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Research article

Distribution of metals and radionuclides in the lichens *Cladonia rangiferina* and *C. mitis* from the past uranium mining region of Elliot Lake, Ontario, Canada

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HIGHLIGHTS

- Metals levels in lichens have decreased in a survey 40 years after mine closure.
- A new baseline was obtained for U, Th, Pb, As, Cd, Ti and Cs for lichens in the area.
- Cs-137 levels in the lichens reflect worldwide present-day background values.
- The capture rate of elements is slightly different in *C. rangiferina* vs *C. mitis*.

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ABSTRACT

The present study was performed in the Elliot Lake area (Ontario, Canada), a site of uranium mining and milling for nearly 40 years between 1950's and 1990's. Although mining activities ceased in the mid-1990's, the site hosts several tailings management areas (TMAs) which are under ongoing rehabilitation and monitoring. Several surveys using lichens as a biomonitoring tool were completed in the 1980s and the 1990s to assess the levels of contaminants. The present survey aimed to re-visit the historical surveys, and to determine the current status of environmental recovery of the area. Our survey consisted of sampling two lichen species, *Cladonia rangiferina* and *C. mitis*, in an area covering up to 50 km from the former mining operation and the TMAs. The results reported in this work indicated that the levels of metals and radionuclides, diagnostic of mining operations, have decreased over time: particularly, the U, Th and Pb levels in both lichen species dropped by about two orders of magnitude by the 2020's compared to the 1980's. Likewise, the Cs-137 levels in both lichen species reflect present day global background. The study provides a new set of present-day regional baseline elemental concentrations for other metals that are associated with mining (Cd, As, Ti, Cs). Finally, there were weak but statistically significant differences in the levels of some elements (U, Th, Cd) between the two lichens, suggesting these two species might have different capture mechanisms or retention abilities.

1. Introduction

Lichens, accumulators of natural and anthropogenic atmospheric contaminants (Purvis et al., 2013; Garty and Garty-Spitz 2015; Graney et al., 2019; Cwanek et al., 2020; Anderson et al., 2022), have been used as biomonitors and indicators of atmospheric deposition of metals and radionuclides associated with the energy, nuclear, mining or other industries (Beckett 1995; Jeran et al., 1995; Thomas and Gates 1999; Søndergaard and Mosbech, 2022). As radionuclides and metals can persist in lichens for many years, these organisms can preserve past metal

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processing and nuclear disaster radioactivity depositional events (Saunier et al., 2013; Osyczka et al., 2016; Søndergaard et al., 2013, 2020; Sawidis et al., 2010; Savino et al., 2017; Saniewski et al., 2022) for decades after the accidents or the cessation of industrial activities.

The present study was carried out in the Elliot Lake area (northern Ontario, Canada), a region of past large-scale mining and milling (1950s–1990s). Uranium (U), the main resource extracted, plus traces of Thorium (Th), Lead (Pb) and Titanium (Ti) were considered diagnostic elements of the past mining activity in the area (Boileau et al., 1982; Beckett et al., 1982; Nieboer et al., 1982; Fahselt et al., 1995). These elements, along with U- and Th-series radionuclides have been measured in water, sediments, biota (Clulow et al., 1996, 1998a, 1998b). In particular, contamination was reported in cryptogam species, including the lichens *Cladonia rangiferina* and *C. mitis* (Boileau et al., 1982; Beckett et al., 1982; Nieboer et al., 1982; Fahselt et al., 1995; Trembley et al., 1997). The past investigations focused on both regional (macro-) transects of over approximately 50 km from the mining operations, and on localized (micro-) transects adjacent to industrial zones or point sources (<500 m from active tailing ponds, mills or mine exhaust vents, etc.; Beckett et al., 1982). The elements Fe, Ti, and Pb were shown to be indicative of mining operations near the local point sources at the micro-transects. The content of these elements in lichens decreased with distance from the mining operation, the presumed source. The U content in lichens, a principal indicator element of mining operations, decreased with distance from presumed sources at both regional and micro-transect scales in the 1980s. There was also a decrease in the U levels in lichens in the 1990s, after the mining operation had ceased (Fahselt et al., 1995; Trembley et al., 1997). There have been no follow-up lichen surveys of the same (regional) scale conducted in the past 25 years.

All the mines in the Elliot Lake area were closed by 1996, while the tailings deposits of the region have been either revegetated or water covered as components of the mine and mill site closure plans. As regular environmental monitoring does take place (Willianen et al., 1998; Clulow, 2018; Berthelot et al., 2019; Denison Mines Inc, 2019), it is desirable to complement the existing monitoring efforts in the area with a new lichen transect survey to document any residual trends from long-distance or local contamination from mining or quarrying activities, or to confirm recovery. The current levels of metal and radionuclides in area lichens are expected to be much lower than in previous lichen regional surveys carried out in the 1980-s and 1990-s. Further, quantification limits using multi-elemental modern instrumental techniques such as ICP-MS are lower that those of the atomic absorption and X-ray fluorescence techniques used in the 1980s, providing potential detection capacity previously not available. Monitoring data documenting the contaminant levels in lichens is also needed to provide a continuous baseline for pollution assessment (e.g. Seaward 2002; Ohmura et al., 2015), especially in the context of future economic regional development (Darnajoux et al., 2015). The development of a contemporary baseline data is essential for the mining and energy sectors, especially given the potential use of small modular reactors (SMRs) for both mining and remote communities (SMR Roadmap, 2018).

The main elements of interest (EOI) of the present study are U, Th, Pb, and Ti, key diagnostic elements for historical continuity. We also report on the content of elements of toxicological and event monitoring importance such as As, Cd, and ^{137}Cs. Although the toxic elements are not necessarily associated with mining activities in the Elliot Lake area, the data do provide a set of baseline concentrations for the region. The toxic elements (As, Cd) are relevant to mining near Elliot Lake and Sudbury (120–150 km away), with the latter area having a long history of past operations, and intensive toxicological assessment (Wren, 2012). Cesium-137 was globally distributed from past atmospheric weapons tests, reactor accidents, and inadvertent releases from nuclear waste management areas. In the Elliot Lake area, ^{137}Cs was reported in lake sediment columns (Clulow, 2018). Various lichen species have been used worldwide to survey the ^{137}Cs contamination, with just a few of these studies done in Northern Ontario where the content of in lichens is expected to be at background levels.

