USING LICHENS AS BIOINDICATORS OF AIR POLLUTION DEPOSITION NEAR REMOTE MINING OPERATIONS

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ABSTRACT

Lichens are non-vascular plants that serve as excellent bioindicators of air pollutant deposition, as they absorb nutrients directly from the atmosphere, while also readily accumulating atmospheric contaminants. We present two studies where lichens were used as bioindicators near remote mining operations. First, a new research program was implemented in 2008 to map the characteristics of air pollutant deposition using epiphytic lichens as bioindicators in the Athabasca Oil Sands region of northeastern Alberta, Canada. Lichen elemental content will inform patterns of nitrogen and sulphur deposition in the region and a sub-set of lichen samples will be analyzed for trace metals to identify specific pollutant sources that contribute to elemental enrichment in lichen. Second, terrestrial lichens were used to evaluate off-site airborne transport of metals from the Anvil Range open-pit lead-zinc mine in south-central Yukon, Canada. This study indicated elevated lead and zinc concentrations in lichens to 20⁺ km from the mine site and included components to characterize timing and sources of dust transport. Results from these studies can be used to develop spatial predictive models of deposition patterns within the study area which provide an understanding of environmental impacts from mining operations and can improve mitigation of these impacts.

KEYWORDS: oil sands, metals, nitrogen, sulphur, air quality, fugitive dust

INTRODUCTION

Air emissions and fugitive dust (pollutants) resulting from mining and mine-related activities and the potential effects of these pollutants on surrounding ecosystems are of increasing scientific and environmental interest. However, in many contexts, characterization of off-site deposition of pollutant compounds can be extremely difficult. Specific challenges are posed by the lack of technology capable of characterizing air quality across a large landscape, due to high costs associated with deploying and regular maintenance of air monitoring equipment and to the alternating current power that many of these technologies require. Because of these limitations it is logistically difficult and often prohibitively expensive to implement air-quality sampling (passive or continuous) throughout a large remote area at a spatial density that is sufficient to reliably characterize patterns and levels of atmospheric deposition.

One option to address the limitations noted above is to characterize (and potentially monitor) pollutant deposition using biological receptors (e.g., vegetation tissues). This approach presents a cost-effective method to characterize spatial patterns of pollutant deposition across a large study area, and can be used

either in isolation or in conjunction with direct passive or active air-quality measurements. Lichens are biological receptors with specific characteristics that lend themselves to reliable use in air pollution assessment and monitoring programs. Spatial patterns of atmospheric pollutant deposition, including fugitive dust escapement from mining and milling operations and atmospheric emissions from processing and mine fleet operations, can be determined from elemental content in lichens collected near these remote industrial sources.

This paper presents two studies in which lichens were used as bioindicators of air pollution near remote mining operations, as follows:

- 1. Athabasca Oil Sands Study A new research program was implemented in 2008 to map the characteristics of air pollutant deposition using epiphytic lichens as bioindicators in the Athabasca Oil Sands region of northeastern Alberta, Canada.
- 2. Anvil Range Study Terrestrial lichens were used to evaluate off-site airborne transport of metals from the Anvil Range open-pit lead-zinc mine in south-central Yukon, Canada.

These studies demonstrate the utility of using lichens as biomonitors of pollutant deposition and the diversity of objectives that can be addressed using this approach. For each study, methods differ slightly to meet the specific study objectives.

Utility of lichens as bioindicators

Lichens are excellent bioindicators of air pollution because they are very sensitive to dry and wet deposition of airborne pollutants (including nitrogen- and sulphur-based compounds, Farmer et al. 1992; Nash and Gries 2002) and thus serve as an early warning signal for potential air pollution damage to higher plants (Gries 1996). There are two primary characteristics of lichens that make them particularly useful to characterize atmospheric deposition:

- Unlike vascular plants, lichens lack a cuticle or specialized guard cells to control the exchange of water, nutrients, gases, and particles with the external environment. This is an adaptive mechanism that allows lichens to obtain sufficient nutrients from precipitation and other atmospheric sources. However, this physiology also prevents lichens from mediating their uptake of atmospheric pollutants. Consequently, elemental content in lichen reflects atmospheric sources of nutrients and contaminants.
- 2. Lichens lack a vascular system and roots and are therefore not influenced by elements in soils. This lack of interaction with the soil environment removes one of the confounding factors present when using vascular plants as biomonitors for air pollution. This characteristic of lichens is particularly important when studying ecosystems in which there is the potential for both natural soil-borne elemental enrichment and anthropogenic airborne enrichment; for example, this is the typical case around metal mining operations.

