Lichens as Biomonitors of Air Quality around a Diamond Mine, Northwest Territories, Canada

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Lichens are known to be bioaccumulators of atmospheric pollutants and are abundant in the Canadian arctic. Mining in this region may negatively impact the tundra communities and these impacts may be detected by increased accumulation of heavy metals, greenhouse gas constituents, and organic compounds in lichen tissue. The effect of sampling direction and distance from a diamond mine on bioaccumulation in three lichen species, Flavocetraria nivalis, Flavocetraria cucullata, and Cladina arbuscula, was investigated. Eight sample sites were located immediately adjacent to a diamond mine, one in each cardinal and ordinal direction, and six sample sites each were located 30 and 60 km from the mine (cardinal, NE, and SE). Thirty-three major and trace elements, sulfate (SO₄), nitrate (NO₃), ammonium (NH₄), polycyclic aromatic hydrocarbons (PAH), and phthalates were analyzed in lichen tissue and soil. A significant interaction occurred between distance and direction from the mine. Highest concentrations of Al, Cr, Cu, Fe, Ni, Ti, and V in lichen were at the mine site regardless of direction. Highest concentrations for all other elements were at the mine in at least two directions. Although present in lichen tissue, there was no significant difference among sites for Hg, Mn, S, and three phthalates. PAHs were below detection limits in lichen tissue. The effect of direction was dependent on element and species, although concentrations of most elements were greatest east or southeast of the mine site. At distance from the mine, direction had less of an effect on concentrations. Elevated concentrations in tissue did not negatively impact lichen or plant cover or lichen richness. This research strongly suggests selection of sample sites and species can impact results and interpretation of data from air quality monitoring programs that use lichens as biomonitors.

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TMOSPHERIC deposition of contaminants from industrial Aactivities is an issue in arctic regions. Sulfur dioxide and nitrous oxide emissions can reduce soil pH, increase metal mobilization, and alter plant photosynthetic rates (Lechowicz, 1982; Freedman et al., 1990). Vehicle emissions and power generation contribute to greenhouse gas and heavy metal pollution (Bennett and Wetmore, 1997; Allen-Gil et al., 2003). Dust from roads can neutralize soils causing changes in plant community composition (Walker and Everett, 1987; Auerbach et al., 1997). Subsequent changes in plant composition and abundance may result in declines in lichen abundance thereby impacting ecological functions (Cornelisson et al., 2001). Diamond mining, which is an expanding industry in the Canadian North, produces dust during kimberlite extraction that can contain elevated concentrations of calcium, magnesium, sulfate, and heavy metals such as nickel, copper, cobalt, aluminum, and zinc (Baker et al., 2001). The mines rely on fossil fuels for power generation, heating, and vehicles which also contribute to greenhouse gases and acid rain. Deposition of air contaminants on a landscape scale is largely determined by wind and air stability patterns (Tomassini et al., 1976; Dillman, 1996); however, the dispersion and distribution of air contaminants across the tundra is not well understood. Long distance transport has been documented (Macdonald et al., 2000; Kelly and Gobas, 2001) and concentrations of industrial contaminants and their deposition on land are generally greater closest to the pollution source.

One of the greatest advantages of using lichens as part of an air quality monitoring program is the relative ease in gathering detailed information over a large area compared to direct monitoring of air or snow surveys (Garty, 2001). The lack of roots, large surface area, long life span, and high ion exchange capacity enable lichens to effectively bioaccumulate air contaminants. Lichens have been good indicators of sulfate and heavy metal pollution due to vehicle emissions (Garty et al., 1996; Gonzalez et al., 1996); sulfate, copper, and nickel from smelting operations (Alexeyev 1995); and phosphorus, cadmium, chromium, and zinc from phosphate refineries (Dillman 1996). Studies in Europe and Asia have identified pollution zones ranging from hundreds of meters to 100 km surrounding point sources using quantitative or qualitative lichen measurements (Tomassini et al., 1976; Addison and Puckett, 1980; Tynnyrinen et al., 1992; Dillman, 1996). Lichen research in the Canadian North has focused on characterizing the elemental content of lichens and has shown lichens were good indicators of atmospheric deposition (Chiarenzelli et al., 1997). Heavy metal concentrations in the substrates lichens were growing on were not correlated with concentra-

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tions in lichen tissue indicating the source of elements was atmospheric. Kelly and Gobas (2001) found lichens bioaccumulated persistent organic pollutants; pollutants were biomagnified in the food chain as lichens are an important source of food for caribou, which in turn are consumed by wolves and humans.

This research focused on assessing the ability of lichens to bioaccumulate elements and compounds produced by a diamond mine and their use as biomonitors of potential air pollutants in the Canadian arctic. Specific objectives were to determine if element and compound concentrations in lichen tissue in close proximity to a diamond mine were greater than at distances established to detect background levels; to determine if bioaccumulation in lichen was greatest in the direction of prevailing winds; to determine if there was a correlation between contaminant concentrations in lichen tissue and lichen and native plant abundance and diversity; and to determine if lichen species demonstrate the same bioaccumulation ability and pattern.

Materials and Methods

Study Area

Diavik Diamond Mine is located approximately 320 km northeast of Yellowknife, Northwest Territories (NT), Canada. The mine is situated on a 20 km² island, known as East Island, within Lac de Gras. The approximate footprint of the mine site is 7 km². Climate is low arctic characterized by long, cold winters and short, cool summers (Ecological Working Group, 1989). Mean annual temperature at East Island is -9.6°C and mean annual precipitation is 243 mm (Diavik Diamond Mine, 2006). Snow cover remains on average from October to May. Wind speed is generally less than 6 m s⁻¹ with an annual mean speed between 4 and 5 m s⁻¹ (Diavik meterological data 2002-2007). Highest mean wind speeds were recorded in the fall (September to November) and lowest in the winter (January and February). Seasonal and temporal variation in wind direction is reported. In 2005 and 2006 wind was predominantly from the north and northeast; from 2002 to 2004 wind was predominantly from the southwest to southeast.

