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Forest Fertilization Associated with Oil Sands Emissions

Shaun A. Watmough,[1]* Adam Bird,[2] Andrew McDonough,[2] and Eric Grimm[3]

[1]Trent School of the Environment, Trent University, Peterborough, Ontario K9L 0G2, Canada; [2]Environmental and Life Sciences Graduate Program, Trent University, Peterborough, Ontario K9L 0G2, Canada; [3]Environmental Resource Studies, Trent University, Peterborough, Ontario K9L 0G2, Canada

ABSTRACT

The Athabasca Oil Sands in Alberta, Canada, is one of the largest point sources emitters of NO_x and SO_2 in Canada, and there have been widespread concerns over potential ecosystem acidification owing to the acid sensitivity of the base-poor sandy soils in the region. In this study we compared soil and vegetation properties at a jack pine (*Pinus banksiana* Lamb) forest adjacent to one of the largest mines in the region with a jack pine stand located approximately 15 km from the mine. At the site closest to the mine, throughfall deposition of SO_4-S and DIN ($NO_3 + NH_4$) exceeds 30 and 20 kg ha^{-1} y^{-1}, respectively, compared with less than 9 kg ha^{-1} y^{-1} for SO_4-S and less than 2 kg ha^{-1} y^{-1} DIN at the distant site. However, on an equivalence basis, base cation (Ca + Mg + Na) deposition in throughfall at both sites exceeded the combined S and N deposition. Total S and N as well as Ca and Mg concentrations in epiphytic lichens and tree bark were significantly higher at the site adjacent to the mine, reflecting the higher acidic and base cation throughfall deposition. The forest floor at the stand close to the mine had a significantly higher pH, exchangeable Ca, Mg, K and total S concentrations compared with the distant site. The chemistry of deeper mineral soil horizons was more consistent between the two sites. Foliar concentrations of S, Ca, Mg, Fe and Al in jack pine, *Vaccinium vitis-idaea*, *Vaccinium myrtilloides* and *Arctostaphylos uva-ursi* were also higher at the site close to the mine, but these differences were not always significant. Coincidental with differences in atmospheric deposition, herbaceous cover and biomass, especially *A. uva-ursi*, was significantly higher, and terricolous lichen cover was several fold lower at the site closest to the mine. This work indicates that despite high S and N emissions from oil sands activities, forest fertilization and alkalization may be of greater concern than acidification owing to large dust emissions from the mines and the Acid Deposition Management Framework for the region should be modified accordingly.

Key words: oil sands; forests; acidification; eutrophication; alkalization; lichens.

INTRODUCTION

Elevated acid deposition associated with emissions from oil sands activities in Alberta Canada is a concern as this remote environment features extensive upland areas that are acid-sensitive owing to Precambrian bedrock geology with low buffering capacity (Whitfield and others 2010). Consequences of elevated acid deposition can include lower soil pH, depletion of the base cation

pool (reduction in base saturation) and a decrease in the ratio of nutrient base cations (Bc = Ca + Mg + K) to aluminum (Al) in soil solution (Bc/Al) (Reuss and Johnson 1985). Depression of the Bc/Al in soil solution below a critical threshold can impair root function and ultimately impact vegetation health (Cronan and Grigal 1995). Upland forest soils in the region feature extremely low weathering release of base cations and have been identified as potentially at risk of acidifying due to elevated sulfur (S) deposition (Whitfield and others 2010). In response to these concerns, an Acid Deposition Management Framework (ADMF) for the region was developed by stakeholders including industry, regulators, environmental non-governmental organizations and indigenous groups. The primary objective of the ADMF is to maintain chemical conditions such that adverse impacts on biota do not occur (Whitfield and Watmough 2015). Elevated nitrogen (N) deposition is also an emerging concern in the region because of concerns about ecosystem eutrophication that have been documented elsewhere (Bobbink and others 2010; Clark and Tilman 2008; Clark and others 2017; Stevens and others 2004, 2010). Ongoing work is attempting to establish appropriate critical loads for N deposition that may be used to assist management decisions.

Despite these concerns, there have been no documented acidification impacts in the region (Jung and others 2013; Laxton and others 2010), and recent work has shown that high levels of base cation deposition associated with mining activities are essentially ''neutralizing'' the acidic deposition (Watmough and others 2014). In many respects high base cation deposition may be viewed as beneficial because ecosystem acidification is prevented (Watmough and others 2014). However, the ecosystem impacts of alkaline dust on these naturally acidic environments are unknown and understudied. In other regions, high base cation emissions from cement facilities and limestone quarries have led to a suite of undesired consequences including changes in species richness (for example, loss of *Vaccinum* sp.) and a decrease in forest growth/health (Mandre and others 2008; Paal and others 2013; Paoli and others 2015). Mandre and others (2008) for example, reported that Scots pine (*Pinus sylvestris*) trees were heavily impacted (growth, health) by dust emissions in Estonia when soil pH was 6.9–7.9. Impacted sites assessed by Paal and others (2013) had very different species composition compared with un-impacted sites. Lichens, which are a prominent feature of boreal ecosystems, appear particularly vulnerable to alkaline dust (Paoli and others 2015). Further, Macdonald (2015) examined plant community composition at 19 jack pine stands in the region and reported that vascular plant richness was positively correlated with base cation deposition, despite the majority of sites being located some distance (> 20 km) from the main industrial activities.

To adequately manage industrial emissions from oil sands activities, a better understanding of the potential ecological impacts of both acidic (S + N) and base cation deposition is required. In this study we compared soil and vegetation properties in two similar jack pine stands located close (< 3 km—high deposition) and distant (15 km—low deposition) from one of the largest mines in the region to assess whether differences in policy-relevant soil properties (for example, pH) and plant community composition differed between the study forest areas. We hypothesized that the site closest to the mines would have elevated base cation, S and N concentrations in soils and plant tissues and that plant community composition would differ, with an increase in vascular plants and a decrease in lichen cover associated with a fertilization effect.

