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Determination of elemental baseline using peltigeralean lichens from Northeastern Canada (Québec): Initial data collection for long term monitoring of the impact of global climate change on boreal and subarctic area in Canada

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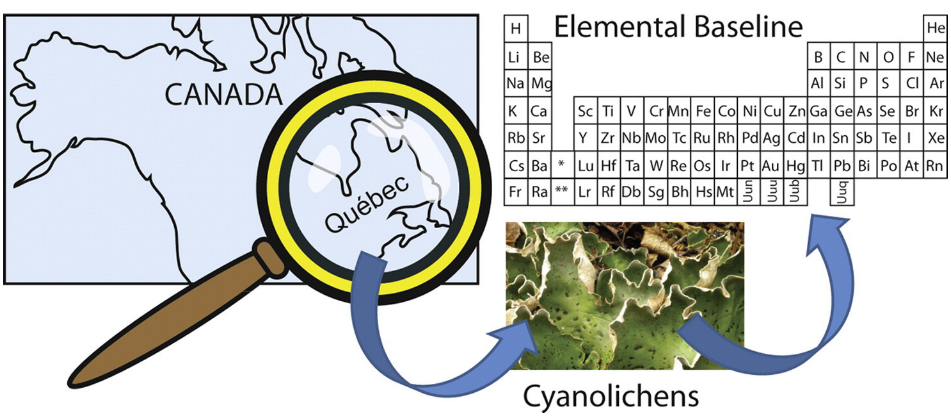
GRAPHICAL ABSTRACT



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ABSTRACT

Northeastern Canada is mostly free of anthropogenic activities. The extent to which this territory has been impacted by anthropogenic atmospheric depositions remains to be studied. The main goal of our study was to establish background levels for metals in boreal muscicolous/terricolous macrolichens over non-urbanized areas of northeastern Canada (Québec). Concentrations of 18 elements (Na, Mg, Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, and Pb) were determined for three species of the genus *Peltigera* (*Peltigera aphthosa* (L.) Willd. s.l., *Peltigera neopolydactyla* (Gyeln.) Gyeln. s.l., *Peltigera scabrosa* Th. Fr. s.l.), and *Nephroma arcticum* (L.) Torss., along a 1080 km south–north transect and along a of 730 km west–east transect. We report that elemental contents in the sampled lichen thalli are very low and similar to background levels found in other studies performed in pristine places (high elevation or remote ecosystems) throughout the world.

Overall, our results demonstrate that most of the boreal and subarctic zone of Québec (northeastern Canada) is still pristine. The elemental baseline established in these lichen populations will contribute to

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monitor metal pollution in boreal and sub-polar ecosystems due to global climate change and future industrial expansion.

1. Introduction

Climates of the northern hemisphere will undergo significant changes in the next decades. By the end of this century, according to the 2013 International Panel for Climate Change (IPCC) report, the average temperature in boreal and sub-polar regions is expected to rise from 3 to 11 °C, the snow and ice cover of the northern hemisphere will be reduced by up to 50%, and the annual precipitation in high latitudes will increase from 10 to 40% compared to 2005 (Logan et al., 2011; scenarios RCP 2.6 and RCP 8.5 in Working Group I Contribution to the IPCC Fifth Assessment Report, 2013). In addition to these environmental concerns, global warming offers new economic opportunities that will likely further impact these natural boreal and arctic habitats. In the next 20 years, the Government of Québec plans to expand economic activities northward as part of the Canadian strategy to increase the exploitation of natural resources in its northern regions (Gouvernement du Québec, 2014). That development would inevitably impact boreal and subarctic ecosystems.

Lichens have been used as biomonitors in countless studies (Nash and Gries, 1995; Sloof, 1995; Conti and Cecchetti, 2001; Garty, 2001; Jeran et al., 2002; Nimis et al., 2002; Wolterbeek, 2002; Nash, 2008c; Seaward, 2008); lichens are ubiquitous, slow growing and long living symbioses, able to tolerate high levels of metal contaminants (Seaward, 2007; Nash, 2008c). They are particularly abundant in boreal and arctic regions where they can be the dominant photoautotrophs (Seaward, 2008). While some studies have reported the elemental content of lichens from northwestern Canada (Tomassini and Puckett, 1976; Puckett and Finegan, 1980; Nash and Gries, 1995; Chiarenzelli et al., 2001), Ontario (Tomassini and Puckett, 1976), southern Québec (Evans and Hutchinson, 1996; Aznar et al., 2008) and Greenland (Riget et al., 2000), data from northeastern Canada are limited to specific metals of health concern in the reindeer food industry, generally Pb, Cd and Hg (Crête et al., 1992).