The study area is within the Takijuq Lake Upland Ecoregion of the Southern Arctic Ecozone (Marshall and Schut 1999). Turbic and static cryosolic soils along with rock outcrops dominate the uplands and organic cryosolic soils dominate the lowlands. Permafrost is deep and continuous. Vegetation is heath tundra with low shrub and ericaceous shrub communities interspersed with wet tussock tundra and eskers. Heath tundra is dominated by *Betula glandulosa* Michx., *Salix* species, *Vaccinium vitis idaea* L., *Vaccinium uliginosum* L., *Ledum decumbens* (Ait.) Lodd. *ex* Steud., *Empetrum nigrum* L., and *Arctostaphylos rubra* (Rehd. and Wilson) Fernald.

Sampling Design

Sampling sites were established within heath tundra on East Island and the adjacent mainland. Eight sites, one in each cardinal and ordinal direction, were located on East Island. Six sites were located 30 and 60 km from East Island in each cardinal direction and northeast and southeast of the mine site.

Field Measurements

Within a site, samples were collected from mesic mid slope positions, where the lichen species of interest were abundant to ensure an adequate sample. Lichens were collected and vegetation was assessed the last week of July 2005. At each site a 1 m² quadrat was randomly located and two additional 1 m² quadrats were located 10 m on either side of the initial quadrat, parallel to the direction of the mine site. Percent canopy cover by plant species was determined. Percent ground cover, 2.5 cm above ground, was determined for vegetation, bare ground, lichen, moss, rock, and animal pellets. While cover of individual lichen species was not assessed, species richness (number of species) was determined. Nomenclature for plants followed Porsild and Cody (1980) and for lichens followed Brodo et al. (2001).

Three terricolous lichen species were selected as bioaccumulators of potential airborne contaminants based on a literature review and a preliminary field survey of the mine site in late June 2005. They were Flavocetraria nivalis (L.) Karnefelt & Thell. (crinkled snow lichen), Flavocetraria cucullata (Bellardi) Kärnefelt & Thell. (curled snow lichen), and Cladina arbuscula (Wallr.) Hale & Culb. (reindeer lichen). Both Flavocetraria species have foliose growth forms and Cladina arbuscula has a fruticose form. All three are green algal lichens, which have a more homogeneous elemental spectrum, preferred for species comparisons (Nash and Gries, 1995). Approximately 5 g samples of each species were collected from the area surrounding each quadrat. Samplers wore nitrile gloves to prevent contamination and lichens were stored in paper bags. A total of 60 samples were collected for Flavocetraria cucullata, 58 for Flavocetraria nivalis, and 49 for Cladina arbuscula; less than full replication was due to low abundances at some sites.

Samples of the soil on which lichens were growing were collected at each site. A composite sample of the top 10 to 15 cm of soil was taken adjacent to each 1 m² quadrat. Vegetation and lichens were removed from sample locations before soil collection. A total of 60 soil samples was collected.

Laboratory Measurements

At the University of Alberta laboratory, plastic forceps were used to remove soil, plant, and other debris from lichen samples and plant and other debris from soil samples. Lichen samples were lightly rinsed with distilled water to remove finer particulate matter and samples were air dried. Nitrile gloves were worn when handling lichens. Samples were submitted to a commercial laboratory for analyses. All results reported are in mg kg⁻¹ dry weight.

All lichen material was pulverized and ground at the laboratory. Only plastic implements were used and grinding equipment was washed between samples with a non corrosive interference free detergent. Following washing, equipment was rinsed three times with deionized water; the last rinse was analyzed with the samples. If samples were subsampled into plastic bags or jars, an equivalent storage container was analyzed with samples. QA/QC procedures for all analyses included, per batch, a blank carried through preparation, digestion, and analysis, a duplicate sample to determine

precision, and a certified reference material. Sulfate (SO₄), nitrate (NO₂), and ammonium (NH₂) were analyzed using ion chromatography (APHA 4110B and EPA 300.7). A 1:5 water extraction was performed and the extract filtered. Anions and cations were separated using the DIONEX System equipped with an appropriate ion exchange column and a self regeneration suppressor to improve sensitivity. As ions separated they were detected with a conductivity cell detector. Trace elements, silver (Ag), aluminum (Al), barium (Ba), beryllium (Be), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), lithium (Li), molybdenum (Mo), nickel (Ni), lead (Pb), tin (Sn), strontium (Sr), thallium (Tl), vanadium (V), and zinc (Zn), were determined through inductively coupled plasma mass spectrometry (EPA 200.3/200.8). Subsamples were digested in a microwave in a sealed Teflon vessel with deionized water, nitric acid, and hydrofluoric acid, then analyzed with an ELAN 6000. Major elements boron (B), calcium (Ca), potassium (K), magnesium (Mg), sodium (Na), iron (Fe), manganese (Mn), phosphorous (P), sulfur (S), silicon (Si), titanium (Ti), and uranium (U) were determined using inductively coupled plasma optical emission spectrometry (EPA 200.3/200.8). Digestion was the same as for trace metals. Mercury (Hg), selenium (Se), arsenic (As), and antimony (Sb) were analyzed by continuous hydride generation atomic absorption spectrometry (APHA 3114). A sample (wet for Hg, dry for As, Se, and Sb) was digested in a sealed bottle at 95°C for 6 h with hydrochloric acid, sulfuric acid, and potassium persulfate; the sample was then filtered and made to volume. Mercury was analyzed at this stage and two subsamples taken, one for As and Sb and one for Se. Each subsample was mixed with hydrochloric acid to create a 50% matrix; Se was reduced by heating and As and Sb were reduced by treatment with potassium iodide; samples were then analyzed. Boron, Li, Si, U, and Hg were tested for in a subset of 12 samples, one sample from each cardinal and ordinal direction on East Island and each cardinal direction 60 km from the island. Elements for analyses were selected based on Canadian Council of Ministers of the Environment (CCME, 1999), Alberta Tier 1 (Alberta Environment 1994) criteria for contaminated soils, Northern Contaminant Program metals of concern (Fisk et al., 2003), and elevated levels found in lichen tissue at a neighboring mine site (Kidd et al., 2003).