The present study, therefore, explores the potential use of lichens as a monitoring tool to examine the background levels of contaminants in an area recovering from past mining activities. The specific aims of the study are:

- to estimate current levels of selected elements;
- to confirm whether active tailings management shows content decreases, compared to levels documented in the previous decades;
- to obtain a new baseline data of EOIs of both toxicological and/or economic importance for the area, using modern instrumentation which features lower limits of quantification, compared to earlier studies performed several decades ago;
- to explore how the behavior and distribution of EOIs differ on an element basis.

2. Materials and methods

2.1. Study area and lichen species

The study was conducted in the Elliot Lake area of northeastern Ontario. The area was the subject of earlier studies (Beckett et al., 1982; Fahselt et al., 1995; Akerman et al., 2021). Uranium was extracted from the quartz-pebble conglomerate host rock, and milled in the facilities from the 1950s to the 1990s (Berthelot et al., 2019; Davé, 2011). Conventional uranium mineral processing was combined with leaching for extraction; the facilities have been decommissioned since (Sapsford et al., 2012; Berthelot et al., 2019). Approximately 100 million tonnes of tailings are still present in the area, for a combined area of more than 9 km^2. The tailings are now under a vegetated cover or submerged under water (Berthelot et al., 2019).

The sites were chosen along a ~50 km regional transect from Massey to North of Elliot Lake, Ontario (Figure 1 and Table S1). Sites 1–11 are referred to as "regional transect". When possible, three replicate samples of *Cladonia rangiferina* and *C. mitis* were taken at each of these locations. A 120 m micro-transect (site 12) was located ~2 km west of Quirke Lake, adjacent a now decommissioned mine exhaust vent (Beckett et al., 1982). The micro-transect consisted of a collection of 10 individual *Cladonia rangiferina* lichen samples, at 10–15 m intervals from the location of the (closed) exhaust vent (*C. mitis* was not available in these locations).

2.2. Sampling and sample treatment

The sampling sites were chosen in openings between large trees to optimize input from aeolian sources and minimize tree drip. Sites with a minimum amount of overlying ground vegetation cover were located at least 50 m from roads (Boileau et al., 1982; Steinnes et al., 1992; Akerman et al., 2021). Consistent sample volumes were achieved by using a 10 cm (diameter) by 5 cm (high) Al ring. Fresh nitrile gloves were used at each site, plus samples were manipulated using plastic or stainless steel spades and/or ceramic knives to minimize cross-contamination. The lichen samples were individually placed inside brown paper bags in a polycarbonate clamshell box for transport to the analytical facility. All equipment was washed with distilled water, and cleaned with alcohol wipes between sample collection sites.

The samples were transported to the laboratory within 15 h of sampling, and were air-dried under ambient conditions in half open polycarbonate boxes, covered with paper bags. Extraneous material such as pine needles, leaves, etc., was carefully removed with plastic tweezers. Whole lichens were then placed between individual sheets of food-grade parchment paper and manually ground using a ceramic mortar and pestle.

2.3. Sample analysis

The natural and artificial radionuclides content was analyzed for gamma emitters using a Canberra GC1020 high purity Ge detector, controlled by a DSA-1000 processor and Genie 2000 software (Caron and Mankarios, 2004; Caron et al., 2007). Finely ground air-dried lichens in

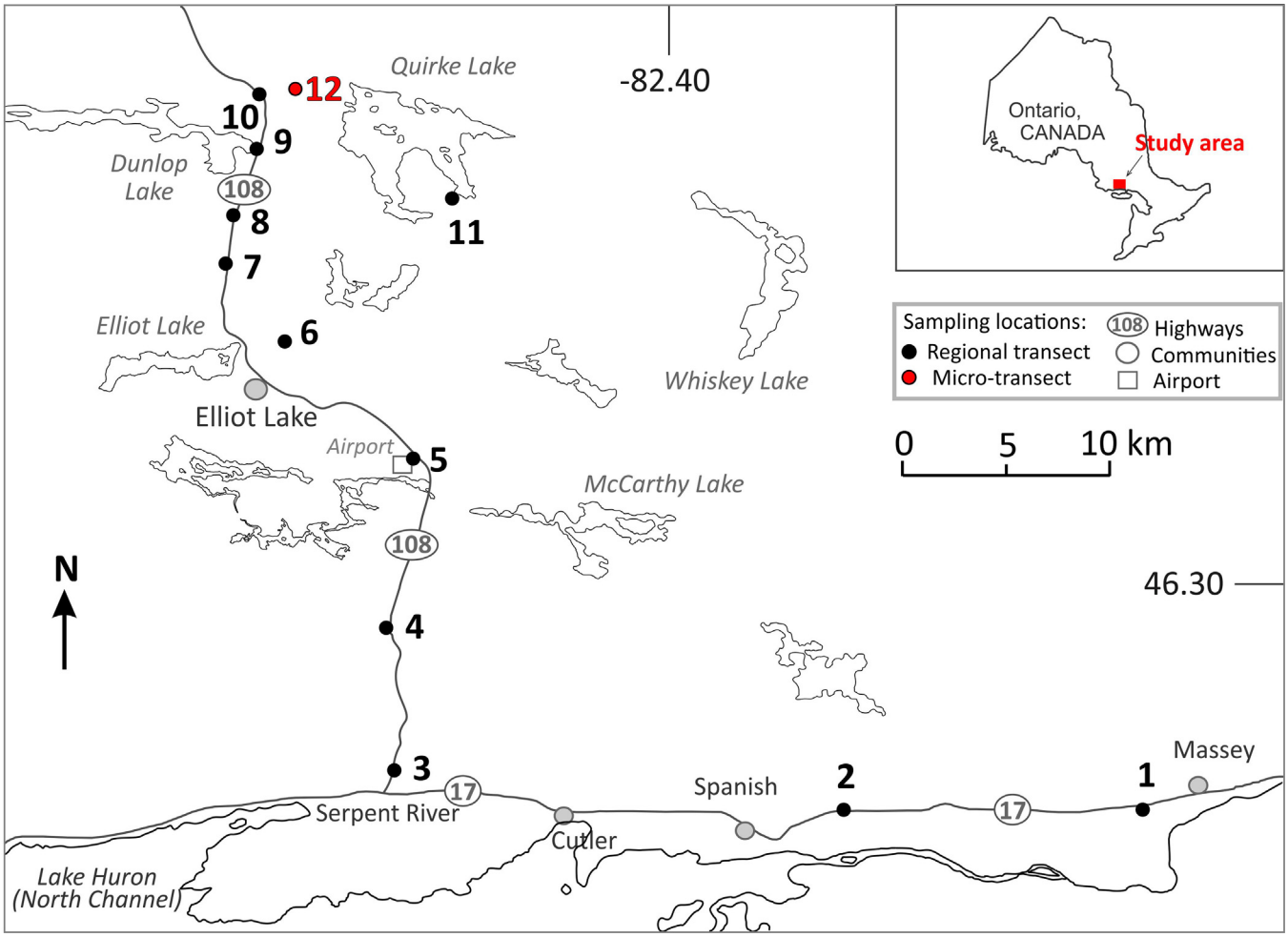

Figure 1. Location of the sampling stations.