The above characteristics make lichens not only useful bioindicators, but also very sensitive to changes in air quality. Lichens typically are one of the most sensitive ecosystem components, and thus can serve as "early-warning" indicators in air quality and environmental effects monitoring programs.

Accumulation of elements in lichens occurs by particulate trapping, active uptake of anions, passive absorption of cations, and ion exchange (Nieboer et al. 1978). Lichens are subject to continual wetting

and drying cycles (sometimes daily or weekly, depending on rain and fog events). When lichens are wet, nutrients and contaminants deposited on the lichen surface are absorbed and are later concentrated in the lichens when dry (Nieboer et al. 1978). However, particulate trapping can occur when the lichen is either wet or dry. During periods of rain, the nutrients and contaminants stored in the lichen are slowly leached. The residence of elements in lichen is different for macronutrients and for metals. Macronutrients (i.e., nitrogen, sulphur, potassium, magnesium, calcium) are relatively mobile and their concentrations in lichen can change seasonally (Boonpragob et al. 1989). Whereas, trace metals (e.g., cadmium, lead, zinc) accumulate in lichen over time and are less mobile than macronutrients. Trace metals are slowly released from the lichen with time (Garty 2001) and metal concentrations in lichen tend to decrease with improved air quality.

Lichen elemental content has been used in many studies to map pollutant deposition or to characterize pollution gradients in relation to sources (some examples include: Addison and Puckett 1980; Bargagli and Mikhailova 2002; Bruteig 1993; Gartner Lee et al. 2006; Gombert et al. 2003; Sloof and Wolterbeek 1991; Zakshek et al. 1986). Lichens can be used to document spatial and temporal changes in air pollution because they are widespread and are long-lived perennial organisms (Nimis et al. 2002). Effects of air pollution on lichen chemistry and on lichen communities can be monitored to determine depositional patterns from sources. Such studies can use lichens to map pollutant deposition or describe pollution gradients in relation to sources (some examples of such studies include: Bargagli et al. 1987; Branquinho et al. 1999; Diamantopoulos et al. 1992; Gailey et al. 1985; Pfeiffer and Barclay-Estrup 1992; Vestergaard et al. 1986).

Approaches for Using Lichens as Bioindicators

Lichens can be collected to determine the average elemental content for a given population, which can provide an understanding of spatial patterns of atmospheric deposition in the study area (Figure 1, conceptual model). While analyses of lichen chemistry (elemental concentrations) do not provide a measurement of total deposition at a site (due to the leaching/flux discussed above), they do serve as a useful tool for informing relative patterns of deposition. Regular monitoring of elements in lichen can capture increases or decreases of pollutants in lichens over time, which reflects overall patterns of atmospheric deposition. By relating elemental content in lichens to modeled atmospheric deposition values estimated through other methods (e.g., passive air-quality monitoring), a relationship between the various approaches for understanding deposition patterns can be developed. Additionally, elemental content in lichen can be compared to other measures of pollution effects at a study site, such as physiological responses of lichens or vascular plants, or changes in lichen community composition. For studies that involve long-term monitoring with repeated site visits, and/or in conditions where lichens are low in abundance (urban areas, heavily polluted sites, etc.), lichen transplants can be used to assess air pollution deposition and impacts on lichen growth and vitality.