Phthalates and polycyclic aromatic hydrocarbons (PAHs) were assessed in a subset of eight samples collected on East Island and at 60 km from the mine site in each cardinal direction. Phthalates and PAHs have long been recognized as relevant pollutants; however, only recently has there been evidence they accumulate in plant tissue (Carlberg et al., 1983; Mueller and Koerdel, 1993; Slaski et al., 2000). PAHs and phthalates were analyzed using gas chromatography and mass spectrometry (EPA 3640/3540/8270). Subsamples were mixed with anhydrous sodium sulfate; a sample was extracted in a Soxhlet extractor, dried, concentrated, and subjected to gel permeation chromatography to remove lipid, proteins, and polymers which may interfere with GC/MS analysis. Calibration standards were performed daily, a blank processed per batch, and internal and surrogate standards met with each sample.

Texture, pH, total organic and inorganic carbon, total Kjeldahl nitrogen, and percent saturation were determined to character-

ize the soil at each site. SO, was determined by saturated paste and inductively coupled plasma optical emission spectrometry (APHA 3120B). NO₃ and NH₄ were determined by colorimetry (APHA 4500) with samples extracted in a 1:5 ratio with water and analyzed with a Technicon colorimeter. Major and trace metals were determined through inductively coupled plasma mass spectrometry (SW 846-3050/6020). Subsamples were digested with nitric acid and hydrogen peroxide; hydrochloric acid was added to the initial digestate and refluxed; the sample was then diluted to volume and analyzed by ICP-MS. Mercury, As, Sb, and Se were analyzed by continuous hydride generation atomic absorption spectrometry (see lichen tissue for details). PAHs and phthalates were analyzed using gas chromatography and mass spectrometry (EPA 3540/8270). Sample extraction was by Soxhlet extractor. The gas chromatograph was equipped with a narrow bore, fused silica capillary column and the sample analyzed in the selected ion monitoring (SIM) mode. Soil data were used to assist in confirming the source of tissue contaminants as atmospheric versus substrate (see Wolterbeek and Bode, 1995 and Chiarenzelli et al., 1997).

Data Analyses

Data were tested for normality with the Shapiro-Wilk Test and homogeneity of variance with Levene's Test. Due to nonnormal distribution and many groups with non-homogeneous variance, nonparametric methods were employed. The Scheirer Ray Hare Test, a two way analysis of variance (ANOVA), was conducted to determine effect of sampling location, sampling direction and their interaction on element and compound concentrations in lichen tissue, plant cover, lichen cover, and richness (Sokal and Rolf, 1995). Kruskal-Wallis Tests, one way ANOVAs, were conducted on B, Li, Hg, Si, S, U, PAHs, and phthalates as there were only sufficient samples to test distance. The Mann-Whitney U Test was used for post hoc comparisons between groups. Bivariate correlation analysis (Spearman's rho, n = 60) was performed to compare element and compound levels in lichen tissue to soil concentrations and lichen and plant cover and diversity. Analyses were conducted in SPSS 14.0 (SPSS Inc., 2005) using a *p*-value of 0.05 to balance Type 1 and Type 2 errors.

Results and Discussion

Greenhouse Gas Constituents

Sampling location and direction interactions significantly affected SO_4 , NO_3 , and NH_4 tissue concentrations in *Flavocetraria nivalis*, SO_4 and NO_3 in *Flavocetraria cucullata*, and SO_4 and NH_4 in *Cladina arbuscula*. Sampling location alone had a significant effect on NH_4 in *Flavocetraria cucullata* tissue and NO_3 in *Cladina arbuscula* tissue. SO_4 and NH_4 concentrations were significantly higher at the mine except in the west and depending on species concentrations were two to three times higher then at other sampling sites (Fig. 1a). At the mine SO_4 was significantly greater in the northwest, north, northeast, and east compared to more southerly directions (Fig. 1b). Although highly variable within a site, concentrations were highest in the northwest, although concentrations were high in all directions except southwest.

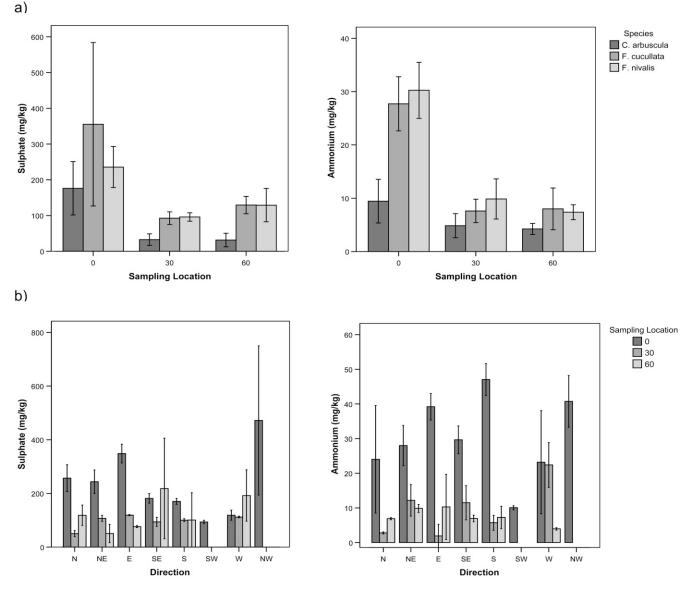


Fig. 1. Effect of (a) lichen species and (b) distance (km) and direction (*Flavocetraria nivalis* only presented) on sulfate and ammonium accumulation in lichen tissue in proximity to a diamond mine, NT. Error bars represent ± 2 SE.

