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Establishing trace element concentrations for lichens and bryophytes in the ring of fire region of the Hudson Bay Lowlands, Ontario, Canada

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Abstract Peatlands dominate the landscape of the Hudson Bay Lowlands in Ontario, Canada. Recently, mineral deposits of chromium (Cr), nickel (Ni), and copper (Cu) were discovered in the region and anticipated future industrial mining operations have the potential to impact the environment. Lichens and bryophytes are considered excellent biomonitors and indicators of deposition, deriving their nutrients directly from the atmosphere. Trace element concentrations in lichens and bryophytes have not been reported in the Hudson Bay Lowlands. Here, we seek to determine the baseline trace element concentrations of six non-vascular species (*Evernia mesomorpha*, *Bryoria* spp., *Cladonia stellaris*, *Cladonia stygia*, *Sphagnum fuscum*, and *Sphagnum capillifolium*) common to the region, explore linear relationships of trace elements with iron (Fe) as a signature of particulates with geogenic origin, and calculate trace element enrichment factors. Thalli, foliage, and peat (0–30 cm) were collected from 55 locations between 2013 and 2018 and analyzed for trace elements. Thalli and foliar concentrations are among the lowest reported in the broader literature and differ substantially from peat. Fe concentrations were significantly correlated (Pearson's $r \geq 0.8$) with aluminum (Al), titanium (Ti), and vanadium (V) in all six species. Enrichment factors show some anthropogenic deposition effects non-vascular organism chemistry. Most trace element concentrations in lichens and bryophytes are indicative of long-range atmospheric transport of dust, but some is attributed to industry, with only minimal inclusions from the local area. Epiphytic lichens are well suited for ongoing atmospheric biomonitoring as industrialization commences.

Keywords Non-vascular · Plants · Bog · Fen · Enrichment · Deposition · Background · Iron · Peatlands

Introduction

The Hudson Bay Lowlands in Canada is the second largest peatland complex in the world (Ulanowski & Branfireun, 2013) spanning from western Quebec through northern Ontario and into northeastern Manitoba (Sjors, 1959). When compared to the larger West Siberian Lowlands, the Hudson Bay Lowlands is considered relatively pristine, lacking broadscale intensive industrial development (Ulanowski & Branfireun, 2013). As a result, the

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region provides quality habitat for numerous subarctic flora and fauna (Peterson et al., 2013).

Recently, vast mineral reserves of chromium (Cr), copper (Cu), and nickel (Ni) were discovered in the southcentral Hudson Bay Lowlands (Ontario) on the traditional territory of the Cree in a region colloquially known as the "Ring of Fire" (Mungall et al., 2010). The remoteness, saturated conditions, and limited upland ecosystems of the region pose logistical and financial challenges for developers. Nonetheless, many organizations support industrial mining efforts in principle, including the prospect of open pit mining.

Fugitive dust emissions from open pit mines and unpaved roads can influence ecosystem biogeochemistry (Watmough et al., 2019). Establishing biomonitoring chemical or stoichiometric baselines of sensitive receptors are valuable tools for land managers before industrialization begins (Ellis & Schneider, 1996). While a considerable body of scientific literature exists on the Hudson Bay Lowlands (Adshead, 1983; Handa et al., 2002; Hattori et al., 2016), trace element concentrations of lichens and bryophytes are unknown. Establishing a baseline chemical composition of these non-vascular organisms is important as they are often considered the most sensitive ecosystem receptors and are used as biomonitors and bioindicators of air quality (Geiser & Neitlich, 2007; Nimis et al., 2002). Furthermore, positive linear relationships between iron (Fe) and titanium (Ti) in lichen thalli are often indicative of ambient atmospheric deposition relatively free of anthropogenic activity, providing a benchmark of background environmental conditions (Nieboer et al., 1978; Puckett & Finegan, 1980; Takala et al., 1994; Wu et al., 2021).

Considering the uncertain industrial future of the region and the prospect of using lichens and bryophytes to monitor atmospheric deposition from industrial activity, we seek to establish a range of trace element concentrations of two epiphytic lichens (*Evernia mesomorpha* and *Bryoria* spp.), two terricolous lichens (*Cladonia stellaris* and *Cladonia stygia*), and two bryophytes (*Sphagnum fuscum* and *Sphagnum capillifolium*) common to peatlands in the region. Furthermore, we seek to determine if there are linear relationships between various metals and Fe indicative of geogenic minerals and calculate trace element enrichment factors in the non-vascular organisms to establish if they have been traditionally exposed to atmospheric deposition from long-range transport.

Materials and methods

Hudson Bay Lowlands site characterization

The sub-polar Hudson Bay region has a microthermal climate due to the influence from arctic air and sea ice (Packalen et al., 2014). Mean annual temperature of the study region is −1.2 °C (30-year mean, Neskantaga First Nation Weather Station) and precipitation is approximately 700 mm $year^{-1}$ (Environment and Climate Change Canada, 2021). The area has a unique geological form relative to the rest of North America. Discontinuous permafrost predominates the southcentral region of the Hudson Bay Lowlands, including the study area here, while continuous permafrost is present north of the study region. Permafrost is absent at the southern extent of the Hudson Bay Lowlands. The entire Hudson Bay Lowlands sits atop Precambrian igneous rock which is overlain by limestone (Ordovician and Silurian) and glacial till. Isostatic rebound continues in the Hudson Bay Lowlands after it was infilled with water and sediment (Tyrell Sea Clay) following the disappearance of the Laurentide Ice Sheet approximately 12,000 years ago, allowing the vast peatland complex to develop (Hattori & Hamilton, 2008).

Aside from exploratory drilling localized within the centre of the proposed mining area, there is very little industrialization within the region. On a broader scale, the Hudson Bay Lowlands have experienced increased warming due to anthropogenic climate change (Ruhland et al., 2013).