MATERIALS AND METHODS

The region of northeastern Alberta surrounding the town of Fort McMurray lies in the Boreal Plains ecozone (Environment Canada 1996; Figure 1). The landscape in this region features prominent areas of muskeg peatland, numerous lakes and ponds, and uplands dominated by jack pine and trembling aspen (*Populus tremuloides*). Mineral soils in upland regions are generally acid-sensitive, being Eluviated Dystric Brunisols or, less commonly, Orthic Gray Luvisols (Agriculture and Agri-Food Canada 1998). Typical parent materials include coarse glaciofluvial and till deposits, but coarse materials of aeolian origin are also found in the region. One forest stand (57°4.427′N, 111°35.674′W) is close (< 3 km) to one of the largest open pit mines in the region, while the distant site (57°7.360′N, 111°25.628′W) is an additional 12 km further from the mine and main industrial emission sources. Mean (29 years) annual temperature and precipitation are approximately 0.96°C and 419 mm, respectively (Environment and Climate Change Canada 2015). Industrial activity in the region began in the late 1960s and has resulted in an increase in SO_2, NO_x and NH_3 emissions (Clair and Percy 2015; Wang and others 2012). In 1967 for example, SO_2 emis-
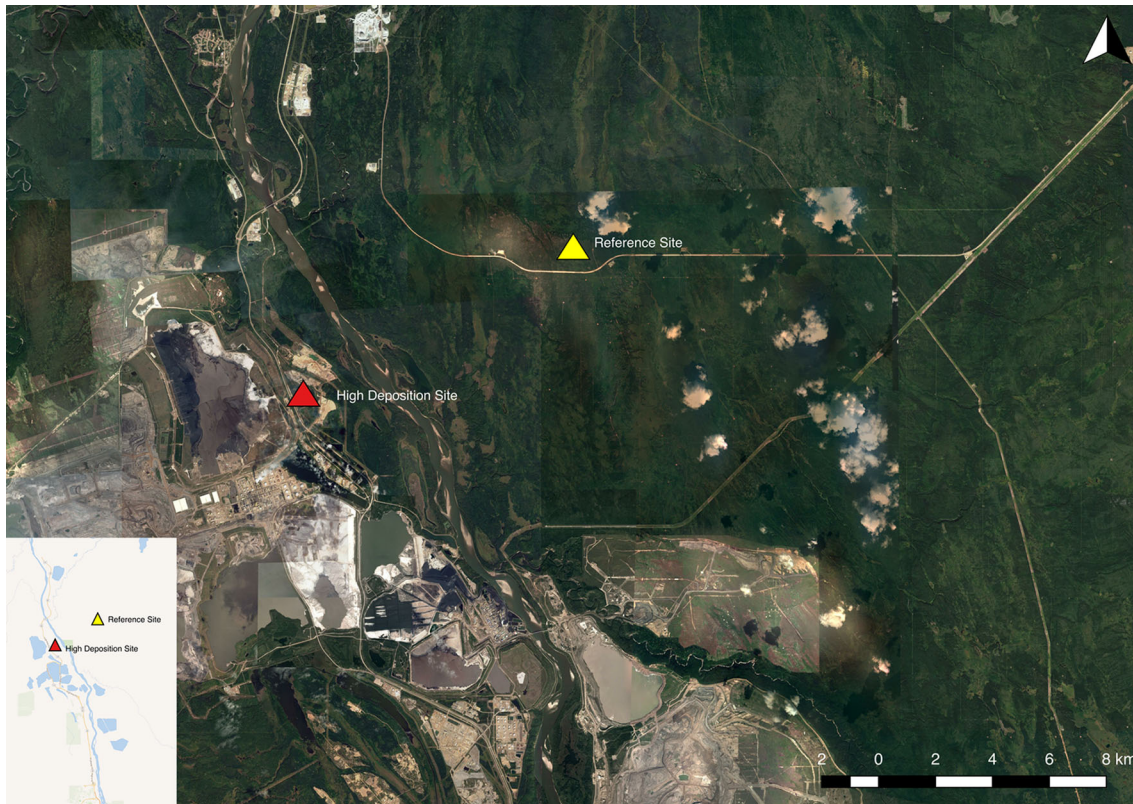
Figure 1. Location of the close and distant forest stands in the Athabasca Oil Sands region of Canada.

sions were estimated to be 132 t day^{-1} peaking in 1995 at 478 t day^{-1} (Clair and Percy 2015). NO$_x$ emissions are less well documented and arise from multiple sources, but Clair and Percy (2015) reported that NO$_x$ emissions increased from around 50 t day^{-1} in 1995 to almost 250 t day^{-1} in 2012. In the present study, measurement of atmospheric deposition fluxes of S and N (NO$_3$-N and NH$_4$-N) at the site (throughfall and open) began in 2008 and continued for three years; base cation (BC) deposition (Ca, Mg, Na) was observed over a 12-month period in 2009–2010 (see Fenn and others 2015; Watmough and others 2014). At the distant site, atmospheric deposition of base cations, SO$_4$-S and DIN was measured using IER columns between 2010 and 2011.

In each forest stand, three randomly selected 20 m by 20 m plots aligned with cardinal directions were established within the two jack pine forests for soil and vegetation analyses. The two stands are similar with respect to topography, soil type and stand age/type to the Terrestrial Environmental Effects Monitoring (TEEM) forest monitoring plots in the region (Clair and Percy 2015) but are not part of this monitoring program. However, the distant site is close (< 1 km) to one of the long-term TEEM plots (JPH4). There was no obvious physical disturbance (harvesting or insect/pathogen infestation) at either site, and forest stand age, density and basal area were comparable and similar to those that are part of the TEEM network (Table 1; Percy and others 2012).

Table 1.   Selected Jack Pine (Pj) Characteristics at the Sites Close (3 km) and Distant (15 km) from the Main Syncrude Mine in the Athabasca Oil Sands

	Bark pH	Basal area (m^2 ha^{-1})	Stem density (ha^{-1})	Height (m)	1st year-100 needle mass (g)	2nd year-100 needle mass (g)	3rd year-100 needle mass (g)
Close	4.6 ± 0.1**	21.4 ± 2.9	1083 ± 192.2	12.2 ± 0.74	0.8 ± 0.0	1.1 ± 0.0	1.3 ± 0.0
Distant	3.9 ± 0.1**	23.8 ± 2.3	1083 ± 117.6	14.5 ± 0.55	0.8 ± 0.0	1.3 ± 0.1*	1.3 ± 0.1

*Values are based on the average of three plots (± SD). Asterisks indicates significant difference (*p < 0.05; **p < 0.01).*

Field Sample Collection

Field sampling at both sites was conducted in mid-July. Soil samples were collected from three different soil pits at three depths (0–10, 15–25 and 40–50 cm), as well as five samples of the forest floor (LFH) within each of the three plots at both sites. The depths roughly comprised the Ah, upper B and lower B horizons. Five samples of the terricolous lichen *Cladonia mitis*, as well as five samples of the three dominant ground vegetation species (*Vaccinium vitis-idaea*, *Vaccinium myrtilloides* and *Arctostaphylos uva-ursi*) were collected from each study plot. Dwarf shrub foliage was removed from the stem and collected. Portions of lichen and bryophytes were lifted from the forest floor intact. All biomass types were transported in paper bags and returned to the laboratory for further processing. Three samples of the corticolous lichens *Hypogymnia physodes* and *Evernia mesomorpha* were also randomly collected at each study site. Within each plot, tree bark samples were collected from five different jack pine trees, as well as three biomass samples collected by removing all vascular plant biomass (excluding trees) within three 25 cm by 25 cm quadrats in each of the three study plots in both forest locations. Pine needles (all 3 years) from two mature *Pinus banksiana* trees per plot were also collected. Upon collection, needle growth years were visually identified and separated by year for chemical and biomass analysis.