At all sampling sites, NO₃ concentrations were low, ranging from 1.1 to 3.1 mg kg⁻¹ and accumulation pattern was inconsistent. Increased NO₃ concentrations are a concern in tundra ecosystems as they are nitrogen limited and additions could result in significant ecological change (Woodin and Marquiss, 1997). Soil NO₃ was below detection limits confirming N limitations in the region. Lichen tissue concentrations of NO₃ and NH₄ were much lower than those reported from other industrial activities (Addison and Puckett, 1980; Tynnyrinen et al., 1992; Takala et al., 1994; Bennett and Wetmore, 1997). Epiphytic lichens were sampled in most of these studies and Bennett and Wetmore (1997) found terricolous lichens had lower element concentrations than epiphytic species.

Kimberlite and processed kimberlite contain low but leachable levels of SO_4 (Baker et al., 2001). Lichen tissue SO_4 concentrations have been infrequently reported although in this study they were similar to those at another diamond mine in the region (Kidd et

al., 2003). Tissue pH was significantly higher at the mine (median 4.2) than other sites when lichen species were grouped (3.9 and 4.0, respectively; Kruskal Wallis $X^2 = 15.20$, P = 0.001). Soils in the area are moderately acidic. Lichen SO₄ concentrations increased from 30 to 60 km (Fig. 1b) in some directions with concentrations considerably higher at 60 km than at the mine in southeast and west directions. This suggests sites are influenced by activities outside the monitoring radius, although there is no development within 30 km in most directions.

Elements

Sampling location and direction interactions had a significant effect on most element concentrations in the three lichen species with a few exceptions. For *Flavocetraria cucullata* sampling location and direction significantly affected Pb concentrations and location affected Na. For *Cladina arbuscula* sampling location and direction had significant effects on Cr and location on Pb, Mo, and Sr. Most elemental concentrations were significantly higher at the mine site in all directions than at other sampling locations. There was no significant difference among sample sites for Hg, Mn, and S in any species and in two of the three species for P and Zn. The lack of statistical significance in an easterly direction for *Flavoce-traria nivalis* and in all directions for *Cladina arbuscula* resulted from a small sample size (n = 2) due to insufficient lichen material. Location comparisons were not significant at P = 0.05 but were at P = 0.10, although numerical data clearly demonstrate differences. For example in *Flavocetraria nivalis*, Al was 48 times greater, Cr was 24 times greater, and V was 11 times higher in the east at the mine than at other sampling locations (Table 1).

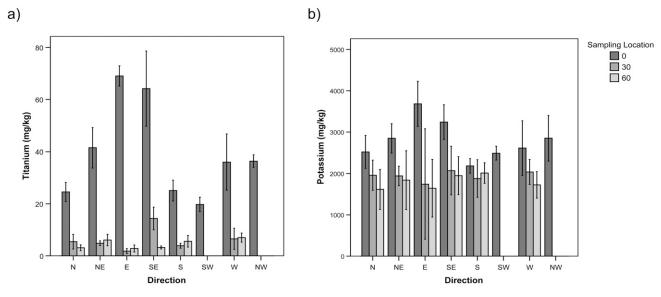
For many elements, patterns of accumulation were similar in lichen species, as illustrated for selected elements in Table 1. Highest values on East Island were consistently in the southeast and/or east for Al, Ba, Cd, Cu, Cr, Fe, Mo, Ni, Pb, Sr, Ti, and V. At 30 km, element concentrations were considerably reduced in all directions with highest values remaining at the southeast sampling site. Barium, Cd, and Sr were highest in the north and northeast. By 30 km, there was no effect of direction on Cu or Pb. At 60 km, there was greater divergence in pattern. Strontium was significantly greater in the south and V in the northeast. These elements numerically increased in the west, northeast, and/or south compared to 30 km (Fig. 2a).

Macronutrients such as Ca, Mg, K, and P were significantly higher in lichen tissue by the mine, in the southeast, compared to other locations (Table 1 and Fig. 2b). Potassium was significantly greater in the east, and P and Ca had numerically high concentrations in the east. Magnesium was significantly greater in the west; Na was significantly greater on East Island in all directions except west. Na concentrations were 5 to 20 times higher depending on direction and species. There were no differences in macronutrients among or between sampling sites at 30 and 60 km.

Direction resulted in unique accumulation patterns for some elements and species (Table 2). Thallium, Be, Ba, Co, Se, and Sn

Table 1. Mean concentration of selected elements in tissue (mg kg ⁻¹
± SE) of Flavocetraria nivalis (L.) Karnefelt & Thell. (crinkled snow
lichen), Lac de Gras, NT. <i>Flavocetraria cucullata</i> and <i>Cladina</i>
arbuscula have similar patterns in accumulation.

Element	Direction	East Island	30 km	60 km
Aluminum	North	746 (80)	107 (8)	40 (10)
	Northeast	1152 (121)	115 (8)	137 (24)
	East	2160 (105)	44 (17)	67 (2)
	Southeast	1536 (168)	326 (42)	63 (10)
	South	646 (15)	67 (12)	151 (36)
	West	1203 (280)	184 (51)	136 (16)
Barium	North	27 (0.47)	29 (0.61)	19 (0.75)
	Northeast	29 (0.79)	32 (0.78)	25 (0.51)
	East	38 (1.50)	27 (0.45)	16 (0.10)
	Southeast	48 (2.48)	26 (0.89)	23 (1.71)
	South	35 (0.22)	22 (1.11)	30 (1.67)
	West	50 (6.72)	27 (1.62)	33 (1.130
Chromium	North	4.73 (0.77)	1.23 (0.03)	0.47 (0.17)
	Northeast	7.40 (0.50)	0.10 (0.00)	1.30 (0.26)
	East	12.00 (1.47)	0.45 (0.05)	0.50 (0.00)
	Southeast	11.17(1.23)	3.53 (0.12)	0.67 (0.15)
	South	4.23 (0.20)	0.53 (0.09)	0.93 (0.15)
	West	9.83 (2.51)	2.13 (0.20)	0.87 (0.07)
Lead	North	1.66 (0.07)	0.51 (0.02)	0.38 (0.05)
	Northeast	2.11 (0.08)	1.02 (0.51)	0.77 (0.19)
	East	5.24 (0.30)	0.30 (0.03)	0.32 (0.02)
	Southeast	2.78 (0.10)	0.47 (0.04)	0.38 (0.03)
	South	1.49 (0.06)	0.61 (0.09)	0.50 (0.07)
	West	1.45 (0.12)	0.76 (0.20)	0.63 (0.07)
Calcium	North	4183 (66)	3203 (177)	3647 (413)
	Northeast	5117 (149)	3983 (420)	3490 (251)
	East	5833 (26)	3290 (560)	3790 (130)
	Southeast	5790 (386)	3377 (75)	2737 (79)
	South	5987 (329)	2313 (48)	4020 (393)
	West	5620 (245)	3830 (72)	4593 (658)
Magnesium	North	460 (19)	136 (9)	297 (12)
-	Northeast	1133 (35)	890 (63)	903 (48)
	East	1083 (72)	684 (58)	1080 (30)
	Southeast	1643 (119)	842 (46)	763 (33)
	South	1173 (24)	779 (38)	888 (45)
	West	1563 (112)	889 (61)	768 (70)