In the context of a global warming mediated economic development in northern regions, defining background levels for metal contaminants in lichen species from northeastern Canada (Québec) is urgently needed. Our study provides a baseline dataset for future biomonitoring surveys designed to evaluate the impact of human activities in northern Québec and contributes to the overall understanding of biogeochemistry in boreal regions.

In this study, we measured the elemental composition of four species: *Peltigera aphthosa* (L.) Willd. s.l., *Peltigera neopolydactyla* (Gyeln.) Gyeln. s.l., *Peltigera scabrosa* Th. Fr. s.l., and *Nephroma arcticum* (L.) Torss, collected along two transects (1080 km south–north and 730 km east–west) covering a large fraction of northeastern Canada. These lichen-forming fungi from the families Peltigeraceae and Nephromataceae (Peltigerales; Lecanoromycetes; Ascomycota) are associated with cyanobacteria (*Nostoc* spp.) or a combination of *Nostoc* and a unicellular green alga (*Coccomyxa* sp.) and are ubiquitous in boreal and subarctic regions (Vitikainen, 1994; Miadlikowska and Lutzoni, 2000, 2004; Brodo et al., 2001; Martínez et al., 2003).

2. Materials and methods

2.1. Lichen sampling

The sampling for this study is derived from a sampling designed specifically for a project focusing on fungal endophytes of the boreal biome (endobiodiversity.org). Additional specimens were collected for a revisionary taxonomic study of the genus *Peltigera* (www.peltigera.lutzonilab.net) and for this study. All lichens were collected in August 2011 in the Province of Québec, along a 1080 km south–north (SN) transect (from SN2, 48°37′58″N 73°2′20″W to SN9, 57°49′36″N 73°11′45″ W) and a 730 km east–west (EW) transect (from W50, 50°54′11″N 69°33′56″W to E400, 51°37′5″N 59°9′1″W) (Fig. 1A–B). Because of their abundance and broad distribution in boreal forests, four species were collected along both transects: *P. aphthosa* s.l., *P. neopolydactyla* s.l., *P. scabrosa* s.l., and *N. arcticum*. An ongoing molecular systematic revision of the genus *Peltigera* by Miadlikowska et al.(e.g., 2014) strongly suggest that the focal species contain multiple taxonomic entities, which are likely to be recognized at the species level. Therefore, the current broad species concept (s.l.) is used throughout the text.

We selected our biological material based on their biogeochemical relevance and availability in nature. The peltigeralean lichens selected for this study are living on mosses, which are of particular importance to nitrogen inputs in boreal forest (DeLuca et al., 2002), and are known to fix nitrogen. Therefore, they will provide a better evaluation of the potential impact of atmospheric depositions on the boreal forest biogeochemistry. Moreover, *Peltigera* species were found throughout the boreal belt as part of a study on endophytic and endolichenic fungi of the boreal biome (see endobiodiversity.org) and are present in the arctic, i.e., beyond the tree line. The latter point is important because the choice of this genus and *N. arcticum* enables a sampling for atmospheric deposition beyond what is possible with arboreal lichens.

Nine sampling sites (SN1–SN9) were equally distributed along the SN transect, approximately one at each 150 km segments (Fig. 1A–B). At each sampling site along the SN transect, individual thalli were collected at three sub-sites, one central sub-site and two sub-sites about 2 km away (in opposite directions) from the central sub-site, for a maximal distance of 4 km from the two most distant sub-sites. Within each sub-site, lichens were collected at three microsites, where two of the three microsites were 30 m away from the central microsite for a total distance of approximately 60 m from one terminal microsite to the other. For this study we used lichen thalli collected at sites SN2 to SN9, as no lichen thalli were found at SN1 (black spruce dominated forests of La Mauricie National Park). On the EW transect (Fig. 1A–B), the sites were distributed from a central point (EW0) at a doubling distance toward the west up to about 650 km (400 miles) west of that central point (W1.5, W3, W6, W12.5, W25, W50, W100, W200, W400). For this study we used lichens collected at sites up to W50, inclusively, as not enough lichen thalli were found at W100 and no peltigeralean lichens were found at W200 and W400. No sub-sites were established along the EW transect, however three microsites were sampled as for the SN transect. For the east arm of this transect, only sites E50, E100, E200 and E400 were sampled (Fig. 1A–B). A summary of the lichens sampled for this study can be found in Sup. Info. Table S1. Lichens were air dried, cleaned from soil, plant and other organic debris, and then stored in paper bags at room temperature in the dark before further processing.

