses as biomonitors of heavy metal depositions in the Canadian High Arctic.

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Introduction

Atmospheric heavy metal emissions from anthropogenic sources have received increasing attention due to their strong effect on biotic systems through biomagnification and neurotoxicity (Van Oostdam et al., 2005). Transport and deposition of atmospheric contaminants into arctic ecosystems has been previously established (Sturges and Barrie, 1989; Wania and Mackay, 1993; Ford et al., 1995; Gamberg et al., 2005). Biomagnification of contaminants through successive trophic levels of food chains is higher in polar regions than in lower latitudes (Gamberg et al., 2005; Van Oostdam et al., 2005). Many Canadian arctic terrestrial and marine fauna that occupy higher trophic levels are consumed as part of traditional human diets (Van Oostdam et al., 2005). Initially low concentrations of contaminants deposited onto arctic vegetation can reach toxic levels in these fauna for human consumption (Gamberg et al., 2005). In the Canadian Arctic, bryophytes (particularly mosses) often form the dominant vegetation in terrestrial and freshwater ecosystems, yet their use for investigating long-range contaminants is lacking. Although mosses are not commonly grazed in temperate regions, in arctic ecosystems they are consumed by a variety of herbivores (e.g., Peary caribou, muskoxen, lemmings, and snow geese; Prins 1981; Longton, 1997). Recent studies of heavy metal accumulation in Canadian arctic biota has focused on polar bears (Rush et al., 2008), arctic hare (Pedersen and Lierhagen, 2006), birds (Braune and Scheuhammer, 2008; Wayland et al., 2008), or fish (Campbell et al., 2005; Evans et al., 2005; Gantner et al., 2009). Studies of abiotic systems have focused on glacier ice cores (Cheam et al., 1998; Zheng et al., 2007), marine systems (Crane et al., 2001; Kirk et al., 2008), atmospheric aerosols (Mercier et al., 2001; Gong and Barrie, 2005), and lake sediments (Outridge et al., 2002, 2005; Michelutti et al., 2009). Accumulation of heavy metals that indicate anthropogenic influence have been found in both biotic and abiotic components of arctic ecosystems.

Atmospheric anthropogenic emissions of heavy metals are transported to and deposited in the Arctic via wet and dry deposition of particulate matter (Rao, 1982; Harrison, 1986). Their transport to remote polar regions is controlled by global circulation patterns. The circumpolar westerlies (Polar Vortex) dominate the high arctic region and form an extensive low pressure system (O'Connor, 1961). When the Polar Vortex becomes strongly amplified, ridges and troughs (Rossby Waves) form, which span temperate to arctic regions (Hare, 1969). Contaminants are transported via these air masses from mid-latitude industrial regions to high latitudes. Seasonal changes in the Polar Vortex can impact the origin of air masses (and therefore contaminants) to the Arctic (Raatz, 1991).

BRYOPHYTES AS BIOMONITORS

The most extensive use of bryophytes (particularly mosses) as biomonitors of atmospheric and freshwater contamination has been in Europe (Rühling and Tyler, 1968, 1970, 1971; Rambaek and Steinnes, 1980; Rao, 1982; Ross, 1989; Bates, 2000; Aceto et al., 2003; Harmens et al., 2007; Harmens et al., 2008). Since the first atmospheric study (Rühling and Tyler, 1968), the European Heavy Metals in Mosses Survey has been established, which includes 32 countries that provide data on 10 heavy metals at five-year intervals (Harmens et al., 2007). In North America, bryophytes have been used as biomonitors of atmospheric heavy metal deposition to a lesser extent and have been predominantly restricted to boreal or subarctic localities (e.g., Gignac, 1987; Ford et al., 1995; Pott and Turpin, 1998; Chiarenzelli et al., 2001) and Greenland (Riget et al., 2000).

Bryophyte morphology facilitates high heavy metal accumulation (Rühling and Tyler, 1970; Schofield, 2001; Salemaa et al., 2004).

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Assimilated heavy metals are derived from wet-dry deposition or passive uptake from substrates through adsorption and cation exchange (Brown, 1982; Bates, 2000; Chiarenzelli et al., 2001; Glime, 2007; Harmens et al., 2008). Unistratose leaves and uniseriate rhizoids provide a high surface/volume ratio that enhances cation exchange (Bates, 2000; Glime, 2007). Mosses can accumulate, sequester, and tolerate concentrations that are often toxic to other taxa. (Mouvet, 1984; Shaw, 1987; Shaw and Schneider, 1995; Martins and Boaventura, 2002). As well, selected moss species are indicators of substrates with high levels of specific heavy metals.

Using mosses provides inexpensive and density-rich sampling methods in contrast to conventional precipitation analyses, which require establishment and maintenance of numerous collectors (Steinnes, 1995; Harmens et al., 2004, 2007, 2008). Bryophyte biomonitoring is less prone to contamination given their ability to accumulate higher trace metal concentrations than rainwater (Steinnes, 1995; Harmens et al., 2007, 2008). Furthermore, the use of both field collections and herbarium specimens expands the potential spatial and temporal record of heavy metal accumulation (Herpin et al., 1997; Weiss et al., 1999; Farmer et al., 2002, Glime, 2007; Shotbolt et al., 2007).

The objectives of this study are to: (i) Provide a baseline record of seven trace element concentrations from terrestrial bryophytes collected in the Canadian High Arctic: lead (Pb), copper (Cu), chromium (Cr), arsenic (As), nickel (Ni), zinc (Zn), and cadmium (Cd). (ii) Determine the effect of habitat (xeric, mesic, and hydric) on heavy metal concentrations in three bryophyte species from a single locality. (iii) Compare heavy metal concentrations and enrichment factors between high arctic and low latitude populations. (iv) Use Pb-isotope ratios to determine the source of Pb deposition in Canadian high arctic vs. lower latitude specimens. (v) Compare heavy metal concentrations, enrichments, and Pb-isotope ratios in mosses collected in 1983 and 2007 from a single high arctic locality.

Materials and Methods

HIGH ARCTIC STUDY SITES

Bryophyte samples were collected from three Canadian high arctic localities on Ellesmere Island in 2007: Piper Pass (82°11′N, 68°30′W), 800 m a.s.l.; Sverdrup Pass (79°08′N, 79°39′W), 300 m a.s.l.; and Orske Bay (77°7′N, 79°47′W), 2 m a.s.l. (Fig. 1, Table 1). The first site is located within Quttinirpaaq National Park on a fault block at the southern end of Piper Pass on the Hazen Plateau. This remote locality was chosen for its minimal anthropogenic disturbance. The fault block ($\sim$15 km^2) is characterized by diverse bedrock assemblages, including Permian sandstone outcrops intruded by metamorphic diabase dikes and scattered with chert erratics (Trettin, 1994).

Sverdrup Pass is a 75-km-long deglaciated valley bisecting central Ellesmere Island that is bounded on the north and south by the Agassiz and Prince of Wales icefields, respectively (Fig. 1). This locality has been characterized as a polar oasis with a diverse flora and rich fauna (e.g., Henry et al., 1986; Breen and Lévesque, 2006). Field collections were primarily restricted to the southern slopes near the Teardrop Glacier, which are dominated by gneiss and granitic bedrock.

