

Coupling lead isotopes and element concentrations in epiphytic lichens to track sources of air emissions in the Alberta Oil Sands Region

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Abstract

A study was conducted that coupled use of element concentrations and lead (Pb) isotope ratios in the lichen *Hypogymnia physodes* collected during 2002 and 2008, to assess the impacts of air emissions from the Alberta Oil Sands Region (AOSR, Canada) mining and processing operations. The lichens selected from the 2002 data set were from 15 samples sites collected on an N-S and E-W grid centered between the oil sands processing sites. The lichens selected for analysis in 2008 were collected using a stratified, nested circular grid approach radiating away from the oil sands processing sites, and included 121 sampling sites as far as 200 km from the mining and processing operations. Spatial analysis indicates three main element groupings including a geogenic source (aluminum and others) related to oil sands mining, an oil processing source (vanadium and others) and a grouping that is likely related to biogeochemical processes (manganese and others). An exponential decrease in concentration of the geogenic grouping of elements versus distance from the mining sites was found, whereas near source concentrations of elements typically associated with oil processing are more homogeneous spatially than the geogenic elements. The mining and oil processing related element groupings are superimposed over the elemental signature that reflects lichen biogeochemical processes. The ranges in Pb isotope ratios were similar in 2002 and 2008, suggesting that sources of Pb accumulated by the lichens did not change substantially between 2002 and 2008. The Pb isotope ratios from lichens collected beyond 50 km from the mining and processing sites cluster into a grouping with a $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of 0.8650 and a $^{208}\text{Pb}/^{206}\text{Pb}$ ratio near 2.095. This grouping likely reflects the regional background Pb isotope ratio signature. The lowering of the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios near the mining and processing operations indicates other Pb sources, likely related to the oil sands mining and processing, are contributing to the Pb source signature. This assessment was confirmed through the analysis of source and stack samples. The Pb isotope ratios were a better predictor of the extent of the source impacts than the element concentrations because the Pb isotope ratios are not affected by either the metabolic processing of elements by the lichens or moisture related controls on atmospheric deposition processes at the collection sites.

The main goals for this project to determine (i) the efficacy of using Pb isotopes to assist in identifying the sources of atmospherically deposited air pollutants in the AOSR, and (ii) whether coupling Pb isotopes with elemental concentrations can help to elucidate the causes for spatial differences in the accumulation of elements by epiphytic lichens in relation to emission sources were successful. An approach that couples Pb isotopes, spatial analysis, and element concentrations is recommended for future source attribution studies in the AOSR.

1. Introduction

In the Alberta Oil Sands Region (AOSR), there are both natural and anthropogenic air emission sources. The anthropogenic sources include oil sand mining, oil extraction and refining facilities, and transportation sources. Natural sources include forest fires and wind blown dust from soils. Assessing regional scale effects of air pollution sources in the AOSR is difficult due to logistical constraints. Roadway infrastructure and electrical services are lacking outside the mining and processing facilities. As an alternative to direct atmospheric measurements, plant species can be used as surrogates in air quality studies. Lower order (e.g., mosses, lichens) and higher order (e.g., jack pine, aspen) plant species are possibilities for use as biological indicators of air quality over large spatial scales in the AOSR (Addison and Puckett, 1980; Puckett, 1988; Nash, 1995).

Lichens are commonly used in bio-monitoring studies to determine spatial and temporal gradients in air pollution (Conti and Cechetti, 2001; Purvis et al., 2004). Epiphytic lichens obtain most of their nutrients from the atmosphere in the form of wet and dry deposition of aerosols and gases (Nash, 1989). Lichens do not contain waxy cuticles or root systems like vascular plants, and likely exchange materials across their entire surface (Nash, 1996). They can be sensitive to air pollutants, particularly SO_2 and NO_x , and have served as an indicator of adverse environmental conditions on local, regional and global spatial scales (Nash, 1996; Getty et al., 1999; Garty, 2001; Bergamaschi et al., 2002) as well as temporal scales in transplantation experiments (Spiro et al., 2004; Rusu et al., 2006; Ayrault et al., 2007; Bergamaschi et al., 2007). Effects of air pollution on lichen communities (shifts in populations and spatial diversity) and the elemental composition of their tissue can be measured to determine pollutant deposition patterns from emission sources (Nash, 1989; Garty 2000a, 2000b). These spatial features in lichen elemental concentrations offer opportunities to apply receptor modeling in examining the basis for such differences in regard to pollutant emissions and their accumulation in the lichens (see Landis et al., this volume). In ideal cases, mining and processing facilities and their predominant metal emissions provides unique elemental fingerprints for source characterization.

In addition to elemental composition, the distributions of Pb isotopes can be used to determine the relative contribution of sources of air pollution. Pb has four major isotopes, 204, 206, 207, and 208. ^{208}Pb is formed from the radioactive decay of ^{232}Th , ^{207}Pb from ^{235}U , and ^{206}Pb from ^{238}U . ^{204}Pb is referred to as common Pb (has no radioactive parent, and is much less abundant than the other isotopes). The uranium and thorium parents have differing decay rates resulting in predictable changes in Pb isotope ratios (Faure, 1986). The Pb isotope ratios from source materials reflect the age of the Pb incorporated into the parent material (e.g., ore deposit, coal, sediments, oil, oil sands) which is preserved during the subsequent industrial process that emitted the Pb into the environment (Ault et al., 1970; Graney et al., 1995). Following emission from high temperature processes such as smelting, coal combustion, or oil refining, Pb species typically nucleate or condense into atmospheric aerosols very quickly. Pb isotope ratios are not believed to undergo significant fractionation during the industrial processes or subsequent biogeochemical processes resulting in Pb accumulation by the lichens.

In North America Pb isotope ratios from lichens have been used to track metal source, transport, and deposition processes in southern Quebec (Carignan and Gariépy, 1995), and other parts of northeastern North America (Carignan et al., 2002) and western Canada (Simonetti et al., 2003). The results from these studies suggest that in consort with metal concentrations, the use of Pb

isotope ratios from lichens can be used to differentiate between sources of Pb bio-accumulated within the lichens on local, regional, and global scales.

The main goals for this project were to (i) determine the efficacy of using Pb isotopes to assist in identifying the sources of atmospherically deposited air pollutants in the AOSR, and (ii) whether coupling Pb isotopes with elemental concentrations can elucidate the causes for spatial differences in the accumulation of elements in epiphytic lichens in relation to emission sources. An integrated analysis combining Pb isotopes, distance from known sources, and selected element concentrations demonstrates that both goals for this project were met and this technique may be successfully applied in future source attribution studies.

2. Materials and Methods

The sensitivity of lichens to pollutants may be species specific, in part influenced by morphology and other factors (Nieboer et al., 1978). Metal accumulation by lichens can also be species dependent (Garty, 1979; Nash, 1989) in part because of physiological differences in lichen species (Cercasov et al., 2002; Bergamaschi et al., 2007). For purposes of this hybrid source attribution effort, it was decided to focus on analysis of one species of lichens from the AOSR rather than combining results from several species. In the AOSR, *Hypogymnia physodes* was an ideal choice because it is an epiphytic lichen that is commonly used in air quality monitoring due to its widespread distribution and tolerance to SO₂ (Garty, 2001). Previous studies in the AOSR (Berryman et al., 2004, 2010) have shown that *Hypogymnia physodes* exhibited distinct spatial variations in their total sulfur (S) and total nitrogen (N) elemental composition in relation to distance from known emission sources.

The methods used to collect the lichens are described in detail in Berryman et al. (2004, 2010). Briefly, all lichen samples were collected during the summer in 2002 and 2008 from the tips of tree branches. GPS was used to obtain the sample location coordinates and elevation at each collection site. The field personnel that harvested the lichens classified the sample location stand characteristics into ecosite based designations. The ecosite classification that was used followed an edaphic grid of moisture and nutrient regimes suitable for northeast Alberta (Beckingham and Archibald, 1996), supplemented by the addition of fens and bogs (Vitt et al. 1996). Samples from 15 locations and 5 duplicate samples (from a total of 44 samples) from the 2002 collection campaign were selected for inclusion in this study. The 2002 samples were collected on a N-S and E-W grid centered between the two main oil sands processing sites. The 2008 data set included lichens collected from 369 sites using a stratified, nested circular grid approach radiating away from the oil sands processing sites. Samples from 121 sites were selected for elemental and Pb isotope ratio determinations in this effort. This included lichens from sites as far as 200 km from the mining and processing locations. Comparisons of results from 2002 and 2008 will determine if temporal changes are apparent between the data sets. Bulk source and stack samples were also collected and analyzed for source apportionment purposes (see Landis et. al. in this volume for details on the bulk source samples and Chow and Watson in this volume for details on stack samples).

Edgerton et al. (this volume) provides a detailed description of the lichen and source sample digestion and elemental analysis methods. Briefly the elements were extracted from the lichens in an H₂O₂-HNO₃-trace HF mixture using microwave digestion. The concentrations of the elements in the extracts were analyzed using a Perkin Elmer Elan 9000 DRC ICP-MS at ARA

Inc. Aliquots of the lichen and source sample digests that had been used for the multi-element determinations were subsequently measured for stable Pb isotope ratios at the U.S. Environmental Protection Agency National Exposure Research Laboratory (EPA NERL) using a Thermo Scientific (Franklin, MA) Element2 inductively coupled plasma high resolution magnetic sector field mass spectrometer (ICP-SFMS). The method that was developed to measure the Pb isotope ratios included: (i) self-aspiration of sample through a cyclonic spray chamber with an uptake rate of $200 \mu\text{l min}^{-1}$ to maximize signal stability; (ii) optimization of the detector dead time in the scanning speed operation mode (the dead time calculation is used to optimize the accuracy of the Pb isotope ratio measurements); (iii) utilization of low resolution detection mode to produce flat-topped peak shapes; and (iv) use of a narrow mass width window (10% of the peak top-width) scanned at a high sweep rate. The concentration levels determined to minimize detector signal processing inefficiencies was assessed by analysis of National Institute of Standards and Technology Standard Reference Material 981 (NIST SRM 981, Pb Isotope Standard) at varying concentrations levels (from 0.10 ppb – 5 ppb). Optimal isotope ratio results were found when Pb concentrations were lower than 2.0 ppb.