petri dishes (d = 5 cm, sample depth ~1.5 mm) were placed directly on top of the detector. Samples were counted for 22h. Efficiency calibration was performed using 100 μL of an aqueous multi-isotope standard QCY-48 (AEA Technologies, Burlington, MA), spiked into a vegetative standard (CLV-1 CRM, Natural Resources Canada), and air-dried. This spiked standard was counted using the same geometry (5 cm dia. x 1.5 mm) as the sampled lichens. Both spiked standard and lichens had the same texture. A background reading (19h) was performed and used for spectral correction (Williamson et al., 2014). The activities (^{137}Cs) were decay corrected for the sampling date August 07, 2020.

For the ICP-MS, the samples were prepared for the elemental analysis by multi-acid digestion using a closed vessel microwave system (Questron Technologies), following the EPA 3052 procedure (U.S. Environmental Protection Agency 1996) commonly used for the digestion of various matrices, including mosses and lichens (Cowden and Aherne, 2019; Fortuna et al., 2017, 2021). Samples of lichens (0.500 ± 0.002 g) were digested in a mixture of HNO_3 (9 ml), H_2O_2 (2 ml) and HF (1 ml; TraceMetal™ Grade, Fisher Chemical™) at 180 °C. Following the microwave digestion, the next steps were done at 95 °C using a programmable Qblock (Questron Technologies): a first evaporation was done to bring down the volume to 1 ml (for about 7–10 h); following this, 4 ml of HCl were added, and the samples were evaporated again to 1 ml volume (for 2–4 h). After these two steps, 5 ml of HNO_3 were added to the samples and kept for 2h in a hot block covered with reflux caps; the samples were then cooled down, topped up with Milli-Q water up to 25 ml and placed into a refrigerator until subsequent analysis. Elemental concentrations were quantified with a Thermo iCAP-Q instrument, with Ru–Re internal standard, calibrated with acid-matrix matched synthetic solutions. Lower reporting limits were estimated from average reagent blank (+3 SD of the blank). Relative uncertainties on the analyses were based on the standard deviations of the normalised intensities obtained for the 8 replicate measurements. The QA/QC procedures included sample preparation blanks, reagent blanks, duplicates and certified reference materials (CRMs). The difference between measurement duplicates was better than 10%. The CRMs used were: BCR-482, Lichen standard (*Pseudevernia furfuracea*; Quevauviller et al., 1996; IRMM, Belgium), and CLV-1 (Natural Resources Canada). The recoveries of the reported elements were 91 % for As, 93% for Cd, and 92% for Pb (BCR-482); and 98 % for U (CLV-1).

2.4. Linear regression and statistical analyses

Linear regression analyses and the Pearson correlation coefficients (r) were obtained using the MS Excel spreadsheet (Analysis ToolPak Add-in, Office 16). A high correlation coefficient (r) is interpreted to infer that the two measured variables might have a common origin. The Grubb's test (Graphpad.com) was used to examine the data for the presence of outliers. The differences in slopes were obtained using the approach from Real-Statiscics, comparison of the slopes for two independent samples (www.real-statistics.com/; the calculations were done using MS Excel).

3. Results

3.1. Distribution of the elements

Table 1 (a, b) summarize the concentrations of the EOIs, with Table 1 (c) summarizing the sample-to-sample and analytical variabilities among

replicates. Table 2 presents the activity concentrations of ^{137}Cs in *C. rangiferina* and *C. mitis*. Additional data is available in supplementary materials (see Tables S2–S5).

The U and Th concentrations were less than 1 μg/g, which is well below the levels reported by Boileau et al. (1982) and Fahselt et al. (1995). The Gamma spectroscopy data indicates the presence of low levels of radionuclides in the lichen samples, with primarily short-lived U and Th decay products. Uranium (mostly U-235) was below quantifiable levels. The levels of U, Th, Pb and Ti in lichens at the northern sites were slightly more elevated than compared at the southern "background" sites. However, this is not a statistically significant trend (Grubb's test for outliers, $P < 0.05$). When compared to historical levels from the 1980s (Boileau et al., 1982) and the 1990's (Fahselt et al., 1995), the concentration ranges of three diagnostic elements (U, Th and Pb) have decreased markedly over the last few decades (also see Figure 2). However, the measured Ti levels have not changed noticeably in this period (Figure 2). The Th/U concentration ratios are similar to those derived from the data of Fahselt et al. (1995); see Figure 3.

The distribution of As, Cd and Cs over the regional and micro-transects is different from the diagnostic elements (Table 1; Figure S1 a, b), with no obvious "hot spot", suggesting that the measured concentrations reflect regional background values. Although Cesium-137 was detected in 9 out of 76 samples for *C. rangiferina* and *C. mitis* (Table 3), the

Table 2. ^{137}Cs activity concentrations in lichens collected in the Elliot Lake area, 2020.

Site number	Species	^{137}Cs, Bq/kg**
1	*C. rangiferina*	26 ± 6
2	*C. rangiferina*	42 ± 7
	C. mitis	51 ± 8
3	*C. mitis -1*	20 ± 6
	C. mitis -2	24 ± 6
4	*C. mitis*	17 ± 3
5		N/D*
6	*C. rangiferina*	20 ± 6
7	*C. rangiferina*	21 ± 6
	C. mitis	27 ± 6.5
8		N/D*
9		N/D*
10		N/D*
11	*C. rangiferina*	23.6 ± 6
12		N/D*

* N/D: not detected.
** corrected to sampling date August 07, 2020.

Table 1. Mass concentration of EOIs (μg/g, n = 3 replicates except for station 4, n = 2; regional transect); (a) *C. rangiferina*; (b) *C. mitis*; (c) typical sample-to-sample variability and analytical errors for both lichen species (refer to Tables S1 to S5 in suppl. inf. for details).