The third site is a lowland at Orske Bay on southwestern Ellesmere Island (Fig. 1). The site is dominated by Devonian carbonate bedrock and sandstone (Trettin, 1994). The single Orske Bay specimen was collected just above sea level ($\sim$2 m), growing at the base of a sandstone outcrop next to a remnant, dried pond.

TAXON SAMPLING

A total of 57 field and herbarium (University of Alberta Cryptogamic Herbarium [ALTA]) collections were used for habitat, latitudinal, and temporal heavy metal accumulation comparisons (Table 1). These included three species (Fig. 2) that represent distinct habitat preferences: *Hylocomium splendens* (Hedw.) B.S.G. (5 localities, 29 specimens), *Racomitrium lanuginosum* (Hedw.) Brid. (2 localities, 20 specimens), and *Pseudocalliergon brevifolium* (Lindb.) Hedenäs (1 locality, 8 specimens). Voucher information, locality, and habitat preference of each specimen is presented (Table 1).

Hylocomium splendens is a widespread mesic species that is distributed from temperate and boreal forests to arctic tundra, growing on moist acidic to neutral soils and humus (Steere, 1978). It has a prostrate habit that forms extensive wefts on forest floors or erect tufts in tundra habitats. This is the key taxon used in bryophyte biomonitoring programs of Europe (Harmens et al., 2008) and therefore used here for comparison. *Racomitrium lanuginosum* is an arctic-alpine, xeric species that forms highly branched erect to prostrate tufts on dry, exposed rock. Its morphology is designed to rapidly absorb moisture from the atmosphere. The leaves have highly papillose, long-acuminate hyaline points with erose-dentate margins that facilitate wet deposition from the atmosphere (Crum and Anderson 1981). As a taxon with a preference for xeric habitats, *R. lanuginosum* is primarily restricted to atmospheric deposition of heavy metals. *Pseudocalliergon brevifolium* is an arctic-alpine taxon restricted to hydric habitats, including calcareous fens, ponds, and tundra depressions (Steere, 1978). It is an emergent to often submerged species that has long irregularly branched stems. It represents a taxon that receives maximum ground water influence for heavy metal accumulation.

MOSS HEAVY METAL AND PB-ISOTOPE ANALYSIS

The moss specimens were analyzed for heavy metal concentrations and lead (Pb)-isotopic ratios. Lead is an ideal element for tracing the origin of atmospheric heavy metal deposition. It is relatively easy to analyze, has four stable isotopes, is non-mobile in environmental archives, and is emitted from a variety of sources (i.e., mining, metal industries, and fuel combustion; Bindler et al., 2001; Bollhöfer and Rosman, 2001). The residence time of Pb-bearing aerosols is approximately 10 days in the atmosphere (Settle and Patterson, 1991). Pb-isotopic ratios have specific signatures that indicate the source of local and long-range atmospheric transport and discriminate between natural and anthropogenically derived Pb emissions (Bindler et al., 2001; Bollhöfer and Rosman, 2001; Komárek et al., 2008). These ratios have been used to identify the region of origin of Pb emissions around the globe (Sturges and Barrie, 1987, 1989; Mercier et al., 2001; Simonetti et al., 2003; Michelutti et al., 2009).

Sampling bryophyte tissue for heavy metal analysis followed the protocols outlined by the European Moss Survey and Buse et al. (2003). Field collections were placed into paper bags, air-dried, and stored at room temperature (20–25 °C) until sampling for heavy metal analysis. Apical segments ($\sim$2 cm) of moss stems were removed and cleaned of surficial detritus. Tweezers were cleaned with double distilled, de-mineralized water between specimen sampling to prevent cross-specimen contamination.

Samples were analyzed for heavy metal concentrations on a Perkin Elmer Elan 6000 quadruple Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The instrument conditions were ICP-RF 1300W in dual detector mode with a flow rate of