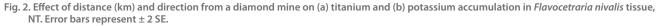


Table 2. Mean accumulation of elements in three lichen species sampled at a diamond mine on East Island, 30 and 60 km from the mine. Units are mg kg⁻¹ (\pm SE); samples from all directions within a sampling location are pooled.

	Species	East Island	30 km	60 km
Aluminum	Flavocetraria nivalis	1126 (111)	146 (26)	101 (13)
	Flavocetraria cucullata	2654 (175)	322 (55)	189 (24)
	Cladina arbuscula	4356 (541)	420 (50)	309 (39)
Boron	Flavocetraria nivalis	4.00 (0.41)	-	2.75 (0.75)
	Flavocetraria cucullata	4.25 (0.48)	-	1.75 (0.48)
	Cladina arbuscula	5.00 (0.71)	-	2.00 (0.58)
Cobalt	Flavocetraria nivalis	0.86 (0.06)	0.56 (0.15)	0.47 (0.10)
	Flavocetraria cucullata	0.87 (0.04)	0.35 (0.07)	0.23 (0.03)
	Cladina arbuscula	2.45 (0.81)	0.29 (0.05)	0.18 (0.03)
Copper	Flavocetraria nivalis	1.59 (0.08)	0.84 (0.05)	0.87 (0.04)
	Flavocetraria cucullata	2.55 (0.12)	1.05 (0.06)	1.06 (0.03)
	Cladina arbuscula	2.39 (0.28)	0.99 (1.82)	0.96 (0.03)
Lithium	Flavocetraria nivalis	1.38 (0.52)	_	0.25 (0.00)
	Flavocetraria cucullata	3.05 (0.67)	_	0.25 (0.00)
	Cladina arbuscula	3.38 (1.28)	_	0.25 (0.58)
Phosphorous	Flavocetraria nivalis	962 (45)	652 (30)	664 (24)
	Flavocetraria cucullata	982 (71)	900 (61)	960 (30)
	Cladina arbuscula	680 (80)	565 (52)	659 (30)
Sodium	Flavocetraria nivalis	965 (49)	570 (58)	574 (63)
	Flavocetraria cucullata	1365 (97)	845 (30)	829 (38)
	Cladina arbuscula	1160 (159)	261 (35)	310 (29)
Strontium	Flavocetraria nivalis	20 (1)	13 (1)	14 (1)
	Flavocetraria cucullata	11 (0)	5 (0)	5 (0)
	Cladina arbuscula	11 (1)	4 (0)	4 (0)
Uranium	Flavocetraria nivalis	1.12 (0.45)	_	0.03 (0.00)
	Flavocetraria cucullata	1.84 (0.57)	_	0.03 (0.00)
	Cladina arbuscula	1.24 (0.38)	_	0.03 (0.00)
Zinc	Flavocetraria nivalis	30 (1)	33 (2)	32 (1)
	Flavocetraria cucullata	31 (1)	31 (1)	33 (1)
	Cladina arbuscula	168 (69)	18 (1)	18 (1)

concentrations were considerably numerically greater in *Cladina arbuscula* southeast, southwest, and east of the island. In *Cladina arbuscula* Be was more than 100 times greater than CCME guidelines for soil, Se up to 25 times, and Tl close to guidelines in half these samples. Beryllium and Se were below detection limits at most other sampling sites. Diavik reports the highest dust deposition northeast and southeast of the mine (Diavik Diamond Mine, 2004), which may explain elevated concentrations in these directions. However, these elements were not elevated in the northeast in any species and not in the southeast for *Flavocetnaria*.

A number of elements were elevated in *Flavocetraria* from the 30 km northeast sampling site. Selenium was up to 25 times greater than CCME guidelines for contaminated soil; Sb and Ag were considerably greater, and Sb was above soil quality guidelines in one sample; Co was 10 times greater than in other directions, except west; As had high concentrations in *Flavocetraria nivalis*. The same accumulation pattern at 30 km was not found in *Cladina arbuscula*; these elements were elevated, and often above CCME guidelines, at the south sampling site. Elevated concentrations north or northeast of the mine may result from cumulative effects of airborne pollution since Ekati Diamond Mine is 30 km north northwest and its Misery Pit is 10 km north northeast of Diavik; the two are connected by a haul road.

Polycyclic Aromatic Hydrocarbons and Phthalates

Tissue concentrations of PAHs were below detection limits for the three lichen species. Of the eight phthalates analyzed, three were present in all three lichens in concentrations above detection limits. Of the 12 lichen samples submitted for analyses, 75% contained di-*n*-butyl phthalate (DBP), 50% contained diisobutyl phthalate, and 17% contained diethyl phthalate. No significant differences were found between East Island and 60 km from the island. Mean (± SE) concentrations of di-*n*-butyl, diisobutyl, and diethyl phthalate in *Flavocetraria nivalis* on East Island were 1.13 (0.33), 1.63 (0.55), and 0.18 (0.05) mg kg⁻¹ and in *Flavocetraria cucullata* were 1.07 (0.46), 1.00 (0.27), and 0.27 (0.17) mg kg⁻¹, respectively.