Tree Health and Ground Vegetation Assessments

Tree health assessments using the Ecological Monitoring and Assessment Network (EMAN) protocol (Environment and Climate Change Canada and Canadian Forest Service 2004) were conducted upon every tree within each study plot at both the close and distant locations. Tree crown condition was used to assess tree health, placing each tree into one of four categories; crown class 1 refers to a healthy tree (< 10% crown dieback), class 2 refers to a tree with greater dieback (11%-50%), class 3 refers to a tree in severe decline (> 50% crown dieback), and trees with a crown class of 4 were assessed to be dead. Ground vegetation surveys were conducted within each plot by assessing the ground vegetation present at each site by measuring the percent cover of each species within a 1 m by 1 m quadrat. Ten assessments were conducted within each 20 m by 20 m study plot. To assess differences in plant communities between locations, species richness, Simpson's and Shannon–Weiner diversity indices were calculated.

Laboratory Analysis

Soil Samples

All soil samples were air-dried and sieved through a 2-mm mesh before being analyzed. Mineral soil and forest floor samples were analyzed to determine organic matter content, pH, exchangeable base cation saturation and cation exchange capacity (CEC). Soil organic matter (SOM) content was determined by measurement of loss on ignition after heating oven-dried soils at 400°C for 12 h in a muffle furnace. Soil pH was measured in deionized water after a 60-min equilibration period (for example, Lozano 1987), using a 1:4 mass ratio. A two-step un-buffered salt extraction was used in the determination of exchangeable base cations and CEC (Lozano 1987). Exchangeable base cations were removed from soil exchange sites with 1.0 M ammonium chloride and analyzed by flame atomic absorption spectrophotometry (Varian™ 240FS). Sodium chloride was subsequently used to displace the NH_4, with concentrations in the extracts measured by colourimetry (SEAL™ AutoAnalyzer 3 Quattro) and used to quantify CEC. Soil samples were also analyzed for CNS by combustion analysis.

Vegetation Samples

Subsamples of ground lichen, epiphytic lichens, ground vegetation and tree bark were air-dried and ground using electric grinders, and chemical analysis was conducted using the pulverized sample. A portion of each ground vegetation sample was also rinsed with 75 ml of B-pure water (25 ml three times) in order to remove any possible base cations from fugitive dust that had been deposited as dry deposition. Samples were cold-digested in concentrated nitric acid (HNO_3) for 8 h and then hot-digested at 100°C for 8 h before being filtered using a P8 fast-flow paper filter and diluted for instrumentation. All samples of lichens, ground vegetation and tree bark were analyzed for Ca, Mg, K and Na and selected trace metals (for example, Fe, Al, Mn) using a PerkinElmer Inductively Ion Coupled Optical Emission Spectrometer (7000 Dual View). Acid-only blanks and apple leaf standards (NIST 1515) were included with each digestion to check for contamination and element recovery, respectively. The mean recovery rate for the selected analytes ranged from 73 to 87%. Carbon and N concentrations were determined on an Elementar Macro CNS analyzer using dried (60°C) and pul-

verized samples. Biomass of 100 randomly collected needles for each age class for each tree was also determined.

Data Analysis

For all statistical tests, mean values for each of the three study plots at each site were used. All datasets were assessed using a Shapiro–Wilks normality test. Differences in soil chemistry and vegetation parameters between sites were assessed using a two-way two-sample independent Student's t test and a Mann–Whitney U test in the case of non-parametric distributions. All analyses were performed using the stats package in the R software environment (R Core Team 2017).

RESULTS

Throughfall Chemistry

Sulfur, NO_3-N, NH_4-N, Ca, Mg and K inputs measured in throughfall using ion exchange resins differed greatly between the two locations (Table 2). At the site closest to the mine, throughfall SO_4–S deposition was 34 kg ha^{-1} y^{-1} compared with around 8 kg ha^{-1} y^{-1} at the distant site (Table 2). Similarly, inorganic N deposition at the site closest to the mine was around 21 kg ha^{-1} y^{-1} compared with less than 2 kg ha^{-1} y^{-1} at the distant sites and at both sites NO_3-N represented about 60% of the total dissolved inorganic N deposition (Table 2). Throughfall deposition of SO_4-S and DIN at the site close to the mine was approximately four times greater than inputs measured in bulk deposition (Table 2). Despite the high level of acidic (S + N) deposition at the site closest to the mine, Ca + Mg + Na deposition in throughfall exceeded (on an equivalence basis) the combined input of S and N (3.10 vs 2.18 keq ha^{-1} y^{-1}) and was much higher than base cation deposition at the distant

site (Table 2). Throughfall base cation deposition was dominated by Ca, which amounted to 37 kg ha^{-1} y^{-1} at the site closest to the mine compared with 6 kg ha^{-1} y^{-1} at the distant site. Magnesium and Na were similarly about 6 times higher in throughfall at the closest site to the mine compared with the distant site (Table 2).

Soil Chemistry

The site closest to the mine receiving elevated S and N and base cation throughfall deposition had significantly higher exchangeable Ca, Mg and Na concentrations as well as total S content and a significantly higher pH in the surface (LFH) soil horizon compared with the distant site (Figure 2). Soil organic matter and N concentration were also significantly higher in the mineral soil at the site closest to the mine compared with the distant site. Soil chemistry measured at the deepest soil horizon (40–50 cm) was generally more consistent between the two sites with the exception of SOM that was consistently higher at the site close to the mine (Figure 2).