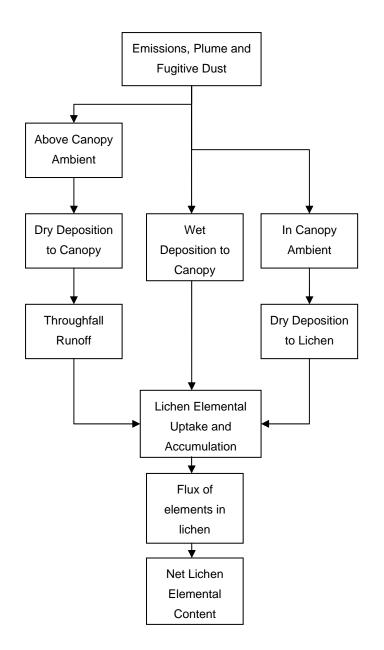


Figure 1. Conceptual model showing pathways from pollutant sources to deposition to elemental accumulation in lichen.

Regular monitoring of lichen communities (i.e., community surveys of species presence and abundance) can be used to assess changes in lichen community health as indicated by shifts in lichen species composition and relative species abundance. Some lichen species are more tolerant to air pollutants than others. For example, in polluted sites, most lichen species sensitive to air pollution are either absent or in decline and overall lichen diversity is low. This effect can be caused by different mechanisms, for example SO₂ can have direct inhibitory (toxic) effects to lichens, reducing overall lichen abundance and species richness in a community (Nash and Gries 2002). Other pollutants such as nitrogen may actually stimulate colonization and growth of some nitrophilic lichen species, altering lichen species diversity and community composition through alteration of inter-specific competitive relationships. As noted above,

because of the sensitivity of lichens to changing air-quality conditions, monitoring shifts in species abundance and diversity in lichen communities can serve as an early-warning indicator of adverse ecological effects of air pollution, however this approach is not implemented in the two studies presented here.

Sample Design and Implementation

Sample locations are established to provide elemental lichen content for sites located across the perceived deposition gradient for the pollutants of interest (e.g., sample sites along a distance/direction gradient(s) from the key sources). Along this deposition gradient, sample sites may be randomly located, or may be located following a modified grid or transect approach. Sampling intensity is typically greater near the main pollution sources, as both deposition and variation in deposition is typically greatest closer to sources. Both epiphytic and/or terrestrial (ground-dwelling) lichens may be targeted for sampling and elemental analysis (see Table 1). Epiphytic lichens represent the best indicator of atmospheric pollutants for forested ecosystems as they have greater exposure to pollutants than terrestrial species that are protected under the forest canopy. Terrestrial lichens are excellent indicators in non-forested areas, although there is greater potential for elemental leaching due to exposure to standing water or surface run-off. However, terrestrial lichens tend to grow in mats allowing for quick field collection of large samples, whereas collection of epiphytic lichens requires more time.

Target lichen species are selected based on two criteria:

- 1. Species are ubiquitous and abundant across the study area. This maximizes the probability that sufficient sample material can be collected for laboratory analyses; and,
- 2. Species are moderately tolerant to pollutants. This is necessary to ensure that species targeted for collection will be present at near-source higher-deposition sites, as well as at sites farther from the source(s).

By collecting a composite sample of many lichen individuals from multiple locations, a range of ages are captured, providing a more accurate representation of the overall lichen population within a site.

Table 1. Lichen species collected for elemental analysis in the Athabasca Oil Sands and Anvil Range studies.

Study	Lichen Species	Growth Form	Habit	Pollution Tolerance
Athabasca Oil Sands	Hypogymnia physodes	Foliose	Epiphytic	Tolerant
Study	Evernia mesomorpha	Fruticose	Epiphytic	Intermediate to tolerant
Anvil Range Study	Cladina mitis	Fruticose	Ground	Sensitive
			Dwelling	

Field sampling and lichen cleaning protocol all follow L. Geiser's methods for the U.S. Forest Service Air Quality Monitoring Program in the Pacific Northwest (Geiser 2004). The mass of lichen (dry weight) collected in the field is determined based on the type of laboratory elemental analyses that will be conducted.