Commonly used as a plastic softener, DBP is considered a human carcinogen. Only one arctic study, Carlberg et al. (1983), tested for and found phthalates in a combined sample of lichen and moss tissue. As they were present in equivalent amounts at the mine and reference sites, their presence cannot be attributed to the diamond mine. Long range transport of other POPs has been internationally recognized in arctic regions (Kelly and Gobas, 2001). In the laboratory, lichens were in contact with plastic for short periods of time during sample preparation, and although highly unlikely this cannot be completely ruled out as a source of phthalates. Natural sources, including plants, of phthalic acid and phthalate esters have been reported (Anjou and von Sydow 1967; Graham 1973); however, further research is required to determine the environmental importance of these sources. If bioaccumulated in lichen tissue this would be the first documented case of long distance transport of this group of contaminants in the Canadian arctic. Thus further testing is highly desirable.

Soil Tissue Correlations

Although lichens do not uptake nutrients from a substrate (Garty, 2001), it is necessary to confirm the source of pollutants as atmospheric and not soil. The majority of elements analyzed were below detection limits in soil. Soil and tissue concentrations did not correlate for most elements and compounds, indicating atmosphere, not substrate, was the source. Calcium (Spearman's rho, *r* = 0.272, *P* = 0.041), Mg (*r* = 0.310, *P* = 0.019), and P (r = 0.396, P = 0.002) in *Flavocetraria nivalis* tissue were significantly positively correlated with soil concentrations suggesting an influence of crustal material. Manganese was significantly correlated in tissue and substrate samples for two of the three lichen species (Flavocetraria nivalis, r = 0.616, P = 0.000; Flavocetraria *cucullata*, r = 0.356, P = 0.006), and a significant Zn (r = 0.280, P = 0.032) soil tissue correlation was found for *Cladina arbuscula*. Di-n-butyl phthalate was found in a few soil samples; however, there was no correlation between tissue and soil samples.

Effect of Lichen Species

While the pattern of element and compound concentrations in the three lichens with distance and direction from the mine site was similar, concentrations at a given sampling site were

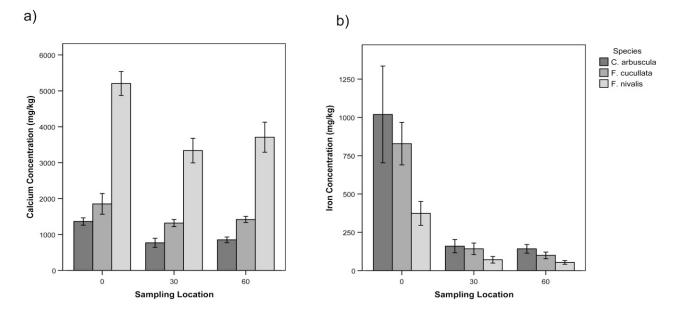


Fig. 3. Effect of species on (a) calcium and (b) iron concentration in lichen tissue collected at 0, 30, and 60 km from a diamond mine, NT. Error bars represent ± 2 SE.

variable (Table 2). *Flavocetraria nivalis* had considerably higher accumulations of Ca, Cd, Mg, Mn, and Sr, and both *Flavoce-traria* species accumulated more NH_4 , Fe, P, K, and Na. *Cladina arbuscula* accumulated significantly more Al, As, Ba, Fe, Li, Mo, Tl, Sn, and Si on East Island; however, this was location specific with higher concentrations on East Island but lower concentrations at other locations. For example, *Flavocetraria nivalis* was the highest and *Cladina arbuscula* the lowest accumulator of Ca at all sampling locations; the pattern was opposite for Fe (Fig. 3). For most sampling locations, *Flavocetraria cucullata* was the moderate accumulator of elements and compounds.

The magnitude of the difference between mine and off-mine sites for each species was similar, except for Ba (1.5, 3, and 25 times for *Flavocetraria nivalis*, *Flavocetraria cucullata*, and *Cladina arbuscula*, respectively), Co (2, 4, and 14 times), and Tl (0, 3, and 24 times). While species accumulation patterns among sampling locations were similar, considerable deviations existed for Be, Se, and Zn. All three were highest in *Cladina arbuscula* at East Island, but Be and Se were below detection limits in *Flavocetraria* and Zn was similar between locations. NO₃–N was 17 times higher in *Cladina arbuscula* on the mine than off with no difference between locations for *Flavocetraria*. *Cladina arbuscula* had the greatest extreme values.

Morphological and structural differences play a role in accumulation of airborne contaminants. In this study *Cladina arbuscula* was just as likely to accumulate elements as foliose species. Conversely Chiarenzelli et al. (1997) found fruticose lichens such as *Cladina arbuscula* bioaccumulate less heavy metals than foliose lichens like *Flavocetnaria*. Puckett and Finegan (1980) found finely divided thalli were more likely to accumulate particulate matter, and *Cladina arbuscula*'s branched form may assist in accumulation. Thin, flat surfaces in *Flavocetnaria nivalis* are ideal for intercepting particulate matter and maximizing surface area to dry weight ratio resulting in higher element concentrations (Nieboer et al., 1972). *Flavocetraria cucullata* combines the two growth forms and curled flaps on the branches may secure particulate matter to its surface and reduce wind or water erosion. *Cladina* species lack a cortex, often composed of fungal hyphae with gelatinous walls (Brodo et al., 2001). This morphological difference may assist or hinder its ability to bioaccumulate (Garty, 2001). Nonparticulate elements such as S and K are not as affected by these structural differences compared to metals such as Pb, Ni, Cr, and Al which adhere to particles (Garty, 2001). These are important factors when selecting a lichen species for a biomonitoring program.