2.2. Mineralization and analysis of samples

Elemental analyses were performed on individual thalli. Healthy looking parts of lichen thalli were oven dried (70 °C, 24 h), weighted (0.5 ± 0.02 g) and inserted in 55 mL Teflon® vessels with 10 mL of concentrated nitric acid (HNO_3, trace metal grade, Fisherbrand). Digestions were performed with a MARS Xpress Microwave assisted digestion system at 170 °C for 1 h. Digested samples were recovered in 15 mL conical centrifuge tubes and stored at 4 °C prior to analysis. Procedural blanks

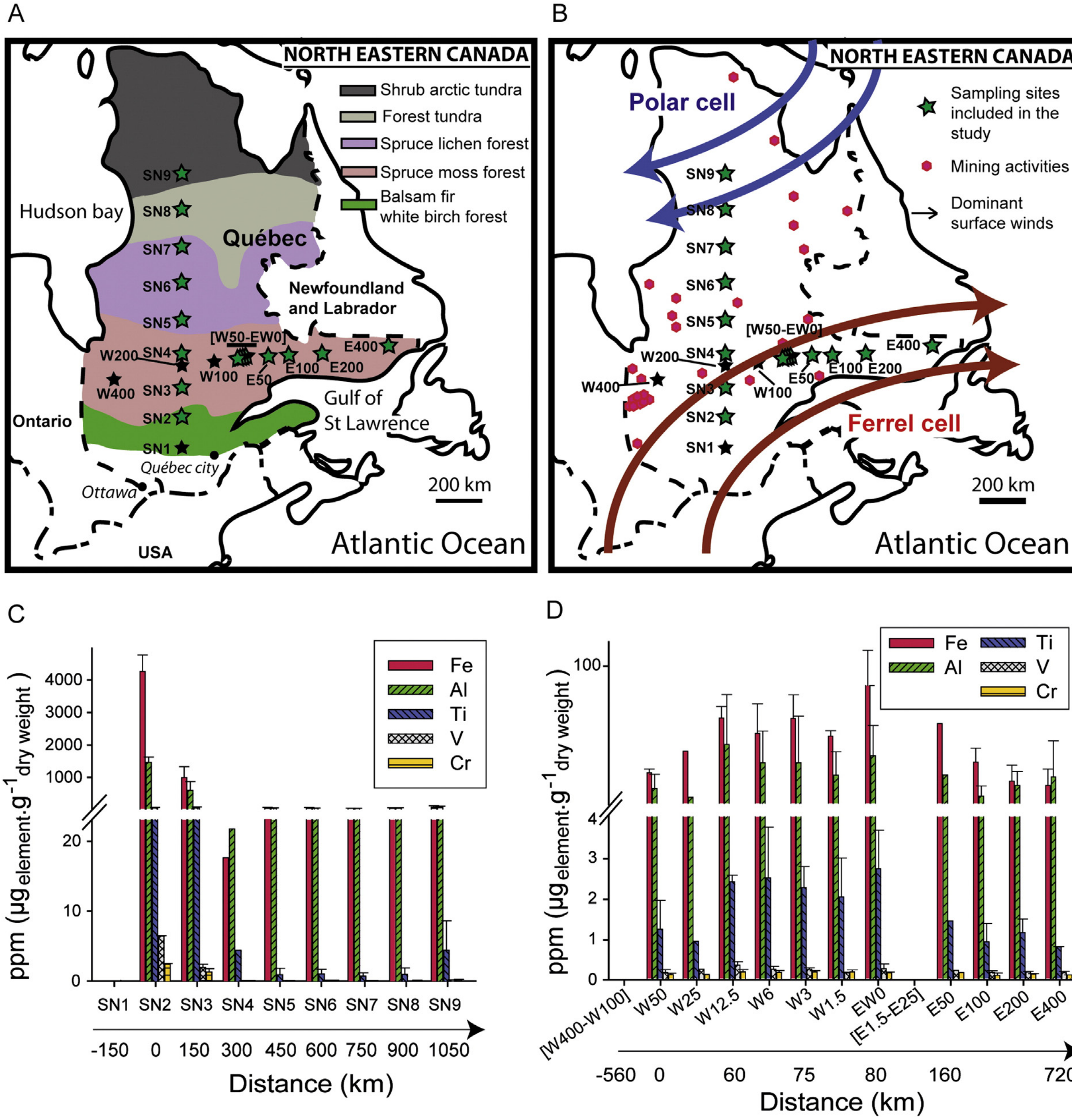

Fig. 1. Sampling sites in Québec and comparisons of Fe, Al, Ti, V, and Cr contents along transects. (A) Geographic localization of sampling sites with main vegetation zones (Gouvernement du Québec, 2013b). (B) Geographic localization of the main mining activities in Québec (Gouvernement du Québec, 2013a) and directions of dominant winds. For both panels, stars represent sites sampled as part of a separate study (endobiodiversity.org). Green stars represent sites from which *Peltigera* and *Nephroma* specimens were used for this study. (C) Comparison of some metals along a south–north (SN) oriented transect and (D) along an east–west (EW) oriented transect. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

were done for every set of digestions. All elemental quantifications of Na, Mg, Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd and Pb were done on a Thermofisher XSeries II Inductively-Coupled Plasma Mass Spectrometer (ICP-MS) and PlamaLab software v2.6.1.335. Rhodium was used as an internal standard and the accuracy of measurements was tested using CRM SLRS5 (NRCC). Replicability was below 5% for all elements (except for Ti 12% and Fe 6%) and repeatability was below 10% for all elements, except for Mg (19%), Ti (27%) and Fe (17%). Element recovery was assessed by spiking a dummy lichen sample (constituted of a mix of 100 digested lichens) with a multi-element standard solution (See Sup. Info. Table S2). Full duplicates (selection, digestion, measurement and data processing) were performed to control the validity of the method. Results were reported in μg of element per g of oven dry weight lichen ($\mu g \cdot g^{-1}$ of dry weight).