Laboratory Analysis

Elemental analyses of lichen samples are dependent on study-specific objectives. For example, the Athabasca Oil Sands study is focused primarily on total nitrogen and sulphur content in lichens, as these compounds:

- 1. are emitted in substantial quantities from oil sands operations (upgrading or other extraction processes and large diesel equipment fleets) and other combustion sources in the region; and,
- 2. have potential roles in ecosystem health through soil acidification and nutrient fertilization, imbalances and eutrophication.

In addition to nitrogen and sulphur analyses in the Athabasca Oil Sands study, a sub-set of the lichen samples will be analyzed for a suite of trace elements using sensitive techniques such as inductively coupled mass spectrometry (ICP-MS) to recover elements from the lichen samples. The purpose of this analysis is to allow inferential determination of emission source types contributing to nitrogen and sulphur deposition at sample sites.

In contrast, the primary focus of the Anvil Range study was on metals associated with the mined ore body, particularly lead and zinc. In this case, the major fugitive dust sources were assumed to be the crusher/surge pile/mill complex/concentrate load-out and the tailings impoundment. Although nitrogen and sulphur were present in mine vehicle emissions, the remote and isolated location and the relatively low combustion emissions from this operation made these compounds of less interest than the metals associated with the mining operation. In the Anvil Range study, lichen (and soil) samples were analyzed using ICP-MS where the suite of analyzed elements included, but was not restricted to aluminum, antimony, arsenic, bromine, cadmium, caesium, chromium, sodium, cobalt, iron, lanthanum, lead, magnesium, manganese, mercury, nickel, scandium, selenium, thorium, tungsten, vanadium, and zinc.

ATHABASCA OIL SANDS STUDY

Rapid industrial development in the Athabasca Oil Sands (AOS) region of northeastern Alberta has resulted in increased emissions of acid-forming compounds, such as sulphur dioxide (SO₂) and nitrogen oxides (NO_x), and airborne particulates containing trace metals (Pauls et al. 1996). Extended periods of enhanced deposition of these pollutants and their products can alter ecosystems both directly and through soil and surface-water acidification or eutrophication. There is a recognized lack of empirical data for historical and current pollutant deposition fields, and this lack of information represents a critical gap in AOS regional air-quality and ecological monitoring and modeling programs. Thus at present we are unable to confirm predicted deposition patterns at the regional scale, which would help to establish a more reliable link between air pollutant emissions and their possible effects on ecosystems. Lichens are a cost-effective indicator for collecting reliable, high-density information across the AOS region and help to overcome challenges associated with limited access and the extensive range and intensity of deposition

within this region. For these reasons, a region-wide lichen bioindicator project was initiated in 2007 and implemented in 2008.

Objectives

The AOS lichen bioindicator project was designed to accomplish two main objectives:

- 1. Map spatial patterns of total sulphur and nitrogen concentrations in two epiphytic lichen species to document patterns and extent of relative air pollution deposition for the AOS region.
- 2. Identify and apportion the sources of pollution/enrichment in lichens at the study sites (i.e., lichen receptor modeling and source apportionment).

Maps of nitrogen and sulphur concentrations in lichens will provide information on relative patterns of pollutant deposition across the study area, while source apportionment will allow us to link these findings directly to emissions sources or source types in the region. These results can then be compared to predictions from plume transport-dispersion modeling, and thus can be used to refine future in-depth air quality or effects-related studies. Furthermore, results from this study will inform future regional monitoring programs focused on assessing the cumulative effects of air pollutants to selected sensitive ecosystems in the region.

Study Design

Epiphytic lichen samples were collected from 359 forested sites in a study area centred on the major oil sands mining operations and extending out in a 150-km radius from this centre-point. This study area covers the perceived deposition gradient for the pollutants of interest (e.g., sampling sites along distance/direction gradient(s) from the key sources) and is approximately 7,068,600 ha in area (roughly 70,000 km², or over 10% of the land area of the province of Alberta). Sampling layout was based on a modified grid established in radial strata, such that sampling frequency was greatest near the main sources (Suncor Energy Inc. and Syncrude Canada Ltd. operations). A sub-set of the lichen sample locations were integrated with locations of established air-quality monitoring equipment (including conventional passive samplers, continuous monitors and ion-exchange resin columns) to develop cross-correlations between lichen concentrations of nitrogen and sulphur and air-quality measurements of nitrogen and sulphur-based compounds. Sampling of lichen epiphytes was restricted to specific forested vegetation community types within a similar age-class to control for variability that may be associated with various forest communities. At all study sites, samples of both epiphytic lichen species (Table 1) were collected where possible, with duplicate samples collected at a sub-set of sites to assist in laboratory quality assurance and control.