Lichen and source sample digests typically required a five fold or greater dilution to achieve the less than 2 ppb sample concentration needed for Pb isotope ratio determination. A bracketing technique was then used to correct for mass bias during the Pb isotope ratios measurements (Krachler et al., 2004; Yip et al., 2008). This mass bias correction is instrumentation dependent, and is now recognized as a conventional procedure needed during the measurement of Pb isotope ratios to optimize the accuracy of the results (Yip et al., 2008). In this study, correcting for mass bias was achieved by analyzing an aliquot of NIST SRM 981 before and after every lichen or source sample extract. The average of the Pb isotope ratios from the bracketing samples was used to correct the results from the lichen sample for ICP-SFMS mass bias (Krachler et al., 2004). Each of the diluted lichen and source sample extracts was sequentially analyzed four times between the NIST SRM 981 runs. The relative standard error from the four sets of sequential measurements was averaged to determine the relative precision of the isotope ratio measurements. All Pb isotope ratio results using the ICP-SFMS are reported using two sigma relative standard error notation. In this study, it was found that high precision isotope ratios could be obtained on samples with Pb concentrations as low as 0.10 ppb. Using an uptake rate of $200 \mu\text{l min}^{-1}$ and 10 minutes per set of 4 analyses resulted in a sample consumption of 2 ml of sample per Pb isotope ratio determination.

3. Results

3.1 Theory for Using Pb Isotopes to Help Identify Sources

There are several methods to depict results from Pb isotope ratio measurements. Plotting results as $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratios (y-axis) versus $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios (x-axis) often yields either linear arrays or triangular fields of data points (Sondergaard et al., 2010). Individual datum on such plots typically reflects the age of the Pb incorporated into the parent material (e.g., ore, coal, sediments, oil, oil sands) which is preserved during the subsequent process that emitted the Pb into the environment. Results in linear arrays or triangular fields indicate homogenization processes that mix Pb from several sources (Faure, 1986). In Figure 1 the variance in $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios from several of the major ore and coal deposits from North America has been plotted. On $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ plots such as Figure 1, older Pb will be found in the upper right quadrant of the diagram, and younger Pb in the lower left quadrant

due to the differences in the age of the Pb incorporated into the samples of interest. The decrease in $^{207}\text{Pb}/^{206}\text{Pb}$ ratios from old to young Pb reflects the difference in decay rate of the parent ^{235}U and ^{238}U isotopes. The difference in $^{208}\text{Pb}/^{206}\text{Pb}$ can reflect differences in the amount of parent ^{232}Th and ^{238}U . Source materials with higher thorium concentrations generate higher $^{208}\text{Pb}/^{206}\text{Pb}$ ratios. Coupling elemental concentrations on the y-axis versus either distance or Pb isotope ratios on the x-axis can yield additional insights related to the source of the Pb and other elements.

3.2 Comparing Results from 2002 and 2008

The $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios measured in this study (Figure 2a-b) define a field in which mixing from several Pb sources is suggested. The differences in the Pb isotope ratios are significant (based on two sigma relative error as noted in Figure 2a) and several end member compositions and groupings are apparent. The endmembers (samples with the lowest and highest isotope ratios) may represent a fingerprint for specific air emission sources. This possibility will be discussed later. Note that there is a similar range in isotope ratio fields in 2002 and 2008, suggesting sources of Pb incorporated into the lichens have not changed substantially between 2002 and 2008.

When examining the relation between the Pb isotope ratios versus distance from the oil sands processing facilities (Figure 3a and b), the lowest $^{207}\text{Pb}/^{206}\text{Pb}$ (and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios, not shown here) are found closest to the processing sites, and the highest $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios are found in the samples 50 km or more from the processing sites. Based on source sample analysis (to be discussed in detail later), lower $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios found near the processing sites reflect contributions from the Pb in the bitumen from the oil sands superimposed over the Pb sequestered in the matrix of the parent materials. The samples collected beyond 50 km from the processing site cluster into an isotope ratio grouping with a $^{207}\text{Pb}/^{206}\text{Pb}$ ratio near 0.8650 and a $^{208}\text{Pb}/^{206}\text{Pb}$ ratio near 2.095. This grouping could reflect a regional background Pb isotope ratio signature because the matrix in the oil sands deposits (the sand and clay components) is the main component in the soil at the distal sites. However global scale transport processes may also contribute to the Pb isotope signature at the distal sites, this possibility will be explored in the discussion section. The lowering of the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios as one approaches the processing sites indicates other Pb sources (related to the oil sands processing) are influencing the measured Pb isotope ratios. The $r^2 > 0.70$ power law function fits for the isotope ratio versus distance relation suggests source proximity is the major determinant of isotope composition in the AOSR lichens.

Combining Pb concentration in lichens and distance from the oil processing facilities revealed a similar concentration distance relation in 2002 and 2008 (Figure 3 c and d). Of note is the limited difference in Pb concentrations between the proximal and distal sites. The r^2 value for the power law function fits for the Pb concentration versus distance is < 0.30 . This suggests that proximity to sources is not the only factor that influences Pb concentrations in lichens. There seems to be an exponential decrease in Pb concentrations between 0 and 50 km from the oil processing sites (proximal sites), versus greater variability in the concentrations at the more distal sites (greater than 50 km). The spatial distribution could reflect the size and morphology of aerosols that transport Pb to the lichens. The deposition velocity, or the speed at which an aerosol will deposit to lichens, is inversely proportional to the mass median aerodynamic diameter (Landis and Keeler, 2002). Therefore, the observed exponential decreases in element concentrations near mining sources is consistent with the emission of large coarse mode particles during the oil sands

mining process (abrasion followed by suspension). During the processing of the oil sands, the Pb source incorporated into the lichens may be different, and reflect Pb transformation during processing to a volatile phase, with subsequent incorporation into secondary fine mode aerosols. Secondary aerosols smaller size distribution would result in lower deposition velocities and a smaller near field deposition gradient than the larger primary particles. Another possibility is that the variability in the Pb concentrations at the distal sites may also be related to differences in the host vegetation at the sampling sites, which affected how Pb was accumulated by the lichens. To address these possibilities, the relations between other elements and Pb isotope ratios needs to be examined.

3.3 Coupling Pb Isotopes and Metal Concentrations in Lichens

To help explain the significance of the Pb concentration and isotopic data, we need to consider that concentrations of metals in lichens in the AOSR probably reflect source differences, as well as source proximity, and the biogeochemistry of lichens (Addison and Puckett, 1980). Comparing other elements to Pb from a source and process perspective would likely involve assessing differences between (i) elements from geogenic wind-blown dust sources versus (ii) those from oil sands processing versus (iii) those that may reflect the nutrient and metabolic needs of lichens which could be related to ecological variables as well as air quality factors. To assess these possibilities, we examine the spatial distribution of a likely representative element from the geogenic group (Aluminum, Al), the oil sands processing group (Vanadium, V) and an element from the nutrient group (Manganese, Mn) coupled with Pb isotope ratio findings.

An examination of the distance from the source versus concentration results, suggest metals such as Al (and several others) are likely emitted as coarse mode particles near the processing site (Figure 4). This is reflected in an exponential decrease in Al concentration versus distance in 2002 and 2008 (Figure 4a and b) and the resulting $r^2 > 0.75$ for the power law best fits. Al concentration versus Pb isotope ratio plots in 2002 and 2008 (Figure 4c and d) indicate a cluster of samples with high $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios when Al concentrations were low, and a greater range in, and lower $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios, when Al concentrations were enhanced. In 2002 and 2008, Al concentrations and Pb isotope ratios displayed similarities from a distance from source perspective. The larger 2008 data set allowed the Al concentrations versus Pb isotope ratios to better define groups of samples from a distance from source perspective, and confirmed major enhancement of Al concentrations within 20 km from mining sites suggested by the 2002 samples.

Combining V concentration, Pb isotope ratios and distance using the 2008 data set results in groupings of samples (Figure 5a-b) similar to the Al results. The exponential decay in V concentrations away from the processing sites is also expressed by a good fit using a power law regression.

Combining Mn concentration, Pb isotope ratios and distance from the 2008 data set indicate a different type of behavior for this micronutrient than found for the Al and V (Figure 5c-d). Mn concentrations in lichens seem to increase away from the mining and processing sites, and the power law fit for this relation is not as well defined. Unlike Al and V, and Pb; the lowest concentrations of Mn are typically found at locations that are closest to the mining and processing sites. Comparing Mn concentration versus Pb isotopes yields a J shaped pattern,

suggesting that the source of the Pb (and other elements), as reflected in $^{207}\text{Pb}/^{206}\text{Pb}$ ratios, has some relation to Mn accumulation (or lack thereof) by the lichens (Figure 5c-d).

3.4 Contouring Lichen Concentrations to Aid in Spatial Assessments

Another way to express the relation between Pb isotopes and elemental concentration is through use of contoured results of spatial distributions. A graphical contouring program (SURFER v10, Golden Software, Boulder, CO) was used to visualize such spatial relations. In Figure 6a the distribution of the 2008 lichen sample sites is plotted on a UTM E and UTM N grid system. Note the grid ends at the sample collection points to minimize extrapolation during the contouring process. The generation of the concentration contours involved kriging of the concentration data without smoothing the results. An example of the contouring results is presented for Al in Figure 6b. The highest Al concentrations in the lichens are centered over the three main open pit mining operations which are located within the 50 km on a side grid cell square bounded by UTM 450000 – 500000 East and 630000 - 635000 North. As will be discussed in the source apportionment chapter in this volume (Landis et al.), other elements including Fe, La and Ce have a spatial distribution similar to that of the Al, and reflect similarities in sources and subsequent deposition. Elements such as V (as well as Ni, Mo) reveal a pattern that is more homogeneous (uniform) than the geogenic elements (Figure 6c). This type of spatial distribution for V and related elements would be expected from emission of secondary aerosols with subsequent fine particle deposition to the lichens. This spatial distribution of measured concentrations of V related elements in lichens is similar to the modeled pattern for the deposition of S expected from secondary aerosol emissions from the oil processing facilities (see Davies chapter this volume). The lowest $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratios are centered over the mining and processing sites, in consort with the highest Al and V concentrations (Figure 6c and d).

The topography generated by Surfer for the sampling domain (Figure 6f) was based on the GPS measured elevation at all 369 of the lichen sample collection sites. The gently northward dipping topographic relief of the Athabasca River drainage basin is well expressed, as are the higher elevations on the plateau located to the northwest of Ft. McMurray. This regional difference in elevation exerts some control on the resulting element concentrations and Pb isotope ratios in the lichens. The elongation of the low $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios in the north-south direction may directly reflect the topographic expression of the Athabasca River Valley (Figure 6f). And the coupled Pb isotope and V concentration pattern in lichens may reflect near surface enhanced atmospheric deposition processes in the river valley. $^{207}\text{Pb}/^{206}\text{Pb}$ ratios greater than 0.8600 and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios greater than 2.090 dominate outside of the topographic lows, except for an area just southwest of Ft. McMurray which may represent the impacts from traffic along the main roadway corridor.