2.3. Statistics

Due to the close structure of the metal content, our data set was transformed using centered log-ratio (clr) (Aitchison, 2003; Filzmoser et al., 2009a, 2009b). Then, a principal component analysis (PCA) of compositional data was performed in order to reduce the size of the data set by highlighting factors that explain variation in the composition of the thalli. While many studies (e.g., Puckett and Finegan, 1980; Monaci et al., 2012) have used classical PCA, this is the first time compositional PCA is being used on data from lichen. The compositional biplot must be analysed in term of ratio of elements; the center of the plot represents the average composition, and links between arrows represent the ratio between elements. Due to the large number of variables, results from the PCA were separated into two different types of graphs (see Sup.

Info Supplementary methods for details on compositional biplot interpretation and description). All statistics were performed using R software v2.15.2 with RStudio, Composition, FactomineR, Stats and Nortest pack (R development core team; http://www.cran.r-project.org). Medians and median absolute deviations were used as estimators of central tendency and dispersion to conveniently show non-transformed data.

3. Results and discussion

3.1. Principal component analysis

3.1.1. Major southern anomaly

A first PCA analysis performed on all data (Sup. Info. Fig. S1) highlighted a major anomaly associated with the southernmost sampling sites (i.e., SN2 and SN3). PC1 clearly separates SN2 and SN3, which show a higher ratio of terrigenous insoluble elements such as Fe, Al, Ti, V to soluble elements such as P, Mg, K and Mn, from all other sites (Sup. Info. Table S3 and Fig. S1B). This difference among sampling sites is likely due to their southern geographic location and proximity to pollution rather than their bioclimatic domain (Fig. 1A–B). SN3 is located in the spruce moss domain, which is the same bioclimatic domain as for SN4 and yet, thalli sampled at SN3 show high metal contents, compare to SN4 (Fig. 1A, C). It is also worth noting that while we sampled different bioclimatic domains, samples were collected where black spruce was the dominant tree (as much as possible).