Project Status

Field sampling of lichens was completed in August-September 2008. Over 800 lichen samples were collected, cleaned, and further processed (drying, grinding) and nitrogen and sulphur analyses are in progress at the University of Minnesota Research Analytical Laboratory. The sub-set of samples that will be used for additional trace elemental analysis will be selected following a review of the completed nitrogen and sulphur dataset. Once results from lab analyses are received, statistical analyses and geo-

spatial modeling will be conducted to predict/interpolate deposition patterns of nitrogen and sulphur across the study area and to identify factors influencing these patterns. Following analysis of trace elements in the lichens, source apportionment analysis will identify and quantify specific source types contributing to pollutant-loading in lichens, such as bitumen upgrader stacks, diesel fleets, tailings impoundments, in-situ extraction operations, light vehicle traffic, and potential biogenic sources such as wildfire.

ANVIL RANGE STUDY

The Anvil Range Mine Complex is located approximately 200 km north-northeast of Whitehorse, Yukon, and contains open pit lead-zinc mines operating from approximately 1968 to 1998. Results from a pilot study in 2002 indicated elevated concentrations of elements attributed to airborne contamination originating from the mine complex site. In response to these findings, a multi-year integrated terrestrial effects study was established. This study included sampling and analysis of lichen, soils and moss transplants to test for evidence of cumulative and/or ongoing deposition related to the activities of the Anvil Range Mine and to determine the relative spatial patterns of this deposition. As with the AOS study, lichens were chosen as a key component of the biomonitoring program due to the remote nature of the site and to the lack of availability of other air-quality or deposition information for the study area.

Objectives

The study conducted at Anvil Range was a multi-year sequential study conducted during 2002-2005. The integrated objectives of this study were to:

- 1. determine whether off-site deposition of mine-related elements had occurred, and if so, characterize the spatial distribution of deposition; and,
- 2. determine whether airborne deposition is ongoing or historic.

Study Design

Terrestrial lichen samples were collected from over 300 sites surrounding the Anvil Range mine complex, where sites were located directly adjacent to mine facilities and out to a maximum distance of approximately 50 km from the mine site. Sample layout in the first year of study was based on eight transects radiating out from the mine facilities at cardinal and ordinal directions. Sample site selection in subsequent years was based on spatial data gaps identified through geostatistical analysis (Kriging) of results from previous sampling years (2002 and 2004). Due to substantial topographic constraints in the Anvil Range area, sampling was not grid-based as in the AOS study, but was based on a semi-regular selection of sample points on a topographic map of the study area (made prior to field visit). Similar to the AOS study, sampling intensity was greatest near to the mine facilities and decreased with increasing distance from the mine complex.

A particular challenge of the Anvil Range study was the presence of soil materials naturally enriched in the elements of interest (lead and zinc) and thus the possibility that natural mineralization of surficial geologic materials was a potential source contributing to elemental levels in lichens. This challenge was addressed by careful selection of a reference site that was located far from the mine complex where fugitive dust deposition was not expected, but that was located in an area of known mineralization in order to simulate pre-disturbance conditions at the Anvil Range mine site. The use of lichens in this study was important as there is no mineral uptake from the soil by these non-vascular plants (as described above); therefore all elements present in the lichen were from dust sources, either natural or anthropogenic. Lichen sampling intensity at the reference site was high, similar to that used in the study areas located near the mine complex. Soil sampling and analysis was also conducted at a sub-set of sampling locations at the reference site, to provide information on metal concentrations in soils. Soil samples were collected from the surface organic horizons (theoretically representative of the same deposition conditions affecting lichens), from subsurface organic horizons (pre-dating the mine development and thus reflective of pre-mining deposition conditions), and from subsurface mineral horizons (reflecting natural mineralization unaffected by anthropogenic deposition).