The concentrations of elements in lichens that may reflect metabolic needs differ from those of the geogenic and oil processing groups (Figure 7). Zn (Figure 7a) is depleted in the lichens near the mining and processing sites. The depletion trend seems to follow the surface topography to some extent, following preferential air flow along the topographic expression of the river valleys (to the north). The baseline value for Zn concentrations is 25 ppm, this may reflect minimum nutrient/metabolic needs of the lichens. Mn depletion in the lichens is greatest near the mining and processing sites, and this inverse concentration trend is more pronounced than the Zn well beyond the visible footprint of the oils sands operations (Figure 7b). The Mn depletion trend also

seems to follow the surface topography, to some extent mirroring the Zn. The baseline value for Mn concentrations seems to be 40 ppm, possibly reflecting minimum nutrient/metabolic needs for the lichens. The highest Mn concentrations occur at the highest topographic elevations (on the plateaus to the northwest of Ft. McMurray). The distribution of the Pb concentrations in the lichens is unlike that of Zn and Mn (Figure 7c). There seems to be high concentrations of Pb near the mining operations as well as the city of Ft. McMurray. In contrast, locations with higher concentrations of K away from the mining and processing sites (Figure 7d) appear to correspond to locations with lower Pb concentrations.

Some of differences in the spatial variation of elements such as Zn, Mn, Pb, and K may be related to differences in the vegetation that host the lichens, which in turn reflect variability in soil moisture and nutrient regimes at the collection sites. Hydrology, canopy, open water and edge fetch, as well as vegetation type are important factors in aerosol capture and deposition dynamics. This study was not designed to directly assess the synergy between these parameters. However, as a first approximation for grouping synergistic effects, we used the ecosite classifications from Berryman et al. (2010) to group the lichens from the 121 sample locations into wet and dry site designations based on soil moisture regime. The dry sites (n=61) were *Jack Pinus* and mixed hardwood dominant, and the wet sites (n=60) included bogs and fens where Black Spruce and Tamarack were common.

To assess whether this soil moisture regime parameter could account for variability observed in Pb concentrations away from the mining and processing facilities, Pb concentrations and isotope ratios versus distance were plotted using the wet versus dry site designation (Figure 8a-b). In addition, results from paired two sample t-tests were computed to aid in this graphical assessment (Table 1). The paired two sample two tests were chosen so a distance variable could be included in the analysis. Only the distal samples, samples located greater than 50 km from the processing sites, were included in the statistical analysis to avoid complexities from near source contributions. The concentrations and Pb isotope ratios from samples at similar distances from the processing sites, but differing soil moisture regimes, could thereby be compared to one another. The $P(T \cdot t)$ for the matched sample distance variable was 0.005 (Table 1), and comparison to this value will be used as the significance determinant for this study. Dry versus wet site was found to have a significant impact on Pb concentrations in lichens away from the mining and processing sources ($P < 0.005$), the lichens from the wet sites contained higher Pb concentrations than the dry sites. However, the variance in Pb isotopes does not seem to be soil moisture regime dependent ($P > 0.005$). To further test this wet-dry dependence hypothesis, a spatial distribution plot for K (Figure 8c) and V (Figure 8d) is provided. Outside of the mining areas, highest K and S concentrations correspond to dry sites ($P < 0.005$ in Table 1), especially where *Jack Pinus* is prevalent. The behavior of V, Mo, and Al was different from that of Pb and K, concentrations for these elements do not seem to be soil moisture regime dependent ($P > 0.005$ in Table 1).

The relation of element concentrations in lichens to soil moisture regime may reflect processes directly associated with the host vegetation including stem flow and canopy density or architecture interactions, in addition to humidity gradients and source proximity. The specific reasons for our wet-dry findings will require further study, of more importance for this work was that ecosite type does not seem to influence the Pb isotope ratios (Figure 8b). It appears that the Pb isotope ratios are a more robust indicator of source impacts than Pb concentrations. This

finding allows us to explore the possibilities of using source samples in conjunction with lichen samples to apportion sources and their impacts on spatial scales.

3.5 Source Samples

Source samples from the oil sands mining and processing operations, including raw oil sand from mining operations and exposures along the Athabasca River, mine haul road materials, coke, fly ash, stack samples, tailings sand, and vehicle emissions were collected from the AOSR (Landis et al., this volume). ARA Inc. provided the extracts from the digested source samples that were diluted at EPA NERL and then measured for Pb isotope ratio determinations using ICP-SFMS. The results from the samples were grouped into several categories for ease of interpretation (Figure 9a). The processed oil sands materials cluster into a group of points with the lowest $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios. The Pb isotope ratios from the stack samples overlap those from the processed oil sands materials. The tailings sand clusters into a group of points with the highest $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios. The raw oil sands have mid-range $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios.

Based on the results displayed in Figure 9a, the isotopic composition of the source materials in the AOSR region includes an end member (source) that is related to the oil processing operations, as well as a tailings sand end member. The raw oil sands would include a mixture of the Pb within the bitumen and additional Pb in the earth materials that compose the matrix of the oil sand reservoir. In simplest terms from a regional context, the background (distal samples) should include Pb from the sand and clay matrix of the oil sand reservoir over which the Pb isotope signature of the bitumen has been superimposed. When the isotope ratio results from the source samples are compared to those from the lichens (Figure 9b), the lichens proximal to the mining and processing sites were found to overlap the raw oil sands isotope ratio field, whereas the more distal lichens overlap the tailings sands fields. None of the lichen samples have an isotopic signature that is dominated by the processed oil sand signature. The end member contributions to the lichen samples can be calculated using mixing equations to approximate the source of the Pb to individual lichen samples. For example if it is assumed that only (i) oil processing and (ii) tailings sand end members contributed Pb to the lichens, at most 50% and as little as 1% (or less) of the Pb in the lichens could come from the oil processing end member (from the Pb in the bitumen). However the two end member solution likely overestimates the oil processing end member contribution, because a third end member, fugitive dust from mining oil sands, is likely also a significant source of Pb. Other forms of source apportionment are needed to better constrain contributions, particularly the importance of fugitive dust emissions from the mining operations. Source apportionment will be the focus in a subsequent chapter (Landis et. al, this volume).

4. Discussion

4.1 Other Studies that Document Emissions of Metals from Point Sources of Pollution in Canada

The emissions of trace metals from point sources in Canada has typically involved characterizing impacts from smelters (Simonetti et al., 2004; Telmer et al., 2004; Gallon et al., 2006; and Aznar et al., 2008) rather than oil sands processing facilities. Telmer et al. (2004) indicated exponential decreases in metal concentrations with distance from the Horne smelter (Rouyn, Quebec) based on results from snow pack sampling. They suggested metals in the snowpack represented

emissions from the smelter (Cu, Pb and others) as well as contributions from background sources and smelter emissions (Sr, Al and others) versus metals from only background sources (K, Rb, Mn, and Cs). Their sampling extended to distances as far as 50 km from the smelter and they suggested that wet and dry deposition occurred within 15 km from the smelter, but wet deposition predominated beyond 15 km from the stack. Gallon et al. (2006) examined variation in Pb isotope ratios in lake sediments to suggest evidence of emissions from the Horne smelter could be found in lake sediment 10, 25 and 150 km from the smelter, but not in lake sediment collected 300 km away from the smelter. Simonetti et al. (2004) used metal concentrations and Pb isotope ratios in conjunction with sampling within plumes from aircraft and on the ground sampling to identify impacts from the Horne smelter. They suggested that the Pb isotope ratios in ground level pollution reflected contributions from the local (smelter) as well as global (Eurasian) sources, but that apportioning contributions from the sources was difficult because the Pb isotope and metal contribution signal from the smelter was not homogeneous.

All of these studies suggested exponential decreases in metal concentrations with distance from point sources of emissions similar to the spatial gradients found in this study by using atmospheric deposition and lake sediment records, rather than the biomonitors used in this study. In contrast, Aznar et al. (2008) is an example of a study that merged deposition patterns from smelter emissions through use of Pb isotope ratios in lichens. Their results indicated contamination declined exponentially with distance from a copper smelter in Quebec but was only detectable at distances 30 km or less from the smelter. Further examples of results from coupling Pb isotopes with lichens as bio-monitors in other types of atmospheric deposition studies are summarized in Section 4.3.

4.2 Controls on Metal Concentrations and Accumulation by Lichens in the AOSR

As documented in Edgerton et al. (this volume), the metal concentrations in *Hypogymnia physodes* from the AOSR are lower than those in lichens from urban areas and locations near smelters (Doucet and Carignan, 2001; Bergamaschi et al., 2007; Spiro et al., 2004). And the concentrations for many metals in *Hypogymnia physodes* from distal collection sites in the AOSR are comparable to those lichens from remote locations such as the Himalayas (Bergamaschi et al., 2002). This suggests that from a metal accumulation standpoint, lichens at distal locations in the AOSR (greater than 50 km from processing and mining sites) do not have elevated concentrations, and concentrations in lichens within 50 km from the major sources in the AOSR are not as elevated as at other industrial and urban sites.

However several caveats when comparing these *Hypogymnia physodes* concentration results to those from other lichen studies should be noted. Although there have been numerous studies in which metal concentrations have been measured in lichens (for example see references from Conti and Cechetti, 2001), how metals are accumulated by epiphytic lichens is a source of ongoing debate. Physiological differences in lichen species may make comparisons between studies difficult, as studies that have compared species have noted (Cercasov et al., 2002; Bergamaschi et al., 2007). To avoid need for interspecies comparisons was a major reason only *Hypogymnia physodes* was chosen for this study. *Hypogymnia physodes* is also known to be tolerant of acidic environments that include high SO₂ concentrations as well as low pH conditions (Hauck 2011) likely present near oil processing facilities.

Some authors suggest metal accumulation in lichens may be element specific reflecting metabolic needs. Chiarenzelli et al. (2001) found that major and micronutrient needs as reflected in Zn, K and Ca concentrations in lichen tissue had relatively consistent values regardless of lichen species. And they suggested that particulate deposition rather than substrate was the likely source for much of the variation in other metals incorporated into the lichen tissue. Others suggest canopy foliage and stem flow contributions would also affect metal deposition rates to lichen surfaces. The metals within these particles on the thalli may be solubilized by acid deposition or organic acids generated by the lichens (Nash, 1989). Solubilized metals can bind to ion exchange sites on cell walls or pass through cell membranes (Nash and Gries, 1995). However, lichens also have methods to concentrate metals on exterior surfaces to avoid passage through the cell membrane. Williamson et al. (2004) observed that lichens sequester Ca in the form of the Ca-oxalate weddellite on *Hypogymnia physodes* surfaces. This metal fixation on external surfaces could be an avoidance mechanism to limit possible toxic effects. In other cases, neutralization of acidic compounds may occur in areas with high aerosol concentrations of carbonate minerals producing products such as gypsum on lichen surfaces (Garty and Garty-Spitz, 2011).