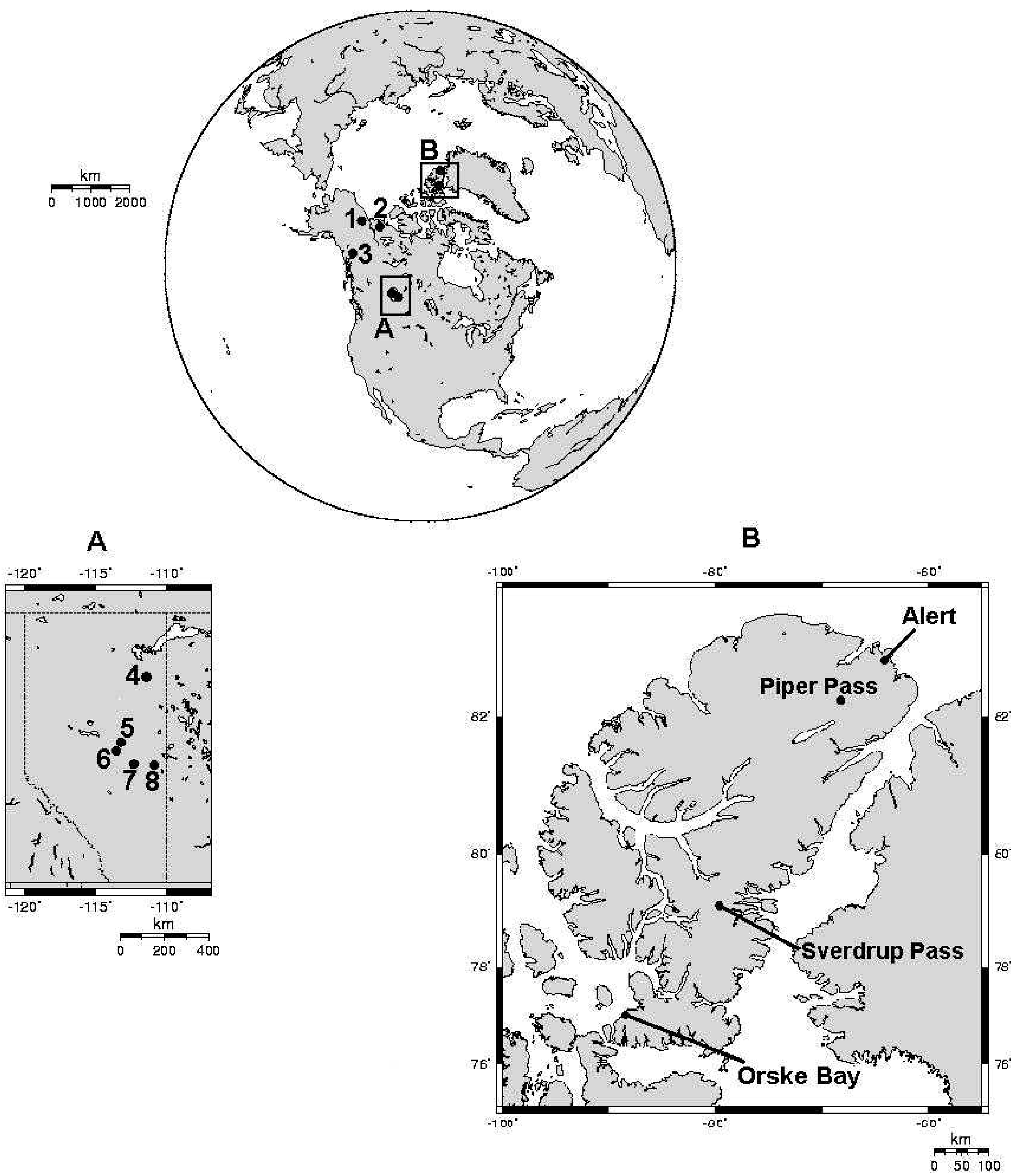

FIGURE 1. Locations of moss specimens used for heavy metal and Pb isotope analysis. Multiple bryophyte collections were made on Piper Pass, Sverdrup Pass, and Orske Bay on Ellesmere Island. Specimen numbers from Table 1 are provided for lower latitude sites: 1 = HM-56, Yukon; 2 = HM-95, Northwest Territories; 3 = HM-34, Yukon; 4 = HM-94, Alberta (Fort McMurray area); 5 = AT-4 and 6 = HM-67, Alberta (Athabasca area); 7 = HM-64, Alberta; 8 = HM-68, Alberta. Alert is mapped on Ellesmere Island for reference, but no moss specimens were collected from this locality.

1 mL/min. The analytical procedure used is outlined in Doucet and Carignan (2001) and Simonetti et al. (2003). Approximately 100 mg of stem apices were wet digested in 1N nitric acid. Samples were not ground or homogenized prior to analysis to reduce potential contamination from mortars and pestles. Concentrations (ppm) of Pb, As, Cr, Ni, Cu, Zn, Cd, and aluminum (Al) were determined for all samples. Detection limits for these elements were 0.03 ppm, 0.06 ppm, 0.05 ppm, 0.06 ppm, 0.03 ppm, 0.08 ppm, 0.04 ppm, 0.2 ppm, and 0.06 ppm, respectively. Each heavy metal concentration is given on a dry weight (g) basis

TABLE 1

Moss specimens used in heavy metal analyses: locality and year of collection, taxon, habitat, sample number, and voucher information (collector and collection #) is presented. All specimens are deposited in the University of Alberta Cryptogamic Herbarium (ALTA).

Locality & Year	Taxon	Habitat	Sample #	Voucher
Piper Pass 2007	*R. lanuginosum*	xeric	HM-23	Wilkie 72
			HM-26	Wilkie 75
			HM-31	Wilkie 84
			HM-35	Wilkie 58
			HM-59	Wilkie 86
			HM-66	Wilkie 99
			HM-69	Wilkie 94
			HM-71	Wilkie 76
			HM-79	Wilkie 90
			HM-82	Wilkie 56
Piper Pass 2007	*H. splendens*	mesic	HM-24	Wilkie 42
			HM-25	Wilkie 57
			HM-29	Wilkie 83
			HM-30	Wilkie 48
			HM-32	Wilkie 59
			HM-57	Wilkie 91
			HM-58	Wilkie 50
			HM-61	Wilkie 63
			HM-80	Wilkie 33
			HM-81	Wilkie 70
Piper Pass 1983	*H. splendens*	mesic	HM-9	La Farge C-4
			HM-36	La Farge C-9
			HM-44	La Farge C-16M
			HM-73	La Farge C-159
			HM-86	La Farge C-27
			HM-87	La Farge C-15
			HM-88	La Farge C-17
			HM-89	La Farge C-16
			HM-90	La Farge C-18
			HM-91	La Farge C-11
Piper Pass 2007	*P. brevifolium*	hydric	HM-33	La Farge 12659
			HM-62	Wilkie 98
			HM-63	La Farge 12657
			HM-65	Wilkie 97
			HM-72	La Farge 12654
			HM-74	Wilkie 111
			HM-78	Wilkie 60
			HM-85	La Farge 12785
Sverdrup Pass 2007	*R. lanuginosum*	xeric	HM-39	Wilkie 115
			HM-40	Wilkie 162
			HM-49	Wilkie 149
			HM-53	Wilkie 134
			HM-60	Wilkie 124
			HM-75	Wilkie 136
			HM-76	Wilkie 143
			HM-77	Wilkie 154
			HM-83	La Farge 13082
			HM-84	Wilkie 140
Orske Bay-2007	*H. splendens*	mesic	HM-70	Wilkie 166
Yukon-2007	*H. splendens*	mesic	HM-34	La Farge 13107
			HM-56	Froese LocU
NWT-2007	*H. splendens*	mesic	HM-95	Davey 224
Alberta 2007	*H. splendens*	mesic	AT-4	Terpsma 20
			HM-64	La Farge 13154
			HM-67	Wilkie 173
			HM-68	Davey 127
			HM-94	Wilkie 167

Notes: *H.* = *Hylocomium*; *R.* = *Racomitrium*; *P.* = *Pseudocalliergon*. Piper Pass, Sverdrup Pass, and Orske Bay are all Ellesmere Island localities in Nunavut.

(heated to a constant weight at 40 °C) and is the average of three measurement replicates. Reagent blanks were included to ensure concentrations of trace elements were negligible. Continued calibration verifications were followed to correct instrumental drift between measurements. Duplicate analyses were carried out every 10 samples to determine heavy metal variability, following Ross (1989).

Lead isotopic composition was determined separately from concentration values using the ICP-MS in dual detector mode. The isotopes of ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb peak intensities (abundances) were measured. Repeated measurements (n = 10) of the NIST SRM 981 Pb isotope standard yielded an average external reproducibility (2σ) of ±0.4% amu^{-1} (i.e., 0.5%, 0.4%, and 0.4% for the ^{206}Pb/^{204}Pb, ^{206}Pb/^{207}Pb, and ^{208}Pb/^{206}Pb values, respectively).

Determination of Enrichment Factors (EF) is a common method to identify and evaluate the influence of anthropogenic activity on global element cycles. In this method metal concentrations are 'normalized' to that of aluminum, which is used as a standard for elements derived from crustal erosion in the High Arctic (Doucet and Carignan, 2001; Simonetti et al., 2003; Gong and Barrie, 2005). The EF calculation is defined as $[\text{metal/Al}]_{\text{sample}}/[\text{metal/Al}]_{\text{Earths crust}}$. EF calculations are based on generalized global element concentrations of the Earth's continental crust (Taylor and McLennan, 1995). An EF value >10 (i.e., 10 times larger than crustal values) is considered an indication of anthropogenic influence following previous studies (Carignan and Gariépy, 1995; Chiarenzelli et al., 2001; Doucet and Carignan, 2001; Simonetti et al., 2003; Zheng et al., 2007). Reimann and de Caritat (2000, 2005) outlined several inherent limitations of using these globally averaged values: (1) elements have a natural fractionation during transfer from the crust to the atmosphere; (2) there is neglect for differential solubility of minerals during alteration in the environment; and (3) there is neglect of impact of biogeochemical processes. They suggested that EF values are appropriate for a regional context, rather than site specific enrichments. With EF values, Pb-isotopic ratio data and raw trace element concentrations are presented.

