Chapter 14

Method for Extraction and Multi-element Analysis of *Hypogymnia Physodes* Samples from the Athabasca Oil Sands Region

E. S. Edgerton^{*}, J. M. Fort, K. Baumann, J.R. Graney, M.S. Landis, S.Berryman and S. Krupa^e *Corresponding author: *e-mail address: <u>eedgerton@atmospheric-research.com</u>}*

Abstract

A microwave-assisted digestion technique followed by ICPMS analysis was used to measure concentrations of 43 elements in *Hypogymnia physodes* samples collected in the Athabasca Oil Sands Region (AOSR) of northern Alberta, Canada. Analysis of multiple Standard Reference Materials, replicate samples and digestion blanks indicate that 34 elements were routinely quantifiable in small samples of lichens (25-30 mg) from the AOSR. Analysis of As and Se was performed by dynamic reaction cell ICPMS techniques to minimize polyatomic interferences and improve detection limits. Data from 121 sampling locations show that concentrations of many elements are higher (factors of 1.5-3) near the oil sands operations (i.e., within 50 km) than further away (i.e., beyond 50 km). Statistical analysis shows that many of the 34 elements (particularly the Rare Earth Elements) are highly correlated, but others only have weak correlations with a few other elements. Linear regression of element concentrations versus Al indicates a range of behavior across elements that likely reflect multiple accumulation processes. Comparison with previous studies of *Hypogymnia physodes* shows that elemental concentrations within the AOSR are generally comparable but often towards the lower end of those reported for remote and background areas of the northern hemisphere. Sb and Pb concentrations, in particular, are among the lowest reported for *Hypogymnia physodes*.

1. Introduction

Epiphytic lichens have been used for more than half a century to assess environmental effects of air pollution (Tuominen, 1967; Hawksworth and Rose, 1970). Numerous studies have used

native or relocated lichen specimens to determine global distribution of radionuclides from thermonuclear weapons tests (Ferry et al, 1967), heavy metal concentrations in remote, high elevation regions (Bergamaschi et al. 2002), depleted uranium in war zones (Di Lella et al. 2003), heavy metal gradients in and around industrial facilities (Nieboer et al. 1972; Gailey et al. 1985), and to recolonize areas with low or absent populations of once native species (Bennett et al, 1996). This chapter describes the digestion and analytical method used to quantify elemental concentrations in *Hypogymnia physodes* samples collected in the Athabasca Oil Sands Region (AOSR) of northern Alberta, Canada. As described in other chapters of this book, the objective of this work is to quantify spatial gradients and atmospheric sources of elements in *Hypogymnia physodes*, and, ultimately, assess potential effects of emissions from extraction and processing operations within the AOSR. *Hypogymnia physodes* was chosen for this work because it is relatively pollution tolerant and found at most of the forested sites in the AOSR; hence, it is a good candidate species for defining deposition gradients across the region.

Several factors were considered in the selection of digestion and analytical techniques. First, we wanted to perform a complete digestion in order to measure both mineral-bound and organicallybound elements. Given the variety of oil production operations in the AOSR from mining to refining, we would expect particulate emissions in a broad range of sizes (ultra-fine to supercoarse), chemical states and chemical matrices. Complete digestion of the lichen samples was therefore necessary to bring all size and source categories into solution. Second, we needed a large number of elements (major, minor and trace) to account for the potentially large number of sources and processes (natural and anthropogenic) that could contribute to lichen concentrations. Third, we wanted a technique that could be used on relatively small sample sizes (i.e., 25-50 mg). This was necessary to ensure that there would be sufficient sample mass for replicate analyses, independent analyses of Hg isotopes, polyaromatic hydrocarbons (PAHs), and for archival. Finally, we needed a solution that was amenable to Pb isotope analysis. Based on these considerations, we selected microwave-assisted digestion with a sequential peroxide and acid addition procedure, followed by analysis via inductively coupled plasma-mass spectrometry (ICPMS). Details of the lichen digestion and analytical procedures, statistical analysis, and comparison to results from other multi-element lichen studies are the major components covered in this chapter.

2. Materials and Methods

2.1 Lichen Samples

Samples of *Hypogymnia physodes* were collected by the WBEA Terrestrial Environmental Effects Monitoring program (TEEM) in 2008, during which more than 800 lichen samples were collected from 369 circular plots roughly 0.4 hectare in size (see Figure 1). The lichen sampling protocol followed methods developed by the U.S. Forest Service Air Quality Monitoring Program in the Pacific Northwest, with a few modifications (Berryman et al., 2010). Lichens were collected from tree branches at a height of at least 1.5 m from the forest floor and placed in clean, unused metalized polyester Kapak bags. Samples were collected from a minimum of six overstory trees, primarily jack pine (*Pinus banksiana*) or black spruce (*Picea mariana*), in or near each study plot. Duplicate samples (field replicates) were collected when sufficient material was available. The ecosite phase or wetland type was also classified for each stand and the plant community type was described (following classifications in Beckingham and Archibald, 1996 and Vitt et al., 1996).

Following collection, samples were air-dried the same day, and cleaned to remove host plant material and other debris. Samples were then dried at 65° C for 2 hours and sealed in clean envelopes. Aliquots of each sample were then analyzed for total-sulfur (total-S) and total-nitrogen (total-N) concentration at the University of Minnesota Research Analytical Laboratory (UMRAL; Berryman et al., 2010). Total-S concentration was determined with a LECO Corp. Sulphur Determinator (Model No. S144-DR) by dry combustion of a 100-150 mg aliquot covered by tungsten oxide in an oxygen atmosphere at 1350 °C. The sulfur detector was calibrated with three LECO plant reference materials (LECO 1026, orchard leaves; LECO 1025, orchard leaves; LECO 1010, tobacco leaves). Total-N concentration was determined with a LECO Corp. FP-528 Nitrogen Analyzer by dry combustion of a 150-500 mg aliquot in a gel capsule. The nitrogen analyzer was calibrated using three LECO plant reference materials (LECO 1006, rice flour; LECO 1026, orchard leaves; and, LECO 1052, ethylenediaminetetraacetic acid). Total-S and total-N concentrations from the 369 sample sites were 378-1783 µg/g and 5645-26799 µg/g, respectively.

Samples used for the multi-element study were obtained from the subset of 121 circled sites in Figure 1.

The sample selection strategy for multi-element analysis involved a staged approach.

The first group of 50 targeted lichen samples with either:

- high N and S concentration;
- low N and S concentration;
- high N:S ratio; or
- low N:S ratio.

The next group of 20 samples were selected to focus on:

- high N and S samples near the main oil sands production operations;
- low N and S (background) sites to the far north of the study area; and
- low N and S (background) sites to the east near the Saskatchewan/Alberta border.

The last group of 51 samples were used to fill in around sites of interest from the first 70 samples and to ensure that roughly equal numbers of samples had been selected from proximal sites (i.e., <50 km from the mid-point between the two main oil processing facilities, n=61) and distal sites (n=60). As discussed in the Graney et al., (this volume), sample selection was also designed to select an equal number of sites from locations with similar soil moisture conditions based on the ecosite phase classification noted during lichen collection (specifically wet versus dry sites).

2.2 Sample Digestion

Prior to digestion for multi-element analysis, lichen samples were ground and homogenized in a SPEX (Metuchen, NJ) 8000M ball mill equipped with zirconium balls. Grinding was performed at the University of Michigan laboratory of Dr. Joel D. Blum.