Plot establishment and characterization

Between 2013 and 2015, 55 peatland (39 bogs and 16 fens) non-destructive permanent monitoring stations were established in and around the proposed development zone colloquially known as the Ring of Fire in the Hudson Bay Lowlands (Fig. 1). Two vegetation plots (25 m^2) separated by a minimum of 100-m distance were randomly established in each peatland. Bogs are dominated by black spruce (*Picea mariana*) with a mean basal area of 2.7 m^2 ha^{-1} (±0.4 standard error (SE)) and stem density of 1888 stems ha^{-1}

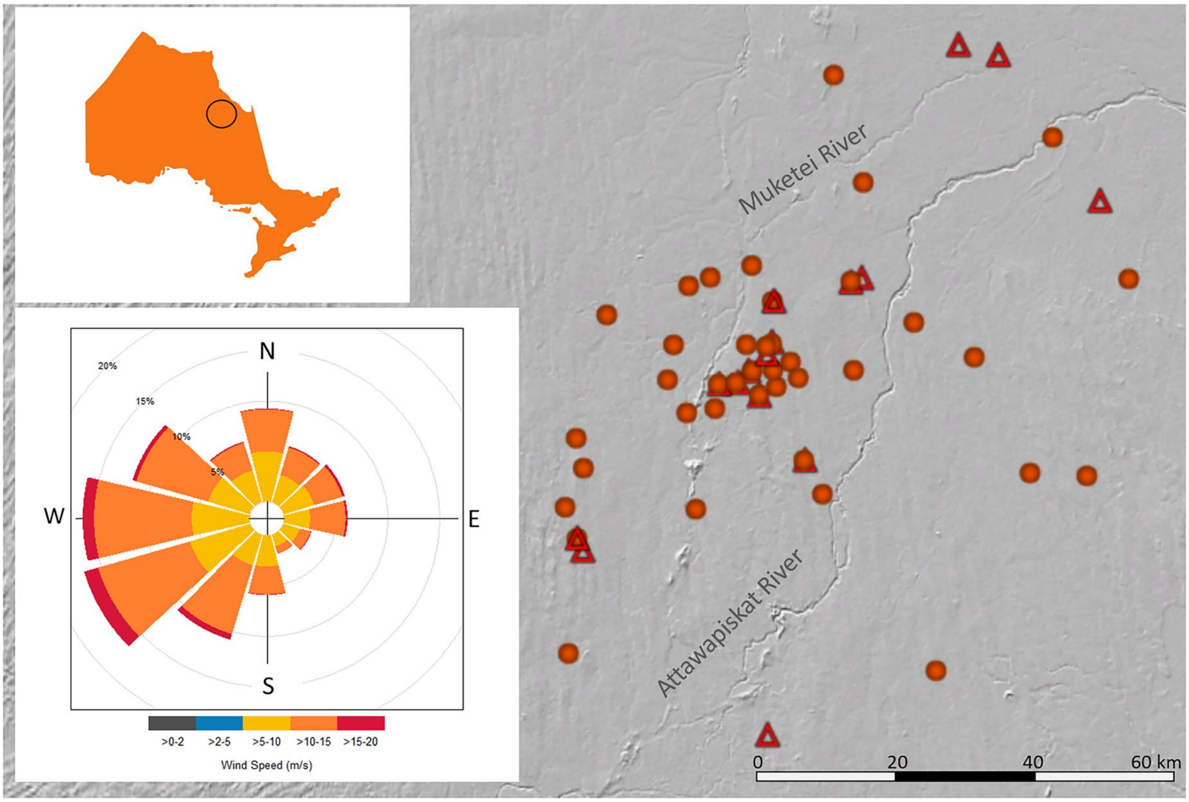

Fig. 1 Study location in the Ring of Fire area of the Hudson Bay Lowlands, Ontario, Canada, overtop a digital elevation model highlighting low relief. Top left inset shows the Ring of Fire area (open black circle) in Ontario; bottom left inset shows prevailing wind direction and wind speed (m s^{-1}) between 2010 and 2018 (data obtained from Environment and Climate Change Canada, 2021); solid circles, bogs ($n = 39$); open triangles, fens ($n = 16$)

(±244 SE). Basal area (2.1 m^2 ha^{-1} (±0.6 SE)) and stem density (1557 stems ha^{-1} (±285 SE)) are similar in fens but tree species composition is dominated by tamarack (*Larix laricina*). Epiphytic lichens are common in both bogs and fens and are present on both living and necrotic branches.

Non-vascular plant collection

A composite sample of six common (present at > 30% of the sites) non-vascular plants characteristic of peatlands in the region was randomly collected outside of each non-destructive permanent monitoring plot for trace element analysis. Terricolous lichens *Cladonia stellaris* and *Cladonia stygia* and bryophytes *Sphagnum fuscum* and *Sphagnum capillifolium* were collected between 2013 and 2015, whereas epiphytic lichens *Evernia mesomorpha* and *Bryoria* spp. were collected during 2018 from necrotic branches of both living and non-living trees. All samples were stored in sterile laboratory-grade paper bags and housed in climate-controlled chambers (4 °C) for no longer than 7 days before transportation to the laboratory.

Peat collection

During 2018, three peat samples (30 cm length × 10.2 cm diameter) from 20 randomly selected peatlands within the 55-site monitoring network were collected from the top 30 cm of the organic soil profile. Peat was extracted by cutting organic soil along the circumference of the cores to a depth of 30 cm. Cores were inserted around the separated peat and the bottom was cut flush with the core. Caps were added on both ends to seal the peat and porewater inside. After removal, caps were sealed with multiple layers of tightly wrapped Parafilm and placed upright in climate-controlled chambers for upwards of

7 days before transportation to the laboratory. Cores remained upright during on-site cap sealing, storage, and transportation.

Laboratory preparation and trace element analysis of lichens, bryophytes, and peat

Sample preparation

In the laboratory, epiphytic lichens were separated from bark and debris using forceps. Following debris removal, the entire thallus (epiphytic lichens) was prepared for analysis. Conversely, only capitula and apical tissue (*Sphagnum* and *Cladonia* species, respectively) were removed and prepared for analysis (after all debris was removed). Lichens and mosses were not washed during the preparation procedure. All samples, including peat, were dried at 70 °C for a minimum of 72 h. Once dried, samples were ground to a fine powder using an electric grinder.