Statistical analyses using a non-parametric Wilcoxon Range Test (SPSS, 2006) were performed to compare heavy metal concentrations, EF, and Pb-isotope ratios between (1) bryophyte habitats, and (2) temporal data from a single locality. Heavy metal concentrations included As, Cd, Cr, Cu, Ni, Pb, and Zn. EF comparisons focused on As, Cr, Cu, Ni, Pb, and Zn. Pb-isotope ratios included ^{206}Pb/^{207}Pb, ^{206}Pb/^{204}Pb, ^{208}Pb/^{207}Pb, ^{208}Pb/^{204}Pb, and ^{208}Pb/^{206}Pb. P-values $\leq$ 0.05 for individual tests were considered statistically significant.

HABITAT COMPARISON

A comparison of heavy metal concentrations from species representing a dry-wet gradient was made from a single high arctic locality (Piper Pass) to assess habitat effect (Fig. 3). *Racomitrium lanuginosum* (xeric), *Hylocomium splendens* (mesic), and *Pseudocalliergon brevifolium* (hydric) were collected over a 15 km^2 area composed of various bedrock types (Trettin, 1994). Multiple bedrock substrates in a single locality have been shown to have little impact on heavy metal concentrations and enrichment in mosses and lichens (e.g., Lounamaa, 1956; Chiarenzelli et al., 2001).

LATITUDINAL COMPARISON

Specimens of *Racomitrium lanuginosum* from Sverdrup Pass and Piper Pass were compared to assess high latitude, inter-locality

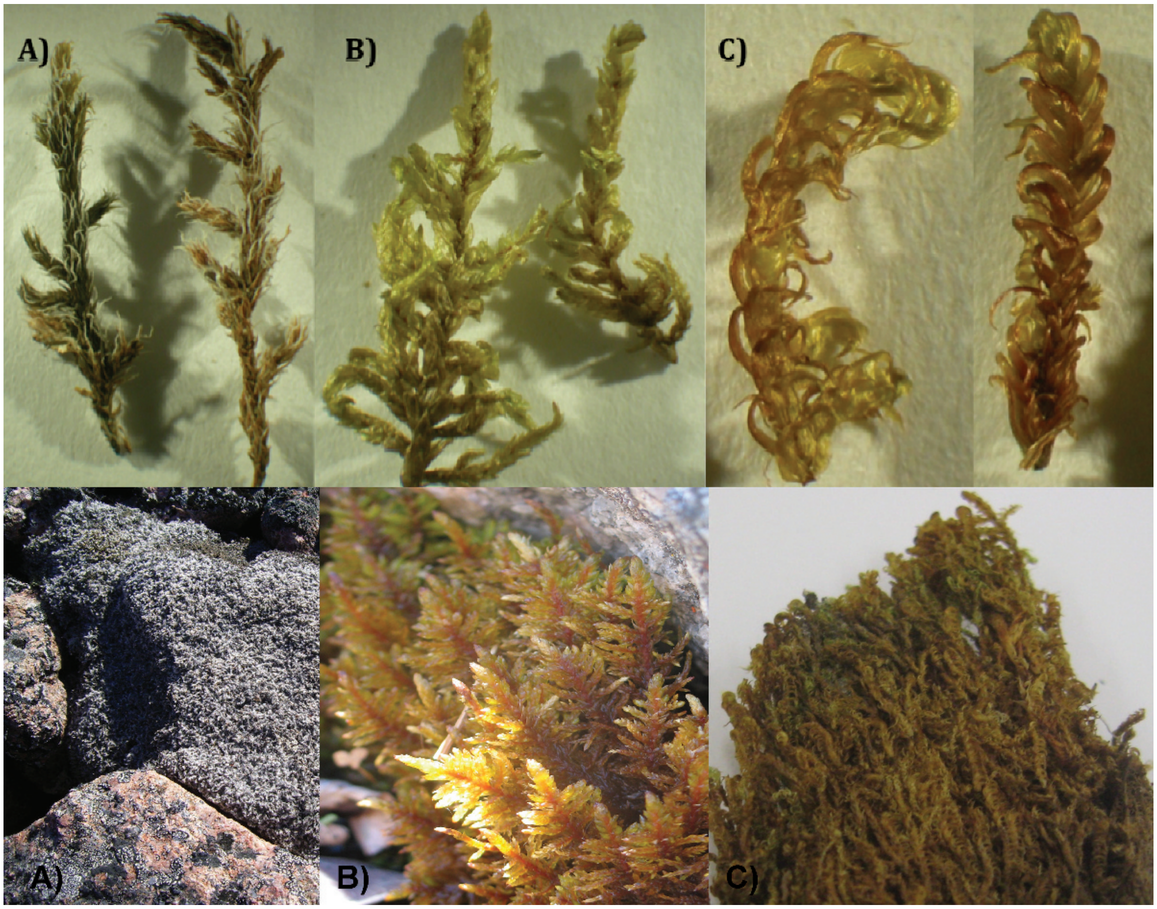

FIGURE 2. Moss taxa used for heavy metal analyses. (A) ***Racomitrium lanuginosum*** **(*DW75* ALTA) (xeric); (B)** ***Hylocomium splendens*** **(*DW63* ALTA) (mesic); (C)** ***Pseudocalliergon brevifolium*** **(*DW60* ALTA) (hydric).**

variation of heavy metal concentrations and Pb-isotopic ratios. Inter-latitudinal differences were compared using low latitude (Yukon, Northwest Territories [NWT], and Alberta) and high latitude (Ellesmere Island, Nunavut) specimens of *Hylocomium splendens* (Fig. 1, Table 1). All specimens were collected at least 5 km from a main road or urban area, following specimen collection protocols outlined by the European Moss Survey (Buse et al., 2003). Inter-latitude samples were also used to determine Pb-isotope ratios variation. Mean Pb-isotope ratios from the high arctic moss specimens (this study) were plotted with Komárek et al. (2008) summarized Northern Hemisphere ratios and Mercier et al. (2001) Alert atmospheric aerosols ratios (Fig. 4).

TEMPORAL COMPARISON

A temporal comparison of heavy metal accumulation in *Hylocomium splendens* assessed differences from a single high arctic locality. Field collections from the Southern Piper Pass fault block (~15 km^2) made in 1983 (CLF) were compared to samples collected from the same site in 2007.

Results

ANALYTICAL QUALITY

Trace element concentrations, EF, and Pb-isotope ratios are presented in Tables 2, 3, and 4, respectively. All samples indicated within and between site variation for heavy metal concentration and EF data (Tables 2 and 3). Duplicate heavy metal analyses produced ≤10% variation between replicates. Pb-isotope ratios showed less variation than heavy metal concentrations or EF data from the high arctic localities (Table 4).

HABITAT COMPARISON

All of the 2007 samples from Ellesmere Island (Piper Pass, Sverdrup Pass, and Orske Bay) indicated EF values >10 for As, Cr, Cu, Ni, and Zn (Table 3). EF values for Pb were just below 10. Samples from distinct habitats showed no significant ($p \leq 0.05$) difference for heavy metal concentrations and EF data. In general, *Pseudocalliergon brevifolium*, representing hydric habitats, had higher heavy metal concentrations and EF values than the xeric or mesic taxa (Fig. 3).