Some authors suggest that the trapping of relatively large particles on the lichen thalli is a main cause of elevated concentrations of metals in lichens (Garty, 1979). Irregularities in surfaces of lichens as well as in the shapes of particles may affect attachment to thalli. Williamson et al. (2004) used SEM-EDX to examine particulate matter on the surfaces of transplanted lichen thalli near a copper smelter in Karabash Russia. They suggested particles < 2.5 micron in diameter were less efficiently captured by *Hypogymnia physodes* than larger particles. This may suggest that coarser particles from abrasion from the mining operations in AOSR would be more effectively captured by *Hypogymnia physodes* in comparison to finer particles generated from the oil processing facilities. Some authors suggest that lichens do not capture and accumulate metals in a manner resulting in increasing concentrations within the lichens. Rather, metal accumulation and removal may reflect equilibrium, steady state processes (Williamson et al., 2004, Spiro et al., 2004) in which metal incorporation and metal loss both take place. The Spiro et al. (2004) study was conducted near smelting operations in Russia, and documented through the use of the Pb isotope ratios, that Pb within transported lichen tissue quickly undergoes exchange processes. Their results indicate that lichens produce a transient record resulting from the accumulation and loss of Pb in lichen tissues. Such steady state processes suggest that lichens may not act as a passive bioaccumulator of pollutants, but continually recycle some of the metals, perhaps as a detoxification mechanism. This recycling process may explain why the Pb concentrations in the lichens from the AOSR are not elevated as might be expected and why Pb isotope ratios rather than concentrations are a more robust method for source attributions. So although metal concentrations in lichens will reflect proximity to metal sources in the form of spatial gradients, they may not quantitatively reflect metal emission and deposition rates. Pb isotopic ratios would therefore be a more robust way to monitor transport and deposition processes, because Pb isotopic ratios would reflect source profiles regardless of concentration gradients affected by metabolic processes.

To our knowledge, the increase in Mn, and possibly Zn, concentrations with distance away from mining and processing operations in the AOSR has not been noted in other studies in urban or industrial areas. Some authors suggest that the Mn (and perhaps Zn) is incorporated into the lichens by leaching from the canopy, after translocation to the canopy through root system

induced processes, rather than from atmospheric deposition (Ceburnis and Steinnes, 2000). This suggests that Mn and Zn accumulation in lichens may be influenced by canopy interactions reflecting ecological variables. Another possibility for near source depletion in Mn concentrations suggested by Hauck (2008) is that *Hypogymnia physodes* is Mn sensitive and may use the production of depsidone physodalic acid to reduce Mn uptake while not inhibiting the uptake of Fe and Zn.

In summary, the physiological processes on and within the lichens that control metal accumulation are complex (Pawlik et al., 2002; Hauck, 2007). And the methods by which particles and gases are dry and wet deposited onto lichens reflect a complex interplay between site factors such as microclimate, nutrient supply, air pollution and forest fires in northern coniferous forests Hauck (2011). These site factors might all affect metal accumulation rates in lichens in the AOSR. In the case of AOSR, the concentrations of elements in *Hypogymnia physodes* are within the range found in numerous studies, and may be on the lower end of the range typical for urban areas (see Edgerton et al., in this volume). Further study is needed to determine the reasons for the spatial gradients in Mn and other elemental concentrations in lichens in the AOSR including (i) characterizing the size and chemical composition of aerosols, specifically the importance of fugitive dust on controlling deposition fluxes (ii) the importance of S species and their interaction with fugitive dust emissions on controlling pH on lichen surfaces, and (iii) the influence of relative humidity gradients between wet and dry ecosites. This moisture gradient may affect dry versus wet deposition and transformation processes, perhaps on an element by element basis.

4.3 Other Work that examined Pb Isotopes in Lichens

Studies in which metal concentrations and Pb isotopes in lichens have been measured for source attribution are listed in Table 2. The studies in Table 2 included both determinations of anthropogenic versus natural impacts, as well as local versus regional source contributions. A summary of findings from studies in Table 2 that are most pertinent to AOSR source attribution issues follow.

The work of Carignan and Gariépy (1995) was probably the first study that tried to use Pb isotope ratios from lichens to constrain impacts from a major point source of emissions, in this case the Noranda Smelter in Quebec. The Noranda smelter often used massive sulfide ore from the Kidd Creek deposit as smelter feed. As noted from Figure 1, Kidd Creek ore has very high $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios, and the lichens collected closest to the Noranda smelter had the highest $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios (Figure 10). A spatial gradient was also apparent in the other samples, with lichens from south Quebec having lower ratios than those from the mid Quebec and Hudson Bay regions. Although the Pb isotopes from lichen samples collected near the smelter did not overlap directly with those of ore deposits from Kidd Creek, the lichens near the smelter contained evidence of smelter air emission impacts from a Pb isotope ratio perspective. This study found that, at least on a regional scale, point source emission impacts can be found in the Pb isotope ratios from lichens. It should be noted that the source signature from this smelter is very different in Pb isotope space from the processed oil sands signature from the AOSR. The Kidd Creek ores have very high $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios in comparison to source materials from the AOSR.

In a follow up 2002 study by Carignan et al., Pb isotope ratios from lichens in eastern North America indicated several source signatures (Figure 11a). Samples from northern Quebec contained high $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ once again suggesting some contributions from the Kidd Creek ore deposits were being released to the atmosphere in the stack emissions from the smelter near Noranda. In contrast samples from the northeast U. S. had the lowest $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios, which could indicate contributions from coal- and oil-fired power plants as well as other anthropogenic sources that contained Pb from ore deposits from Missouri (see Figure 1). Samples from eastern Canada had higher $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios than those from the Northeast U.S. suggesting differences in anthropogenic emissions from Canadian sources. Samples from the St. Lawrence River valley are likely mixtures from Canadian and U.S. sources. The Pb isotope ratios from the AOSR lichens in this study cover the entire range found in the Carignan et al. (2002) study (Figure 11a), although the Pb sources in the AOSR are very different from those in eastern North America. Reasons for these similarities and differences will be explored below.

In a study by Simonetti et al. (2003), Pb isotope ratios from lichens in western North America were collected. The results suggested north – south spatial gradients in Pb isotope ratios were present within the data set. Only the samples from the northern portion of their sampling domain are presented here (Figure 11b), these would be the samples closest to the AOSR and might provide values for background conditions in the AOSR away from the oil sands processing sources. In Figure 11b, the samples from the Northwest (NW) territories and British Columbia exhibited the widest range in Pb isotope ratios, whereas the samples from the Yukon were more restricted in Pb isotope space. Several samples from northern Alberta were included in this study, and the results overlapped with those from the other sample sites. Although the Pb isotope ratios from the Simonetti et al. (2003) study directly overlap with those from the AOSR from this investigation, no cluster of data points that might be used to constrain a regional background value for the AOSR area are apparent. Results from aerosol studies may be needed to provide better insights for defining the regional background in the AOSR.

4.5 Comparing Pb Isotope Ratios in Aerosols to those in Lichens from the AOSR

The results from the global scale Bollhoefer and Rosman aerosol studies (2001, 2002) indicate a wide range of values on Pb isotope ratio plots (Figure 12). Samples of aerosols from Canadian cities tend to have higher $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios than those from cities in the United States. The difference in Pb isotope ratios in aerosols collected in Canada and the U.S. is believed to be due to isotopic differences in Pb ore sources used in industrial processes. If one mixes Pb from predominantly Canadian sources (Kidd Creek ore, Sudbury ore, British Columbia ore, and New Brunswick ore in Figure 1) and compares that Pb isotope signature to predominantly U.S. sources (Idaho ore, Pennsylvania and West Virginia coal, and Missouri ore in Figure 1) one would expect that Canadian cities would have higher $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios in aerosols than those from the U. S. The difference between the Canadian and U.S. aerosols in Pb isotope space was noted in several studies by Sturges and Barie (1987, 1989) and has been used by other investigators to help apportion emissions between U.S. and Canadian sources.

The samples from Mexico City, cities in Japan, and Moscow from the Bollhoefer and Rosman (2002) study tend to have higher $^{208}\text{Pb}/^{206}\text{Pb}$ ratios than sites from Canada and the U.S. (Figure 12). This finding indicates a more thorogenic source of Pb is present in those samples. This

thorogenic Pb signature is now commonly reported in studies of aerosols from China, and indicates global scales differences in U – Th reservoirs. However, if one compares the results from the Bollhoefer and Rosman (2002) versus those of Simonetti et al. (2003), there is little evidence for global scale transport and deposition of thorogenic Pb to northwestern Canada. That is the background Pb isotopic signature in the AOSR seems to be dominated by regional rather than global sources.

Also of note from the Bollhoefer and Rosman (2002) study are the low $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios from Tampa and New York. Oil fired power plants are a major source of electricity in those regions of the U.S. These low isotopic ratios are similar to the processed oil sands values from the AOSR, and suggest that combustion of fuel oil may have an isotopic signature that is distinct from coal deposits and other Pb emission sources as previously suggested by Hurst (2002). With the continuing decrease in Pb concentrations in gasoline across the globe, further study is needed to determine if coal and oil sources have discernible differences in Pb isotopes that might be used in future source apportionment studies to assess impacts from fossil fuel use.

5. Conclusions

The concentrations of elements accumulated by lichens in the AOSR reflected proximity to oil sands mining and processing operations as well as ecosite variability at the lichen collection sites. Spatial analysis indicates three main element groupings including a geogenic source (Al and others) related to oil sands mining, an oil processing source (V and others) and biogeochemical processes (Mn and others) affected element accumulation in lichens.

- An exponential decrease in concentration of the geogenic grouping of metals versus distance from the mining sites was found, whereas near source concentrations of metals characteristic of oil processing have a more homogeneous spatial distribution than the geogenic materials. The mining and oil processing related elements are superimposed over the elemental signature that reflects the nutrient needs of the lichens.
- There is some enhancement in Pb concentrations within lichens at the proximal sites (<50 km from mining and processing operations), but Pb concentration enhancement is limited compared to other elements from the mining and processing groups. Elevated concentrations of Pb at the distal sites reflects ecosite differences, wet sites have higher Pb concentrations than dry sites. The other elements from the mining and processing groups have concentrations that are less influenced by ecosite.

There are major differences in Pb isotope ratios at proximal versus distal locations. The ecosite type does not affect the Pb isotope ratio distribution at either the proximal or distal sites.

- The samples collected beyond 50 km from the mining and processing sites cluster into a Pb isotope ratio grouping with a $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of 0.8650 and a $^{208}\text{Pb}/^{206}\text{Pb}$ ratio near 2.095. This grouping likely reflects the regional background Pb isotope ratio signature. The lowering of the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios near the mining and processing operations indicates other Pb sources, likely related to oil sands mining and processing, are contributing to the Pb source signature.

- The source attribution based on Pb isotope ratios in lichens was confirmed by source and stack sampling. The lowest $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios were from the processed materials and stack samples, which reflect contributions from the Pb in the bitumen component of the raw oil sands. The highest $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios were from the tailings materials, which includes the Pb in the sand and clay matrix from the raw oil sands. The $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios from the lichens collected at the distal sites are similar to those from tailings materials. This result suggests Pb from the sand and clay fraction of the soils at distal locations, is the major contributor to the regional background Pb isotope signature.