The relative abundance of cyanolichens further supports the hypothesis of an anthropogenic origin of the southern anomaly. Some lichens are known to be susceptible to anthropogenic nitrogen deposition, nitrogenic acid rain and other city-derived sources (Nash, 2008a, 2008b). No *Peltigera* and *Nephroma* species were found at SN1, W400 and W100 and were nearly absent from SN2, SN3, SN4 and W200 (Sup. Info. Table S1). These southern and western most sites are located in the proximity of active mining areas (Fig. 1B) and near urbanized and industrialized areas (along the Saint Lawrence River). The location of these sampling sites relative to the mining sites and cities is also consistent with dominant winds in the region (Fig. 1B). Thus, the lack of lichens in the southern most portions of these transects could be due to metal pollution and/or to enhanced nitrogen pollution from urbanized areas. This could also explain the overall distribution of some of these lichen species (e.g., *N. arcticum*) in Québec (see Brodo et al., 2001). Further dedicated research, including a more intensive survey, is required to clearly establish the role of human activities on the abundance of cyanolichens in the region.

Because our main objective was to determine baseline metal contamination levels, samples collected at SN2 and SN3 (Sup. Info. Tables S1 and S3) were excluded from further analyses. A new PCA was performed without samples from SN2 and SN3 (Fig. 2). Results highlight that samples from SN4 to SN9 and W50 to E400 can hardly be differentiated based on their geographical location (Figs. 1, 2B). This is unexpected considering the large territory and bioclimatic range covered by the sampling, especially along the SN transect. This finding suggests that elemental deposition in most of northern Québec is homogeneous. Only few and small geographic anomalies could be revealed and likely reflects local conditions (natural and anthropogenic, See Sup. Info Supplementary discussion 2.1 for details).

3.1.2. Elemental composition of thalli

The variable biplot (Fig. 2) shows comparable repartition of elements between the two first PCs when compared to the one obtained with the first analysis (compare Figs. 2A and Sup. Info. Fig. S1A). Those two first PC explain >40% of the total variance of the dataset. PC1 opposes Ti and other terrigenous elements such as Fe, Al and V to more soluble elements such as Zn, P, and K. We can distinguish several clusters of correlated variables. On the left quadrants, a first group contains mostly insoluble terrigenous elements such as Fe, Al, Ti, V and Cr. The high ratio stability between those five elements strongly suggests that they are

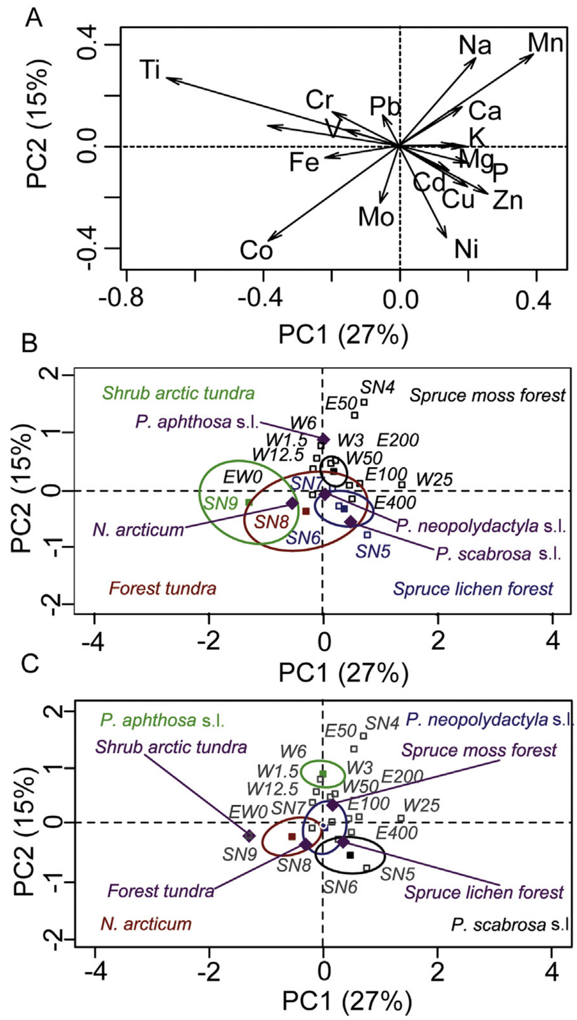

Fig. 2. Correlations among elements and the effect of bioclimatic zones and species on data structure. (A) Correlation among elements projected on the first two principal components. Variable plots highlighting bioclimatic domains (B) and lichen-forming species (C). In (B) centroids of geographical sampling points are highlighted with the color of their bioclimatic domains location. For clarity purpose, individuals are not shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