LATITUDINAL COMPARISON

Samples from all three localities on Ellesmere Island had similar Pb-isotope ratios (Table 4). A comparison of inter-locality samples of a single species, *Racomitrium lanuginosum*, showed that ratios between Piper Pass and Sverdrup Pass were not significantly different. The high arctic moss samples showed distinct and unique Pb-isotope ratios in comparison to northern hemisphere values presented in Komárek et al. (2008) (Fig. 4). Pb-isotope ratios of bryophyte samples from Alberta, Yukon, and NWT were distinct from Ellesmere Island specimens (Fig. 4; Table 4). Samples from the Yukon and NWT had similar Pb-isotope ratios that were distinct from the Albertan and high arctic specimens (Fig. 4; Table 4).

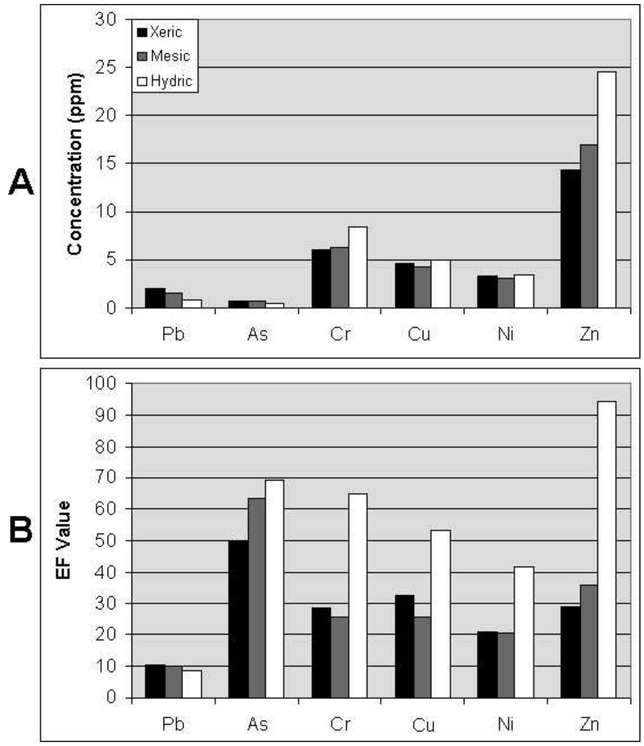

FIGURE 3. (A) Habitat comparison of average heavy metal concentrations and (B) Enrichment Factors (EF) from *Racomitrium lanuginosum* (xeric), *Hylocomium splend*ens (mesic), and *Pseudocalliergon brevifolium* (hydric) collected from a single high arctic locality (Piper Pass).

Heavy metal concentrations and EF were consistently higher in lower latitude samples than those of Ellesmere Island (Fig. 5; Table 3). The highest concentrations and EF values were from Albertan specimens. Heavy metal concentrations between high arctic localities (Piper Pass and Sverdrup Pass) were not significantly different.

TEMPORAL COMPARISON

Hylocomium splendens specimens from Piper Pass collected in 1983 showed EF $>$ 10 for As, Cr, Cu, Ni, Pb, and Zn (Table 3). Given a 24-year interval between sampling (1983 and 2007), there was a decrease in concentration values for all heavy metals except Zn, which showed an increase (Fig. 6). No significant difference of heavy metal concentrations, EF, or Pb-isotope ratios was found between 1983 and 2007 using non-parametric analyses.

Discussion

ANALYTICAL QUALITY

Our data show a similar amount of variation within a species and between analyses in heavy metal concentrations, EF, and Pb-isotope ratios (i.e., $<$10%) as has been observed in other botanical biomonitoring studies (Ross, 1989; Simonetti et al., 2003; Harmens et al., 2007, 2008). Variation of trace element concentrations within a single moss species has been attributed to morphological differences between populations caused by microhabitat/microclimate factors unique to each sampling site (Braune et al., 1999; Gerdol et al., 2002; Chiarenzelli et al., 2001). These include conditions that affect growth rates, productivity, and adsorption. Therefore, heavy metal concentration variation in data may be inherent to the use of plant material as biomonitors. Variation within our data of heavy metal concentrations, EF, and Pb-isotope ratios indicate changes in temporal, latitudinal, and habitat data that require further monitoring to establish long-term trends. Although there was variation within our data, the trends observed correlated well with other high arctic proxies. This suggests that bryophytes are useful high arctic biomonitors of atmospheric heavy metal deposition.

HABITAT COMPARISON

Racomitrium lanuginosum, *Hylocomium splendens*, and *Pseudocalliergon brevifolium*, exemplars of a xeric-hydric gradient from a single locality, showed no statistically significant difference between heavy metal concentrations and therefore the resultant uptake rates. Our results do indicate a general increase in heavy metal concentrations and EF in hydric habitats, although not significantly different from mesic and hydric habitats (Fig. 3). This suggests that different habitats (xeric, mesic, and hydric) received equivalent amounts of the heavy metals analyzed. Further, hydrological runoff from the local bedrock did not significantly affect concentrations between these moss taxa, given the apical stems tested. This contrasts with selected studies, which used bulk samples of xeric, arctic plants that indicate larger amounts of contaminants due to slower growth rates (e.g., Hutchison-Benson et al., 1985). However, other studies show no significant difference of heavy metal accumulations between moss taxa and indicate that they can be used interchangeably (Chiarenzelli et al., 2001; Galsomies et al., 2003; Harmens et al., 2008). Arctic terrestrial systems have been shown to accumulate less long-range transported contaminants than freshwater and marine systems (Braune et al., 1999; Gamberg et al., 2005). An increased abundance of contaminants in high arctic freshwater and marine systems has been attributed to the transfer of contaminants from terrestrial systems during spring snowmelt (Braune et al., 1999). One area of research to pursue is the effect of habitat gradient on contaminants with different mobilities in the environment (i.e., mercury and organic pollutants).

LATITUDINAL COMPARISON

Pb-Isotope Ratios

Three localities on Ellesmere Island (Piper Pass, Sverdrup Pass, and Orske Bay) show similar Pb-isotopic ratios between all species, suggesting a common atmospheric source for heavy metal to this region. Pb-isotope ratios of mosses from Ellesmere Island correspond to those in other high arctic environmental archives: Alert atmospheric aerosols (Sturges and Barrie, 1989; Mercier et al., 2001; Gong and Barrie, 2005), lake sediment profiles (Outridge et al., 2002; Michelutti et al., 2009), and glacial ice cores (Zheng et al., 2007).