(a) *C. rangiferina*

Site number	U	Th	Pb	Ti	As	Cd	Cs
1	0.008	0.023	0.42	10	0.068*	0.074	0.108
2	0.027	0.090	0.53	26	0.094	0.084	0.252
3	0.010	0.034	0.50	14	0.084	0.059	0.123*
4	0.006	0.020	0.32	9	0.076	0.063	0.244
5	0.015	0.060	0.83	39	0.118	0.092	0.076
6	0.016*	0.045	0.34	13	0.082	0.060	0.036
7	0.011	0.039	0.57	17	0.092	0.076	0.116
8	0.037	0.170	0.66	77	0.156	0.066	0.152
9	0.037	0.090	1.13	30	0.108	0.110	0.079
10	0.014	0.037	0.88	15	0.077	0.083	0.053
11	0.017	0.080	0.83	21	0.104	0.049	0.086

(b)*C. mitis*

Site number	U	Th	Pb	Ti	As	Cd	Cs
1	0.007	0.021	0.47	10	0.063*	0.058	0.055
2	0.025	0.084	0.66	34	0.116	0.060	0.185
3	0.011	0.038	0.44	16	0.103	0.066	0.133*
4	0.008	0.024	0.57	11	0.080	0.052	0.112
5	0.012	0.040	0.59	20	0.099	0.078	0.077
6	0.019	0.038	0.29	16	0.085	0.054	0.052
7	0.018	0.055	1.09	24	0.111	0.079	0.159
8	0.037	0.145	0.63	75	0.163	0.048	0.084
9	0.024	0.094	0.81	37	0.108	0.090	0.055
10	0.028	0.061	0.28	24	0.082	0.054	0.051
11	0.012	0.044	0.70	15	0.088	0.118**	0.157

(c) variabilities

Parameter	U	Th	Pb	Ti	As	Cd	Cs
Sample to sample variability (%)	20.9	19.3	24.0	22.7	17.0	22.2	27.3
Range	7.3–55	3.4–40	4.8–59	8.1–70	4.4–79	5.8–49.4	3.2–80
Analytical variability (%)	2.0	1.3	1.5	3.0	5.1	8.3	1.3
Range	1.3–4.3	0.9–1.8	0.9–3.7	1.9–4.3	2.4–6.8	3.7–12.5	0.7–2.8

* Average after removal of one outlier value (see suppl. Information).
** Outlier station for Cd, not used in statistical analyses; also see supplementary information.

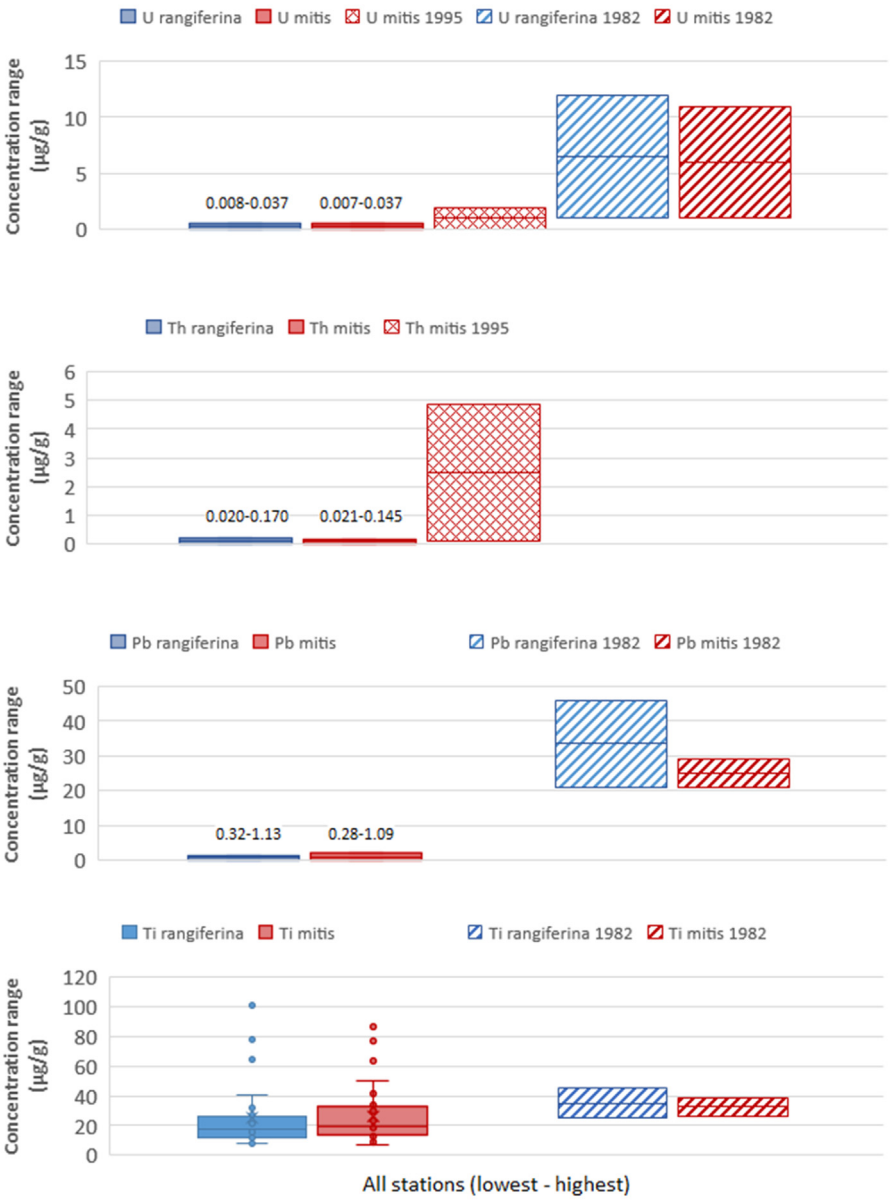

Figure 2. Comparison of the concentration ranges for U, Th, Pb and Ti for the two lichen species in this work (left) and available historical concentrations (Fahselt et al., 1995; middle, U and Th only; Boileau et al., 1982; patterned bars, right, U, Pb, Ti). All are for regional values.

distribution of this radionuclide did not show any discernible regional trend.

At site 12 (the micro-transect), the distribution of the elements in lichens did not display a discernible trend for the EOIs. The last sampling point (120 m) shows higher concentrations for Th, Pb, Cs and Ti, but not for U, As and Cd (Grubb's test, $P < 0.05$), compared to the rest of the micro-transect.

3.2. Correlations

3.2.1Correlations between elements

Table 3 (a, b) shows the correlation coefficients (r) of the EOIs between elements for the regional transect. The U levels in lichens, when plotted against Th, Ti and As, showed high r values (significant at the $P < 0.05$ level), suggesting that these elements have a similar origin. The r values between the U levels in lichens and Pb, Cd and Cs were low, suggesting different origins and/or different capture/retention processes by lichens. The plots of Th concentrations against Ti and As also showed significant r values, but low r values were found for Pb, Cd and Cs. The Pb levels had a weakly significant r value with Cd, but and no significant correlation with Ti, As and Cs. The measured Ti levels were correlated with As, but not with Cd or Cs. Neither the Cd nor Cs concentrations displayed significant correlations with the other EOIs. These observations were consistent for both lichen species.