Aliquots of homogenized lichen samples (25-35 mg) were digested in batches of 30-35 in a sequential peroxide and acid addition procedure similar to that developed by Jalkanen and

Hasanen (1996) using a MARS Express (CEM Corp., Matthews, NC) microwave digestion system. The first digestion step included addition of 2.0 mL of 30 % ultrapure H_2O_2 (J.T.Baker Ultrex-II) with heating to 100 °C for 10 minutes to break down organic matrices. After cooling, 1.0 mL of ultrapure HNO₃ (J.T.Baker Ultrex-II) plus 0.25 mL of ultrapure HF (J.T.Baker Ultrex-II) were added to each vessel and heated to 180 °C for 10 minutes to dissolve the mineral matrices. After cooling, 5 mL of ASTM Type II ultrapure (18.2 M Ω ·cm) water was added to each vessel and heated to 180 °C for 20 minutes. Digestates were then vacuum filtered through a Whatman #541 ashless paper filter and brought up to a final volume of 25 mL with ultrapure water. Each batch included 2-3 digestion blanks, 2-3 replicate samples and 1-2 aliquots each of two standard reference materials (SRMs). The SRMs were: (i) Community Bureau of Reference (BCR) 482 (elements in lichens); and (ii) National Institute of Standards and Technology (NIST) 1648a (urban particulate matter). Digestion aliquots for BCR482 and NIST 1648a were in the range of 25-30 mg and 1-2 mg, respectively.

2.3 Multi-element Analysis via ICPMS

Sample extracts were analyzed with a Perkin Elmer/Sciex dynamic reaction cell (DRC) II inductively coupled plasma-mass spectrometer (ICPMS) for 43 elements. Operating conditions for the ICPMS are shown in Table 1. Two independent reference solutions and one SRM (NIST 1643e, trace elements in water) were analyzed to confirm the ICPMS calibration, and ten digestion spikes (0.1-1.0 ppb) were analyzed to assess matrix interferences and estimate method detection limits. Arsenic (As) and selenium (Se) were measured using the DRC function of the ICP-MS to reduce polyatomic interferences and improve detection limits. The DRC is located before the quadrupole chamber and uses a reagent or collision gas to reduce interfering ions using charge transfer/collision-induced and chemical dissociation. In this case oxygen was used as the reagent gas for As (quantified as ⁷⁵As¹⁶O) and ammonia was used as the reagent gas for Se (quantified as 78 Se) in the DRC. Multiple dilutions (2x, 5x and 10x) were performed on each digestate to optimize quantification. Data were then reviewed for SRM recoveries, replicate precision and stability of concentrations across dilutions. Following data review, the 5x dilution was used for purposes of reporting and analysis. Several samples were also analyzed at the USEPA-NERL using a ThermoFinnigan Element2 high resolution magnetic sector field ICPMS (HR-ICPMS) to estimate potential polyatomic interferences around amu 75 that hinder

quantification of ⁷⁵As (i.e., ⁴⁰Ar³⁵Cl, ³⁹K³⁶Ar) and to confirm that ⁷⁵As¹⁶O measured by ARA accurately represented As concentrations.

3. Results and Discussion

3.1 Detection Limits

Method detection limits (MDLs) for each element are shown in Table 2. Method detection limits were calculated using a slight modification of EPA method 200.1 (40 CFR Appendix B, part 136) as three times the standard deviation of the digestion spike concentrations times the student t's value for a 99% confidence interval. Also shown in Table 2 are the minimum observed concentrations for each element in the 121 sample data set. For most elements, the minimum observed concentration was one or two orders of magnitude greater than the MDL, suggesting that the method used for lichen sample digestion and analysis in this study is well suited for trace element quantification. However, this was not the case for Be, Nb, Pt, Sn, Ta and W (italicized in Table 2). For these elements, concentrations were below the MDL anywhere from 1% of the time (Nb) to 50% of the time (Pt), and were rarely present at concentrations more than 2-5 times the detection limit.

Table 2 shows two sets of results for As and Se, one for analysis in normal mode (⁷⁵As, ⁷⁷Se) and the other for analysis via DRC (⁷⁵As¹⁶O, ⁷⁸Se). The DRC-mode MDLs are roughly an order of magnitude lower than the normal-mode MDLs. Subsequent discussion of As and Se in this chapter therefore refers specifically to DRC-mode concentrations. Figure 2 shows a scatter plot of the USEPA HR-ICPMS analysis of ⁷⁵As versus the DRC-mode ICPMS analysis of ⁷⁵As¹⁶O. Results show a strong correlation ($r^2 = 0.914$) with a slope near unity (0.985), suggesting that the DRC-ICPMS method is appropriate for measurement of sub-part per billion (in solution) concentrations of As. In contrast, results for normal mode ⁷⁵As, indicate poor comparability with the USEPA HR-ICPMS. This is indicated by a weak correlation ($r^2 = 0.379$), a slope of 0.66 and a significantly negative intercept (-0.51). These results suggest that historical As data for lichens should be viewed with caution, unless the analytical technique in question has been demonstrated to be largely artifact-free.

3.2 SRM Recoveries

Recovery data for certified elements in solid phase SRMs are shown in Table 3. Results show good recovery (\pm 10%) and high reproducibility (\pm 5%) for most elements. The two exceptions are Cr and Ti, with recoveries of 35% and 76%, respectively, in urban particulate matter (NIST 1648a) and 80% and 129%, respectively, in lichen (BCR 482). Several previous studies have also reported low recoveries for Cr in NIST 1648a when using similar digestion techniques (Jalkanen and Hasanen, 1996; Rasmussen et al., 2007).

3.3 Lab Replicates

Results of laboratory replicate extractions are summarized in Table 4 as the median absolute percent difference (MAPD) and the standard deviation (SD) of percent differences between replicates. MAPD is a useful statistic because it conveys the midpoint of the absolute deviations from exact agreement. For example, the MAPD for Al in Table 4 indicates that half of the replicate samples agreed within ±3.2%. MAPD ranges from 1.2% (Ca) to 22.3% (W) and SD ranges from 3.0% (Fe) to 73.5% (Pt). In general MAPD is <5% and SD is <10% for the majority of elements. These findings indicate that the samples were well homogenized in the grinding process and that measurement precision for the most part is adequate to detect relatively small (10-20%) differences between sampling locations. Exceptions include Be, Bi, Nb, Pd, Pt, Sn, Ta, Tl and W, elements with concentrations typically only a factor of 2-3 above the method detection limit. Given the relatively low concentrations and poor reproducibility of these 9 elements, they will be excluded from further discussion in this chapter.