Seasonal fluctuations in heavy metal concentrations in the High Arctic have been observed in Alert atmospheric aerosols (Sturges and Barrie, 1989; Mercier et al., 2001; Gong and Barrie, 2005) and ice cores of the Agassiz Ice Cap from Ellesmere Island (Cheam et al., 1998). These fluctuations indicate different source regions for heavy metals deposited in the High Arctic (Sturges and Barrie, 1989; Mercier et al., 2001; Gong and Barrie, 2005). Pb-isotope ratios ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$, and $^{208}Pb/^{206}Pb$) from our data plot close to the natural aerosol component observed by Mercier et al. (2001) from Alert on Ellesmere Island. These ratios were attributed to a natural radiogenic end-member observed in early fall that originates in the Canadian Arctic Islands and

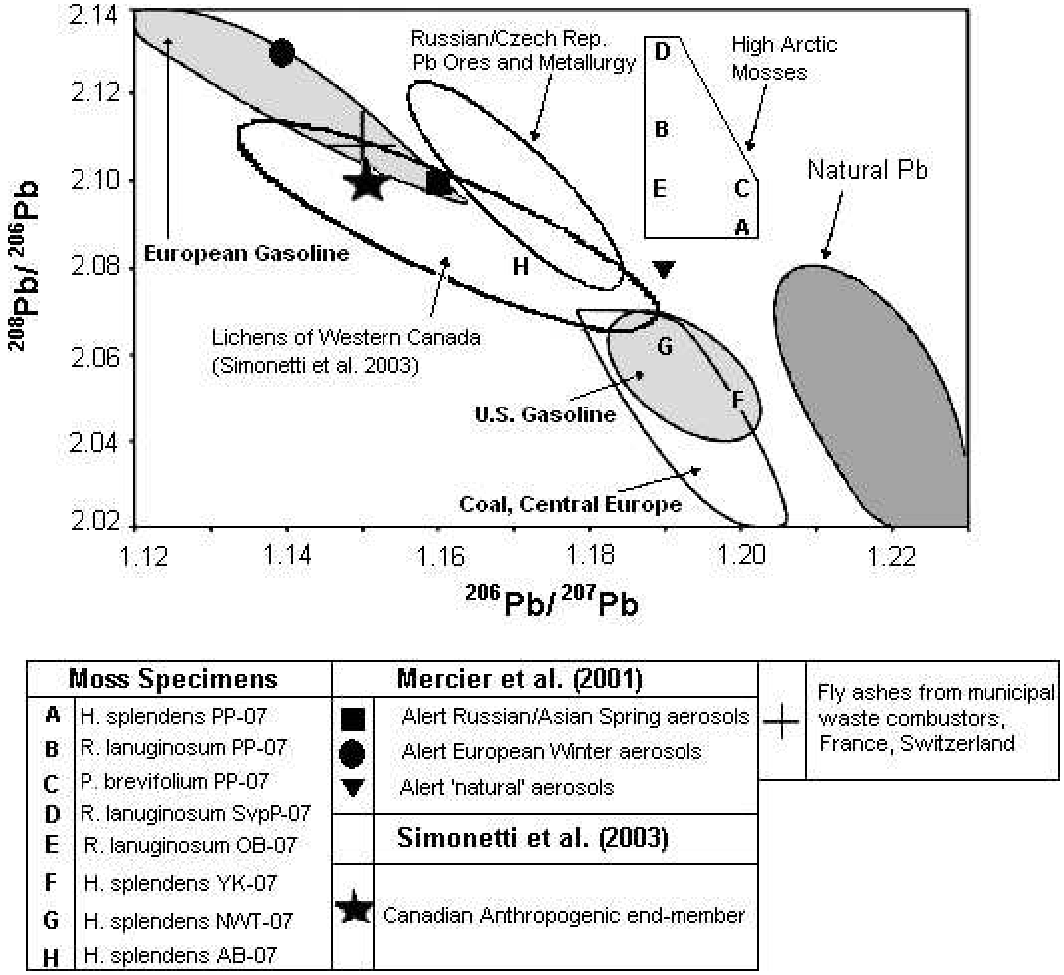

FIGURE 4. Modified plot of $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ ratios summarized by Komárek et al. (2008). Averaged bryophyte Pb-isotope ratios collected in 2007, Alert arctic aerosols from Mercier et al. (2001), the summarized lichen ratios of Western Canada from Simonetti et al. (2003), and the Canadian Anthropogenic end-member from Simonetti et al. (2003) were plotted in relation to summarized northern hemisphere Pb-isotopic ratios. PP—Piper Pass, SvpP—Sverdrup Pass, OB—Orske Bay, YK—Yukon, NWT—Northwest Territories, AB—Alberta.

TABLE 2

Average trace element concentrations (ppm) and standard deviations (1σ) for moss specimens.

Species	Locality and Year collected	*n*	Sample	Element Concentration (ppm) Al	As	Cd	Cr	Cu	Ni	Pb	Zn
R. lanuginosum	Piper Pass-2007	10	Average	859	0.69	0.02	6.03	4.65	3.25	1.97	14.37
			1σ	814	0.57	0.04	1.52	0.96	1.93	1.64	11.31
H. splendens	Piper Pass-2007	10	Average	609	0.69	0.09	6.17	4.27	3.02	1.45	16.92
			1σ	239	0.27	0.06	1.30	0.96	1.11	0.52	7.86
P. brevifolium	Piper Pass-2007	10	Average	385	0.48	0.15	8.43	4.96	3.42	0.83	24.56
			1σ	183	0.23	0.24	2.63	1.00	1.24	0.46	4.45
H. splendens	Piper Pass-1983	10	Average	619	0.76	0.14	8.70	5.8	3.54	1.95	16.82
			1σ	196	0.32	0.06	5.60	1.09	1.51	0.91	5.50
R. lanuginosum	Sverdrup Pass-2007	10	Average	488	0.50	0.10	5.05	2.96	2.38	1.21	12.72
			1σ	274	0.21	0.07	2.92	2.14	1.03	0.61	6.80
R. lanuginosum	Orske Bay-2007	1	HM-70	134	0.09	0.00	6.44	3.95	1.56	0.28	10.64
H. splendens	Yukon-2007	2	Average	59	1.90	0.130	6.35	5.20	1.20	0.35	31.06
			1σ	12	2.69	0.07	0.04	0.04	0.14	0.01	5.96
H. splendens	NWT-2007	1	HM-95	146	3.68	0.12	4.15	6.92	4.73	0.53	28.92
H. splendens	Alberta-2007	5	Average	125	1.71	0.08	3.98	3.65	1.73	0.36	16.67
			1σ	100	1.56	0.05	2.66	2.67	1.75	0.24	12.31

Notes: Aluminum is reported for calculations of enrichment factors (EFs). *n* = number of samples; NWT = Northwest Territories; *H.* =*Hylocomium*; *R.* = *Racomitrium*; *P.* = *Pseudocalliergon*.

TABLE 3

Average and median enrichment factors (EFs) values for heavy metals (As, Cr, Cu, Ni, Pb, and Zn) from moss specimens.