deposited all together. This first group certainly reflects the deposition of element as particles from pedogenic (orogenic) or anthropogenic origins (mining activities). A similar pattern with high correlation of terrigenous materials was reported for the first component of PCA from most studies on elemental deposition conducted in pristine areas (Puckett and Finegan, 1980; Monaci et al., 2012). A second group, in the lower-right quadrant, composed of numerous elements (K, Mg, P, Zn, Cu, Cd and Ni), may point at depositions from anthropogenic origin such as mining industries (i.e. Ni, Cu) and agricultural activities (P and K). However, the low levels of Ni, Cu and Zn (Sup. Info. Table S3–S7) suggest that anthropogenic sources, if any, must be scarce. A third group of elements (Na, Ca and Mn) is found in the upper-right quadrant (Fig. 2B) and might reflect leaching of easily soluble nutrients from the surrounding vegetation (Carlisle et al., 1966; Chou and Chen, 1976; Schmull and Hauck, 2003). However, source apportionment of elements that play a role in lichen physiology (Mn, Ca, Na, P, K) should be performed with care. Soil analysis at sampling sites is needed to determine more accurately the origin of trace metals.

Overall, the biplots (Fig. 2) suggest that metal content of lichens from large parts of the boreal zone of Québec mostly reflect atmospheric deposition of particles from pedogenic sources and transfer of soluble elements from surroundings (i.e., vegetation leaching). The contribution of anthropogenic sources, if any, is likely low.

3.1.3. Lichen species

When considering the different lichen-forming species with regard to the first two components (Fig. 2C), all species have narrow confidence ellipses ($p = 0.95$), reflecting intraspecies homogeneity. Regarding PC1, none of the species could be well separated from each other. Moreover, all centroids are close to the center of the plot (i.e. the average composition). This result demonstrates that the accumulation of metals originating from the deposition of particles is quite similar regardless of the four species we examined.

When comparing metal content for each species separately (Fig. 3, Sup. Info. Fig. S2, Tables S4–S7), there is no clear difference in the metal content of the thalli. Only few elements seem to differ in abundance in some species (e.g. Ni). However, these differences could reflect more their geographic distribution than a difference in species behavior with regard to these metals (See Sup Info Supplementary discussion 2.2 for details).

Nonetheless, our results show that all species have comparable overall elemental composition throughout most of our sites; from W50 to E400 and SN4 to SN9 (Figs. 2C, 3, Sup. Info. Table S8), suggesting that these four peltigeralean species do not significantly affect the quality of metal monitoring, at least for the level of contamination recorded here. The pertinence of the selected species for future biomonitoring surveys will strongly depend on their ability to accumulate elements and survive under high element exposures. Samples collected close to anthropogenic activities (SN2 and SN3, in this study; Alaska and Siberia, data not shown), suggest that the selected species (*P. aphthosa* s.l., *P. neopolydactyla* s.l. and *P. scabrosa* s.l.) can efficiently monitor anthropogenic perturbations (i.e., metal deposition), while *N. arcticum* seems to be more sensitive to anthropogenic perturbations and could potentially be of use as a bioindicator. Further dedicated studies are required to fully establish the potential of these species as biomonitors or bioindicators.