The Pb isotope ratios are a more robust indicator of source contributions than the Pb concentrations. The Pb isotope ratios are a better predictor of the extent of the source impacts on the lichens than Pb concentrations because the Pb isotope ratios are not affected by either metabolic processing or ecosite related controls on atmospheric deposition.

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7. References

- Addison, P.A., Puckett, K.J., 1980. Deposition of atmospheric pollutants as measured by lichen content in the Athabasca oil sands area. *Canadian Journal of Botany* 58, 2323-2334.
- Ault, W.A., Senechal, R.G., Erlebach, W.E., 1970. Isotopic composition as a natural tracer of lead in the environment. *Environmental Science and Technology* 4, 305-311.
- Ayrault, S., Clochiatti, R., Carrot, F., Daudin, L., Bennett, J. P. 2007. Factors to consider for trace element deposition biomonitoring surveys with lichen transplants. *Science of the Total Environment* 372, 717-727.
- Aznar, J.C., Richer-Lafleche, M., Cluis, D., 2008. Metal contamination in the lichen *Alectoria sarmentosa* near the copper smelter of Murdochville, Quebec. *Environmental Pollution* 156, 76-81.
- Beckingham, J.D. and J.H. Archibald. 1996. Field Guide to Ecosites of Northern Alberta. Northern Forestry Centre, Forestry Canada. Northwest Region. Edmonton, Alberta.

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.

Bergamaschi, L., Rizzio, E., Giaveri, G., Loppi, S., Gallorini, M., 2007. Comparison between the accumulation capacity of four lichen species transplanted to a urban site. *Environmental Pollution* 148, 468 - 476.

Berryman, S., Geiser, L. & Brenner, G., 2004. Depositional gradients of atmospheric pollutants in the Athabasca Oil Sands region, Alberta, Canada: an analysis of lichen tissue and lichen communities. Lichen Indicator Pilot Program 2002-2003. Final Report Submitted to the Terrestrial Environmental Effects Monitoring (TEEM) Science Sub-committee of the Wood Buffalo Environmental Association (WBEA). Fort McMurray, Alberta, Canada.

Berryman, S., Straker, J. Krupa, S., Davies, M., Ver Hoef, J., 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 Terrestrial Environmental Effects Monitoring (TEEM) Science Sub-committee of the Wood Buffalo Environmental Association (WBEA). Fort McMurray, Alberta, Canada.

Bollhoefer, A., Rosman, K. J. R., 2001. Isotopic source signatures for atmospheric lead: The Northern Hemisphere. *Geochimica et Cosmochimica Acta* 65 (11), 1727–1740.

Bollhoefer, A., Rosman, K.J.R., 2002. The temporal stability in lead isotopic signatures at selected sites in the Southern and Northern Hemispheres. *Geochimica et Cosmochimica Acta* 66 (8), 1375–1386.

Carignan, J., Gariépy, C. 1995. Isotopic composition of epiphytic lichens as a tracer of the sources of atmospheric lead emissions in southern Que'bec, Canada. *Geochimica et Cosmochimica Acta* 59, 4427-4433.

Carignan, J., Simonetti, A., Gariépy, C., 2002. Dispersal of atmospheric lead in northeastern North America as recorded by epiphytic lichens. *Atmospheric Environment* 36, 3759-3766.

Ceburnis, D., Steinnes, E., 2000. Conifer needles as biomonitors of atmospheric heavy metal deposition: comparison with mosses and precipitation, role of the canopy. *Atmospheric Environment* 34, 4265-4271.

Cercasov, V., Pantelica, A., Salagean, M., Caniglia, G., Scarlat, A. 2002. Comparative study of the suitability of three lichen species to trace-element air monitoring. *Environmental Pollution* 119, 129–139.

Chiarenzelli, J., Aspler, L., Dunn, C., Cousens, B., Ozarko, D., Powis, K., 2001. Multi-element and rare earth element composition of lichens, mosses, and vascular plants from the Central Barrenlands, Nunavut, Canada. *Applied Geochemistry* 16, 245-270.

- Cloquet, C., Carignan, J., Libourel, G. 2006. Atmospheric pollutant dispersal around an urban area using trace metal concentrations and Pb isotopic compositions in epiphytic lichens. *Atmospheric Environment* 40, 574–587.
- Cloquet, C., Carignan, J., Libourel, G. 2006. Isotopic composition of Zn and Pb deposition in an urban/periurban area of northeastern France. *Environmental Science and Technology* 40, 6594 – 6600.
- Cloquet, C., De Muynck, D., Sinoret, J., Vanhaecke, F., 2009. Urban/peri-urban aerosol survey by determination of the concentration and isotopic composition of Pb collected by transplanted *Hypogymnia physodes*. *Environmental Science and Technology* 43, 623 - 629.
- Conti, M.E., Cecchetti, G., 2001. Biological monitoring: lichens as bioindicators of air pollution assessment a review. *Environmental Pollution* 114, 471-492.
- Dolgoplova, A., Weiss, D. J., Seltmann, R., Kober, B., Mason, T. F. D., Coles, B., Stanley, C. J. 2006. Use of isotope ratios to assess sources of Pb and Zn dispersed in the environment during mining and ore processing within the Orlovka-Spokoinoe mining site (Russia). *Applied Geochemistry* 21, 563-579.
- Doucet, F. J., Carignan, J. 2001. Atmospheric Pb isotopic composition and trace metal concentration as revealed by epiphytic lichens: an investigation related to two altitudinal sections in eastern France. *Atmospheric Environment* 35, 3681–3690.
- Faure, G., 1986. Principles of isotope geology. New York: John Wiley & Sons.
- Gallon, C., Tessier, A., Gobeil, C., Carignan, R., 2006. Historical perspective of industrial lead emissions to the atmosphere from a Canadian smelter. *Environmental Science and Technology* 40, 741-747.
- Garty, J., Galun, M., Kessel, M., 1979. Localization of heavy metals and other elements accumulated in the lichen thallus. *New Phytologist* 82, 159–168.
- Garty, J., 2000a. Environment and elemental content of lichens. In: Markert, B., Friese, K. (Eds.), *Trace Elements—Their Distribution and Effects in the Environment*. Elsevier Science B.V., Amsterdam, pp. 245–276.
- Garty, J., 2000b. Trace metals, other chemical elements and lichen physiology: research in the nineties. In: Markert, B., Friese, K. (Eds.), *Trace Elements—Their Distribution and Effects in the Environment*. Elsevier Science B.V., Amsterdam, pp. 277–322.
- Garty, J. 2001. Biomonitoring atmospheric heavy metals with lichens: Theory and application. *Critical Reviews in Plant Science* 20 (4), 309–371.
- Garty, J., Garty-Spitz, R.L., 2011. Neutralization and neoformation: Analogous processes in the atmosphere and in lichen thalli - A review. *Environmental and Experimental Botany* 70, 67-79.

- Getty, S. R., Gutzler, D. S., Asmerom, Y., Shearer, C. K., Free, S. J. 1999. Chemical signals of epiphytic lichens in southwestern North America; Natural versus man-made sources for airborne particulates. *Atmospheric Environment* 33, 5095–5104.
- Graney, J. R., Halliday, A. N., Keeler, G. J., Nriagu, J. O., Robbins, J. A., Norton, S. A., 1995. Isotopic record of lead pollution in lake sediments from the northeastern United States. *Geochimica et Cosmochimica Acta* 59, 1715–1728.
- Hauck, M., Huneck, S., 2007. Lichen substances affect metal adsorption in *Hypogymnia physodes*. *Journal of Chemical Ecology* 33, 219–223.
- Hauck, M., 2008. Metal homeostasis in *Hypogymnia physodes* is controlled by lichen substances. *Environmental Pollution* 153, 304–308.
- Hauck M., 2011. Site factors controlling epiphytic lichen abundance in northern coniferous forests. *Flora* 206, 81–90.
- Hurst, R.W., 2002. Lead isotopes as age-sensitive, genetic markers in hydrocarbons: 2. kerogens, crude oils, and unleaded gasoline. *Environmental Geosciences* 9, 1–7.
- Krachler, M., Le Roux, G., Kober, B., Shotyk, W., 2004. Optimising accuracy and precision of lead isotope measurement (^{206}Pb , ^{207}Pb , ^{208}Pb) in acid digests of peat with ICP-SMS using individual mass discrimination correction. *Journal of Analytical Atomic Spectrometry* 19, 354 – 361.
- Landis, M.S., Keeler G.J., 2002. Atmospheric mercury deposition to Lake Michigan during the Lake Michigan mass balance study. *Environ. Sci. Technol.* 36, 4518–4524.
- Monna, F., Aiuppa, A., Varrica, D., Dongarra, G., 1999. Pb isotope composition in lichens and aerosols from eastern Sicily: insights into the regional impact of volcanoes on the environment. *Environmental Science and Technology* 33, 2517–2523.
- Monna, F., Poujol, M., Losno, R., Dominik, J., Annegarn, H., Coetzee, H., 2006. Origin of atmospheric lead in Johannesburg, South Africa. *Atmospheric Environment* 40 (34), 6554–6566.
- Nash III, T.H., 1989. Metal tolerance in lichens. In: Shaw, A.J. (Ed.), *Heavy Metal Tolerance in Plants: Evolutionary Aspect*. CRC Press, Boca Raton, FL, pp. 119–131.
- Nash, T.H., Gries, C., 1995. The use of lichens in atmospheric deposition studies with an emphasis on the Arctic. *Science of the Total Environment* 160, 729–736.
- Nash III., T.H., 1996. Nutrient, elemental accumulation and mineral cycling. In: Nash III., T.H. (Ed.), *Lichen Biology*. Cambridge University Press, Cambridge, pp. 136–153.

Nieboer, E.A., D.H.S. Richardson, and F.D. Tomassini. 1978. Mineral uptake and release by lichens: an overview. *The Bryologist* 81(2): 226-246.

Pawlik-Skowron' ska, B., Sanita di Toppi, L., Favali, M.A., Fossati, F., Pirszel, J., Skowron' ski, T., 2002. Lichens respond to heavy metals by phytochelatin synthesis. *New Phytologist* 156, 95–102.

Puckett, K.J., 1988. Bryophytes and lichens as monitors of metal deposition. In: Nash III, T.H., Wirth, V. (Eds.), *Lichens, Bryophytes and Air Quality*. Cramer, Berlin- Stuttgart, pp. 231–267.

Purvis, O. W., Chimonides, P. J., Jones, G. C., Mikhailova, I. N., Spiro, B., Weiss, D., Williamson, B. J. 2004. Lichen biomonitoring in one of the most polluted areas in the world. *Proceedings of the Royal Society of London* 272, 277–285.