Sample		EF-As	EF-Cr	EF-Cu	EF-Ni	EF-Pb	EF-Zn
Piper Pass-2007							
R. lanuginosum	Average	49.9	28.9	32.6	20.8	10.6	29.2
n = 10	Median	48.0	25.5	30.7	19.3	9.6	28.3
Piper Pass-2007							
H. splendens	Average	63.5	25.7	25.6	20.5	9.9	35.8
n = 10	Median	64.3	23.7	21.6	20.4	9.9	29.1
Piper Pass-2007							
P. brevifolium	Average	69.6	65.0	53.4	41.7	8.5	94.5
n = 8	Median	61.9	47.1	42.1	38.2	8.4	65.6
Piper Pass-1983							
H. splendens	Average	66.8	34.4	32.5	23.5	13.3	32.1
n = 10	Median	71.2	23.2	31.8	20.7	11.3	33.4
Sverdrup Pass-2007							
R.lanuginosum	Average	16.9	29.6	24.7	14.8	8.9	24.2
n = 10	Median	16.7	24.4	21.9	13.9	9.0	16.1
Orske Bay-2007							
R. lanuginosum							
n = 1	HM-70	35.2	110.2	94.6	46.6	8.4	89.6
Yukon-2007							
H. splendens	Average	50.4	51.1	60.4	30.3	16.6	101.8
n = 2	Median	50.4	51.1	60.4	30.3	16.6	101.8
NWT-2007							
H. splendens							
n = 1	HM-95	330.9	65.2	152.5	129.9	14.6	224.3
Alberta-2007							
H. splendens	Average	172.2	248.7	217.9	118.6	23.2	414
n = 5	Median	145.1	216.6	236.7	104.4	22.0	300.5

Notes: *n* = number of specimens analyzed; Piper Pass, Sverdrup Pass, and Orske Bay are all high arctic localities on Ellesmere Island. *H. splendens* = *Hylocomium splendens*; *R. lanuginosum* = *Racomitrium lanuginosum*; *P. brevifolium* = *Pseudocalliergon brevifolium*. HM-70 and HM-95 are specimen numbers from Table 1.

coastal areas of West Greenland. Mercier et al. (2001) suggested that this natural component represents dust particles derived from erosion of local bedrock exposed during the summer and autumn seasons when snow/ice cover is at a minimum. Mercier et al. (2001) reported two additional seasonal end-member Pb-isotope ratios from Alert aerosols: (i) Russian/Asian emissions were predominant in late spring and early summer (Fig. 4; Table 3); (ii) Western/Northwestern European non-radiogenic Pb-isotope ratios were observed in late fall and winter (Fig. 4; Table 3). Analyses of moss apices are unable to detect seasonal fluctuations since they represent an average of 1–2 years of heavy metal deposition. Further, seasonal precipitation at Alert is predominantly during August–October (Dominé et al., 2002; Gong and Barrie, 2005; Meteorological Service of Canada Website, 2009); during this time atmospheric heavy metals would be transferred to the terrestrial system via wet deposition. This supports the hypothesis that deposition of atmospheric Pb and other heavy metals to the High Arctic is predominantly in the fall.

France and Blais (1998) attributed similar Pb-isotope ratios in high arctic vascular plants to long-range transport from U.S. atmospheric emissions. However, the Polar Vortex represents a barrier to northerly movement of air from southern Canada and the United States to the Canadian High Arctic; instead airflow is generated from Eurasian sources (Raatz, 1991). The Pb-isotope ratios and low Pb EF (<10) observed in the 2007 moss samples reflect naturally derived Pb of the Canadian Arctic Archipelago deposited from fall aerosols. Thus, the contribution of Pb from anthropogenic emissions is small compared to local geological sources in these northern mosses.

Moss samples from mid-latitude localities (Yukon and NWT) have distinct Pb-isotope ratios from those of lower latitudes (Alberta) and the High Arctic (Fig. 4; Table 4). The Albertan specimens are similar to those previously reported for western Canada (Bollhöfer and Rosman, 2001; Simonetti et al., 2003). Mosses from the Yukon and NWT have similar Pb-isotopic ratios to those reported from U.S. gasoline emissions (Fig. 4). However, similar Pb-isotope ratios from lichens of the Yukon and Northwest Territories have been attributed to local weathering and deposition of Silurian-Devonian-Mississippian shales (Simonetti et al., 2003). These two contrary interpretations of the Pb-isotope ratios, along with the proximity of our samples to Alaska and U.S. gasoline emissions, warrant further investigation.

Concentrations and EF

High arctic moss samples were collected from remote locations with minimal influence from direct anthropogenic emissions such as smelters. Detection of anthropogenic enrichments in these moss samples indicates long-range, atmospheric transport of heavy metals. Consumption of mosses by herbivores would facilitate the transfer of atmospherically derived heavy metals into arctic food webs. Ihl and Barboza (2007) have observed an increased consumption of mosses by arctic ruminants. Although mosses have less nutritional content than other arctic vegetation, these ruminants consumed more mosses due to shifting grazing ranges caused by climate change. Arctic mosses may have an additional and unstudied role in linking atmospheric contaminants through bioaccumulation in arctic terrestrial food webs.

Heavy metal concentrations and EF of lower latitude specimens indicate a larger amount of anthropogenic deposition than high arctic specimens, given their proximity to industrial activity (Fig. 5). Lower abundance of heavy metals in northern localities was also observed in lichens of western Canada (Simonetti et al., 2003) and in lake sediments (Outridge et al., 2002). This decreasing trend of heavy metals at higher latitudes has been attributed partially to lower precipitation rates in high arctic localities (Outridge et al., 2002). Lower precipitation rates decrease wet deposition of atmospheric heavy metals in terrestrial and freshwater systems.

TEMPORAL COMPARISON

Temporal changes of heavy metal deposition to the Canadian Arctic have been investigated in several different environmental archives such as lake sediment profiles (Michelutti et al., 2009), glacial ice cores (Cheam et al., 1998; Zheng et al., 2007), and atmospheric aerosols (Gong and Barrie, 2005). Lake sediment profiles from a single high arctic (NW Greenland) locality and several low arctic localities (Baffin Island) have revealed non-significant reduction in atmospheric deposition of heavy metals over the last ~140 years (Michelutti et al., 2009). As well, other proxy data from high arctic ice cores (Cheam et al., 1998; Zheng et al., 2007) and atmospheric aerosols (Gong and Barrie, 2005) indicate a general reduction of heavy metals, although non-significant. European contamination studies utilizing mosses have also noted a general reduction in heavy metal concentrations over the past few decades (Steinnes et al., 2003; Poikolainen et al., 2004;

TABLE 4

Average and standard deviation (1σ) Pb-isotope ratios of bryophytes from each study area and years collected are presented along with values of arctic aerosols presented in Mercier et al. (2001).