Vegetation and Lichen Cover and Deposition

Environmental guidelines do not exist for plant tissue, therefore the impact of elevated tissue concentrations on plants and wildlife, including caribou which rely on lichens as their primary food source, is not known. Soil quality guidelines exist for many elements analyzed; the majority of tissue concentrations fell much below these limits. Environmental soil quality guidelines do not exist for all trace elements (e.g., Al, Ca, Mg, Mn, P, K, Na, Ti) as some are natural elements in soils and abundance is site specific. These metals and minerals also result from industrial activities, in particular soil disturbance, road construction, and increase of airborne dust (Addison and Puckett, 1980; Tynnyrinen et al., 1992). Kimberlite and processed kimberlite dust is a direct source of Al, Cr, Ni, Sr, Co, Cu, Hg, Pb, Mo, and U (Baker et al., 2001); all of which were elevated in lichen tissue at and near the mine site.

Besides elevated concentrations of metals and other potential pollutants in lichen tissue, overall reduced lichen and plant health has been reported in proximity to industrial activities (Walker and Everett, 1987; Alexeyev, 1995). In this study there was a significant interaction between sampling location and direction for all plant and lichen groups except shrubs. Vegetation cover was dominated by *Salix* species, *Betula glandulosa*, and ericaceous shrubs. Mean cover on East Island, at 30 and 60 km Table 3. Correlations between lichen cover and plant cover and element concentrations in three lichen tissue selected as bioaccumulators of elements and compounds. N = 60. Significant correlations are in italic.

	Lichen	nen cover Ericaceo		shrub cover	Graminoid cover	
	r	Р	r P		r	Р
Ammonium						
Flavocetraria nivalis	-0.171	0.199	0.273	0.038	0.077	0.564
Flavocetraria cucullata	-0.275	0.034	0.189	0.148	-0.297	0.021
Cladina arbuscula	-0.246	0.099	0.038	0.801	0.050	0.740
Arsenic						
Flavocetraria nivalis	-0.162	0.275	0.265	0.045	0.056	0.676
Flavocetraria cucullata	-0.265	0.041	0.449	0.000	0.037	0.778
Cladina arbuscula	0.207	0.154	0.306	0.033	0.017	0.908
Nitrate						
Flavocetraria nivalis	-0.013	0.924	-0.068	0.614	0.105	0.433
Flavocetraria cucullata	-0.105	0.423	-0.114	0.384	-0.270	0.037
Cladina arbuscula	-0.363	0.013	0.057	0.708	0.132	0.380
Magnesium						
Flavocetraria nivalis	-0.378	0.003	0.305	0.020	0.027	0.838
Flavocetraria cucullata	-0.221	0.089	0.109	0.407	-0.148	0.260
Cladina arbuscula	-0.087	0.552	0.193	0.184	-0.098	0.504
Manganese						
Flavocetraria nivalis	-0.469	0.000	0.089	0.507	0.392	0.002
Flavocetraria cucullata	-0.363	0.004	-0.028	0.833	0.258	0.046
Cladina arbuscula	-0.141	0.335	0.062	0.674	0.354	0.013
Phosphorus						
Flavocetraria nivalis	-0.103	0.443	0.278	0.034	-0.197	0.138
Flavocetraria cucullata	0.106	0.421	0.020	0.882	-0.297	0.021
Cladina arbuscula	-0.048	0.745	0.209	0.150	-0.066	0.654
Thallium						
Flavocetraria nivalis	bdl†	bdl	bdl	bdl	bdl	bdl
Flavocetraria cucullata	-0.168	0.200	0.286	0.027	-0.052	0.692
Cladina arbuscula	-0.109	0.457	0.289	0.044	-0.208	0.152
Zinc						
Flavocetraria nivalis	0.329	0.012	-0.064	0.634	-0.306	0.020
Flavocetraria cucullata	0.062	0.637	-0.219	0.092	-0.397	0.002
Cladina arbuscula	0.015	0.919	0.121	0.408	-0.244	0.091

† bdl- below detection limit.

was forbs 1, 0, and 1%; graminoids 2, 1, and 1%; shrubs (nonericaceous) 6, 4, and 7%; and ericaceous shrubs 30, 21, and 25%. Although there was an interaction, there was no obvious pattern in plant cover with direction. Lichen cover was significantly greatest 30 km from the mine (26%) and lowest on East Island (10%) but there was no significant difference in cover between the mine and 60 km (12%; Mann Whitney U = 214.00, P = 0.959). Mean number of lichen species ranged from 5 to 12 species per sample site. Mean number of lichen species at East Island (10) was significantly greater than at 30 km (seven species) but not significantly different than at 60 km (eight species) (Mann Whitney U = 156.5, P = 0.127).

In this study, a few significant correlations between decreases in lichen and plant cover and increases in element or compound concentrations in lichen tissue were found (Table 3). Manganese was the only element consistently negatively correlated with cover of lichens and positively correlated with graminoids. Ericaceous cover was consistently positively correlated with As and Tl. Forb and shrub cover were not affected by any element or compound measured. Lichen richness was significantly positively correlated with Al, Ba, Ca, Cr, Cu, Fe, Mo, Sr, Ti, and V in all three lichens with these elements explaining approximately 30% of the variation (R^2 ranged from 0.285 to 0.422). Surprisingly, the elements and compounds that were positively correlated with lichen cover were not statistically significant. Plant and lichen abundance may only be effective measures of air quality for extremely polluted environments, where lichen deserts have been reported.

Background Levels

Two detailed studies have been conducted on lichen and elemental concentrations in the NT and their results can be used to confirm background levels in this study (Table 4). Puckett