All samples were stored in accredited laboratory method glass containers and housed in climate-controlled rooms designed for proper sample preservation. All samples were analyzed the year they were collected.

Trace element analysis in lichens, mosses, and peat

Samples were prepared for inductively coupled plasma-mass spectrometry (ICP-MS) by weighing 1.00 g of dried material (lichens, mosses, or peat) into digestion tubes. Aliquots were then heated at 100 °C for 30 min, then increased to 250 °C for an additional 60 min and finally to 500 °C for 3 h. After cooling, 5 mL of double deionized water, 3 mL of concentrated nitric acid (HNO_3), and 9 mL of hydrochloric acid (HCl) were added to the digestion tubes. Samples were sealed with disposable glass caps and placed onto a hot block for digestion. Digestions occurred by sequentially increasing temperatures over time. Samples were heated for 60 min at 40 °C, increased to 70 °C for an additional 60 min, and finally for 165 min at 110 °C. Once the samples cooled, three drops of hydrogen peroxide (H_2O_2) were added to the digestion tubes followed by re-heating at 100 °C for 15 min. Once cooled, samples were diluted as needed and analyzed.

For every 40 samples, three blanks and two certified reference materials (National Institute of Standards and Technology pine and rye grass) were analyzed as a quality control measure. Recoveries of certified reference materials were required within 20% of the expected concentrations. Beryllium concentrations in lichens and moss were unreliable and were not included in this work. Detection limits for ICP-MS are in the parts per billion (ppb) range. Burr (2015) and Kryukova (2016) provide a detailed description of the accredited laboratory method.

Statistical analysis and general computation

Statistical analyses were carried out using a two-step process. Firstly, all trace elements were compared with Fe to determine if linear relationships existed (Pearson's correlation). Secondly, linear regression was conducted on trace elements that had coefficients of correlation $(r) \geq 0.8$ with Fe among all non-vascular species considered. We applied the coefficients of correlation threshold (≥ 0.8) to ensure linear equations have robust predictive power.

Additionally, trace element ($r \geq 0.8$ with Fe) enrichment factors (EF) were calculated using Fe as the normalizing factor (Eq. 1) to identify possible sources of anthropogenic deposition in the region, originating from long-range transport.

$$\mathrm{EF} = \left(L_{\mathrm{te}}/L_{\mathrm{Fe}}\right)/\left(S_{\mathrm{te}}/S_{\mathrm{Fe}}\right) \quad (1)$$

where L_{te} is a given trace element concentration (μg g^{-1}) in tissue of a given non-vascular species, L_{Fe} is the Fe concentration (μg g^{-1}) in tissue of that same non-vascular species, S_{te} is the trace element concentration (μg g^{-1}) of the Earth's Upper Continental Crust (Taylor & McLennan, 1995; Wu et al., 2021), and S_{Fe} is the Fe concentration of the latter.

We are aware of the complications of using trace element concentrations from the continental crust to calculate EFs (Reimann & De Caritat, 2000); however, given the vastness of these peatlands and the saturated organic nature of the soil, we feel it is best to apply the upper continental crust concentrations, as upland soil is minimal in the region. Furthermore, trace elements were only considered enriched in non-vascular tissue once the EFs exceeded 10. This process has been applied elsewhere and compensates for trace element variability in the continental crust (Wu et al., 2021). All analyses were carried out in R ($\alpha = 0.05$) (RCoreTeam, 2020).

Results

Lichen metal concentrations

The base cations (K > Ca > Mg > Na) had the highest concentrations of all analytes. Notably, mean K concentrations exceeded 3000 μg g^{-1} in both *Sphagnum* species. Contributions of Al, Fe, and Zn were also considerable. Iron concentrations (~400 μg g^{-1}) were the highest in the epiphytes (*Evernia mesomorpha* > *Bryoria* spp.), whereas means were roughly ≤ 200 ug g^{-1} for terricolous cryptogams. Antimony (Sb), selenium (Se), thallium (Tl), and molybdenum (Mo) were among the lowest concentrations for all trace elements but similar among all species (Table 1).

Pearson's correlation between Fe and trace elements of cryptogams

Considering geogenic Fe complexes are constituents of atmospheric deposition in remote regions free of industrial activity (Mahowald et al., 2009), we wanted to determine if trace elements were correlated with Fe in the non-vascular organisms.

Numerous trace elements were significantly correlated with Fe for all six species assessed. For example, the coefficients of correlation for Al, Ti, and V tightly ranged between 0.87 and 0.99 ($p < 0.001$). By contrast, significant coefficients broadly ranged between 0.5 and 0.96 for Sb, Cr, and Co across all species ($p < 0.01$).

Manganese, K, and Zn concentrations of thalli and foliage were not significantly ($p > 0.05$) related to Fe

Table 1 Mean trace element concentrations (μg g^{-1}) and standard errors for various non-vascular plants in the Hudson Bay Lowlands, Ontario, Canada