Bark, Lichen and Vascular Plant Chemistry

Jack pine bark and epiphytic lichens, which are often used as biomonitors of atmospheric deposition, had significantly higher concentrations of N, S, Ca and Mg at the mine site compared with the distant site, reflecting the differences in throughfall deposition, although the relative differences in concentration between the two sites were lower than measured in throughfall (< 2 fold compared with 6 fold) (Table 3). Jack pine bark also had a significantly higher pH at the site closest to the mine compared with the distant site (Table 1). Chemical differences between sites in the terricolous lichen (C. mitis) were generally less pro-

Table 2. Annual Open (bulk) and Throughfall (TF) Deposition (kg ha^{-1} y^{-1}) at the Sites Close (3 km) and Distant (15 km) from the Main Syncrude Mine in the Athabasca Oil Sands

kg ha^{-1} y^{-1}	SO_4-S	NO_3-N	NH_4-N	Ca	Mg	Na
Close						
Open	8.7	3.2	2.2	18.1	2.6	2.2
TF	34.0	12.2	8.4	36.9	9.5	10.8
Distant						
Open	6.3	0.6	1.2	n/a	n/a	n/a
TF	8.3	1.0	0.8	6.2	1.4	1.2

n/a not measured.
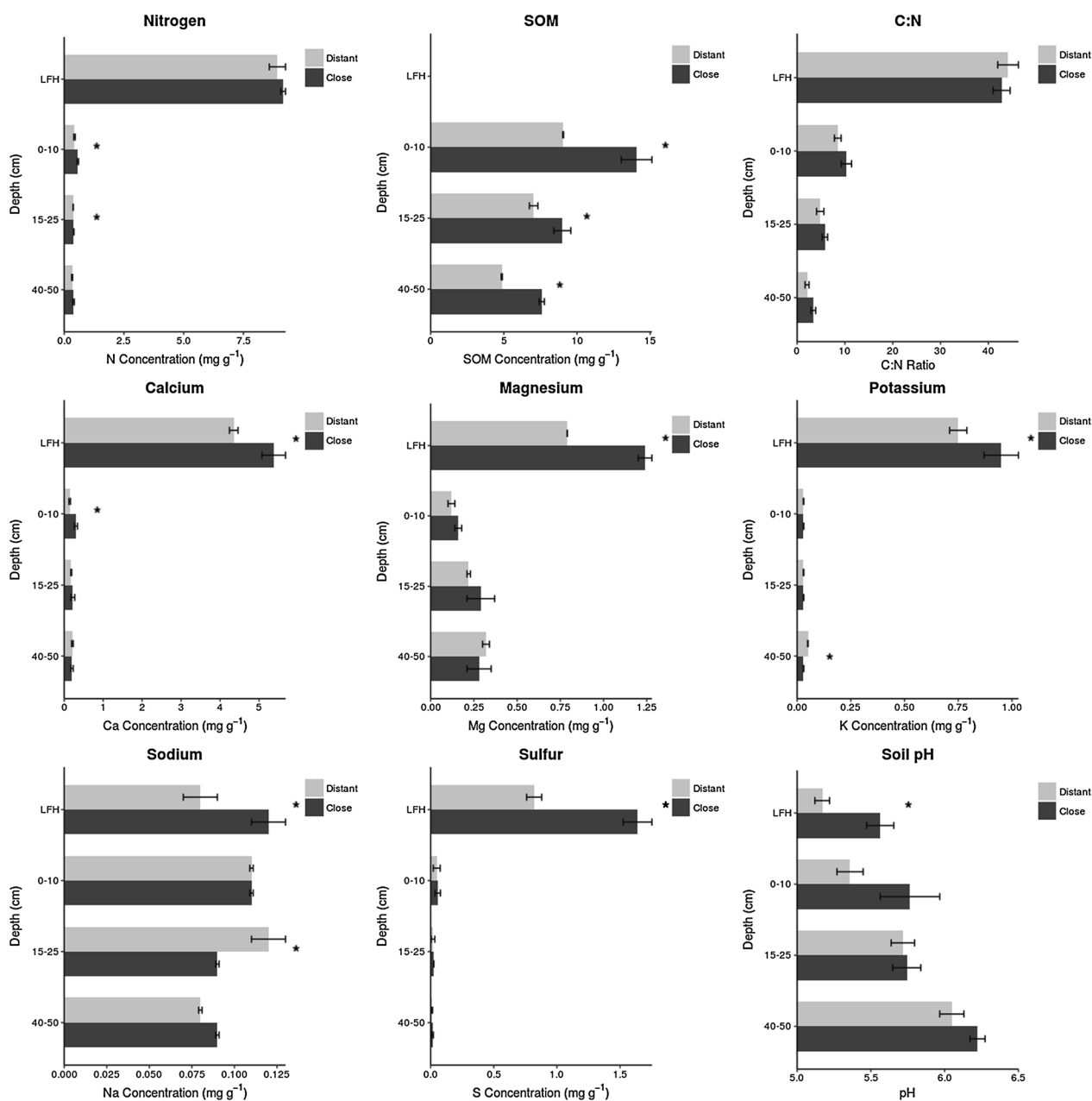
Figure 2. Soil chemical properties (mean ± S.E.) by depth at the sites close (3 km) and distant (15 km) from the main Syncrude mine in the Athabasca Oil Sands. Asterisks indicate significant difference * $p < 0.05$.

nounced than in epiphytic lichens, although base cations, S, N, Mg, Al and Fe were significantly higher at the site closest to the mine (Table 4). Selected trace metals were also measured in jack pine bark and had elevated concentrations of Al, Fe and Zn at the site closest to the mine (Table 3). There were fewer significant differences in the foliar chemistry of vascular plants between the two sites (Table 4). Similar to *C. mitis*, jack pine needles had significantly higher S, Mg, Al and Fe at the site

close to the mine (Table 4). Foliar concentrations of S, base cations, Fe and Al in the three vascular plant species tended to be higher at the site close to the mine, but these differences were not always significant (Table 4). At the site close to the mine, foliar N was only significantly higher in *A. uva-ursi* and was significantly lower in *V. vitis-idaea* compared with the distant site (Table 4). Notably, foliar Mn tended to be approximately 50% lower in vascular plants and *C. mitis* at the site closest to the

Table 3. Mean (± SE) Chemistry of Jack Pine (Pj) Bark and Epiphytic Lichen (*Evernia mesomorpha* and *Hypogymnia Physodes*) at the Sites Close (3 km) and Distant (15 km) from the Main Syncrude Mine in the Athabasca Oil Sands