At the micro-transect, the r values between the concentrations of U and the other EOIs showed only a weak correlation with Th and Pb, but no significant correlations with the other EOIs (Table 3c). The Th concentrations were correlated with Pb, Ti and Cs, while the Pb concentrations were correlated with Ti, Cs, and finally, Ti was correlated with Cs. There were no significant correlations between the other EOIs. Note that only *C. rangiferina* was available at the micro-transect, as mentioned earlier.

3.2.2Correlations of EOIs between lichen species

There was a correlation of the EOI concentrations between both lichen species, except for Pb (Figure 4). These correlations were significant ($P < 0.05$ level). Interestingly, the slopes were between 0.41 to 0.91, suggesting that the capture efficiency for airborne materials of the two

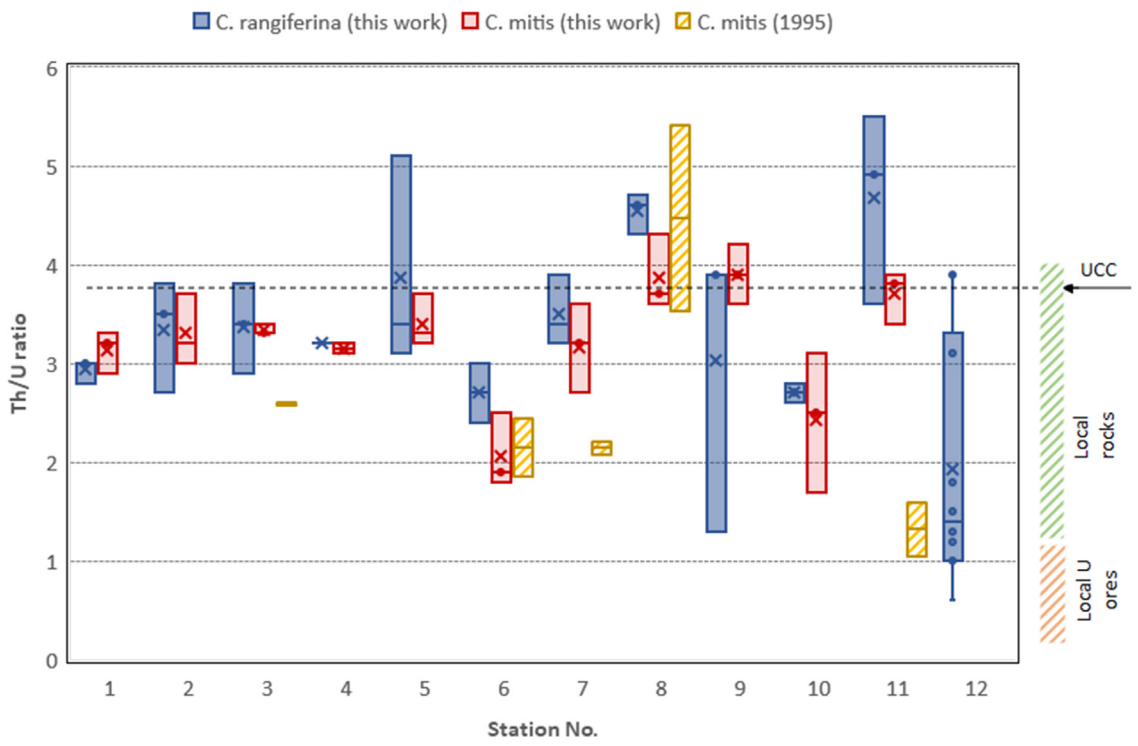

Figure 3. Th/U concentrations ratio in lichens across the study area. The data for *C. mitis* (1995) is included (Fahselt et al., 1995); the correspondence of our stations with distance from Quirke mine No. 2 (ibid) is approximate. Also note: the average ratio for the UCC is from Rudnick & Gao (2003); local rocks and U ores are composites from Al-Hashim and Corcoran (2021); Fedo et al. (1997); Karagiorgakis et al. (2018); Williamson (2014); Sapsford et al. (2012) and Murray et al. (1983).

Table 3. Pearson correlation coefficients (r) between the EOI concentrations for the two lichens; a) *C. rangiferina*, regional transect; b) *C. mitis*, regional transect; c) *C. rangiferina*, micro-transect. Correlations in boldface are significant at the P < 0.05 level. a) *C. rangiferina*.

	U	Th	Pb	Ti	As	Cd
Th	0.837					
Pb	0.549	0.382				
Ti	0.756	0.926	0.355			
As	0.746	0.914	0.429	0.965		
Cd	0.432	0.105	0.607	0.161	0.126	
Cs	0.032	0.122	0.425	0.045	0.010	0.095
b) C. mitis (n = 10 stations for Cd; No. 11 removed)						
	U	Th	Pb	Ti	As	Cd
Th	0.909					
Pb	0.045	0.274				
Ti	0.872	0.978	0.235			
As	0.735	0.896	0.395	0.927		
Cd	0.161	0.063	0.626*	0.110	0.068	
Cs	0.126	0.032	0.528	0.045	0.226	0.330
c) C. rangiferina (n = 10 individual data points, no replicates available)						
	U	Th	Pb	Ti	As	Cd
Th	0.597**					
Pb	0.554**	0.978				
Ti	0.448	0.978	0.953			
As	0.386	0.288	0.255	0.257		
Cd	0.071	0.315	0.365	0.318	0.202	
Cs	0.468	0.905	0.913	0.928	0.528	0.375

*significant at P < 0.053.
**significant at P < 0.1.

lichen species is different, and also that the capture efficiency is variable among contaminants. The slopes were (weakly) statistically different from the expected 1:1 relationship for U, Th, and Cs (P < 0.1 or better). The differences from the 1:1 line were borderline not significant for Ti, As and Cd. In addition to the EOIs, the concentrations of many of the other elements, including the rare earth elements (REE), Sc and Y, also showed high correlation coefficients between the two lichen species (see Fig. S2 in the supplementary information).