Rusu, A.-M., Jones, G.C., Chimonides, P.D.J., Purvis, O.W., 2006. Biomonitoring using the lichen *Hypogymnia physodes* and bark samples near Zlatna, Romania immediately following closure of a copper ore processing plant. *Environmental Pollution* 143, 81-88.

Simonetti, A., Gariépy, C., Carignan, J., 2003. Tracing sources of atmospheric pollution in western Canada using Pb isotopic composition and heavy metal abundances in epiphytic lichens. *Atmospheric Environment* 37, 2853–2865.

Simonetti, A., Gariépy, C., Banic, C. M., Tanabe, R., Wong, H. K., 2004. Pb isotopic investigation of aircraft-sampled emissions from the Horne smelter (Rouyn, Que'bec): Implications for atmospheric pollution in northeastern North America. *Geochimica et Cosmochimica Acta* 68, 3285-3294.

Sondergaard, J., Asmund, G., Johansen, P., Elberling, B., 2010. Pb isotopes as tracers of mining-related Pb in lichens, seaweed and mussels near a former Pb-Zn mine in West Greenland. *Environmental Pollution* 158, 1319 - 1326.

Spiro, B., Weiss, D. J., Purvis, O. W., Mikhailova, I., Williamson, B. J., Coles, B. J., Udachin, V. 2004. Lead Isotopes in Lichen Transplants around a Cu Smelter in Russia Determined by MC-ICP-MS Reveal Transient Records of Multiple Sources. *Environmental Science and Technology* 38, 6522–6528.

Sturges, W. T.; Barrie, L. A., 1987. Lead 206/207 isotope ratios in the atmosphere of North America as tracers of US and Canadian emissions. *Nature* 329, 144-146.

Sturges, W. T.; Barrie, L. A., 1989. Stable lead isotope ratios in arctic aerosols; evidence for the origin of arctic air pollution. *Atmospheric Environment* 23, 2513-2519.

Telmer, K., Bonham-Carter, G. F., Kliza, D. A., Hall, G.E.M., 2004. The atmospheric transport and deposition of smelter emissions: Evidence from the multi-element geochemistry of snow, Quebec, Canada. *Geochimica et Cosmochimica Acta* 68, 2961-2980.

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.

Williamson, B.J., Mikhailova, I., Purvis, O.W., Udachin, V., 2004. SEM-EDX analysis in the source apportionment of particulate matter on *Hypogymnia physodes* lichen transplants around the Cu smelter and former mining town of Karabash, South Urals, Russia. *Science of the Total Environment* 322, 139–154.

Yip, Y.; Chung-wah Lamb, J.; Tong, W., 2008. Applications of lead isotope ratio measurements. *Trends in Analytical Chemistry* 27, 460-480.

Zschau, T., Getty, S., Gries, C., Ameron, Y., Zambrano, A., Nash III., T.H., 2003. Historical and current atmospheric deposition to the epilithic lichen *xanthoparmelia* in Maricopa county, Arizona. *Environmental Pollution* 125, 21–30.

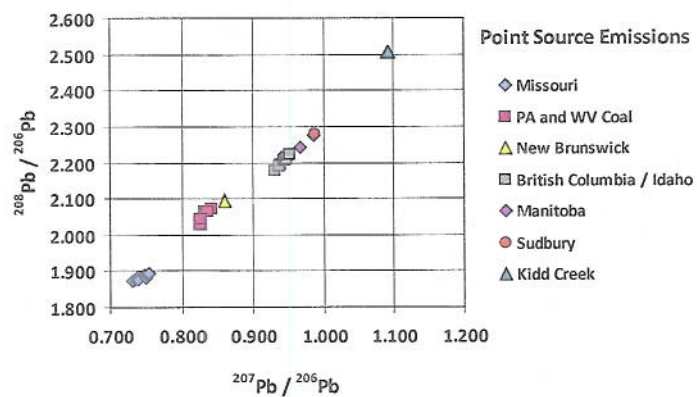


Figure 1. Variance in $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios from several major ore and coal deposits from North America. The sources of data used to construct this plot were compiled in Graney et al. 1995.

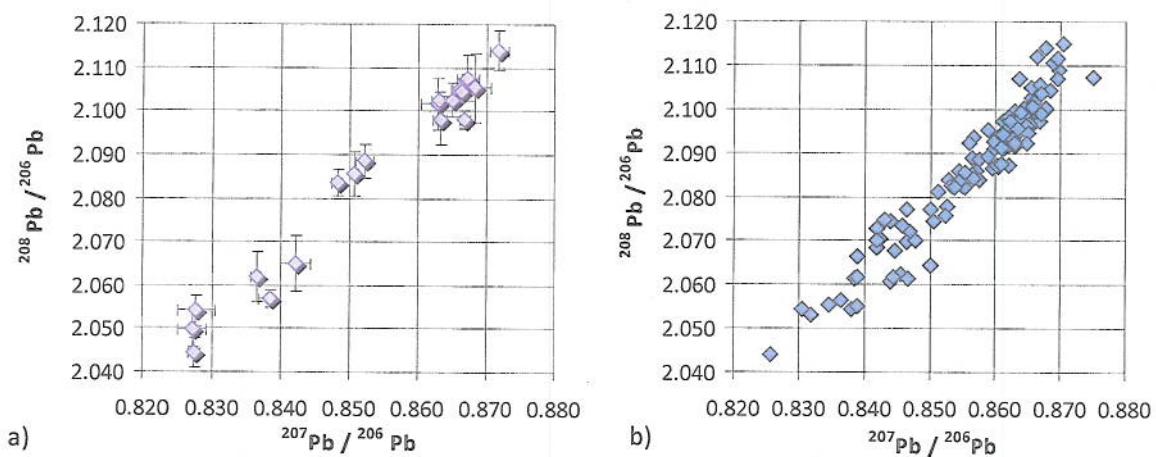


Figure 2. The $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios measured in lichens collected in a) 2002 and b) 2008. 2 sigma error bars are included within a). 2 sigma errors bars not shown in b) for sake of clarity, but are comparable to those displayed in a).

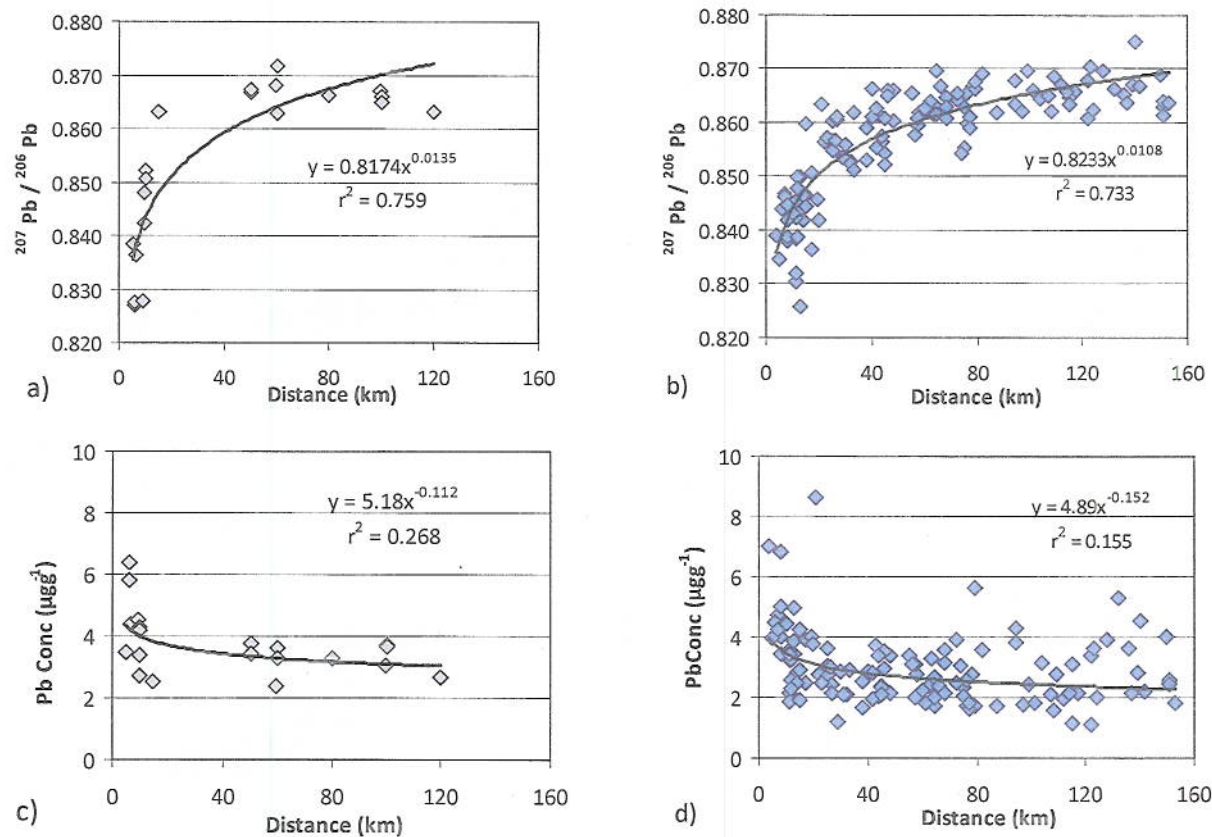


Figure 3. $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios versus distance from the midpoint between the main oil sands processing facilities in a) 2002 and b) 2008; and Pb concentration as a function of distance in c) 2002 and d) 2008. Results from regression analysis using a power law relation displayed on a) - d).