Metal	*Bryoria* sp. ($n = 19$)	*Evernia mesomorpha* ($n = 19$)	*Cladonia stellaris* ($n = 26$)	*Cladonia stygia* ($n = 28$)	*Sphagnum capillifolium* ($n = 22$)	*Sphagnum fuscum* ($n = 29$)
Al	360.8 (±26.4)	430.1 (±18.3)	166.0 (±7.1)	201.3 (±11.4)	142.3 (±10.6)	136.3 (±9.1)
Sb	0.06 (±0)	0.04 (±0)	0.01 (±0)	0.02 (±0)	0.02 (±0.001)	0.03 (±0)
As	0.36 (±0.01)	0.25 (±0.01)	0.08 (±0)	0.11 (±0.01)	0.13 (±0.01)	0.13 (±0.01)
Ba	16.1 (±1.7)	10.0 (±1.6)	4.0 (±0.4)	9.2 (±0.7)	16.0 (±1.3)	12.3 (±0.9)
B	6.27 (±0.22)	1.9 (±0.1)	0.45 (±0.06)	0.77 (±0.1)	1.44 (±0.14)	1.4 (±0.1)
Cd	0.76 (±0.65)	0.31 (±0.18)	0.02 (±0)	0.04 (±0.002)	0.04 (±0.004)	0.1 (±0.03)
Ca	1866.8 (±72.8)	1067.2 (±73)	373.5 (±38.8)	799.9 (±55.9)	1923.5 (±118.4)	1370.1 (±80.6)
Cr	0.51 (±0.03)	0.57 (±0.02)	0.19 (±0.02)	0.21 (±0.01)	0.17 (±0.01)	0.18 (±0.01)
Co	0.09 (±0)	0.08 (±0)	0.03 (±0.002)	0.04 (±0.002)	0.05 (±0.003)	0.04 (±0.002)
Cu	2.13 (±0.08)	1.7 (±0.1)	0.80 (±0.03)	1.1 (±0.04)	1.71 (±0.1)	1.96 (±0.06)
Fe	315.1 (±19.9)	296.8 (±11.9)	98.5 (±3.9)	131.2 (±7.1)	102.4 (±7.1)	96.5 (±6.5)
Pb	3.91 (±0.25)	1.73 (±0.16)	0.36 (±0.03)	1.0 (±0.1)	0.64 (±0.1)	0.55 (±0.12)
Li	0.11 (±0.02)	0.17 (±0.01)	0.30 (±0.05)	0.3 (±0.1)	0.26 (±0.1)	0.34 (±0.05)
Mg	322.6 (±6.1)	243.8 (±4.5)	122.6 (±5.8)	169.5 (±8.8)	473.9 (±29.1)	438.2 (±21.8)
Mn	78.3 (±6.2)	54.7 (±4.6)	29.1 (±4.3)	80.5 (±6.3)	297.5 (±33.9)	265.4 (±18.2)
Mo	0.09 (±0)	0.06 (±0)	0.03 (±0.01)	0.03 (±0)	0.05 (±0.003)	0.09 (±0.01)
Ni	0.54 (±0.03)	0.76 (±0.2)	0.19 (±0.03)	0.24 (±0.02)	0.32 (±0.05)	0.30 (±0.04)
K	1476.3 (±18.6)	1409.1 (±17.3)	769 (±21.8)	901.9 (±31.1)	3314.1 (±159.4)	3842.8 (±155.6)
Se	0.49 (±001)	0.25 (±0.01)	0.09 (±0)	0.09 (±0.01)	0.10 (±0.003)	0.11 (±0.004)
Na	69.0 (±2.3)	66.1 (±3.0)	31.4 (±3.2)	36.8 (±3.3)	179.4 (±15.2)	124.1 (±5.1)
Sr	6.8 (±1.0)	4.0 (±0.7)	0.87 (±0.07)	1.46 (±0.11)	2.3 (±0.2)	1.86 (±0.18)
Tl	0.01 (±0)	0.01 (±0)	0.004 (±0)	0.01 (±0)	0.01 (±0.001)	0.01 (±0)
Ti	15.5 (±0.97)	17.5 (±0.7)	7.3 (±0.5)	7.6 (±0.5)	4.8 (±0.42)	4.62 (±0.4)
V	0.78 (±0.1)	0.7 (±0.03)	0.26 (±0.01)	0.39 (±0.02)	0.27 (±002)	0.28 (±0.02)
Zn	28.1 (±1.2)	24.6 (±0.8)	11 (±0.4)	12.6 (±0.5)	17.6 (±0.8)	14.1 (±0.6)

for any species of consideration. Likewise, Cd values were typically negligible ($p > 0.05$), with a notable exception for both *Cladonia stellaris* and *Cladonia stygia* ($p < 0.01$) (Table S1).

Regression between Fe and trace elements with Pearson's values > 0.8

Trace elements of geogenic origin with limited biological significance are often expressed relative to Fe, considering they are often found mineralized together (Nieboer et al., 1978; Wu et al., 2021). This is particularly relevant for Ti. Here, the Fe to Ti ratio was consistent across all species and ranged between 13.5 and 21.3, with ratios greater than 20 for the *Sphagnum* species (*Cladonia stellaris* [terricolous]: 13.5; *Evernia mesomorpha* [epiphyte]: 17.0; *Cladonia stygia* [terricolous]: 17.3; *Bryoria* spp. [epiphyte]: 20.3; *Sphagnum fuscum* [terricolous]: 20.9; *Sphagnum capillifolium* [terricolous]: 21.3).

In addition to Pearson's correlation, we provide the coefficients of determination (r^2), slope, and intercept for Al, Ti, and V which were strongly correlated (Pearson's) ($r > 0.8$, $p < 0.001$) with those of Fe (Table S2). The coefficients of determination for Al (with Fe) ranged between 0.86 and 0.95 for all species, with Ti between 0.75 and 0.95 and with V between 0.91 and 0.99, the strongest among the four (Fig. 2).

While we report that both epiphytic species had the highest concentrations of Fe and other trace elements when compared with all other cryptogams, the slopes are all relatively similar. For example, Al slopes ranged between 1.3 and 1.7, whereas Ti and V are just above 0. Intercepts (β), on the other hand, were considerably variable. Aluminum for example was positive for *Evernia mesomorpha* ($\beta = 2.67$) and *Sphagnum fuscum* ($\beta = 9.17$), but negative for all others with a low of -48.2 (*Bryoria* spp.) Similar to their slopes, intercepts for Ti and V hovered around 0 (Table S2).

Comparisons of trace elements with iron in organic soil

Unlike non-vascular organisms, there were no relationships between Al, Ti and V, and Fe in organic soils ($p > 0.05$). The range in Fe was large and although most sites (where organic soil was collected, $n = 18$) were weighted towards the low end < 1000 μg g^{-1}, some values were an order of magnitude higher, in some cases greater than 30,000 μg g^{-1} (Figs. S1 through S4). The Fe to Ti ratio was much higher for organic soil relative to cryptogams at 4023 (cryptogam range 13.5 to 21.3).