4. Discussion

4.1. Distribution of the elements and changes in their concentrations

4.1.1. The diagnostic elements (U, Th, Pb, ti)

The concentrations of U and Th have decreased by one to two orders of magnitude since the end of the mining activities (1970's) and permanent closure of industrial mining activities in the 1990s (see Figure 2). This trend strongly suggests that environmental rehabilitation in the area is successful. The concentrations, both regional and near the former industrial sites, are in the range reported for background levels around the world (Anderson et al., 2022). For example, U levels in lichens were in a range of 0.077–1.4 μg/g (in *C. stellaris*, collected in Saskatchewan, Canada; Thomas and Gates, 1999). Chiarenzelli et al., (2001) reported 0.01–0.27 μg/g for U, and from non-detectable values to 1.10 μg/g for Th in various species from Nunavut, Canada. Cecconi et al. (2018) reported background values of 0. 011–0.03 and 0.06–0.17 for U and Th, respectively, in *Pseudevernia furfuracea* in Italy.

The Th/U concentrations ratios in most lichens that we have sampled fall within the range of documented for local geological materials (Figure 3). For the sites south of Elliot Lake (1–4), the Th/U concentration ratio is close to that of the upper continental crust (UCC in Figure 3, Th/U = 3.8; Rudnick and Gao 2003). The values of the ratios we are reporting are in the same range of those from Fahselt et al. (1995). There is more variability between sites at the stations North of Elliot Lake. At

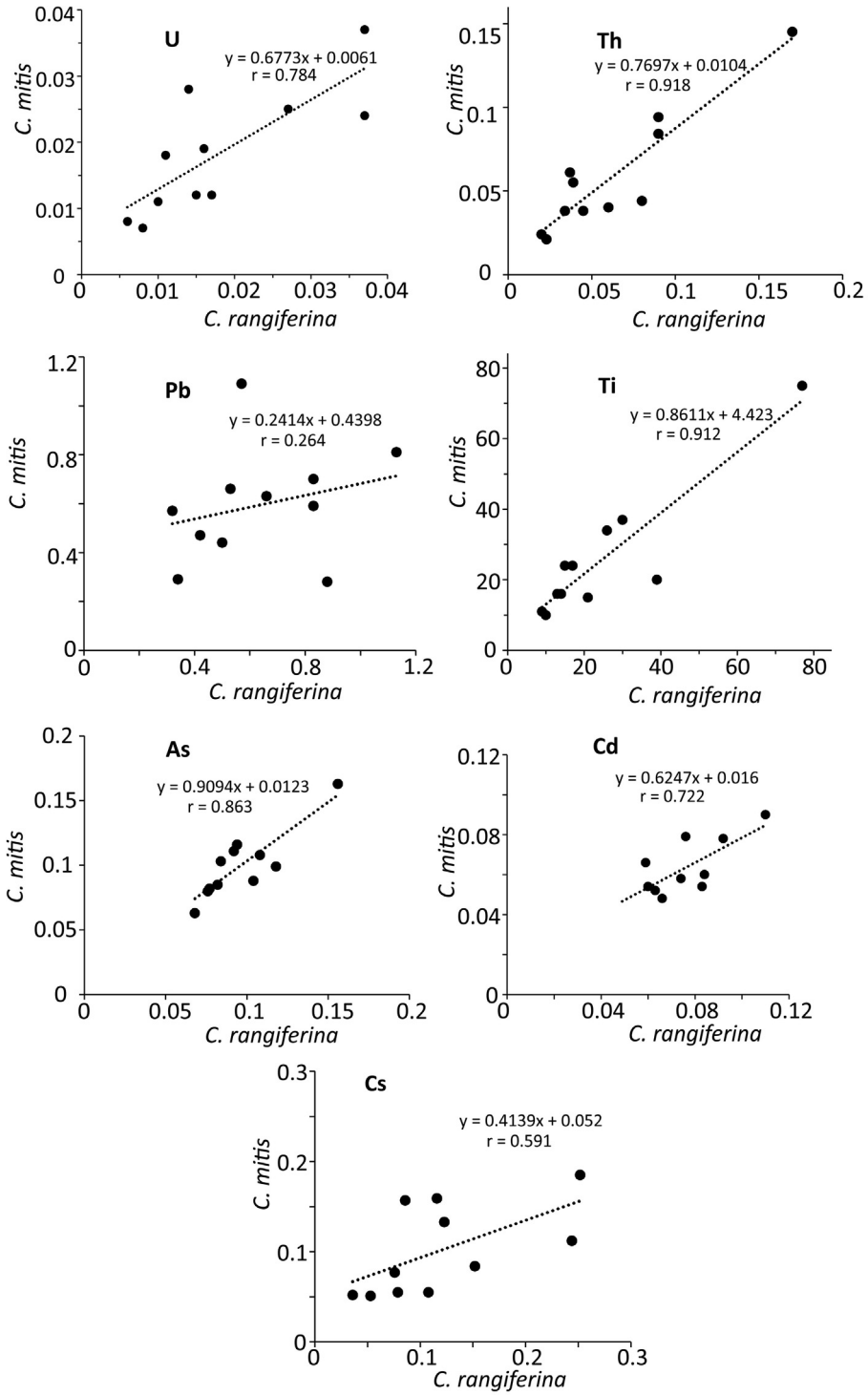

Figure 4. Plots of metal content in lichens (μg/g), *C. rangiferina* vs *C. mitis* (note n = 11 except for Cd, n = 10).

the micro-transect location (site 12), the Th/U mass ratio was generally lower, approaching the values documented for local uranium ores, an observation similar to that reported nearby by Fahselt et al. (1995) for the location of the former sources. This trend, however, is not statistically significant; additional sampling would be needed to confirm this observation.

The Pb concentrations in the lichens that we are reporting are much lower than in 1980 (Figure 2). Beckett et al. (1982) suggested that Pb was the indicator of local emissions only at the micro-transect, postulating that Pb originated from other regional sources, and potentially long-range transport of leaded gasoline at the time. The levels that we are reporting are comparable to those of Akerman et al. (2021). These authors have shown that the Pb distribution in northern Ontario may be explained by the long-range transportation of remote industrial sources, together with some natural background Pb, also transported by prevailing winds. These authors also reported a limited influence of local point sources.

The content of Ti, which is more abundant compared to other EOIs, did not show any noticeable decrease in lichens, compared to the earlier work of Boileau et al. (1982). The median background and post-industrial levels of Ti reported in our work are generally lower than those of previous work in the area (see Figure 2). Ti levels measured in

lichens typically reflect the contents of local dust (Takala and Olkkonen, 1985), and are good indicators of crustal material that could be carried by wind (Nash and Gries 1995; Shotyk et al., 2001). The content of Ti at most of our sites is also comparable to the range of background concentrations known worldwide for this element (e.g. Cecconi et al., 2018; Bargagli et al., 2002; Mróz et al., 2018; Bubash et al., 2020; Takala and Olkkonen, 1985; Darnajoux et al., 2015). In a highly polluted site, Bačkor & Fahselt (2004) reported high levels of Ti (169 μg/g) for *Cladonia pleurota* near the abandoned O'Donnell roast bed near Sudbury, ON, but lower values 19.9 and 32.5 μg/g for lichens in the control site and in recolonized forest.