3.4 Data Overview

Statistical summaries for each of the 34 quantifiable elements are shown in Table 5 for two subsets of sampling sites. The distal group (n=60) includes sites >50 km from the center of oil sand production operations and the proximal group (n=61) includes sites <50 km from the center of oil sand operations. The proximal versus distal site groupings allow us to determine the influence of near field sources in this study, and to compare our results to those from other studies from a local source versus background source contribution perspective. Results show a

broad range of concentrations across elements, but a fairly narrow range of proximal:distal ratios (P/D ratios). Calcium (Ca) is the most abundant element and, on average, represents 1-2 percent of lichen mass. Aluminum (Al), iron (Fe), potassium (K), phosphorus (P) and silicon (Si) are also major elements and can represent 0.1-0.6 % of lichen mass. If we assume that Ca, Al, Fe, K and Si are present as oxides, then, taken together, they account for about 2.5% and 4.8% of sample mass at distal and proximal sites, respectively. Proximal/distal ratios range from 0.6 (Mn) to 3.2 (V) and appear to cluster for the most part into 3 groups: 0.9 ± 0.3 (4 elements), 1.5 ± 0.3 (10 elements), and 2.5 ± 0.3 (20 elements). Alkali and alkaline earth metals compose the group with P/D ratios around 1.5, while Al, Si, most transition metals and Rare Earth Elements (REE) are in the group with P/D ratios around 2.5.

Pearson correlation coefficients (r) for the 121 sample data set are shown in Table 6. In general, there are a large number of significant and highly significant correlations among elements. The highest correlations (r~0.98) are among the REEs (La, Ce, Pr, Nd and Sm) and Al. Interestingly, the non-REEs As and Se are also very highly correlated with the REEs, and with Al and Fe. Several elements, including Cd, P, and Zn exhibit very few significant correlations, while others, including Ca, K, Mg and Pb, exhibit significant correlations with many elements but with r values in a fairly narrow range (i.e., 0.4-0.7). Uniquely, Mn is negatively correlated with most other elements.

Figures 3a through 3f are scatter plots of selected elements versus Al for all lichen samples. Elements were selected to represent major components, REEs, transition metals, trace elements and four elements (P, Mo, Mn and Zn) that exhibit interesting behavior with respect to Al. Al is often used as a normalizing element for comparing lichen concentrations, but very similar relationships would be observed for any of the REEs, given the high correlations between Al and these elements. Each scatter plot contains a best fit regression line (solid) and also a line corresponding to the upper crust element:Al ratio from Taylor and McLennan (1995). The latter is included simply as a point of reference to illustrate relative behavior across groups of elements. As discussed by Reimann and DeCaritat (2000, 2005), a host of geochemical and biochemical processes, in addition to anthropogenic activities, can cause element/Al ratios to depart from the global average. Thus, elemental ratios should be used only as another tool for exploring complex multi-element datasets, rather than as a diagnostic of anthropogenic versus geogenic sources. As detailed in the Landis et al. chapter (this volume) location specific differences in the overburden and the geologic formations that are mined during the extraction of the oil sands are a major reason why element:Al ratios should be expected to depart from the global average in the AOSR.

Si and Fe in Figure 3a exhibit strong correlations with Al and regression line intercepts that are small in relation to observed concentrations. The regression line for Si indicates Si/Al ratios that are lower than the crustal average; however, close inspection suggests there may be two distinct relationships, one of which is near the crustal average and the other about a factor of 2 lower. The Fe/Al slope, on the other hand, is almost a factor of 2 higher than the crustal average. Ca and K differ from Si and Fe in several respects. First, the regression line intercepts are relatively high, suggestive of a process for accumulating Ca and K which is independent of Al. The regression slope for Ca is at least a factor of 10 higher than the crustal ratio, while that for K is not statistically different from the crustal value.

The REEs La, Ce, Pr, and Sm exhibit very strong correlations with Al ($r^2>0.95$) and virtually negligible intercepts (see Figure 3b). Regression line slopes in all cases are roughly 1.7 times the crustal average. The transition elements V, Ni, Cu, and Co exhibit lower correlations with Al than the REEs (see Figure 3c). Regression intercepts are near-zero for V, Ni and Co, while that for Cu is quite large. Regression slopes for V and Ni are 5-8 times the crustal ratio, while those for Cu and Co are 2-3 times the crustal ratio.

The relatively volatile trace elements Se, As, Cd and Pb exhibit interesting and diverse relationships to Al (Figure 3d). Se and As are both highly correlated with Al ($r^2 \sim 0.95$) and exhibit slopes at least a factor of 100 higher than the crustal average. Cd exhibits a very large intercept and negative slope, while Pb exhibits a large intercept and positive slope. Despite the negative slope, observed Cd/Al ratios are at least a factor of 10 higher than crustal ratios across the range of observed concentrations. For Pb, the slope is roughly a factor of 1.5 higher than the crustal value. The elements P, Mn, Rb and Zn show weak to non-significant relationships to Al and dominant intercepts relative to observed concentrations (Figure 3e). Data for Mn, and to a

lesser extent Zn and P, are suggestive of an inverse relationship to Al. P/Al and Zn/Al ratios are invariably much higher than crustal values, while Mn/Al and Rb/Al often approach crustal values. The diversity of Al relationships shown in figures 3a-3e suggests that a range of processes contribute to the accumulation of minor and trace elements in *Hypogymnia physodes* and underscores the need for multivariate analyses, such as principal component analysis, to elucidate source contributions (*Landis et al.*, this volume).

3.5 Comparison with Hypogymnia physodes Data from Previous Studies

Data from previous studies are compared with the distal and proximal subsets of AOSR samples in Table 7. Given the large number of published studies, only a limited cross-section could be included in this discussion. In general, studies were excluded from comparison if they: (i) reported less than 4 elements; (ii) did not present data from a "control" or "background" site; or (iii) employed sample digestion and analytical techniques that were deemed incommensurable with the current study. Data in Table 7 must be approached with caution because they span broad reaches of time and space, and because details of sample collection, site ecology and local sources are unknown or uncontrolled across studies. Graney et al. (this volume), for example, discuss the non-trivial effects of wet versus dry soil conditions that translates to ecological based differences in canopy composition that in turn affect element concentrations in lichens. The studies in Table 7 are listed in order of approximate distance from the AOSR, ranging from about 1200 km for Salt Spring Island, BC, Canada to over 10,000 km for Sagarmatha NP, Nepal. This clearly exemplifies the large geophysical range of *Hypogymnia physodes*, which is one of its preeminent characteristics for biomonitoring studies.

To place the results from this study into context with other work, the following synopsis is provided for several of the studies listed in Table 7.

• Bennett et al. (1996) conducted a transplant study in 1992 to determine whether *Hypogymnia physodes* could be recolonized in the Indiana Dunes National Lakeshore on the south shore of Lake Michigan. Control samples for the experiment were collected from Toft Point in extreme northeast WI and were analyzed for 20 elements via ICPMS.