Trace element enrichment factors

While most elemental enrichment factors were < 10, some were greater (than 10), including Sb, As, B, Mn, and Zn. The latter were typically enriched across all species considered in the study, while enrichment of Ca, Mg, K, and Mo was almost exclusively reported in *Sphagnum*. For Cu, enrichment was evident in the

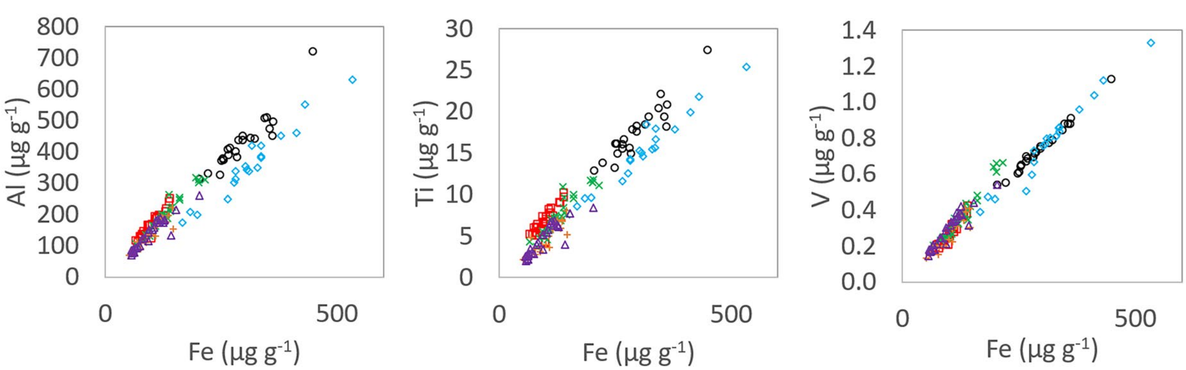

Fig. 2 Relationship between Fe and Al, Ti, and V for non-vascular species in the Ring of Fire region of the Hudson Bay Lowlands, Ontario, Canada. *Y*-axes not standardized. Open black circles, *Evernia mesomorpha*; open blue rhombus, *Bryoria* spp.; red open square, *Cladonia stellaris*; green x, *Cladonia stygia*; red +, *Sphagnum capillifolium*; purple open triangle, *Sphagnum fuscum*

Sphagnum species (EF > 25), but proximal (EF ~ 10) in the lichens, with only the terricolous forms having factors slightly exceeding 10 (Table 2).

Discussion

This work is the first to report trace element concentrations for non-vascular species in the Hudson Bay Lowlands of Ontario, Canada. Despite low thalli and foliar trace element concentrations and the strong linear relationships between Fe and Al, Ti, and V, enrichment factors of other some trace elements suggest anthropogenic deposition sources are a factor. Nonetheless, strong linearity between Fe and the other trace elements is most likely the result of deposition of geogenic origin (Nieboer et al., 1978).

Background concentrations of metals with mining importance in the ring of fire region: chromium, nickel, and copper

Since lichens and bryophytes lack roots and vascular systems, the trace element concentrations presented here are representative of ambient atmospheric conditions in the region. The Cr, Ni, and Cu concentrations are particularly relevant given their mining importance (Chong, 2014) and are among the lowest values we are aware of in the broader literature (Bennett, 1995; Demirbas, 2004; Puckett & Finegan, 1980; Rodushkin et al., 2007; Valeeva & Moskovchenko,

Table 2 Elemental enrichment factors for non-vascular species in the Hudson Bay Lowlands. Elemental enrichment factors were calculated using elemental concentration in Earth's Upper Continental Crust (Taylor & McLennan, 1995; Wu et al., 2021) and normalized to Fe