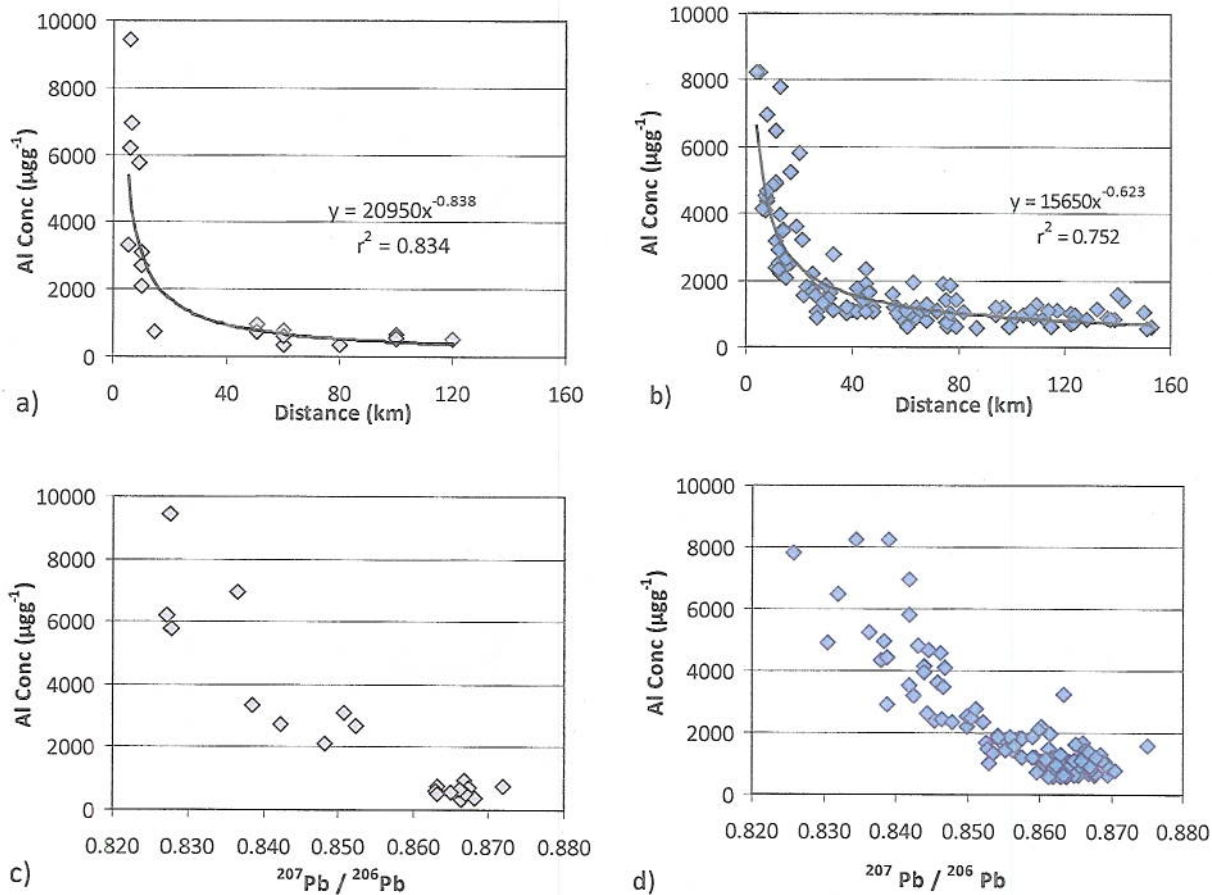


Figure 4. Aluminum (Al) concentrations as a function of distance and from oil sands processing facilities in a) 2002 and b) 2008; and Al concentration versus Pb isotope ratios in c) 2002 and d) 2008. Results from regression analysis using a power law relation displayed on a) and b).

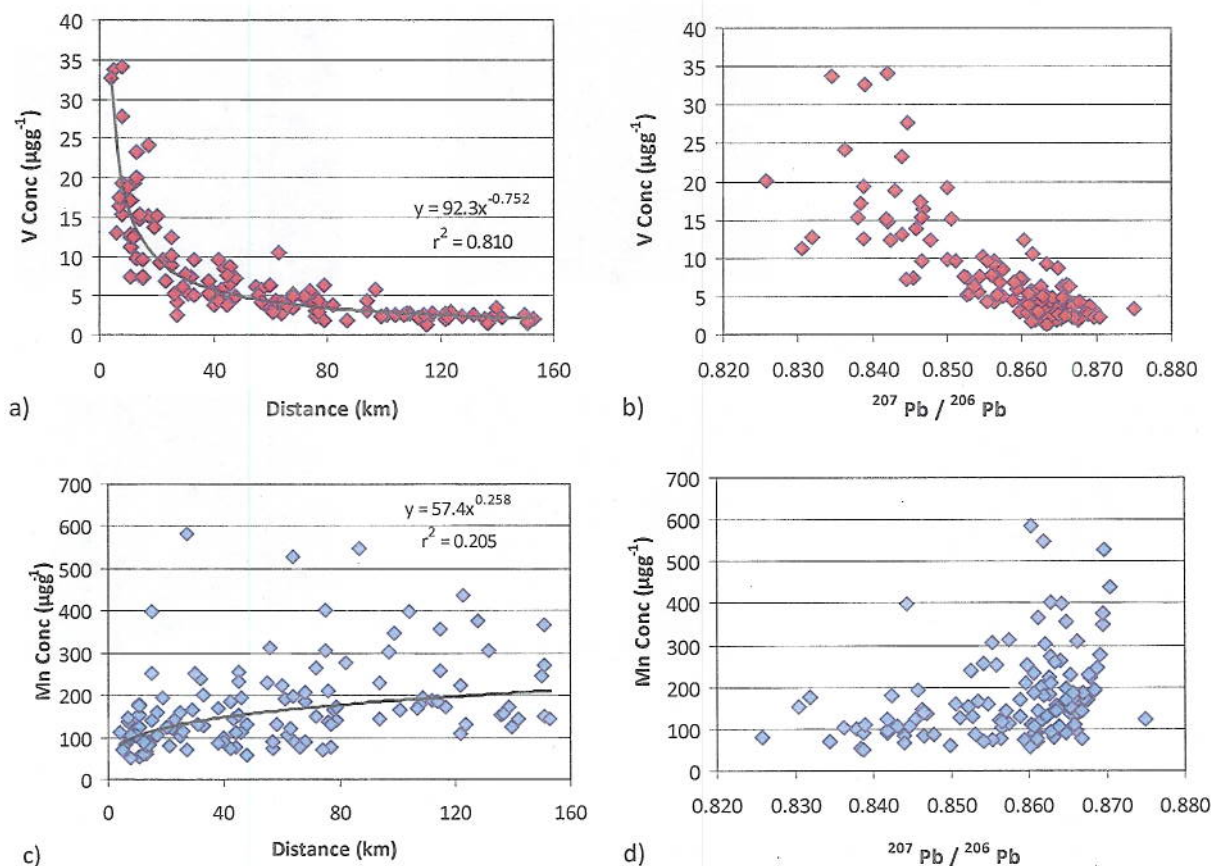
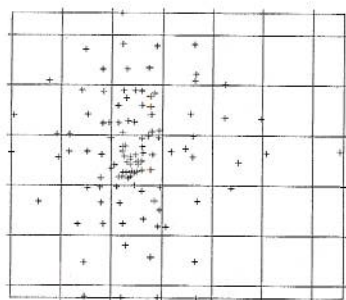
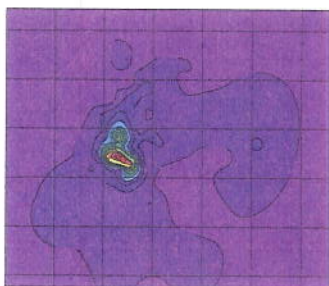


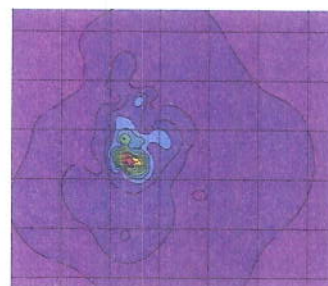
Figure 5. (a) Vanadium (V) concentrations as a function of distance from oil sands production facilities, (b) Vanadium concentration *versus* $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios (c) Manganese concentrations as a function of distance from oil sands production facilities, (d) Manganese (Mn) concentration *versus* $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios. All from the 2008 data set. Results from regression analysis using a power law relation displayed on a) and c).



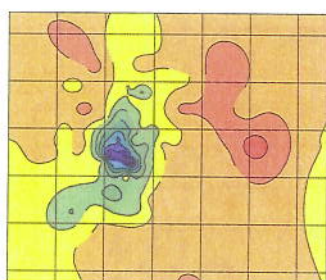
a) Grid overlay for lichen collection sites



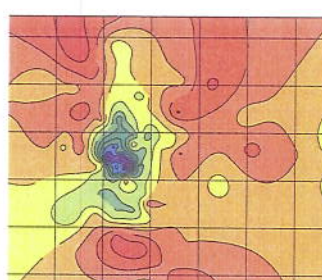
b) Al Concentration



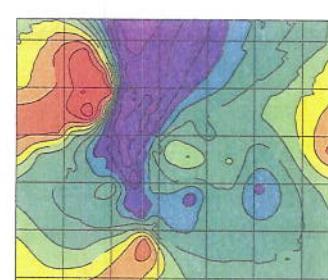
c) V Concentration



d) $^{207}\text{Pb}/^{206}\text{Pb}$ ratios

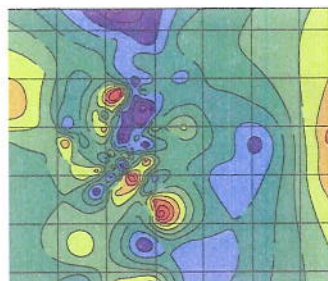


e) $^{208}\text{Pb}/^{206}\text{Pb}$ ratios

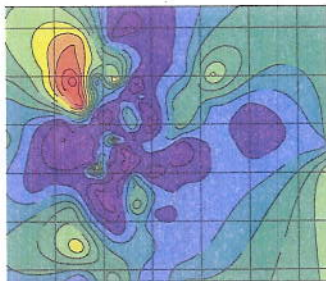


f) Topographic elevation

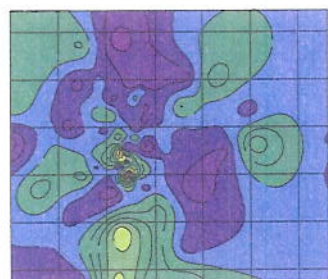
Figure 6. SURFER generated spatial distributions plots from the 121 lichen selection sites from the 2008 dataset. (a) Location of the 121 lichen selection sites on an UTM E and UTM N x-y metric grid. Contoured (b) Al concentrations, (c) V concentrations, (d) $^{207}\text{Pb}/^{206}\text{Pb}$ ratios, (e) $^{208}\text{Pb}/^{206}\text{Pb}$ ratios, and (f) topographic elevation (in meters). Contours grouped and color coded as noted on the bar scales to the right of the figures. All concentrations are in $\mu\text{g g}^{-1}$. Lower concentrations, elevations, and isotope ratios in purple hues, and higher concentrations, elevations, and isotope ratios in redder hues.



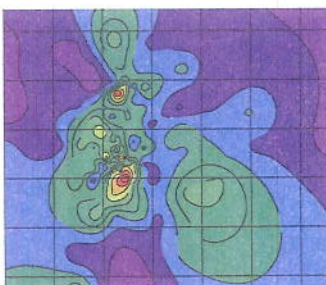
a) Zn Concentration



b) Mn Concentration



c) Pb Concentration



d) K Concentration

Figure 7. Spatial distributions of metal concentrations in lichens collected in 2008 at 121 sampling sites . (a) Zn concentrations, (b) Mn concentrations, (c) Pb concentrations, and (d) K concentrations. See Figure 6 for locations of the sampling sites. All concentrations are in $\mu\text{g g}^{-1}$. Contours grouped and color coded using notation on the bar scales to the right of the figures. Lower concentrations in purple hues, and higher concentrations in redder hues.