- Bergamaschi et al. (2002) performed a study under the auspices of the EV-K2-CNR program to quantify trace element concentrations in lichen samples from remote, high elevation areas. The authors reported data for 20 elements in samples collected from the Sagarmatha National Park at elevations of 3200 m and 5090 m.
- Cloquet et al. (2006) collected samples of several lichen species in and around the city of Metz, France (2006 population c. 300,000). Samples of Hypogymnia physodes were collected at six of the 36 study sites and analyzed for Al, Cd, Cu, Pb and Zn via ICPMS.
- Gailey et al. (1985) conducted a transplant study in 1981 to evaluate accumulation of heavy metals in and around the town of Armadale, a small industrial town in central Scotland. Transplant samples were collected near Tayside, Scotland (80 km northeast of Armadale), in an area distant from heavy metal pollution and analyzed for Fe, Mn, Zn, Pb, Cu, Cr and Ni via AAS.
- Olszowski et al. (2012) conducted a translocation study in rural southwest Poland in 2009-10 to obtain heavy metal data in a region with little historical monitoring. Control samples for this study were collected in the Bory Niemendenski Forest and analyzed for Mn, Zn, Pb, Ni, Cd and Cu via atomic absorption spectrometry.
- Pfeiffer et al. (1992) conducted a survey of metal concentration in lichen samples collected in and around the city of Thunder Bay, Ontario, Canada.
- Valeeva and Moskovchenko (2002) collected samples across the Tyumen Oblast of northwestern Siberia to determine the effect of oil exploration and other human activities on trace element concentrations. A total of 42 Hypogymnia samples were collected and analyzed from 10 sites, including a background site on the Yamal Peninsula.
- The US Department of Agriculture (USDA) published a literature review of nutrient and metal concentrations in 1999 and maintains the National Lichens and Air Quality Database and Clearinghouse (USDA 1999, 2012). Together, these resources contain a wealth of data on numerous lichen species, including *Hypogymnia physodes*, from global studies conducted between 1977 and 1997 and from otherwise unpublished studies in US National Forests conducted between 1986 and 1997.

Inspection of concentration data across sites in Table 7shows relatively large ranges for all elements. AOSR samples tend to exhibit some of the highest concentrations for the major

elements, such as Al, Ca, Fe and K. Ni and V concentrations in the AOSR proximal group also appear somewhat elevated compared to the results from other studies. At the same time, AOSR results include some of the lowest reported concentrations for a number of trace elements, including As, Sb, Cd and Pb. In fact, the Sb and Pb concentrations may be the lowest ever reported for *Hypogymnia physodes*.

4. Conclusions

The methods used in this work are appropriate for multi-element analysis of small (25-30 mg) lichen samples. The microwave-assisted procedure using sequential additions of H_2O_2 and HNO₃+ HF effectively digested the organic and mineral portions of the samples and liberated most elements quantitatively into solution for subsequent analysis. Possible exceptions include Cr and Ti, which showed poor recoveries for NIST 1643a (urban particulate matter) but higher recoveries for BCR 482 (lichen). Matrix matched ICPMS detection limits were found to be suitable for quantification of 34 of the 43 target elements. Multiple analyses of SRMs and duplicate extractions show that accuracy and precision are on the order of 5-15% for many elements. For future studies, larger sample sizes or pre-concentration might be needed to reliably quantify the platinum group elements, plus Be, Bi, Nb, Sn Ta, Tl, and W. As and Se should be analyzed by high-resolution ICPMS or dynamic reaction cell ICPMS to achieve optimum detection limits and to minimize polyatomic interferences. The large dataset produced in this effort shows considerable texture both in terms of inter-element relationships and as a function of distance to the AOSR oil production operations (distal versus proximal subsets). In general, the concentrations reported in this work are well in line with those reported for Hypogymnia physodes samples collected from other parts of Canada, the US and remote areas of the northern hemisphere. The major elements tend to be at or near the upper end of reported concentrations, while a number of trace elements (As, Sb, Pb, Cd) are at or below the lower end of concentrations reported in other studies.

5. Acknowledgements

We thank Justin Straker (Stantec) for his efforts in lichen sample collection and cleaning and Joel Blum (University of Michigan) for lichen sample grinding. This work was funded by WBEA. The EPA through its Office of Research and Development collaborated in this research.

It has been subjected to EPA Agency review and approved for publication. The content and opinions expressed by the authors do not necessarily reflect the views of the EPA, WBEA, or the WBEA membership.

6. References

Beckingham, J.D. and J.H. Archibald. (1996). Field Guide to Ecosites of Northern Alberta. Northern Forestry Centre, Forestry Canada. Northwest Region. Edmonton, Alberta.

Bennett, J. P., Dibben, M. J., Lyman, K. J. (1996). Element concentrations in the lichen *Hypogymnia Physodes* after 3 years of transplanting along Lake Michigan. Environmental and Experimental Botany. 36(3): 255-270.

Bergamaschi, L. Rizzio, E., Valcuvia, M. G., Verza, G., Profumo, A., Gallorini, M. (2002). Determination of trace elements and evaluation of their enrichment factors in Himalayan lichens. Environmental Pollution. 120: 137-144.

Berryman, S., Straker, J., Krupa, S., Davies, M., Ver Hoef, J. and Brenner, G. (2010). Mapping the characteristics of air pollutant deposition patterns in the Athabasca Oil Sands Region using epiphytic lichens as bioindicators. Interim Report Submitted to the Wood Buffalo Environmental Association, Fort McMurray, AB, Canada.

Berryman, S., Straker, J., Krupa, S., Davies, M., Ver Hoef, J. and Brenner, G. (2010). Mapping the characteristics of air pollutant deposition patterns in the Athabasca Oil Sands Region using epiphytic lichens as bioindicators. Interim Report Submitted to the Wood Buffalo Environmental Association, Fort McMurray.

Cloquet, C., Carignan, J., Libourel, G. (2006). Atmospheric pollution dispersion around an urban area using trace metal concentrations and Pb isotope compositions in epiphytic lichens. Atmospheric Environment. 40: 574-587.

Di Lella, L.A., Frati, L., Loppi, S., Protano, G., Riccobono, F. (2003). Lichens as biomonitors of uranium and other trace elements in an area of Kosovo heavily shelled with depleted uranium rounds. Atmospheric Environment. 37:5445–5449.

Ferry, B. W., Baddeley, M. S., Hawksworth, D. L., Tuominen, Y. (1967). Studies on the strontium uptake of the *Cladonio alpestris* thallus. Annales Botanici Fennici: 4. 1-28.
Gailey, F. A. Y., Smith, G. H., Rintoul, L. J., Lloyd, O. L. (1985). Metal deposition in central Scotland, as determined by lichen transplants. Environmental Monitoring and Assessment. 5: 291-309.

Guttova, A., Lackovicova, A., Pisut, I., Pisut, P. (2011). Decrease in air pollution load in urban environment of Bratislava (Slovakia) inferred from accumulation of metal elements in lichens. Environmental Monitoring and Assessment. 182: 361-373.

Hawksworth, D. L., and Rose, F. (1970). Qualitative scale for estimating sulphur dioxide air pollution in England and Wales using epiphytic lichens. Nature. 227: 145-148.
Herzig, R., Liebendörfer, L., Urech, M., Ammann, K., Cuecheva, M., Landolt, W. (1989).
Passive Biomonitoring with Lichens as a Part of an Integrated Biological Measuring System for Monitoring Air Pollution in Switzerland, International Journal of Environmental Analytical Chemistry. 35:1, 43-57.

Jalkanen, L. M. and Hasanen, E. K. (1996). Simple method for the dissolution of atmospheric aerosol samples by inductively coupled plasma mass spectrometry. Journal of Analytical and Atomic Spectrometry. 11: 365-369.

Jeran, Z., Jacimovic, R., Batic, F., SAmodis, B., Wolterbeek, H. T. (1996). Atmospheric heavy metal pollution in Slovenia derived from results of epiphytic lichens. Fresenius Journal of Analytical Chemistry. 354: 681-687.

Nieboer E., Ahmed H. M., Puckett K. J., Richardson, D. H. S. (1972). Heavy metal content of lichens in relation to distance from a nickel smelter in Sudbury, Ontario. Lichenologist. 5: 291-304.