Lichen elemental data were pooled to create an integrated data set, consisting of results from a total of 309 samples obtained over three years. Lichen analytical results were statistically screened to identify non-random patterns (clustering) in the distribution of elemental concentrations. Kriging was then used to interpolate between data points to create a map of spatial patterns of lichen element concentration across the study area. Soils data were also examined to determine the potential contribution of natural mineralized soil materials to elemental enrichment in lichens.

The geostatistical analysis and mapping of elemental concentrations was used to determine the spatial extent and distribution of elevated element concentrations in lichen attributable to airborne deposition of elements from the Anvil Range Mine Complex. Lead was selected as the primary indicator of mining effects in interpretation of lichen results, as initial results in this study showed that elevated lead in lichen extended farthest from the mine complex and that the mine was the leading source of lead enrichment in lichens. Additionally, lead was an effective and stable primary indicator of mining effects because it has relatively low mobility in the environment.

Results

The results of the Anvil Range Mine study clearly indicated that the presence of the mine has resulted in elevated concentrations of several elements in the environment surrounding the mine complex. For example, lead concentrations in lichens near the mine were up to 450 times those concentration of lichens collected at the reference site. The zone of highest elevated lead concentrations was approximately 1,264 ha, or 12.6 km², which is about one-half of the area that was disturbed by mining. Thus, about 500-600 ha of this area is un-mined, but is impacted by high levels of airborne lead from the mine site. The highest lead concentrations in lichen were centred on the northwest mine area, with concentrations generally decreasing with increasing distance from the source. Geostatistical analysis indicated elevated lead concentrations extending 20^+ km from the mine site.

An examination of soils data indicated that although patterns of lead and zinc concentrations in surface organic soil were similar to patterns in lichen, no similar pattern of elemental concentrations was present in subsurface organic or mineral soils. This supports the hypothesis that the spatial pattern of elevated

elemental levels in lichens was originating from the Anvil Range Mine Complex, eliminating the possibility that these levels may be attributed to natural soil dust enrichment.

CONCLUSIONS

The two studies presented in this paper illustrate two different circumstances where lichens are used as bioindicators to monitor and map the effects of anthropogenic air pollutants in remote ecosystems surrounding mining operations. Although these studies differ in their objectives, biophysical settings, and study constraints, they share a number of common elements:

- use of an existing, abundant, and naturally occurring bioindicator (lichens) to provide information on deposition of industrial pollutants;
- use of a study design where sampling is conducted across the projected or anticipated deposition gradient and where sampling intensity is greatest near the major pollutant sources;
- use of similar field protocols for sample collection and storage; and,
- use of geostatistical analytical techniques to interpolate between data collection points to produce maps of modeled concentrations in lichen reflecting deposition patterns across the study area.

Both studies incorporated elements designed to address specific objectives or constraints, or to make use of unique opportunities. For example, the AOS study included co-location of lichen samples with other air-quality measurements to develop models relating lichen nitrogen and sulphur concentrations to other measures of air quality. In addition, the AOS study includes a substantial source apportionment component, to identify source types contributing to observed or projected deposition patterns across the study region. Whereas, the Anvil Range study incorporated soils sampling and the use of a reference site to account for the potential contribution of naturally mineralized soils to metal enrichment in lichen.

The presentation of these studies, and the preceding discussion, is intended to demonstrate that biomonitoring using lichens can be a reliable and cost-effective method for quantifying the extent and patterns of airborne pollutant deposition originating from industrial activities. This approach is particularly applicable in remote locations where other more conventional methods of air quality monitoring may be logistically or economically impractical. Potentially extensive pollutant deposition from industrial activities can make other forms of air-quality monitoring costly and in some cases impossible due to issues of access and available power, whereas lichens naturally occur within the landscape, do not require maintenance and absorb a variety of pollutants, including both trace elements and nitrogen and sulphur compounds directly from the atmosphere and store these elements in the tissues in proportion to patterns of deposition.

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