Trace element	*Bryoria* sp. (*n* = 19)	*Evernia mesomorpha* (*n* = 19)	*Cladonia stellaris* (*n* = 26)	*Cladonia stygia* (*n* = 28)	*Sphagnum capillifolium* (*n* = 22)	*Sphagnum fuscum* (*n* = 29)
Al	0.49 (±0.04)	0.63 (±0.04)	0.73 (0.05)	0.67 (±0.05)	0.6 (±0.06)	0.62 (±0.0625)
Sb	**35.4 (±6.36)**	**24.2 (±3.34)**	**21.7 (±6.69)**	**20.8 (±4.38)**	**41.5 (±9.98)**	**51.5 (±11.5)**
As	**28.3 (±7.98)**	**20 (±1.83)**	**19.8 (±4.97)**	**18.8 (±2.59)**	**29 (±5.94)**	**30 (±7.69)**
Ba	3.51 (±2.01)	2.14 (1.52)	2.52 (±0.97)	4.56 (±1.44)	**10.7 (±4.47)**	8.61 (±3.14)
B	**51.9 (±24.6)**	**14.8 (±3.53)**	**10.3 (±5.19)**	**14 (±6.48)**	**33.9 (±13)**	**34.5 (±14.6)**
Cd	0.88 (±3.27)	0.39 (±1.17)	0.08 (±0.03)	0.10 (±0.03)	0.15 (±0.0782)	0.33 (±0.636)
Ca	7.27 (±1.79)	4.24 (±1.33)	4.38 (±1.94)	7.46 (±2.58)	**23 (±6.82)**	**17.9 (±6.88)**
Cr	1.64 (±0.2)	1.95 (±0.22)	1.93 (±0.78)	1.59 (±0.3)	1.67 (±0.214)	1.96 (±0.584)
Co	1.08 (±0.16)	0.99 (±0.09)	0.97 (±0.20)	1.03 (±0.18)	1.57 (±0.316)	1.65 (±0.357)
Cu	9.82 (±1.65)	8.12 (±1.73)	**11.7 (±2.59)**	**12.1 (±2.74)**	**25.5 (±7.79)**	**31.6 (±11)**
Pb	0.87 (±0.1)	0.41 (±0.16)	0.25 (±0.08)	0.54 (±0.17)	0.42 (±0.0828)	0.36 (±0.196)
Li	0.53 (±0.43)	1.03 (±0.33)	5.24 (±4.13)	4.49 (±3.75)	3.85 (±3.39)	5.36 (±4.06)
Mg	2.88 (±0.8)	2.21 (±0.34)	3.33 (±0.71)	3.58 (±1.08)	**13.3 (±5.4)**	**13 (±4.76)**
Mn	**15.1 (±5.25)**	**11.1 (±4.74)**	**17.1 (±11.6)**	**39.2 (±22.2)**	**180 (±102)**	**186 (±102)**
Mo	6.71 (±1.15)	4.93 (±0.49)	7.56 (±6.14)	5.78 (±1.74)	**12.4 (±4.87)**	**23.4 (±8.91)**
Ni	3.03 (±0.7)	4.74 (±6.22)	3.47 (±2.82)	3.22 (±0.89)	5.33 (±2.62)	5.48 (±3.29)
K	6.31 (±1.93)	6.11 (±1.1)	10.1 (±2.35)	9.26 (±3.1)	**46.3 (±23.8)**	**58.1 (±28)**
Se	1.16 (±0.3)	0.59 (±0.09)	0.62 (±0.15)	0.48 (±0.07)	0.74 (±0.19)	0.81 (±0.200)
Na	0.28(±0.05)	0.28 (±0.07)	0.38 (±0.14)	0.35 (±0.14)	2.2 (±0.742)	1.7 (±0.6)
Sr	2.56 (±2.25)	1.32 (±1.07)	0.89 (±0.30)	1.15 (±0.37)	2.27 (±0.756)	1.93 (±0.535)
Tl	0 (±0)	0 (±0)	0 (±0)	0 (±0)	0.01 (±0.00249)	0 (±0.002)
Ti	0.57 (±0.04)	0.69 (±0.04)	0.87 (±0.27)	0.67 (±0.08)	0.54 (±0.106)	0.55 (±0.097)
V	1.43 (±0.1)	1.46 (±0.03)	1.55 (±0.1)	1.69 (±0.14)	1.51 (±0.197)	1.71 (±0.156)
Zn	**46.4 (±12.5)**	**41.7 (±7.98)**	**57.1 (±15.5)**	**50 (±15)**	**91 (±31.3)**	**79.8 (±31.2)**

Bolded values: trace elements with enrichment factors exceeding 10

2002). Presumably, there are two reasons for this. Firstly, the saturated organic surface layer of the peatlands minimizes local atmospheric particulate entrainment resulting in low rates of dust deposition (Mahowald et al., 2009). Secondly, concentrations here are most likely affected by digestion strength and analytical method (Cook et al., 1997; Neary & Barnes, 1993). For example, Puckett and Finegan (1980) analyzed *Cladonia stellaris* thalli using X-ray fluorescence, a method effectively used to determine totals, and reported Cr concentrations between 1.09 and 2.05 μg g^{-1}. By contrast, Demirbas (2004) reported background concentrations of *Cladonia stellaris* in the same range as Puckett and Finegan (1980) in Europe, which are 5 to tenfold higher than those here, but used a similar HNO_3 digest method, ultimately highlighting the low trace element concentrations in the Hudson Bay Lowlands.

Puckett and Finegan (1980) also report elevated concentrations of Cu and Ni in *Cladonia stellaris* compared to our measurements. They report Cu values ranging between 0.79 and 2.77 μg g^{-1} and a mean Ni concentration of 2.9 μg g^{-1}.

Notable background concentrations have been reported for the other species as well. Demirbas (2004) reported Cr and Cu concentrations for *Evernia mesomorpha* at 1.42 μg g^{-1} and 4.91 μg g^{-1}, respectively, again marginally higher than those from the Hudson Bay Lowlands. Bennett (1995) reported similar background concentrations to those here for both Cr (0.74 μg g^{-1}) and Cu (2.65 μg g^{-1}) for *Evernia mesomorpha* growing at Isle Royal National Park Michigan, USA (~500 km south of Hudson Bay Lowlands).

Globally, concentrations of Cr, Cu, and Ni in *Sphagnum* spp. vary considerably. In Europe for example, median Cr concentrations reportedly range between 0.60 and 13.21 μg g^{-1}. In North America, Gstoettner and Fisher (1997) report 1.68 μg Cr g^{-1} (*Sphagnum* spp.) while Pakarinen and Gorham (1983) reported *Sphagnum fuscum* Cu foliar concentrations between 2.5 and 6.5 μg g^{-1} for species in peatlands of both Canada (Ontario and Manitoba) and the USA (Minnesota).

The Ni concentrations here for *Sphagnum fuscum* (0.3 μg g^{-1}) are comparable with those reported for other remote parts of Canada near Great Slave Lake, Northwest Territories, which ranged between 0.2 and 0.8 μg g^{-1} (Pakarinen & Tolonen, 1976). Similarly, background *Sphagnum capillifolium* concentrations in Italy have been reported at 2.35 μg g^{-1} (Adamo et al., 2003), somewhat higher than those from the study region in the Hudson Bay Lowlands.

Linear relationship between Fe and Al, Ti, and V

The Fe to Ti ratio of Earth's crust is consistently reported between 6 and 8 (Nieboer et al., 1978). Studies relating the mineral composition (ratios) of thalli to geogenic sources have reported similar Fe to Ti ratios as well as a strong correlation between Fe and Ti concentrations in thalli. This suggests atmospheric deposition of entrained mineral particles of lithospheric origin is a strong driver of lichen thalli chemical composition under background conditions (Nieboer et al., 1978). We observed a similar trend here that not only included lichens (*Cladonia stellaris*, *Cladonia stygia*, *Evernia mesomorpha*, and *Bryoria* spp.) but both *Sphagnum fuscum* and *Sphagnum capillifolium* as well. We are not aware of other works that report relationships encompassing these species. The Fe to Ti ratios, however, ranged between 13.5 and 21.3, greater than those of Earth's crust. This may reflect digestion strength, as the aqua regia digests may not have dissolved all metal oxides (Cook et al., 1997; Neary & Barnes, 1993).