Olszowski, T., Tomaszewska, B., Goraina-Wloodarczyk, K. (2011). Air quality in nonindustrialized area in the typical Polish countryside based on measurements of selected pollutants in immission and deposition phase. Atmospheric Environment: doi: 10.1016/j.atmosenv. 2011.12.049.

Pfeiffer, H.N. and Barclay-Estrup, P. (1992). The Use of a Single Lichen Species, *Hypogymnia physodes*, as an Indicator of Air Quality in Northwestern Ontario. The Bryologist. 95(1):38-41. Pilegaard, K. (1979). Heavy metals in bulk precipitation and transplanted *Hypogymnia Physodes* and *Dicranoweisia cirrata* in the vicinity of a Danish steelworks. Water, Air and Soil Pollution. 11: 77-91.

Rasmussen, P. E., Wheeler, A., Hassan, N., Filiatreault, A., Lanouette, M. (2007). Monitoring personal, indoor and outdoor exposures to metals in airborne particulate matter: risk of contamination during sampling, handling and analysis. Atmospheric Environment. 41: 5897-5907.

Reimann, C., DeCaritat, P., (2000). Intrinsic flaws of element enrichment factor (EFs) in environmental geochemistry. Environmental Science and Technology. 34: 5084–5091.

Reimann, C. and DeCaritat, P. (2005). Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factors. Science of the Total Environment. 337: 91–107.

Taylor, S.R. and McLennnan, S.M. (1995). The geochemical evolution of the continental crust. Reviews of Geophysics 33: 241–265.

Tuominen, Y. (1967). Studies on the strontium uptake of the *Cladonio alpestris* thallus. Annales Botanici Fennici 4: 1-28.

USDA Forest Service. (1999). A Review of Lichen and Bryophyte Elemental Content Literature with Reference to Pacific Northwest Species. March 1999.

USDA Forest Service. (2012). National Lichens and Air Quality Database and Clearinghouse. http://gis.nacse/lichenair. Accessed February 21, 2012. Valeeva, E. I., and Moskovchenko, D.V. (2002). Trace-element composition of lichens as an indicator of atmospheric pollution in northern West Siberia. Polar Geography 26(4):249-269.

Vitt, D. H., L.A. Halsey, M.N. Thormann, and T. Martin. (1996). Peatland inventory of Alberta Phase 1: Overview of peatland resources of the natural regions and subregions of the province. National Centres of Excellence. Sustainable Forest Management Centre, University of Alberta, Edmonton, Alberta.

Sample Throughput	
Nebulizer	Elemental Scientific PFA-ST
Spray Chamber	Elemental Scientific PFA Pure Chamber Spray Chamber
	and PFA PureCap Endcap
Injector	Elemental Scientific PFA/Sapphire
Torch	Quartz
Plasma Conditions	
Nebulizer Flow	0.92 L/min
Auxiliary Gas Flow	1.2 L/min
Plasma Gas Flow	15 L/min
Lens Voltage	6.4(v)
RF Power	1.2 kW
Ion Focusing	
Detector Mode	Dual
Analog Stage Voltage	-1750 V
Pulse Stage Voltage	1250 V
Quadrupole Rod Offset (std) [QRO]	-4.50 V
Cell Rod Offset (std) [CRO]	-16.00 V
Discriminator Threshold	25.00 V
Cell Path Voltage (std)[CPV]	-11.00 V
Dynamic Reaction Cell Gas A	Ammonia
Dynamic Reaction Cell Gas B	Oxygen
Cell Gas A Flow	0.6 sccm
Cell Gas B Flow	0.7 sccm
DRC Neb Flow	0.92 L/min
DRC Mode [QRO]	-8.50 V
DRC Mode [CRO]	-1.00 V
DRC Mode [CPV]	-16.00 V
Sampling Parameters	
Mass Range	5-270 AMU
Resolution	0.7 AMU
Uptake	~700uL/min
Number Of Replicates	3
Total Acquisition Time Per Sample	~20min

 Table 1. ICPMS operating conditions.

Element	Analytical Isotope/Mass	LOD (ug/g)	Min. Observed (ug/g)	Element	Analytical Isotope/Mass	LOD (ug/g)	Min. Observed (ug/g)
Al	27	25.3	579	Ni	60	0.063	1.22
As	75	0.389	na	Р	31	8.57	365
As (DRC)	91	0.018	0.108	Pb	208	0.007	1.12
Ba	137	1.53	15.0	Pd	108	0.011	0.019
Be	9	0.018	0.006	Pr	141	0.019	0.063
Bi	209	0.001	0.008	Pt	195	0.004	<0.001
Ca	44	216	2035	Rb	85	0.051	2.08
Cd	114	0.006	0.060	Sb	123	0.003	0.014
Ce	140	0.001	0.576	Se	77	0.133	na
Со	59	0.006	0.189	Se (DRC)	78	0.014	0.232
Cr	52	0.360	0.625	Si	28	61.6	1413
Cs	133	0.009	0.053	Sm	147	0.002	0.049
Cu	63	0.249	1.78	Sn	118	0.052	0.006
Fe	56	15.3	405	Sr	88	0.038	5.23
К	39	1.21	1830	Та	181	0.014	<0.001
La	139	0.005	0.300	Th	232	0.001	0.052
Li	7	0.077	0.720	Ti	49	0.142	14.1
Mg	26	2.11	382	Tl	205	0.001	0.003
Mn	55	0.132	50.3	U	238	0.001	0.024
Мо	98	0.040	0.068	V	51	0.045	1.28
Na	23	1.03	22.1	W	182	0.022	<0.001
Nb	93	0.030	0.028	Zn	68	0.962	26.8
Nd	143	0.002	0.272				

 Table 2. Detection limits and minimum observed concentrations for lichen digestates.

	NIS	5 T-1648 a (n=	10)	BI	RC-482 (n=12	2)
Flomont	Conc.	Mean Recovery	s d (%)	Conc.	Mean Recovery	s d (94)
	<u>(µg/g)</u> 3/1300	100.8	<u>5.u. (70)</u> 5.7	$(\mu g/g)$ 1103	101 3	<u>5.u. (70)</u>
A	115 50	100.8	5.7	1105	101.5 08 1	9.7 9.5
AS Co	113.30 59.100	104.0	5.0	0.03	96.1	0.J 7 1
	50400 72 70	90.3 101 4	5.5	2024	90.0	7.1
Ca	/3./0	101.4	5.9	0.56	88.8	3.7
Co	17.93	98.6	4.5	0.32	97.1	5.7
Cr	402	35.6	8.4	4.12	78.8	9.8
Cu	610	96.4	2.7	7.03	97.2	3.9
Fe	39200	97.5	2.9	804	94.2	4.0
Mg	8130	97.8	5.7	578	93.4	6.3
Mn	790	101.2	1.8	33.0	92.1	4.0
Ni	81.1	103.0	4.7	2.47	96.6	4.4
Pb	6550	101.5	5.0	40.9	88.0	2.2
Rb	51.0	92.8	4.2	7.12	110.3	2.2
Sb	45.4	94.0	11.7	0.35	87.4	9.8
Sr	215	101.0	5.7	10.35	91.7	1.8
Ti	4021	73.6	13.8	34.2	129.1	30.2
V	127	99.5	6.6	3.74	<i>98.3</i>	3.0
Zn	4800	98.0	7.1	100.6	94.9	5.2

Table 3. Recoveries from digested standard reference materials (Bold elements are certified; italicized elements are for reference purposes only).