	Puckett and Fi	negan (1980)	Chiarenzelli et al. (1997)	This study†	
Element	Flavocetraria cucullata	Flavocetraria nivalis	Flavocetraria nivalis	Flavocetraria cucullata	Flavocetraria nivalis
Aluminum	633.8 (600.2)	369.6 (472.3)	na	189.1 (101.7)	100.9 (54.2)
Arsenic	0.26 (0.0)	0.28 (0.24)	0.19 (0.08)	0.39 (0.36)	0.28 (0.23)
Cadmium	na‡	na	0.24 (0.07)	0.04 (0.00)	0.13 (0.04)
Chromium	1.6 (1.1)	1.5 (1.1)	1.18 (0.64)	1.46 (0.83)	0.81 (0.38)
Copper	8.5 (4.7)	6.2 (1.5)	1.98 (1.71)	1.06 (0.15)	0.87 (0.18)
Iron	478 (640)	258 (304)	na	99.7 (43.7)	53.7 (23.8)
Nickel	2.5 (0.6)	2.7 (0.6)	1.92 (1.24)	0.94 (0.36)	1.06 (1.11)
Lead	4.2 (1.9)	5.6 (2.3)	3.23 (0.98)	0.26 (0.06)	0.51 (0.21)
Sulfur	221 (48)	191 (47)	na	325 (50)	275 (50)
Strontium	0.08 (0.04)	0.09 (0.09)	0.02 (0.01)	4.85 (1.34)	13.63 (4.07)
Titanium	62.7 (67.2)	48.1 (49.2)	na	7.5 (4.1)	4.7 (2.1)
Vanadium	1.78 (2.84)	1.2 (2.4)	0.92 (0.50)	0.25 (0.11)	0.14 (0.07)
Zinc	24.1 (11.9)	25.0 (15.1)	25.3 (5.9)	33.1 (6.0)	32.1 (4.0)

+ Mean from sample sites 60 km from the mine pooled among directions.

‡ na- not analyzed.

and Finegan (1980) tested 20 lichen species from 45 sites across the NT for 20 trace elements. Lichen tissue concentrations at 30 and 60 km in this study consistently fell within or below the ranges provided by Puckett and Finnegan. A 1997 study in the Keewatin district, NT (7 km radius) examined 9 heavy metals in 12 lichen species, including *Flavocetraria nivalis* (Chiarenzelli et al., 1997). Elements in *Flavocetraria nivalis* tissue 30 and 60 km from the mine were generally below means reported in the 1997 study, with some considerably lower (e.g., Cd, Cu, Pb, V) (Table 4). Only Zn was consistently found at greater tissue concentrations in this study. Lichen samples are often lightly washed before analyses to remove surface bound particles as tissue accumulation is of interest. This may partially explain the lower background levels in this study compared to other regions, although detailed methods for the other two studies were not reported.

Concentrations of Cd, Cu, Pb, and V were well below mean background levels in lichens. These elements were at lower concentrations at mine and off-mine sites than published background levels from other arctic regions (e.g., Kauppi and Halonen, 1992; Moskovchenko and Valeeva, 2002). Reduced use of leaded gasoline during the past two decades and isolation of the study site from intense development, compared to other arctic regions, may explain the low Pb concentrations in lichens. Pollution with V is often a result of power generation emissions (Allen-Gil et al., 2003) and Cu pollution results from the use of diesel fuel (Garty, 2001). Even though concentrations in the Lac de Gras area were lower than other published values, they were significantly greater at East Island compared to other sample sites.

Thirty kilometers from the diamond mine is sufficient to achieve background levels for most (60%) elements and compounds in lichen tissue. The effect of direction on off-mine samples with high concentrations varied depending on species and element. Sampling in one or two directions may not have detected these elevated values, and sampling only in these directions could erroneously indicate severe contamination. This research strongly suggests that a uniform gradient or pollution zone from the diamond mine cannot be delineated as deposition distance is dependent on contaminant and direction. Variation in the effect of direction on lichen tissue concentrations at greater distances from the point source may be influenced by development outside the study area; however, development is sparse and located beyond the 60 km radius with the exception of the Ekati Diamond Mine. The orders of magnitude difference in most concentrations between mine and off-mine sites, in all directions, provides strong support that deposition is from the point source.

Mines and other industrial developments are point sources of airborne contaminants in arctic regions, although previous studies have not been conducted in the Canadian arctic using lichens as bioindicators. In Finish heath tundra, background levels of S and NO_3 were not obtained in lichen tissue until a distance of 10 km from a strip mine (Tynnyrinen et al., 1992). Effects of a Finish steel works on elemental concentrations in lichen tissue were restricted to 10 km from the plant even though sampling was conducted up to 30 km (Mukherjee and Nuorteva, 1994). In the Russian arctic, Allen-Gil et al. (2003) reported smelting pollution, as measured

in lichen tissue, extended 100 km north of the point source and Walker et al. (2003) found elevated concentrations of air borne contaminants in *Flavocetraria cucullata* and *Cladina arbuscula* tissue 25 to 40 km from a coal mine. In the Canadian Boreal Forest region, high elemental concentrations were found in lichen tissue, including *Cladina arbuscula*, up to 25 km from active mines in the Athabasca oil sands; the highest concentrations were within 10 km (Addison and Puckett, 1980). This study has demonstrated that diamond mine activity results in elevated element and compound concentrations in lichens compared to background levels and detailed sampling at 5 to 25 km from the diamond mine will facilitate delineation of a deposition zone. No previous studies had experimentally tested the effect of direction on the extent of air borne pollution in lichen tissue from a point source.

Conclusions

Mining in the Canadian arctic is a growing industry resulting in potential impacts to the surrounding tundra. Methods to effectively and efficiently measure changes in the adjacent communities and assess impacts are required. This study demonstrated that lichens are effective bioaccumulators of elements and compounds produced by a diamond mine in the Canadian arctic. Lichen tissue by the mine site had elevated concentrations of most elements and compounds tested compared to background levels. Thirty kilometers was sufficient distance from the mine to achieve background levels. Elevated concentrations in lichen tissue do not appear to negatively impact lichen or plant cover and richness. Sampling direction and species of lichen significantly affected accumulation of elements and compounds in tissue; however, there was no consistent pattern. Flavocetraria nivalis and Flavocetraria cucullata were more consistent bioaccumulators than Cladina arbuscula. This research strongly suggests selection of sample sites and lichen species can impact results and interpretation. Sampling a common species, or pooling species, in the predominant wind directions alone is not sufficient to accurately assess deposition of atmospheric pollutants from industrial activities on adjacent communities and potential ecological impacts. Guidelines do not exist for plant tissue, and therefore it is not possible from this study to assess type or magnitude of impact, if any, elevated deposition may have on lichen and plant communities in the Canadian arctic.

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