In general, the distribution of U, Th, Pb, Ti is fairly even for all stations (*C. mitis*), and for the "southern stations" (1–6) for *C. rangiferina* (Table 1; Figure 1; Fiure 1Sa). The levels of metals for *C. rangiferina* are slightly higher at the stations closer to the mining affected area (stations 7–12) than for the southern part. Further, the metal levels observed in the micro-transect (station 12) show some variability on the local scale of tens of meters. The localized higher concentrations of EOIs in lichens at the sites north of Elliot Lake may indicate some metal persistence, probably through particulate resuspension. Similar observations on dust capture by lichens have been reported around the world. For example, Pb persistence in lichens near a former mining area in France 20 years after mines closure was explained by wind-transported dust (Saunier et al., 2013). In other parts in France, REE's in local dust particles from bedrock or soil were found in lichens (Agnan et al., 2014). Osyczka et al. (2016) reported the substrate as the main source of metals in *Cladonia* lichens in a post-industrial area in Poland. In a study from Finland, Takala and Olkkonen (1985) reported that the levels of Ti in lichens were the result of the local minerogenic dust dispersion by winds. Søndergaard et al. (2013) showed that Pb, Zn, Cd were still being deposited as dust and captured by lichens at the historical mining sites in Greenland, 20 years after the mine closure.

4.1.2. The toxic elements (As, Cd, elemental Cs)

The spatial distribution of the toxic elements (As, Cd, Cs) does not show any trend, with no localised "spots" displaying slightly higher concentrations. Baseline data of the toxic elements in lichens in the area is scarce. A regional study of northern Ontario (Sudbury to N. of Kapuskasing, over ~400 km) indicated low levels of As in *Cladonia* lichens (0.11–0.25 μg/g; Arafat and Glooschenko, 1981). This range is somewhat higher but comparable to the values we are reporting in the current study. The Cs elemental concentrations in *C. mitis* from Elliot Lake (Fahselt et al., 1995) ranged from 0.03 to 1.4 μg/g, also comparable to present day values reported here. The Cd content in *Hypogymnia physodes*, collected in Thunder Bay (ON, Canada, ~500 km NW of Elliot Lake) was in the range of 0.2–1.2 μg/g (Pfeiffer and Barclay-Estrup, 1992). Darnajoux et al. (2015) determined a Cd elemental baseline concentration for several *Peltigera* species collected in Québec, Canada. They reported a Cd content of <0.03–1.00 μg/g, which is in a range comparable range to our work.

4.1.3. Cs-137

The activity concentrations of ^{137}Cs in lichens in the sampling area do not show any evident geographical trend, and fall within the ranges reported in recent literature. Particularly, background concentrations have been reported as 9.8 ± 2.8–17.4 ± 1.9 Bq/kg for *C. mitis* (in Alaska), and 17.6 ± 4.5 and 42.1 ± 7.2 Bq/kg for *C. mitis* (in Labrador and in Nunavut, Canada, respectively; Cwanek et al., 2020). This particular radionuclide originates from long-range sources such as nuclear accidents and atmospheric tests, being now present in the ecosystem at background levels which may therefore be captured by lichens without any differentiation between locations. To our knowledge, there is no data on the ^{137}Cs content in lichens from the Elliot Lake area. Clulow (2018) reported detectable levels of ^{137}Cs in sediment columns in Serpent Harbour (near site 3). Levels were 50–100 mBq/g, with only one value exceeding 200 mBq/g at the top of one of the columns. This was interpreted as the consequence of the nuclear bomb testing in the 1950s. A number of studies have attributed the presence of ^{137}Cs in Canadian lichens to global fallout from nuclear weapon tests (Cwanek et al., 2020; Stocki et al., 2016; Hutchison-Benson et al., 1985). Chernobyl (Chornobyl) - derived ^{137}Cs was detected in *C. rangiferina* in Eastern Canada (Smith and Ellis 1990), and in various species in the Canadian Arctic (Taylor et al., 1988). Ellis and Smith (1987) named the Chinese nuclear test carried out in 1980 as another potential source of ^{137}Cs in lichens. More recently, Cwanek et al. (2020) identified the Fukushima fallout signature in some of the Alaskan, but not in Canadian lichen samples. Stocki et al. (2016) detected no increase of radioactivity and no ^{134}Cs which could be attributable to the Fukushima accident in lichen samples from Yukon. However, Fukushima-derived radiocesium was dispersed in the Northern Hemisphere (Hernández-Ceballos et al., 2012; Mészáros et al., 2016), therefore potentially might be present in lichens.

Primary Chernobyl (Chornobyl) or weapon-test related ^{137}Cs is not expected to be currently captured from these sources by lichens because of the time elapsed. Likewise, one could expect only a small contribution from primary emissions from the Fukushima accident, due to the short ^{137}Cs atmospheric effective half-life of 4.7 years (Kinase et al., 2020). These long times, plus the biological processes with short half-lives in lichens (Anderson et al., 2022) would bring these levels to practically zero. We might expect, however, that some of the ^{137}Cs is being recirculated due to dust re-suspension (Kinase et al., 2020) and might thus still be present in the ecosystem (Nimis 1996; Avery 1996).

4.2. Correlations and potential relationships

4.2.1. The EOIs

Elemental uptake by lichens can occur in dissolved or particulate form (Nieboer et al., 1978; Beckett 1995; Branquinho et al., 1999). Nieboer et al. (1982) indicated that trapping of airborne particulate material was the major accumulation mechanism for lichens in the Elliot Lake area. This was also reported for different elements (for instance, U, Th, Ti) and different areas (Beckett et al., 1982; Looney et al., 1985; Fahselt et al., 1995; Jeran et al., 1995; Chiarenzelli et al., 2001; Dias da Cunha et al., 2004). Many of the minerals found in the Elliot Lake that are rich in U and Th also contain trace to significant REE elemental concentrations (Karagiorgakis et al., 2018).

The co-trapping of elements by lichens would provide evidence of similar capture efficiencies or deposition mechanism. Several elements, especially the REE, also show strong linear relationships with U (see suppl. Info), also supporting the role particulate trapping in lichens aerial structures. Chiarenzelli et al. (2001) reported correlations of the element content for many trace elements and REE in lichens (between samples, between species, and lichens vs mosses). These findings implied similar deposition processes from relatively inert (particulate) forms, or similar post-deposition retention processes. Our study is consistent with these findings, namely the uptake of particulate material by lichens from the surroundings (mineral substrates, tailings, exposed floodplains and lakeshores, etc.).