Element	MAPD (%)	SD (%)	Element	MAPD (%)	SD (%)
Al	3.2	4.6	Nd	3.1	4.8
As	1.6	4.9	Ni	2.0	5.7
Ba	2.9	3.9	Р	3.7	5.3
Be	12.6	26.1	Pb	2.1	3.1
Bi	3.3	6.6	Pd	8.9	13.4
Ca	1.2	3.8	Pr	5.1	6.7
Cd	3.6	7.2	Pt	18.5	73.5
Ce	2.1	4.7	Rb	1.7	5.7
Со	3.5	6.8	Sb	5.5	52.8
Cr	2.2	7.3	Se	4.3	5.7
Cs	2.4	4.2	Si	3.3	7.4
Cu	3.9	10.6	Sm	2.4	6.7
Fe	1.9	3.0	Sn	6.4	61.8
K	2.4	3.7	Sr	2.2	4.4
La	3.4	5.5	Ta	5.5	45.0
Li	2.9	4.3	Th	4.2	6.4
Mg	2.3	5.3	Ti	7.9	16.5
Mn	1.4	3.8	Tl	5.5	5.3
Мо	5.2	6.8	U	4.2	6.1
Na	4.5	7.0	V	2.8	5.4
Nb	10.9	29.3	W	22.3	45.5
			Zn	2.6	4.6

Table 4. Summary statistics for replicate extractions (n=19).

	Distal	Proximal	P/D		Distal	Proximal	P/D
Element	(n=60)	(n=61)	Ratio	Element	(n=60)	(n=61)	Ratio
Al	986	2324	2.4	Р	675	722	1.1
As	0.251	0.454	1.8	Pb	2.45	2.92	1.2
Ba	28.2	40.4	1.4	Pr	0.124	0.336	2.7
Ca	10105	18594	1.8	Rb	6.42	8.38	1.3
Cd	0.168	0.152	0.9	Sb	0.022	0.034	1.6
Ce	1.09	2.92	2.7	Se	0.430	0.899	2.1
Со	0.292	0.792	2.7	Si	2615	5765	2.2
Cr	0.978	2.63	2.7	Sm	0.095	0.256	2.7
Cs	0.106	0.175	1.7	Sr	9.9	24.3	2.5
Cu	2.93	3.79	1.3	Th	0.111	0.307	2.8
Fe	711	1932	2.7	Ti	25.6	53.1	2.1
K	2737	3496	1.3	U	0.042	0.091	2.2
La	0.519	1.39	2.7	V	2.94	9.53	3.2
Li	0.95	1.96	2.1	Zn	51.6	46.6	0.9
Mg	570	827	1.5				
Mn	182	116	0.6	Total N	7653	8426	1.1
Мо	0.113	0.332	2.9	Total S	591	813	1.4
Na	39.8	63.0	1.6				
Nd	0.51	1.42	2.8				
Ni	1.93	5.15	2.7				

Table 5. Element concentrations $(\mu g/g)$ in distal (D) and proximal (P) lichen samples.

	Li	Na	Mg	Al	Si	Р	K	Ca	Ti	V	Cr
Li	1.00	.909**	.674**	.984**	.947**	0.05	.489**	.671**	.965**	.907**	.835**
Na	.909 **	1.00	.686**	.934**	.940**	0.07	.465**	.652**	.930**	.837**	.844**
Mg	.674**	.686**	1.00	.682**	.730**	.390**	.718**	.698**	.706**	.551**	.582**
Al	.984**	.934**	.682**	1.00	.952**	0.02	.474**	.649**	.969**	.911**	.835**
Si	.947**	.940**	.730**	.952**	1.00	0.05	.496**	.661**	.980**	.867**	.850**
P	0.05	0.07	.390**	0.02	0.05	1.00	.810**	.292**	0.01	-0.02	0.00
K	.489**	.465**	.718**	.474**	.496**	.810**	1.00	.491**	.468**	.409**	.373**
Ca	.671**	.652**	.698**	.649**	.661**	.292**	.491**	1.00	.654**	.512**	.629**
Ti	.965**	.930**	.706**	.969**	.980**	0.01	.468**	.654**	1.00	.907**	.842**
V	.907**	.837**	.551**	.911**	.867**	-0.02	.409**	.512**	.907**	1.00	.775**
Cr	.835**	.844**	.582**	.835**	.850**	0.00	.373**	.629**	.842**	.775**	1.00
Mn	341**	354**	197*	353**	352**	-0.09	308**	-0.17	358**	387**	349**
Fe	.949**	.908**	.656**	.962**	.916**	-0.05	.402**	.668**	.947**	.896**	.811**
Co	.933**	.878**	.787**	.934**	.945**	0.10	.516**	.742**	.936**	.825**	.830**
Ni	.921**	.844**	.652**	.922**	.897**	0.06	.480**	.642**	.929**	.971**	.811**
Cu	.776**	.776**	.577**	.781**	.800**	0.08	.412**	.504**	.804**	.732**	.687**
Zn	-0.10	-0.03	0.09	-0.11	-0.04	0.16	0.03	.201*	-0.08	-0.10	-0.06
Se	.965**	.888**	.647**	.979**	.917**	-0.02	.443**	.631**	.958**	.938**	.818**
Rb	.438**	.443**	.247**	.469**	.422**	0.10	.337**	0.14	.431**	.380**	.416**
Sr	.435**	.408**	.702**	.406**	.458**	.404**	.544**	.681**	.431**	.293**	.395**
As	.957**	.943**	.694**	.970**	.954**	0.03	.461**	.660**	.960**	.874**	.826**
Mo	.909 **	.848**	.530**	.902**	.850**	0.03	.407**	.560**	.889**	.964**	.786**
Cd	-0.18	-0.09	0.02	-0.17	-0.14	.254**	0.05	0.03	182*	274**	-0.13
Sb	.317**	.360**	.232*	.308**	.337**	0.01	0.11	.274**	.337**	.311**	.479**
Cs	.90 7 ^{**}	.853**	.550**	.913**	.873**	-0.03	.375**	.545**	.887**	.818**	.786**
Ba	.468**	.514**	.620**	.441**	.529**	.391**	.496**	.721**	.487**	.387**	.556**
La	.9 75 ^{**}	.906**	.641**	.981**	.942**	-0.06	.392**	.667**	.968**	.916**	.831**
Се	.9 75 ^{**}	.899**	.636**	.982**	.926**	-0.05	.395**	.661**	.958**	.914**	.825**
Pr	.972 **	.896**	.635**	.982**	.925**	-0.06	.391**	.656**	.957**	.910**	.823**
Nd	.970 **	.895**	.647**	.981**	.928**	-0.06	.392**	.655**	.958**	.907**	.823**
Sm	.966 **	.888**	.647**	.978**	.928**	-0.07	.384**	.646**	.955**	.900**	.820**
Pb	.527**	.641**	.420**	.567**	.608**	-0.14	0.07	.511**	.627**	.542**	.496**
Th	.973**	.899**	.618**	.983**	.919**	-0.07	.377**	.634**	.953**	.911**	.821**
U	.984**	.908**	.656**	.982**	.951**	-0.04	.413**	.640**	.974**	.909**	.836**

Table 6a. Pearson correlation coefficients for elements in *Hypogymnia physodes* (n=121). Asterisks indicate significance at p<0.05 (*) or p<0.01 (**). Part 1: Li-Cr. (Table still needs edits...)