	S (mg/g)	N (mg/g)	C:N	Ca (g/kg)	Mg (g/kg)	K (g/kg)	Na (g/kg)	Al (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Fe (mg/kg)
Pj Bark											
Close	0.5 ± 0.0*	4.7 ± 0.5	105.3 ± 10.9	5.8 ± 0.3	0.6 ± 0.0	0.4 ± 0.0	0.2 ± 0.0	409.5 ± 38.3	83.9 ± 9.5	38.0 ± 5.4	1638.4 ± 251.8
Distant	0.4 ± 0.1*	3.6 ± 0.3	142.1 ± 13.2*	2.9 ± 0.5***	0.2 ± 0.0***	0.3 ± 0.0	0.1 ± 0.0***	192.8 ± 14.7***	61.4 ± 13.9	13.9 ± 2.3*	203.1 ± 36.8***
Evernia mesomorpha											
Close	2.4 ± 0.2	21.4 ± 1.0	17.3 ± 0.4	13.9 ± 3.9	0.91 ± 0.0	2.1 ± 0.2	0.2 ± 0.0	n/a	n/a	n/a	n/a
Distant	1.4 ± 0.1**	14.1 ± 0.9*	29.7 ± 2.0**	4.8 ± 0.2*	0.6 ± 0.0**	2.1 ± 0.1	0.2 ± 0.0				
Hypogymnia physodes											
Close	2.5 ± 0.3	21.2 ± 1.4	16.9 ± 0.7	20.8 ± 2.5	0.9 ± 0.1	1.9 ± 0.3	0.2 ± 0.0	n/a	n/a	n/a	n/a
Distant	1.1 ± 0.1**	11.7 ± 0.9*	35.3 ± 2.6**	13.7 ± 1.7*	0.7 ± 0.0**	2.0 ± 0.1	0.2 ± 0.0				

*Values are based on the average of three plots (± SD). Asterisks indicates significant difference (*p < 0.05; **p < 0.01; ***p < 0.001).*

mine compared with the distant site, although this difference was only significant for 3 of the 5 species (Table 4).

Plant Biomass and Community Composition and Tree Health

Ground vegetation composition (Figure 3) and vascular biomass (Figure 4) differed greatly between the two sites. Ground cover at the distant site was dominated by terricolous lichens (*C. mitis* and *C. stellaris* represent 30% of the cover), with *A. uva-ursi*, *V. myrtiloidies* and *V. vitis-idaea* being the dominant vascular plants that account for approximately 15% of the ground cover in total. In contrast, even though total ground cover at the site close to the mine was similar (60% close vs 55% distant), it was dominated by vascular plants and *A. uva-ursi* in particular (20%) and species richness was higher (17 species vs 11) at the site close to the mine. In contrast terricolous lichens accounted for less than 5% of the ground cover at the site adjacent to the mine (Figure 3). The site close to the mine also had a higher Shannon–Weiner Diversity Index but lower Simpsons Index (Figure 4), but the difference in the Shannon–Weiner Diversity Index between the sites was not significant. Differences in community composition were reflected in vascular biomass, which was approximately twice as great at the site close to the mine compared with the distant site (Figure 4). There was a small, but significant difference in year 2 needle biomass but no significant differences in biomass of the other needle age classes (Table 1). There was also no significant difference in canopy dieback between the two sites (Table 5).

DISCUSSION

The site closest to the mine receives elevated atmospheric S and N deposition in throughfall, and historically there have been concerns that the base-poor soils in the region will acidify, leading to a degradation in forest health (Whitfield and others 2010). Several studies have previously shown that both acidic and base cation deposition decrease exponentially from distance with the industrial center, but the footprint of atmospheric deposition can extend 20 km or more from the main industrial sources (Landis and others 2012; Fenn and others 2015; Watmough and others 2014). The concern arises because S and N deposition measured in throughfall at the site close to the mine is similar to the high acid deposition levels reported in other parts of the world including eastern North America

Table 4. Mean (± SE) Chemistry of 3rd Year Jack Pine (Pj) Needles, *Cladonia mitis*, *Vaccinium myrtilloides*, *Vaccinium vitis-idaea* and *Arctostaphylos uva-ursi* at the Sites Close (3 km) and Distant (15 km) from the Main Syncrude Mine in the Athabasca Oil Sands

	S (mg/g)	N (mg/g)	C:N	Ca (g/kg)	Mg (g/kg)	K (g/kg)	Na (g/kg)	Al (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Fe (mg/kg)
3rd year Pj Needles											
Close	1.3 ± 0.0	10.0 ± 0.2	50.5 ± 1.3	5.7 ± 0.2	1.3 ± 0.6	2.2 ± 0.8	0.4 ± 0.0	484.9 ± 26.5	711.9 ± 55.0	75.2 ± 5.3	154.2 ± 16.0
Distant	1.1 ± 0.0*	9.5 ± 0.2	53.7 ± 1.1	5.2 ± 0.2	0.6 ± 0.1***	2.5 ± 0.2	0.3 ± 0.0	388.6 ± 35.5*	1294.8 ± 61.7***	55.4 ± 3.6**	95.4 ± 7.1***
Cladonia mitis											
Close	0.5 ± 0.1	7.3 ± 0.6	57.5 ± 4.8	0.9 ± 0.0	0.4 ± 0.0	1.6 ± 0.0	0.1 ± 0.0	309.8 ± 18.7	59.7 ± 2.3	19.4 ± 0.5	1570.5 ± 57.6
Distant	0.4 ± 0.0*	5.8 ± 0.2*	71.9 ± 5.1	0.9 ± 0.0	0.3 ± 0.0***	1.4 ± 0.0**	0.1 ± 0.0	158.5 ± 5.8***	124.3 ± 11.0***	20.8 ± 0.6*	606.3 ± 22.1***
Vaccinium myrtilloides											
Close	1.4 ± 0.1	15.8 ± 1.1	28.9 ± 0.4	5.8 ± 0.3	2.3 ± 0.2	4.1 ± 0.2	0.2 ± 0.0	63.8 ± 7.4	1868.4 ± 303.8	9.9 ± 1.3	265.0 ± 20.7
Distant	1.0 ± 0.4	15.8 ± 1.0	29.1 ± 0.7	4.6 ± 0.3**	1.7 ± 0.1*	3.8 ± 0.1	0.1 ± 0.0**	45.9 ± 2.77	3468.3 ± 199.1**	9.0 ± 0.8	88.1 ± 9.8**
Vaccinium vitis-idaea											
Close	0.9 ± 0.1	9.4 ± 0.0	52.7 ± 0.1	5.7 ± 0.2	1.3 ± 0.0	3.0 ± 0.1	0.1 ± 0.0	59.0 ± 12.5	751.2 ± 161.9	17.6 ± 5.9	152.5 ± 34.0
Distant	0.9 ± 0.0	9.7 ± 0.1*	52.9 ± 1.7	5.3 ± 0.5	1.1 ± 0.2	3.2 ± 0.3	0.1 ± 0.0	55.2 ± 1.94	1176.4 ± 144.9	17.2 ± 2.2	66.5 ± 2.8
Arctostaphylos uva-ursi											
Close	0.5 ± 0.1	10.5 ± 0.5	48.7 ± 3.6	5.9 ± 0.2	1.7 ± 0.0	4.4 ± 0.0	0.1 ± 0.0	20.8 ± 4.8	11.8 ± 5.0	28.8 ± 7.1	88.4 ± 22.0
Distant	0.3 ± 0.0	9.0 ± 0.3*	57.4 ± 3.8**	6.1 ± 0.3	1.3 ± 0.1**	4.4 ± 0.1	0.1 ± 0.0*	10.4 ± 0.6	15.0 ± 2.6	19.6 ± 0.2	56.9 ± 12.9