Globally, 95% of atmospheric Fe deposition originates from lithospheric particles that become entrained in air and settle out via wet and dry processes over days to weeks (Mahowald et al., 2009). Models suggest the Hudson Bay Lowlands receive Fe deposition between 0.002 and 0.02 g m^{-2} $year^{-1}$, which is low relative to that of other regions (Mahowald et al., 2009). Additionally, modeled (Mahowald et al., 2009) and empirical air concentrations of Fe (Su et al., 2021) in the Hudson Bay Lowlands strongly agree with one another. As such, we assume the modeled deposition values of Fe are a good representation of what receptors are exposed to. Invariably, this Fe deposition will interact with non-vascular plants that derive their nutrients from the atmosphere (Avila-Perez et al., 2019; Bargagli et al., 2002; Loppi & Bonini, 2000). Furthermore, Mahowald et al. (2009) suggest all Fe deposition in the region originates from North America. With the exception of some eskers, mineral soil exposure is minimal, as the region (Hudson Bay Lowlands) is covered with a deep surface peat layer, largely unbroken from western Quebec through Ontario to Manitoba, Canada (Garrah, 2013); therefore, we assume particulate atmospheric deposition is derived from long-range transport. This is further supported by peat stoichiometry, which did not have the same linear relationships between Fe and Al, Ti, and V.

While we do not have lichen or bryophyte (capitula) biomass estimates for the region, others have shown bogs in Nova Scotia, Canada, can have 2.7 g m^{-2} of epiphytes and 63.8 g m^{-2} for terricolous lichens (Wein & Speer, 1975). Conversely, *Sphagnum* spp. capitula biomass in bogs and poor fens near Ottawa, Ontario, have been reported at 144 g m^{-2} and 160 g m^{-2} (Moore et al., 2002).

Using the biomass data, we can estimate the Fe pool in lichens and bryophytes and compare them with Fe deposition reported by Mahowald et al. (2009). Here, Fe pool estimates for non-vascular plants are around 23,100 μg m^{-2} (mean epiphytes ~ 800 ug m^{-2}; mean terricolous ~ 7300 μg m^{-2}; mean *Sphagnum* spp. capitula ~ 15,000 μg m^{-2}). These estimates compare nicely with atmospheric Fe deposition for the region (2000–20,000 μg m^{-2} $year^{-1}$) (Mahowald et al., 2009) once annual growth rates are considered. For example, lichens have been shown to retain trace elements for up to 5 years (Walther et al., 1990). Some have even suggested older thalli have more ion binding sites than fresh material (Brown, 1991). This would be particularly relevant for the epiphytic lichens here, due to our collection method (whole lichen harvesting).

The high Fe concentrations in some peatlands are most likely the result of exposure to Fe-enriched groundwater (McDonough & Todd, 2020). As a result, it is highly unlikely that Fe complexes found in peat in the area will become atmospherically entrained at quantitatively relevant loads to produce the concentrations and stoichiometry (Fe:Ti and Fe:V) observed in epiphytic lichens. Despite this, we recognize there are considerable mineral deposits that include Fe–Ti–V complexes in the region (Chong, 2014; Rainsford et al., 2017). As a result, aeolian transport of exposed physically weathered rock and soil originating from eskers in the Hudson Bay Lowlands is possible and may have contributed minimally to the linear relationships between Fe and Al, Ti, and V in the non-vascular plants.

Enrichment factors

As atmospheric Fe in the region is most likely geogenic, we believe it is suitable as a normalizing factor when calculating trace element enrichment in lichens and mosses. The EFs suggest that deposition of natural and anthropogenic sources most likely contributes to the chemical composition of non-vascular organisms in the Hudson Bay Lowlands. This is particularly evident for Sb, As, B, Mn, and Zn, which had EFs > 10 across all species.

Aside from soil weathering, Sb can enter the atmosphere via volcano eruptions and automobiles, ultimately leading to biological enrichment (of Sb), relative to Earth's crust (Paoli et al., 2013). Generally, anthropogenic Sb emissions are low in Canada, as most provinces contributed between 0 and 20 kg of Sb in 2010, with Alberta (20–50 kg Sb $year^{-1}$) and Ontario (50–100 kg Sb $year^{-1}$) as the exceptions. Despite low emission rates (2010 data) relative to other countries, some areas of the mid-west and northeastern USA released upwards of 1000 kg Sb during 2010 (Tian et al., 2014). Su et al. (2021) also reported very minor contributions of Sb in the Hudson Bay Lowlands, but suggested a portion arrived from the Great Lakes Region in both Canada and the USA.

While all species show considerable As enrichment, concentrations in lichens are comparable with other *Cladonia* species found in bogs in the boreal forest. Arafat and Glooschenko (1982), for example, reported As concentrations in *Cladonia* species as high as 2.3 μg g^{-1} near Sudbury, while 200 to 450 km northwest, concentrations decreased and were comparable to non-vascular plants here, which ranged between 0.12 and 0.32 μg g^{-1}. Arafat and Glooschenko (1982) attributed the As concentration gradient in *Cladonia* to atmospheric deposition from smelting in both Sudbury and Timmins, Ontario.

The elevated EFs for B in the study region might be the result of both natural deposition, originating from the ocean, and anthropogenic derived from industry. Boron exists as boric acid (H_3BO_3 (*g*)) in the atmosphere which is derived from seawater. Eventually, through long-range transport, B from seawater origin deposits terrestrially as part of its global biogeochemical cycle (Park & Schlesinger, 2002). This source, in addition to B derived via crustal weathering, should inherently lead to elevated enrichment factors in the non-vascular organisms. Conversely, central Ontario receives some industrially derived B emissions from southern Ontario and northeastern USA (Gao et al., 1996). As such, we cannot rule out anthropogenic sources in the Hudson Bay Lowlands, as air masses from the Great Lakes region can reach the Hudson Bay Lowlands (Su et al., 2021). Separating natural and anthropogenic B deposition, however, is not possible in the current study.