Table 6b. Pearson correlation coefficients for elements in *Hypogymnia physodes* (n=121). Asterisks indicate significance at p<0.05 (*) or p<0.01 (**). Part 2: Mn-Mo.

	Mn	Fe	Co	Ni	Cu	Zn	Se	Rb	Sr	As	Mo
Li	341**	.949**	.933**	.921**	.776***	-0.10	.965**	.438**	.435**	.957**	.909**
Na	354**	.908**	.878**	.844**	.776**	-0.03	.888**	.443**	.408**	.943**	.848**
Mg	197*	.656**	.787**	.652**	.577**	0.09	.647**	.247**	.702**	.694**	.530**
Al	353**	.962**	.934**	.922**	.781**	-0.11	.979**	.469**	.406**	.970**	.902**
Si	352**	.916**	.945**	.897**	.800**	-0.04	.917**	.422**	.458**	.954**	.850**
Р	-0.09	-0.05	0.10	0.06	0.08	0.16	-0.02	0.10	.404**	0.03	0.03
K	308**	.402**	.516**	.480**	.412**	0.03	.443**	.337**	.544**	.461**	.407**
Ca	-0.17	.668**	.742**	.642**	.504**	.201*	.631**	0.14	.681**	.660**	.560**
Ti	358**	.947**	.936**	.929**	.804**	-0.08	.958**	.431**	.431**	.960**	.889**
V	387**	.896**	.825**	.971**	.732**	-0.10	.938**	.380**	.293**	.874**	.964**
Cr	349**	.811**	.830**	.811**	.687**	-0.06	.818**	.416**	.395**	.826**	.786**
Mn	1.00	326**	261**	358**	244**	0.17	356**	-0.17	246**	310**	354**
Fe	326**	1.00	.888**	.904**	.744**	-0.16	.964**	.425**	.359**	.945**	.898**
Co	261**	.888**	1.00	.898**	.765**	0.02	.909**	.409**	.558**	.935**	.802**
Ni	358**	.904**	.898**	1.00	.742**	-0.06	.952**	.383**	.406**	.894**	.931**
Cu	244**	.744**	.765**	.742**	1.00	0.00	.737**	.444***	.349**	.803**	.778**
Zn	0.17	-0.16	0.02	-0.06	0.00	1.00	-0.14	306**	.288**	-0.09	-0.10
Se	356**	.964**	.909**	.952**	.737**	-0.14	1.00	.443**	.362**	.944**	.914**
Rb	-0.17	.425**	.409**	.383**	.444**	306**	.443**	1.00	-0.03	.447**	.381**
Sr	246**	.359**	.558**	.406**	.349**	.288**	.362**	-0.03	1.00	.437**	.296**
As	310**	.945**	.935**	.894**	.803**	-0.09	.944**	.447**	.437**	1.00	.885**
Mo	354**	.898**	.802**	.931**	.778***	-0.10	.914**	.381**	.296**	.885**	1.00
Cd	.213*	219*	-0.04	200*	0.10	0.15	229*	0.17	0.03	-0.11	220*
Sb	246**	.317**	.308**	.325**	.364**	0.07	.296**	0.09	0.18	.336**	.352**
Cs	303**	.854**	.857**	.823**	.771**	-0.12	.882**	.634**	.320**	.895**	.827**
Ba	-0.16	.411**	.579**	.477**	.439**	.409**	.394**	0.06	.657**	.463**	.416**
La	339**	.963**	.932**	.935**	.787**	-0.11	.978**	.431**	.395**	.970 **	.917**
Ce	339**	.964**	.925**	.930**	.773**	-0.12	.983**	.438**	.388**	.966**	.915**
Pr	339**	.961 **	.926**	.928**	.769**	-0.12	.983**	.437**	.387**	.964**	.910**
Nd	335***	.959**	.933**	.929**	.766**	-0.12	.982**	.439**	.392**	.966**	.902**
Sm	334**	.953**	.936**	.924**	.760**	-0.12	.978**	.437**	.393**	.963**	.890**
Pb	-0.14	.585**	.524**	.545**	.522**	0.17	.566**	0.04	.249**	.601**	.569**
Th	344**	.960**	.916**	.921**	.767**	-0.12	.981**	.440**	.372**	.961**	.912**
U	344**	.949**	.940**	.925**	.786**	-0.09	.974**	.428**	.406**	.967**	.902**

	Cd	Sb	Cs	Ba	La	Ce	Pr	Nd	Sm	Pb	Th	U
Li	-0.18	.317**	.907**	.468**	.975**	.975**	.972**	.970 **	.966**	.527**	.973**	.984**
Na	-0.09	.360**	.853**	.514**	.906**	.899**	.896**	.895**	.888**	.641**	.899**	.908**
Mg	0.02	.232*	.550**	.620**	.641**	.636**	.635**	.647**	.647**	.420**	.618**	.656**
Al	-0.17	.308**	.913**	.441**	.981**	.982**	.982**	.981**	.978 **	.567**	.983**	.982**
Si	-0.14	.337**	.873**	.529**	.942**	.926**	.925**	.928**	.928**	.608**	.919**	.951**
Р	.254**	0.01	-0.03	.391**	-0.06	-0.05	-0.06	-0.06	-0.07	-0.14	-0.07	-0.04
К	0.05	0.11	.375**	.496**	.392**	.395**	.391**	.392**	.384**	0.07	.377**	.413**
Ca	0.03	.274**	.545**	.721**	.667**	.661**	.656**	.655**	.646**	.511**	.634**	.640**
Ti	182*	.337**	.887**	.487**	.968**	.958**	.957**	.958**	.955**	.627**	.953**	.974**
v	274**	.311**	.818**	.387**	.916**	.914**	.910**	.907**	.900 **	.542**	.911**	.909 **
Cr	-0.13	.479**	.786**	.556**	.831**	.825**	.823**	.823**	.820**	.496**	.821**	.836**
Mn	.213*	246**	303**	-0.16	339**	339**	339**	335**	334**	-0.14	344**	344**
Fe	219*	.317**	.854**	.411**	.963**	.964**	.961**	.959**	.953**	.585**	.960 **	.949**
Со	-0.04	.308**	.857**	.579**	.932**	.925**	.926**	.933**	.936**	.524**	.916**	.940**
Ni	200*	.325**	.823**	.477**	.935**	.930**	.928**	.929**	.924**	.545**	.921**	.925**
Cu	0.10	.364**	.771**	.439**	.787**	.773**	.769**	.766**	.760**	.522**	.767**	.786**
Zn	0.15	0.07	-0.12	.409**	-0.11	-0.12	-0.12	-0.12	-0.12	0.17	-0.12	-0.09
Se	229*	.296**	.882**	.394**	.978**	.983**	.983**	.982**	.978**	.566**	.981**	.974**
Rb	0.17	0.09	.634**	0.06	.431**	.438**	.437**	.439**	.437**	0.04	.440**	.428**
Sr	0.03	0.18	.320**	.657**	.395**	.388**	.387**	.392**	.393**	.249**	.372**	.406**
As	-0.11	.336**	.895**	.463**	.970 **	.966**	.964**	.966**	.963**	.601**	.961**	.967**
Мо	220*	.352**	.827**	.416**	.91 7 ^{**}	.915**	.910**	.902**	.890**	.569**	.912**	.902**
Cd	1.00	-0.10	-0.05	0.00	-0.17	182*	182*	-0.18	-0.17	213*	183*	180*
Sb	-0.10	1.00	.280**	.351**	.321**	.313**	.311**	.308**	.302**	.270**	.308**	.318**
Cs	-0.05	.280**	1.00	.367**	.910**	.909 **	.909**	.90 7 ^{**}	.905**	.470**	.914**	.916**
Ba	0.00	.351**	.367**	1.00	.434**	.416**	.412**	.409**	.402**	.394**	.399**	.441**
La	-0.17	.321**	.910**	.434**	1.00	.998**	.99 7 ^{**}	.99 7 ^{**}	.994**	.608**	.993**	.989**
Ce	182*	.313**	.909 **	.416**	.998**	1.00	.999**	.998**	.996**	.591**	.99 7 ^{**}	.988**
Pr	182*	.311**	.909 **	.412**	.997 **	.999 **	1.00	.999**	.997 **	.592**	.997**	.987**
Nd	-0.18	.308**	.907**	.409**	.99 7 ^{**}	.998 **	.999**	1.00	.999 **	.587**	.995**	.987**
Sm	-0.17	.302**	.905**	.402**	.994**	.996**	.99 7 ^{**}	.999**	1.00	.579**	.993**	.986**
Pb	213*	.270**	.470**	.394**	.608**	.591**	.592**	.587**	.579**	1.00	.579**	.590**
Th	183*	.308**	.914**	.399**	.993**	.997**	.997**	.995**	.993**	.579**	1.00	.988**
U	180*	.318**	.916**	.441**	.989**	.988**	.987**	.987**	.986**	.590**	.988**	1.00