The low values of r for the other elements (e.g., Cd, Cs, Pb) could be explained by processes other than strictly particulate trapping. For example, Cd could be imported by atmospheric transportation as fine particulate matter which could be deposited by both wet and dry deposition processes (Crea et al., 2013). Cd uptake by lichens could take place in dissolved form, both extra- and intra-cellularly (Beckett and Brown, 1984; Paoli et al., 2018). Although Cs as an element is not very abundant naturally, it can act as a carrier of the less abundant ^{137}Cs from soils to plants (Rai and Kawabata, 2020); subsequently, Cs uptake by lichens takes place in a mechanism similar to that of K^+ uptake (Anderson et al., 2022 and references therein; Avery, 1995; Tuominen and Jaakkola 1973). The absence of correlation (low r) with the other EOIs is therefore not surprising. Pb, although related to mining activities in the past, probably originates now mainly from long-range sources, mostly anthropogenic, with limited local input (Akerman et al., 2021). Pb could

come in both dissolved and particulate form (Javed et al., 2017 and references therein). The high r of As with U and Th is not surprising, with As being associated with U and Th in rocks and in tailings in the regions of mining activities, (Pichler et al., 2001; Popic et al., 2011).

4.2.2. The lichen species: EOI levels between C. rangiferina vs C. mitis

The slopes for the linear regressions between *C. rangiferina* and *C. mitis* were different from the 1:1 line for U, Th and Cd. The test for differences in slopes was weakly significant ($P < 0.1$; usually a $P < 0.05$ would indicate significance), while the correlation was significant (r significant at $P < 0.05$). The relationship for Cs between the two species also had a weakly significant correlation coefficient ($r = 0.590$, $P < 0.056$), while the slope was significantly different from the 1:1 line. The slopes of Ti and As between the two lichen species were slightly below the 1:1 line. However, the levels of these two elements between the two lichen species showed a significant correlation (high r values). The two data points for ^{137}Cs for both lichen species pointed out earlier (Table 3, stations 2 and 7) do not show a significant trend. One would expect a relationship, as it was for elemental Cs; more data would be needed to determine its significance. Finally, the Pb concentrations showed no relationship between the two lichen species.

The discussion above raises the point that the two lichen species could have different abilities to capture airborne contaminants. Different bioaccumulations were reported by Fortuna et al. (2021) for *Flavoparmelia caperata* and *Xanthoria parietina*, sampled in two areas near the Italy-Slovenia border and the north-eastern cost of the Adriatic Sea. They showed that Ca and some chalcophiles (Cd, Pb, plus others) were present in higher amounts in *F. caperata*, compared to *X. parietina*. In return, other elements (Cr, Fe, Ti) were more concentrated in *X. parietina*. They reported that the elements Al, Li, Mn, Ni accumulated in similar amounts for both species. Saniewski et al. (2022) also reported different capture abilities for ^{137}Cs for the lichen *Stereocaulon alpinum,* compared to *Cladonia arbuscula*, by a factor of three, in a survey across Europe.

In our work, different abilities of the two lichen species may be due in part to morphological differences (Di Lella et al., 2003; Fortuna et al., 2021) which in turn could result in differences in particle interception. It is also possible that the growth rates of the two lichens are different: the slowly growing *C. mitis* would be expected to have a slightly higher metal concentration and less biomass (Helle et al., 1983). As well, differences in bioaccumulation between species might be explained by local habitat conditions (Saniewski et al., 2022). The emplacement of the lichen in the field matters, as *C. mitis* has the tendency to grow in the open, whereas *C. rangiferina* can better tolerate shade (e.g. Lechowicz and Adams, 1974). Hence, the ability of the latter to capture airborne particulate matter may be impaired by tree cover and may differ from *C. mitis*. Although our findings indicate the possibility that the two lichen species might have accumulated different levels of EOIs, further work is needed to confirm this finding with improved statistics.

5. Conclusions

Present study is a first follow up of 1980s–1990s lichen regional surveys in a zone formerly impacted by extensive mining activities. Our work has provided new baseline data of the concentrations of Elements of Interest (EOI's) and some radionuclides that were associated with mining operations. Our work suggests an amazing environmental recovery of the area over the past several decades. We found a general decrease in contaminant levels in the zone of past mining activities, particularly for U, Th and Pb, but we have detected weak but localized spots to the North of Elliot Lake where some quantifiable contaminants may still be present in an area. In particular, the lichens collected at a localized micro-transect (<10 km from past industrial operations) showed variations of these EOIs by up to an order of magnitude difference over a short distance (~120 m). The toxic elements (As, Cd, Cs), on the other hand, do not show such variations.

This work establishes a latest set of background data for selected elements (including elements diagnostic of past mining, toxic elements, and REE). In particular, such set of data is of practical importance for U and Th, which might be targeted elements for potential future industrial developments and/or the use of SMRs for mining or remote communities. Furthermore, we determined the activity concentrations of Cs-137 in lichens of the area and showed that they evidence present-day global background. The measured values likely reflect local dust re-suspension from previously globally imported ^{137}Cs.

For both lichen species, *C. rangiferina* and *C. mitis*, we found correlations between the concentrations of U, Th, Ti and As. This observation, when coupled with ancillary information on REE abundances, suggest that resuspension and particulate trapping might be a significant mechanism of uptake by lichens. Future sampling and research should be done to investigate the mechanisms. We have also reported that *C. rangiferina* and *C. mitis*, sampled in locations next to one another (<10 m), have different metal contents, suggesting different capture abilities between these two species. Not all elements showed statistically significant differences between the lichen species, but this evidence is sufficient to suggest the use of one lichen species, and not a mixture of lichen species for monitoring purposes.

Declarations

Author contribution statement

Julia Anderson, Ph. D: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Francois Caron, Ph. D: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Peter J Beckett, Ph.D.: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data.

Graeme A Spiers, Ph. D: Conceived and designed the experiments; Analyzed and interpreted the data.

Nykola Lévesque, B.Sc: Performed the experiments.

G. Mark Charbonneau, Ph.D.; Alan Lock, Ph.D.: Contributed reagents, materials, analysis tools or data.

Brad Halvorson, Ph. D: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Heather Dufour, Ph. D: Performed the experiments; Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interest's statement

The authors declare no conflict of interest.

Additional information

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