3.2. Determination of baseline element composition

Because our selected set of data is homogenous in term of composition with respect to species and geography, our baseline estimation was derived using the median and median absolute deviation on the all set (data for species are available in Sup. Info. Table S8). When comparing our results with previously published values from remote areas, including mountainous regions, most elements are in the lowest portion of the range (Table 1). Our results are also very similar to values reported from surrounding boreal and arctic regions, such as in the Northwest Territories (Puckett and Finegan, 1980; Nash and Gries, 1995), and Greenland (Riget et al., 2000), as well as from Antarctic regions (Bargagli et al., 1999). Most elements reported from our study are at the lowest concentration ever reported so far. However it should be stated that comparison between different species are always difficult. The lower elemental content observed in our samples compared to other pristine locations from high elevation such as the Alps, Himalaya or Mount Kenya (Bergamaschi et al., 2004) could reflect differences in erosion dynamics. The Canadian Shield is the result of an early orogenic episode, mountains have a low elevation (culminating at 1700 m in the Province of Québec), and were less likely subject to erosion in the past hundreds of years than the Alps, the Himalaya or Mount Kenya, which originated from more recent orogeneses. Thus, the Canadian Shield likely generated less terrigenous particles. Some recent studies highlighted the pertinence to use thalli margins in order to better evaluate recent pollution sources. For lichen thalli collected in this study, whole thalli and margins provided similar conclusions (see Sup. Info Tables S9 and S10 and Supplementary discussion 2.3 for details).

4. Conclusions

Overall, our results show that a large portion of the boreal biome of Québec (Northeastern Canada) remains pristine. The elemental composition of selected muscicolous/terricolous macrolichens, independent of the species considered here, mostly reflects deposition of particles from pedogenic origin. All lichens are surprisingly homogeneous with regards to their geographic origin. This likely reflects the relative homogeneity in the geological formation of northeastern Canada; mostly the Canadian Shield. Baseline element compositions of studied lichens are very comparable to lichens from the most pristine places in the world (i.e., Greenland, Himalaya, Antarctica and various polar regions). Finally, we showed that in the southern part of the SN transect, the sampled specimens of *Peltigera* spp. were able to monitor anthropogenic perturbations; the intense mining activity in this region was easily recorded in all samples. Also, the use of multivariate analysis in this study underlined small anomalies for specific metals with regard to geography and species, even at low concentration levels. Biomonitoring surveys including several species offer a variety of advantages; (i) it will facilitate sampling (species have different abundances and distributions along both transects) and (ii) it will significantly reduce the odds of losing the reference material over time. Some species are more sensitive than other to perturbation such as nitrogen deposition and acid rain. With future economic developments of boreal regions associated with global climate change, some species could disappear from some regions as a result of anthropogenic activity. The absence or very low abundance of *Peltigera* and *Nephroma* close to intense mining and urbanized areas in the most southern and western part of our transects (SN1 to SN3, W100 to W400) supports this prediction. This study provides a valuable set of data to monitor the impact of global climate change, future urbanization, and mining development in northeastern Canadian ecosystems.

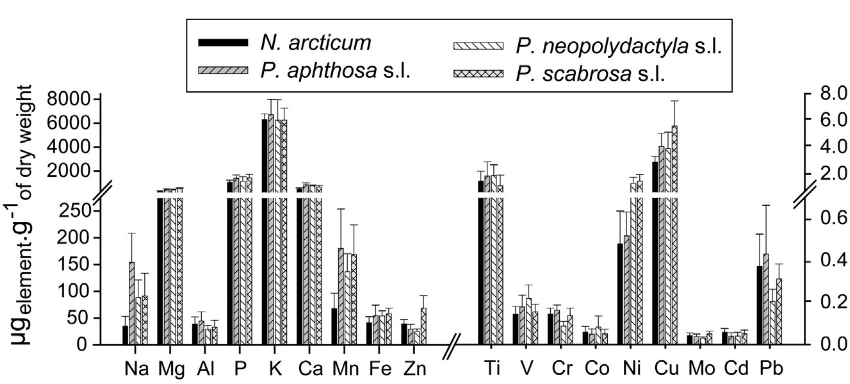

Fig. 3. Element contents for four lichen-forming species. Data from all sites were combined for each species as median and median absolute deviation. *Nephroma arcticum* (n = 31), *Peltigera aphthosa* s.l. (n = 30), *P. neopolydactyla* s.l. (n = 16) and *P. scabrosa* s.l. (n = 33). Samples from SN2 and SN3 were excluded.

Table 1
Baseline concentrations of elements detected from this study compared to previous studies in pristine areas of the world. *Nephroma arcticum*, *Peltigera aphthosa* s.l., *P. neopolydactyla* s.l., and *P. scabrosa* s.l are combined together (data for species are available in Sup. Info. Table S8). Min = lowest value of the final dataset, Max = highest value of the final dataset GM = Geometric mean, AM = Arithmetic mean, SD = Standard deviation, MED = Median, MAD = Median absolute deviation. Elements are sorted by increasing atomic weight.