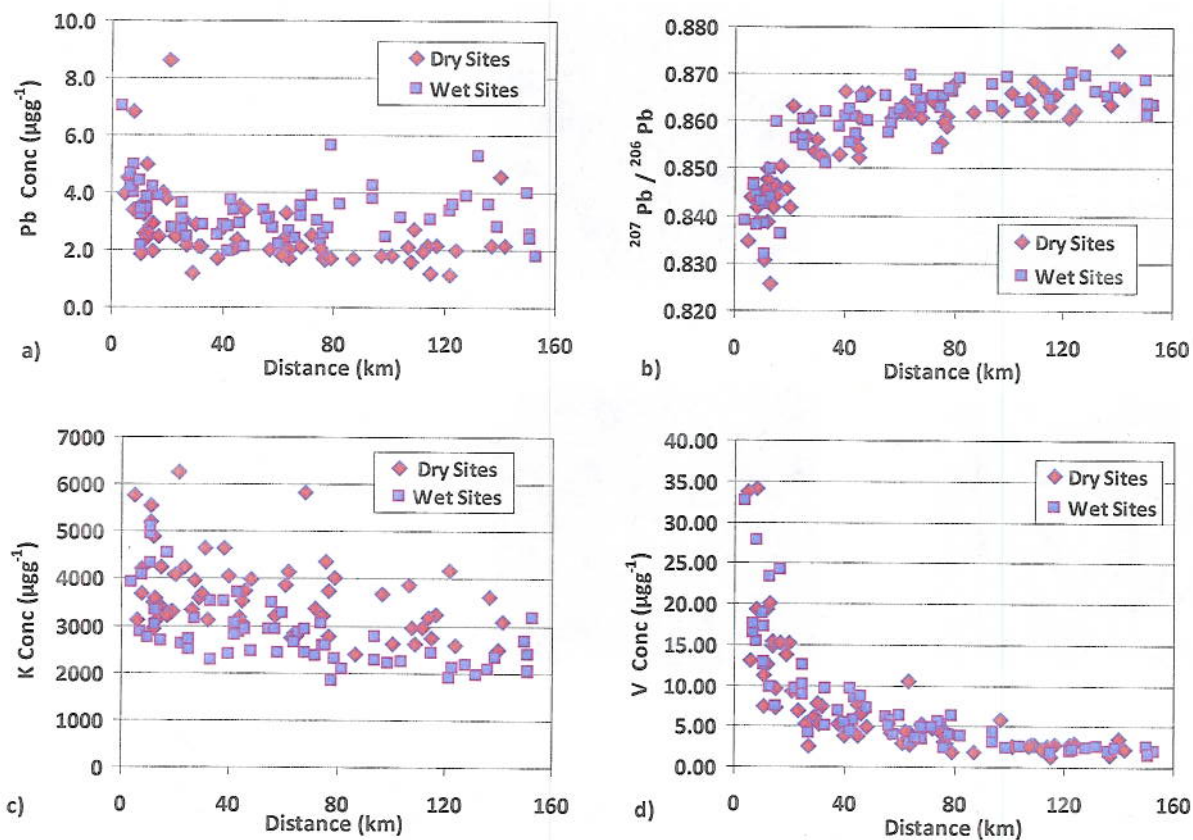


Figure 8. (a) Pb concentration versus distance, (b) $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios versus distance, (c) K concentration versus distance, and (d) V concentration versus distance. Distance refers to the midpoint between the two oil sands processing facilities. Ecosites grouped into wet versus dry sites based on hydrologic characteristics of the soils at the lichen sampling locations.

**Table 1. Results from t-Tests of Paired Two Sample for Means
(from samples > 50 km from processing sites)**

<u>Mean</u>	<u>Dry Sites</u>	<u>Wet Sites</u>	<u>P(T•t) one-tail</u>
Distance (km)	93.82	90.14	0.005
²⁰⁷ Pb/ ²⁰⁶ Pb	0.8636	0.8653	0.022
Aluminum	1068	1004	0.188
Vanadium	3.37	3.72	0.149
Molybdenum	0.130	0.130	0.495
Lead	2.06	3.34	1.48 ^{E-06}
Zinc	47.38	56.59	0.004
Potassium	3316	2493	5.96 ^{E-07}
Sulfur	752	520	6.26 ^{E-07}

Distance is in km, element concentrations in microgram/gram
Dry and Wet Sites refer to Ecosite grouping (see text for explanation)

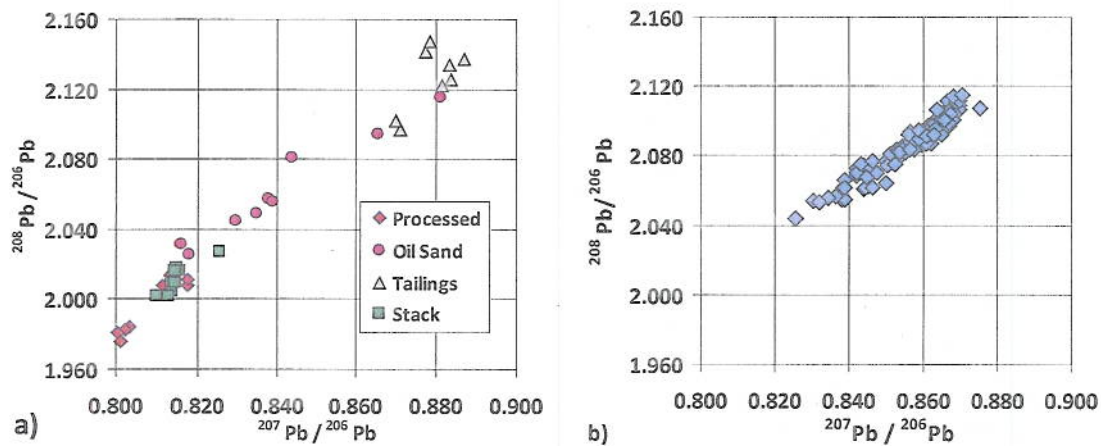


Figure 9. The $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios measured in a) source and stack samples, and b) 2008 lichen samples. The similarities in types of source samples have been grouped by color codes.

Table 2. Synopsis of Previous Studies that used Pb Isotopes in Lichens to aid in Source Attribution

<u>Authors</u>	<u>Date</u>	<u>Location</u>	<u>Study Goals</u>
Carignan and Gariépy	1995	Quebec, Canada	determining impacts near Noranda smelter
Carignan et al.	2002	eastern Canada	follow up from 1995 smelter study, potential for determining Canadian versus United States source contributions
Cloquet et al.	2006a	France	distinguishing between urban anthropogenic sources
Cloquet et al.	2006b	France	used Zn and Pb isotopes, follow up from 2006a study
Cloquet et al.	2009	France	follow up from 2006 studies, included lichen transplants
Dolgoplova et al.	2006	Russia	used Zn and Pb isotopes to assess impacts near mining operations
Monna et al.	1999	Sicily	impact of natural emissions from volcanoes
Monna et al.	2006	South Africa	distinguishing between urban anthropogenic sources
Simonetti et al.	2003	western Canada	latitudinal transects, potential for determining Arctic influences, and Canadian versus United States source contributions
Spiro et al.	2004	Russia	determine smelter impacts on transplanted lichens

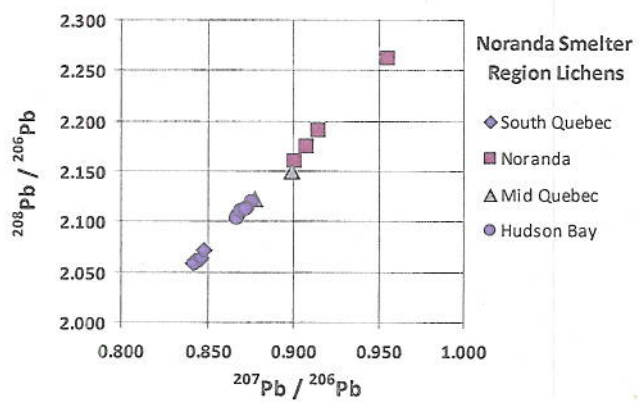


Figure 10. Pb isotope ratios from lichens collected in the Province of Quebec near the Noranda smelter as reported in Carignan and Gariépy (1995).

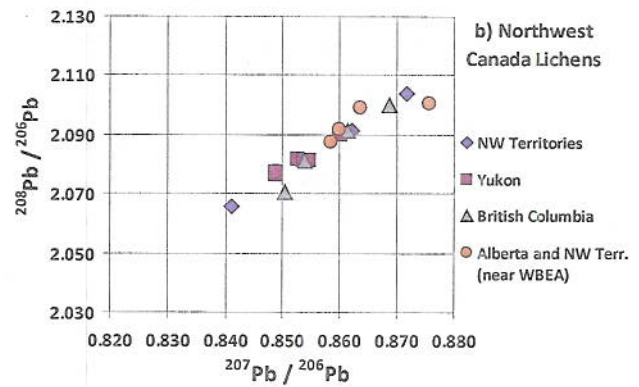
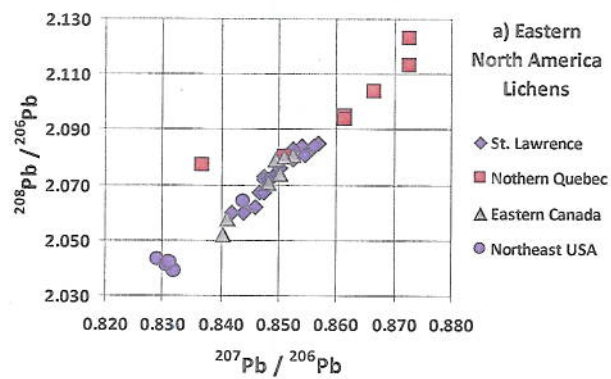


Figure 11. Pb isotope ratios from lichens collected in a) eastern North America as reported in Carignan et al. (2002) and b) northwestern Canada as reported in Simonetti et al. (2003).

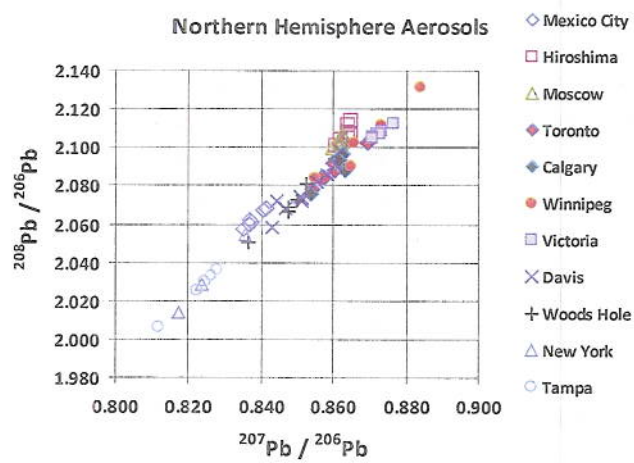


Figure 12. Pb isotope ratios from aerosols collected from several cities in Russia, Japan, Mexico, Canada and the United States as reported in Bollhoefer and Rosman (2002).