Species	Locality and Year Collected	n		$^{206}Pb/^{207}Pb$	$^{206}Pb/^{204}Pb$	$^{208}Pb/^{207}Pb$	$^{208}Pb/^{204}Pb$	$^{208}Pb/^{206}Pb$
H. splendens	Piper Pass-2007	10	Average	1.20	18.74	2.51	39.20	2.09
			1σ	0.01	0.30	0.01	0.64	0.02
R. lanuginosum	Piper Pass-2007	10	Average	1.19	18.59	2.51	39.26	2.11
			1σ	0.01	0.14	0.01	0.39	0.01
P. brevifolium	Piper Pass-2007	10	Average	1.20	18.78	2.52	39.36	2.10
			1σ	0.01	0.19	0.01	0.30	0.02
H. splendens	Piper Pass-1983	10	Average	1.20	18.76	2.51	39.30	2.09
			1σ	0.01	0.16	0.02	0.26	0.01
R. lanuginosum	Sverdrup Pass-2007	10	Average	1.19	18.63	2.52	39.59	2.13
			1σ.	0.02	0.31	0.03	0.54	0.02
H. splendens	Yukon-2007	2	Average	1.20	18.66	2.46	38.30	2.05
			1σ	0.03	0.58	0.04	0.85	0.02
H. splendens	Alberta-2007	5	Average	1.17	18.36	2.46	37.94	2.08
			1σ	0.01	0.07	0.02	0.48	0.03
R. lanuginosum	Orske Bay-2007	1	HM-70	1.19	18.74	2.50	39.43	2.10
H. splendens	NWT-2007	1	HM-95	1.19	18.80	2.46	38.81	2.06
Mercier et al. (2001)								
Alert Spring/Summer Aerosols (A)				1.16	18.1	2.43	38.1	2.10
Alert Late Fall/Winter Aerosols (B)				1.14	17.6	2.44	37.5	2.13
Alert Fall Aerosols "Natural" (C)				1.19	18.5	2.48	38.5	2.08

Notes: n = number of specimens used. *H.* = *Hylocomium*; *R.* = *Racomitrium*; *P.* = *Pseudocalliergon*. Mercier et al. (2001) reported 3 main components in Alert aerosols: (A) Asia/Russian aerosols prominent during late spring and early summer, (B) West/Northwestern Europe found in late fall and winter samples, and (C) Fall natural Pb-isotope ratios for the Canadian Arctic Archipelago. HM-70 and HM-95 are specimen numbers from Table 1.

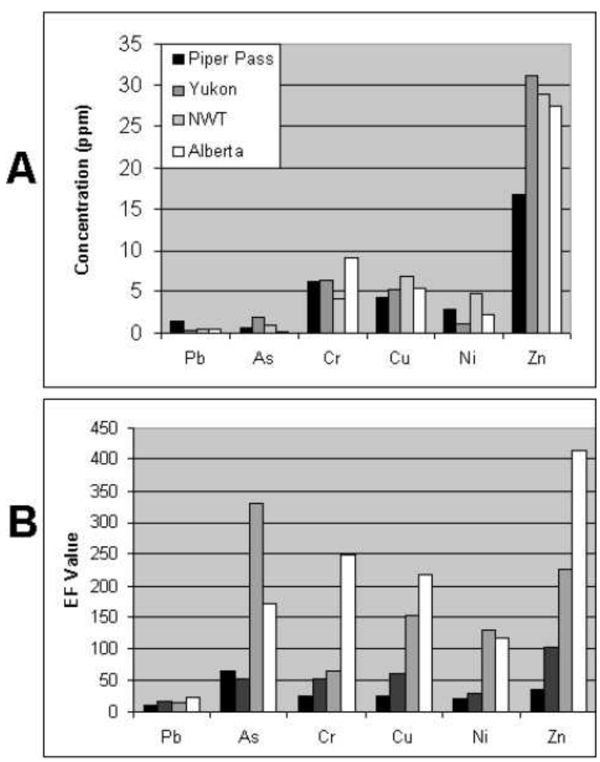

FIGURE 5. (A) Latitudinal comparison of average heavy metal concentrations and (B) EF from *Hylcomium splendens* collected across a latitudinal gradient from Piper Pass ($n = 10$), Yukon ($n = 2$), Northwest Territories ($n = 1$), and Alberta ($n = 5$).

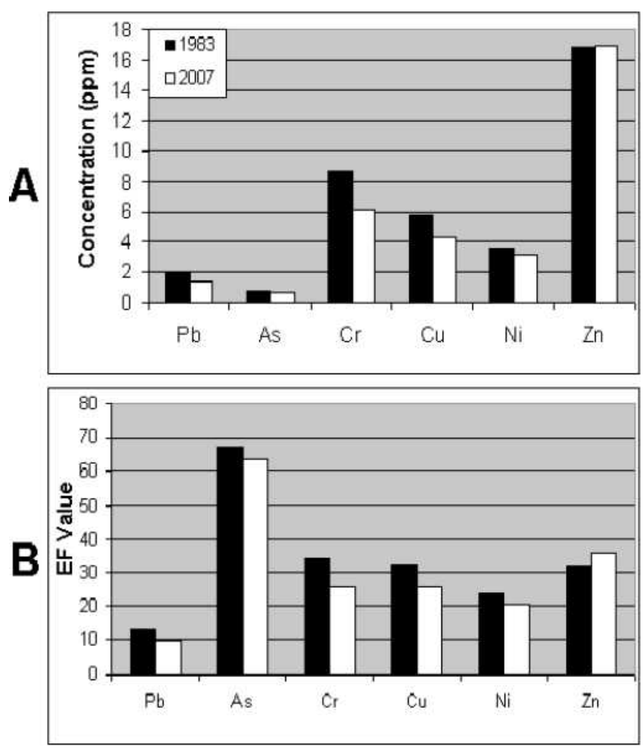

FIGURE 6. (A) Temporal comparison of average heavy metal concentrations and (B) EF from *Hylcomium splendens* collected from Piper Pass from 1983 and 2007 ($n = 10$ each year).

Rühling and Tyler, 2004; Steinnes et al., 2005; Harmens et al., 2007, 2008). Further, the temporal decrease in the long-range transport of contaminants from European sources to the Canadian and Alaskan Arctic has been established (Sturges and Barrie, 1989; Cheam et al., 1998; Mercier et al., 2001; Gong and Barrie, 2005).

Our temporal, site specific data compared ten 1983 samples and ten 2007 samples that show a reduction of contaminants, although non-significant. We cannot establish a trend from our data set, yet it supports decreasing trends observed in other proxy data. To determine if this reduction represents a trend or simply natural oscillation in high arctic terrestrial environments, more data is needed. Continued biomonitoring of the High Arctic is necessary and highly recommended to establish long-term assessment of the terrestrial ecosystem and the impact of contaminants on the higher trophic levels.

CONCLUSION

Steinnes (1995) outlined several potential limitations of using moss samples from polar regions for trace element studies. However, our analyses indicate that arctic mosses are useful and sensitive biomonitors of heavy metals. Our results complement other arctic environmental proxies including: aerosol data (Mercier et al., 2001; Gong and Barrie, 2005), glacial ice cores (Cheam et al., 1998; Zheng et al., 2007), lake sediment cores (Outridge et al., 2002; Michelutti et al., 2009), and temporal trends from European moss data (Harmens et al., 2007, 2008).

Heavy metal concentrations, enrichments, and Pb-isotope ratios from Canadian high arctic terrestrial mosses provide baseline data for future environmental biomonitoring. The taxa utilized are relatively common across North America to facilitate comparative studies. The use of bryophytes for broad scale, long-term biomonitoring of atmospheric contaminants in the High Arctic provides an efficient, inexpensive, less labor intensive method than establishing large-scale precipitation or aerosol monitoring. Their successful use for biomonitoring contaminants in Europe for more than three decades and Gamberg et al.'s (2005) emphasis on the need for new monitoring techniques in the Canadian Arctic suggest that future studies would benefit from the inclusion of mosses and should consider their advantages.

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