*Values are based on the average of three plots (± SD). Asterisks indicates significant difference (*p < 0.05; **p < 0.01; ***p < 0.001).*
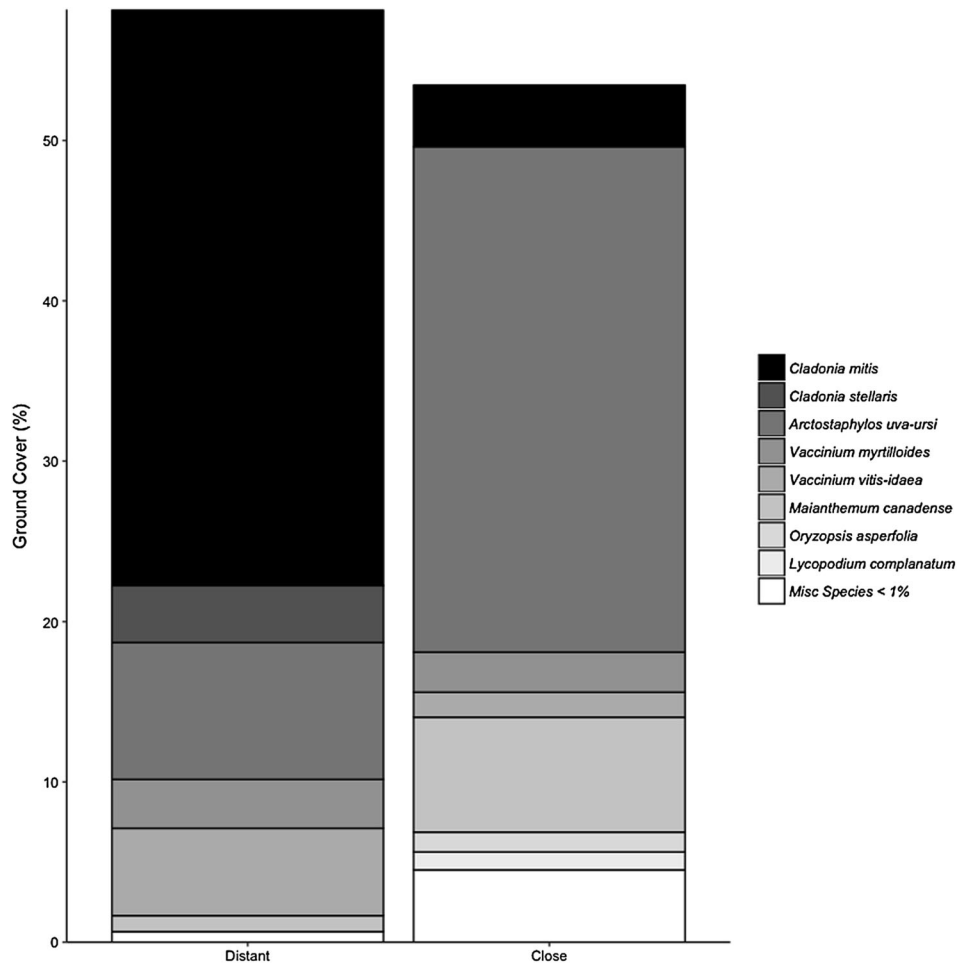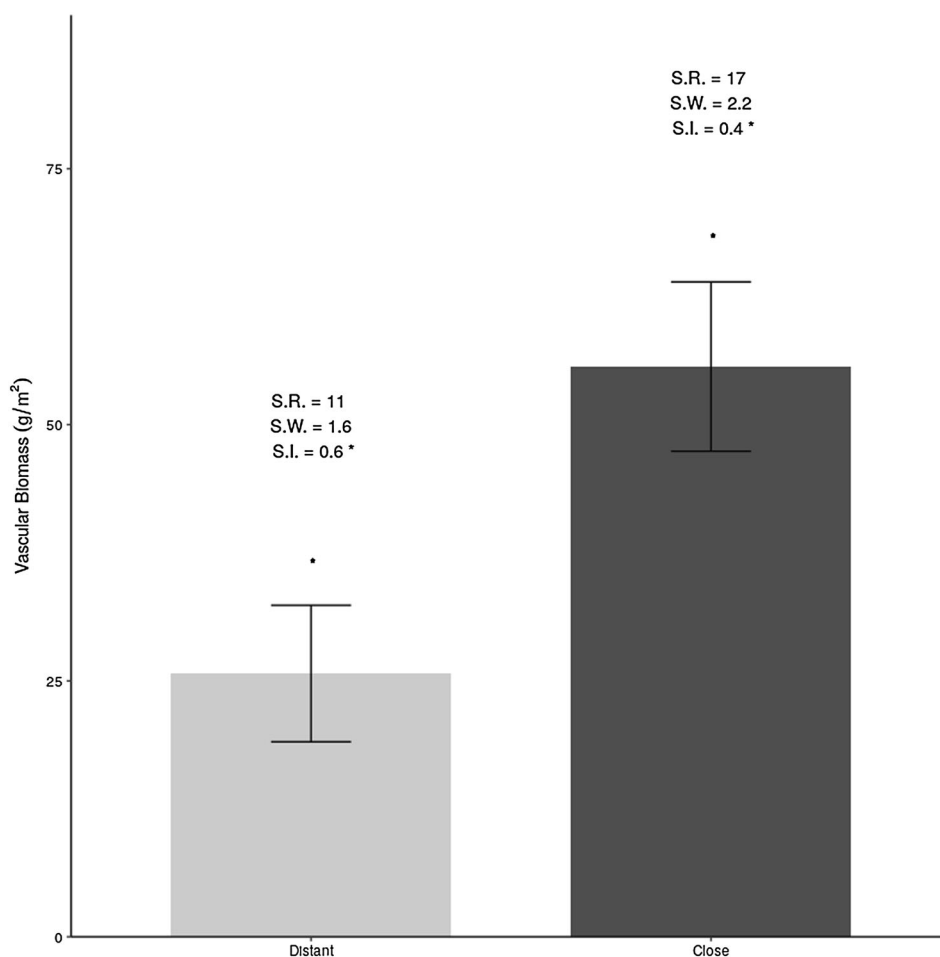
Figure 3. Percentage cover of ground vegetation at the sites close (3 km) and distant (15 km) from the main Syncrude mine in the Athabasca Oil Sands.