Table 6c. Pearson correlation coefficients for elements in *Hypogymnia physodes* (n=121). Asterisks indicate significance at p<0.05 (*) or p<0.01 (**). Part 3: Cd-U.

									Valeeva and					Olszowski	Cloquet	Guttova			
Reference	this study	this study	USDA, 1999	Pfeiffer et al. (1992)	USDA, 1999	Bennett, 1996	USDA, 1999	USDA, 2012	Moskov, 2002	Pilegaard, 1979	USDA, 1999	Cailey et al., 1985	Herzig et al., 1989	et al., 2011	et al., 2005	et al., 2011	Jeran et al., 1996	Bergama: 20	schi et al., 02
Country			CA	CA	USA	USA	USA	USA	Russia	Denmark	Finland	Scotland	p	Poland	France	Slovakia	Slovenia	Sagarmatha	n NP, Nepal
	AOSR	AOSR	Salt Spr.	Thunder	Olympic	northern	Acadia	Nat'l	western			near	Forst						
Location	Distal	Proximal	Is., BC	Bay, ON	NP, WA	IW	NP, ME	Forests	Siberia	"bckgnd"	rural sites	Tayside	Neuenegg	rura	Metz	rural	rural	(3200m)	(m 060 <u>5</u>)
Element/Vr.	2008	2008	pre-1986	1990	pre-1988	1992	pre-1988	1986-1997	1993-02	1977	1985-6	1981	1985	2009	2002-3	2006	2002	1999	1000
PI	986	2324	1948	185	743	580	163	191-880	n.d.	n.d.	n.d.	n.d.	363	n.d.	838	n.d.	n.d.	n.d.	n.d.
As	0.25	0.45	n.d.	0.90	n.d.	2.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.24	0.37	0.43
Ca	10105	18594	13513	n.d.	14500	12593	6795	882-9800	n.d.	n.d.	n.d.	n.d.	25500	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ca	0.17	0.15	n.d.	0.20	0.22	n.d.	0.4	0.4-2.0	0.5	0.58	0.7	n.d.	0.22	0.54	0.31	0.46	11	n.d.	0.04
ů	0.29	0.79	n.d.	n.d.	n.d.	0.3	n.d.	n.d.	0.87	n.d.	n.d.	n.d.	0.43	n.d.	n.d.	n.d.	0.55	0.81	1.87
Ċ.	0.98	2.63	n.d.	n.d.	1.87	1.2	0.4	0.5-6.7	4.6	v î	2.1	1.4	1.8	0.22	n.d.	1.8	n.d.	3.70	2.60
CI	2.93	3.79	2.60	0.80	4.70	<mark>5.3</mark>	2.8	0.8-9.3	9	8.4	7.3	18.5	4.3	3.7	6.7	4.2	n.d.	n.d.	5.00
Fe	711	1932	1549	114	754	622	151	188-954	1013	1100	540	871	480	350	n.d.	n.d.	1253	1659	1843
K	2737	3496	2472	n.d.	2810	2944	2496	n.d.	n.d.	n.d.	n.d.	n.d.	3095	n.d.	n.d.	n.d.	4094	9053	4228
La	0.52	1.40	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.2	1.60	3.50
Mg	570	827	680	n.d.	834	745	695	188-954	n.d.	n.d.	n.d.	n.d.	510	n.d.	n.d.	n.d.	n.d.	3038	3899
Mn	182	116	162	n.d.	255	32.2	205	77-665	270	24	131	4 3	n.d.	n.d.	n.d.	524	n.d.	86.1	1.07
iZ	1.93	5.15	4.10	n.d.	4.00	1.8	11	0.7-3.6	3	11.0	2.6	1.8	n.d.	1.1	n.d.	1.8	n.d.	.p.u	n.d.
Pb	2.45	2.92	60	3.9	38.0	7.8	31	5.3-9.9	17.7	4	18	11	28	6	14.7	8	n.d.	.p.u	14.10
Rb	6.42	8.38	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	14	27.6	15.5
ŝ	0.02	0.03	п.d.	п.d.	n.d.	п.d.	n.d.	ъ.d.	п.d.	п.d.	n.d.	n.d.	n.d.	п.d.	nd.	n.d.	0.35	0.60	1.40
Se	0.43	06.0	n.d.	n.d.	n.d.	1.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.27	0.85	0.25
Λ	2.94	9.53	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.80	2.20
Zn	51.6	46.6	38.0	49.0	53.0	78.4	45	32-125	80	85	86	57	44	55	72	48	06	45.2	31.9

Table 7. Element concentrations ($\mu g/g$) in Hypogymnia physodes from the AOSR and other locations.



Figure 1. Lichen sampling locations. Red circles indicate sites used in this study. Note that <121 circles are shown due to several overlapping locations near mine footprints. Thick lined circle denotes a 50 km radius from center of the oil sands processing operations to differentiate distal and proximal sites.



Figure 2. Scatter plot of EPA HR-ICPMS ⁷⁵As versus ARA DRC-ICPMS ⁷⁵As¹⁶O.



Figure 3a. Scatter plots of major elements (Si, K, Ca and Fe) versus Al.



Figure 3b. Scatter plots of selected REEs (La, Ce, Pr and Sm) versus Al.



Figure 3c. Scatter plots of selected transition metals (V, Ni, Cu, Co) versus Al.



Figure 3d. Scatter plots of selected trace elements (Se, As, Cd, Pb) versus Al.



Figure 3e. Scatter plots of P, Mn, Rb and Zn versus Al.