	Lichen content (μg·g-1, dry weight) This work					Literature						
		Whole lichen (n = 103)			Margin (n = 20)	Himalaya (1)	Kenya (1)	Italy (1)	Greenland (2)	Canadian Arctic (3,4,5)	Chile (6)	Antarctic (7)
Element	Min–Max	AM ± SD	MED ± MAD	GM	GM	AM ± SD	AM ± SD	AM ± SD	GM	AM	AM	AM ± SD
Na	<13–483	126 ± 109	92 ± 61	85	-	-	-	-	-	86–2756[4]	101	222 ± 101
Mg	133–1597	488 ± 195	457 ± 104	457	596	2577 ± 1497	1653 ± 895	1008 ± 249	-	350.8–916.5[4]	-	436 ± 179
Al	15–515	53 ± 69	36 ± 12	40	14	-	-	-	70.1–518	369–940[4]	1289–1691	428 ± 191
P	543–4995	1445 ± 665	1338 ± 354	1337	1980	-	-	-	-	-	1267–1623	963 ± 517
K	3748–10,898	6549 ± 1423	6518 ± 966	6395	9568	4229 ± 1113	4348 ± 1844	4703 ± 608	-	1030–7920[4]	2916	2007 ± 483
Ca	255–2009	778 ± 314	738 ± 158	722	666	-	-	-	-	1100–8200[4]	4300–4946	640 ± 707
Ti	<1–80	3 ± 8	2 ± 1	2	1	-	-	-	-	7–850[3]	-	-
V	0.07–2.20	0.21 ± 0.21	0.16 ± 0.05	0.18	0.11	2.4 ± 1.2	1.8 ± 0.5	0.6 ± 0.1	0.21–0.64	0.17–9.7[3]	2.09	-
Cr	<0.07–1.43	0.19 ± 0.21	0.15 ± 0.04	0.15	0.18	2.5 ± 1.4	2.5 ± 2.0	1.7 ± 1.3	0.17–0.7	0.5–2[3]	2.17	1.3 ± 0.6
Mn	19–1206	169 ± 158	129 ± 64	126	99	55 ± 26	169 ± 138	108 ± 75	-	30.2–84.5[4]	109	11.8 ± 3.9
Fe	18–880	71 ± 88	54 ± 13	57	27	1512 ± 756	1615 ± 792	220 ± 105	90.2–225	50–900[3]	1410	802 ± 402
Co	<0.03–0.79	0.11 ± 0.14	0.06 ± 0.03	0.07	0.02	0.82 ± 0.53	0.39 ± 0.24	0.27 ± 0.12	-	0.08–2.84[3]	-	-
Ni	0.2–4.7	1.0 ± 0.8	0.8 ± 0.3	0.8	0.5	-	-	-	<1–1.1	1.7–5.5[3]	2.63	-
Cu	1.8–23.8	4.9 ± 3.8	3.7 ± 1.1	4.1	5.4	5.9 ± 3.7	5.3 ± 2.0	4.1 ± 3.1	0.594–0.979	0.7–5[3]	4.39–4.49	5.3 ± 5.1
Zn	12–166	51 ± 33	40 ± 15	43	43	34 ± 13	67 ± 32	35 ± 16	10.6–25.1	7–55[3]	44.2–51.0	18.6 ± 4.1
Mo	<0.03–0.33	0.06 ± 0.05	0.05 ± 0.01	0.05	0.03	-	-	-	-	0.07–0.32[4]	-	-
Cd	<0.03–1.00	0.08 ± 0.10	0.06 ± 0.02	0.06	0.14	0.04 ± 0.03	0.14 ± 0.13	0.21 ± 0.10	0.066–0.119	0.03–0.24[4]	0.13–0.28	0.21 ± 0.11
Pb	0.05–3.02	0.43 ± 0.37	0.32 ± 0.12	0.35	0.22	14.0 ± 3.9	3.6 ± 1.9	4.8 ± 1.3	0.77–2.3	0.4–9.2[3]	0.25–1.51	0.54 ± 0.34

Author contributions

J.P.B. and F.L. initiated and conceived the study. J.M. and F.L. collected and identified lichen specimens. R.D. performed all the analysis and wrote the first draft of the manuscript. All authors commented on the final version of the manuscript.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.06.030.

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