(Schindler 1988), Europe (Dise and Wright 1995) and China (Zhang 2006; Guo and others 2010) during the peak of S and N emissions. However, a recent study by Watmough and others (2014) reported on SO_4-S, DIN and base cation deposition in throughfall and in open areas in the region and found that on an equivalence basis, base cation deposition exceeded the combined input of S and N. In this study, despite the fact that the close site receives throughfall SO_4–S and DIN deposition in excess of 30 and 20 kg ha^{-1} y^{-1}, respectively, base cation throughfall deposition was about 30% higher (on an equivalence basis and excluding K that was used as an extractant). In addition, throughfall SO_4 and DIN deposition at the site close to the mine was about four times higher than deposition in open areas (bulk), suggesting that dry deposition comprises a larger fraction of total S and N atmospheric deposition compared with many other parts of North America (Lovett and Lindberg

1993). Landis and others (2012) identified a number of emission sources in the Oil Sands Region including upgrader stacks, fleet emissions and fugitive dust emissions from several sources including haul roads in the mines that are constructed from limestone. Previous modeling studies, however, have failed to adequately account for the fugitive emissions that contain a considerable amount of alkaline dust and hence the potential risk of ecosystem acidification is overstated (Watmough and Whitfield 2015). To date, however, the potential ecological impacts of the high dust levels associated with oil sands activities have not been investigated.

Epiphytic lichen and tree bark tissue had elevated concentrations of S, N, Ca and Mg as well as selected trace metals (tree bark analyzed only) including Al, Fe and Zn at the site closest to the mine compared with the distant site. Epiphytic lichens and tree bark are well-established biomoni-

Figure 4. Mean vascular biomass (+S.D), species richness (S.R.), Shannon–Weiner Diversity Index (S.W.) and Simpsons Diversity Index (S.I.) of all species present at the sites close (3 km) and distant (15 km) from the main Syncrude mine in the Athabasca Oil Sands. Asterisks indicate significant difference *p < 0.05.

Table 5. Percentage of Jack Pine Trees (% dieback ± SD) in Four Dieback Categories at the Sites Close (3 km) and Distant (15 km) from the Main Syncrude Mine in the Athabasca Oil Sands

	0–10% Dieback	11–50%	> 50% Dieback	Dead
Close	30.1 ± 9.4	37.2 ± 0.6	18.6 ± 3.4	14.1 ± 8.4
Distant	43.8 ± 0.8	33.3 ± 4.0	11.8 ± 1.8	11.1 ± 2.7

Values are based on the average of three plots (± SD).

tors, and several studies have similarly reported elevated concentrations of S, N, base cations and many trace metals in epiphytic lichen tissue close to the center of the industrial activities in the oil sands region (Blum and others 2012; Graney and others 2012). In the present study, metal levels in jack pine bark could be up to 8 times higher at the close site compared with the distant site. Although metal levels in lichen tissue are higher close to the

industrial center, it is unknown whether metal concentrations are high enough to adversely impact lichen communities and historically high SO_2 and NO_x have generally been of more concern with respect to ecosystem health in the region (Percy and others 2012). In addition, the pH of tree bark was about 1.0 pH unit higher at the close site, presumably reflecting the high level of alkaline dust deposition. Other studies have similarly found

that the pH of bark of trees growing in the vicinity of cement factories or limestone quarries has a higher pH, and it is well established that bark pH can have a large impact on epiphytic lichen communities (Marmor and others 2010). Finally, atmospheric NH_3 concentrations and NH_4 deposition, which can be toxic to lichens especially, are also elevated close to industrial sources (Fenn and others 2015; Watmough and others 2014). In the present study, NH_4 deposition represented close to half (40%) the total DIN deposition and the sources and potential ecological impact of high atmospheric NH_3 are currently the focus of research in the area.

The higher acidic and base cation deposition at the site closest to the mine is also reflected in differences in the chemistry of the surface soil horizons at the two sites. The pH and base cation (Ca, Mg, K and Na) concentrations in the forest floor were significantly higher at the site closest to the mine, whereas there was generally no significant difference in these chemical parameters in deeper soil horizons indicating that differences in soil chemistry are caused by atmospheric deposition rather than differences in chemistry of the parent material. In contrast, there was no difference in N content of the forest floor although SOM and soil N in the mineral soil were significantly higher at the site closest to the mine. Although elevated base cation deposition offsets the risk posed by acid deposition, elevated dust deposition may have adverse ecosystem impacts that are just as detrimental as acidification (Farmer, 1993). Farmer (1993) reviewed the effects of dust on vegetation and noted that in areas receiving elevated dust emissions plant community structure is altered and that epiphytic lichen and *Sphagnum*-dominated communities are most sensitive. In the majority of studied cases, dust is alkaline in nature as the main sources include limestone quarries and cement factories and limestone dust has been the main concern (Manning, 1971). In a review of the literature, Farmer (1993) identified dozens of studies in which alkaline dust increased the pH of soil or tree bark by 1–2 units and also increased soil base saturation (similar to the present study). In many of these studies, a suite of adverse ecological effects was reported that included altered vegetation communities, impaired tree health and impacted soil fauna communities.