In addition to geogenic Zn sources, there are numerous anthropogenic derivatives including automobile wear, electroplating, and industrial combustion. The remoteness of the study site coupled with the elevated Zn EFs again suggests atmospheric long-range transport. Elevated Zn concentrations are often associated with fine particulates (Schleicher et al., 2020). Wiklund et al. (2020) reported Zn deposition just over 2 mg m^{-2} $year^{-1}$ in northwestern Ontario (west of our study site) and suggested most was likely an anthropogenic derivative from Asia.

Manganese enrichment in lichens and mosses was evident among all species. Using atmospheric cerium/lanthanum ratios, Su et al. (2021) provide limited evidence that atmospheric Mn in the study region was a combination of natural (geogenic and forest fires) and anthropogenic (steel and coal industries) sources. While this helps to somewhat explain the elevated EFs for Mn, it does not explain the palpable differences between lichens and mosses. We speculate this discrepancy could be related to ecosystem cycling (Watmough et al., 2007; Navratil et al., 2007; Avila & Rodrigo, 2004) and *Sphagnum* physiology. *Sphagnum* species (including *Sphagnum capillifolium* and *Sphagnum fuscum*) are known to have a high cation exchange capacity (CEC) relative to other non-vascular organisms (Hajek & Adamec, 2009). Considering Mn is subject to cation exchange processes in the environment (Watmough et al., 2007), any Mn enrichment in throughfall (Watmough et al., 2007; Navratil et al., 2007; Avila & Rodrigo, 2004) at the peatland sites could partition at a higher rate on moss surfaces relative to lichens. This exchange process would also explain the high EFs for the base cations (Ca, Mg, and K) in *Sphagnum fuscum* and *Sphagnum capillifolium*.

Percy and Borland (1984) suggested natural inputs of Mn resulted with a mean *Sphagnum magellanicum* concentration of 244.6 μg g^{-1} for ombrotrophic bogs of eastern Canada (New Brunswick, Nova Scotia, and Prince Edward Island; Peace and Friendship Treaty Lands), which is comparable with results reported here. Nonetheless, future mass balance exercises of Mn and the base cations could help reconcile the elevated EFs in mosses.

Enrichment of Mo was only evident in the *Sphagnum* mosses. Northern peatlands organic soil and *Sphagnum* moss can contain nitrogen-fixing bacteria (diazotrophs) and Mo plays a central role in this process (Warren et al., 2017). The relatively higher portion of Mo to Fe might be explained by the presence of diazotrophs on *Sphagnum spp*. Alternatively, the considerably low concentrations of Mo observed among all species could lead to large variation of EFs and have less to do with deposition or biology.

Copper EFs for the lichens hovered around 10, but like other trace elements, they were considerably higher for the mosses. Air masses from the Great Lakes region can influence the Hudson Bay Lowlands region, including those originating from Sudbury, the home of major Ni and Cu smelting operations (Su et al., 2021; Sofowote & Dempsy, 2015). While Cu emissions from Sudbury have decreased because of modern stack technology, it has not been fully eliminated (Meadows & Watmough, 2012) and might explain the enrichment.

Limitations

For most trace elements, concentrations were highest in the epiphytic lichens relative to terricolous and *Sphagnum* species. Some reports suggest terricolous lichens have a stronger affinity for trace elements than epiphytes given their proximity to mineral soil or dust generated from soil (Osyczka et al., 2016). Here, terricolous lichens and *Sphagnum* spp. grow atop organic soil, thereby lacking contact with mineral soil. With the exception of Fe at some sites, trace element concentrations in surface water in the region are low (McDonough & Todd, 2020; Ulanowski & Branfireun, 2013). These lichens and bryophytes are predisposed to periodic flooding during seasonal changes in peatland hydrology. Water moving across terricolous lichens and *Sphagnum* spp. could effectively remove particulates embedded within hyphae-algae mosaic or from foliage, respectively (Adamo et al., 2007). Surface washing might be responsible for the considerably higher trace element concentrations in epiphytes relative to ground-dwelling lichens and bryophytes as they are only exposed to ambient precipitation. This may limit future atmospheric monitoring if peatland hydrology is impacted by mining. If future industrial operations impact peatland hydrology, terricolous lichens and mosses in bogs may not survive due to flooding or desiccation (Fay & Lavoie, 2009; Waddington et al., 2015); evidently, they will not serve as biomonitors or bioindicators. Despite this, epiphytes should remain strong bioindicators and biomonitors of air quality as industrialization commences, as *Evernia mesomorpha* and *Bryoria* spp. have a moderate range of sensitivity (Laxton et al., 2010; Myllys et al., 2016; Watmough et al., 2019; Will-Wolf et al., 2017) and grow efficiently on necrotic branches (Brodo et al., 2001).

Conclusion

Here, we provide the first account of trace element concentrations in lichens and bryophytes of the Hudson Bay Lowlands, which are among the lowest reported in the broader literature. The linear relationships between Fe and other trace elements, the low overall trace element concentrations, and the generally low EFs in non-vascular organisms suggest the region is relatively pristine. There are some notable exceptions (Sb, As, B, Mn, and Zn,), but separating anthropogenic from natural sources needs more attention in the region. We suggest that epiphytic lichens provide the best biomonitors of atmospheric deposition among all non-vascular organisms considered here.

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Author contribution Andrew McDonough conducted the field and lab work and wrote much of the paper. All the other authors conducted field and lab work and contributed to writing the paper.

Availability of data and materials All data for this work will be made available upon reasonable request.

Declarations

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Consent to participate Not applicable.

Consent for publication We consent.

Conflict of interest The authors declare no competing interests.

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