The two jack pine stands were established on similar soils and had comparable overstory characteristics (stand age/density/basal area), yet there were pronounced differences in understory community composition and vascular biomass. The site close to the mine had a higher mean species rich-

ness (17 compared with 11) and is dominated by vascular plants and *A. uva-ursi* in particular (20%); terricolous lichen accounted for less than 5% of the ground cover. As a consequence, the Simpsons Diversity Index was significantly lower at the site close to the mine. In a recent field survey, MacDonald (2015) examined forest understory composition at 19 jack pine stands established between approximately 15 and more than 100 km from the main industrial center in the region and related a number of vegetation response variables to modeled atmospheric deposition. MacDonald reported that 7 of the 12 vegetation cover and richness variables assessed were related to deposition. The strongest relationships were observed with modeled base cation deposition, whereby there were significant relationships between total species richness and vascular cover (increase from 12 to 22%) and richness (increase from 12 to 18 species). The increase in total richness was almost exclusively due to increased vascular plant richness, which in turn was due to increased richness of forbs and shrubs. There were very few graminoids (grasses or sedges) in the community, and they had extremely low cover. Average cover of *A. uva-ursi* at the five sites with the highest predicted IER base cation deposition in the region was 12.6%, compared to an average of 2.9% at the other 14 sites (MacDonald 2015). Overall these results indicate that herbaceous composition at jack pine stands closer to the mines and receiving elevated base cation deposition is increasingly dominated by vascular plants and *A. uva-ursi*, in particular.

In other regions, high base cation emissions from cement facilities and limestone quarries have led to a suite of undesired consequences including changes in species richness (for example, loss of *Vaccinum* sp.) and a decrease in forest growth/health (Mandre and others 2008; Paal and others 2013; Paoli and others 2015). Other studies have also shown that forest health is adversely impacted by alkaline dust emissions, whereas we found no difference in tree health (canopy condition) or needle mass between the two sites. However, our assessment of tree health is rather rudimentary based on visual assessment of the canopy and other metrics (for example, photosynthesis, tree growth, respiration, secondary chemistry) could prove more insightful. Further, even though base cation deposition at the site is high, it is still likely to be much lower than alkaline dust deposition in close proximity to alkaline quarries or cement factories, where soil or bark pH can be up to 2.0 pH units higher than reference sites (Mandre and others

2008). Notably, foliar Mn in jack pine needles, the three vascular plant species as well as the terricolous lichen were much lower (typically 50%) at the site close to the mine compared with the distant site. This difference in foliar/needle/thali Mn is not reflected in tree bark and most likely reflects the decrease in Mn mobility and plant availability that occurs as soils become more alkaline (Watmough and others 2005). These findings are consistent with the higher pH found at the close site despite the high S and N deposition and are in contrast to other acidification studies that suggest Mn toxicity is responsible for vegetation damage (St. Clair and Lynch 2005).

Elevated DIN deposition may also lead to undesired ecological consequences (see Aber and others 1998; Clark and others 2017; Lovett and Goodale 2011). Many studies worldwide have shown that elevated DIN deposition can lead to a cascade of adverse ecosystem effects including soil acidification, increased NO_3 leaching, altered plant diversity and a decline in tree health (Pardo and others 2011; Gilliam 2006; Stevens and others 2004). One consequence of elevated N deposition is reportedly an increase in soil N, leading to a decrease in soil C/N, an increase in nitrification, soil nitrate leaching and plant N uptake and ultimately changes in species composition (Bobbink and others 2010). In the present study, there was no significant difference in the N content of the forest floor between the two sites, but the N content of the mineral soil as well as soil organic matter was significantly higher at the site close to the mine. The lack of a difference in forest floor N concentration may be due to the contribution of pine needles that did not differ between sites and also because a large fraction of N is re-translocated by plants prior to senescence and we have no measurements of litter N inputs at the two sites. In the present study, foliar N concentrations of the three vascular plant species we studied were generally quite similar, with no consistent differences between sites. Previous work at the site close to the mine also showed that soil nitrate concentrations are barely above detection levels (Watmough and others 2013) and we found no difference in net nitrification rates between the sites (unpublished data) indicating that these symptoms of ''N-saturation'' do not yet exist at the study site, even though the understory composition differs dramatically between the sites.

Other work in jack pine forests in the region has shown that the N concentration (and C/N ratio) in the forest floor and mineral soil as well as potential net N mineralization rates was not correlated with N exposure (Laxton and others 2010). Similarly, nitrification rates were negligible suggesting efficient ecosystem immobilization of current N deposition in the region (Laxton and others 2010). Although differences in N concentration between the two sites were very small, taking into account the larger mass of the mineral soil compared with the organic horizon, we estimate that the soil N content at the site closest to the mine was about 700 kg ha^{-1} higher than the distant site—this would represent about 30 years of current deposition. Ongoing N addition studies at jack pine stands in the region (at rates up to 25 kg ha^{-1} y^{-1} applied over 5 years) have shown that the majority of N is assimilated in the forest floor and soil organic pool, with no increase in vascular plant N availability or soil nitrate leaching (unpublished). Ultimately the N appears to be accumulating in the large mineral soil organic N pool, and hence, changes in soil C/N ratio will likely take a considerable time. We also noted that the soil organic matter was significantly greater at the site close to the mine, but values were still very low ($\sim$ 15 mg g^{-1}), which may reflect alterations in litter decomposition. It should be noted that while this study documents differences in soil and plant chemistry and understory composition between the two sites, the mechanisms for these differences and the interaction between high levels of N and base cation deposition require further study.

CONCLUSIONS

This study clearly documents differences in atmospheric deposition, lichen and plant and soil chemistry between a site located close to oil sands activities with a similar aged stand that is more distant from emission sources. We also noted large differences in understory plant community composition and vascular biomass, but the exact mechanism(s) linking these observations has not been established. Nevertheless, an increase in vascular plant cover related to higher base cation deposition appears to be occurring regionally (MacDonald 2015). The lack of pronounced differences in N concentration in plant tissues indicates that elevated N deposition is not primarily responsible for plant community changes even though the changes are consistent with expectations from increased N deposition. Instead, it may be that base cation deposition is more impactful, either through adverse effects on lichens as shown near quarries or through a fertilization effect (perhaps combined with N and or/P). It is also unknown whether vegetation may be responding to the expected more gradual change in soil chem-

istry. Soil base cation pools at the site close to the mine are 30-40% higher than the distant site. For Ca, this represents about 500 kg ha^{-1} compared with a difference in throughfall of around 30 kg ha^{-1} y^{-1} (that is, 15 years of throughfall deposition). Watmough and others (2014) used MAGIC to simulate changes in soil chemistry caused by dust emissions and found that soils reached 100% base saturation within a few decades. What is lacking, however, is a defined critical end point (surrogate to a Bc/Al ratio used in acidification studies) that links changes in soil chemistry to ecological impacts. It may be that soil base saturation or some other similar index may be better linked to vegetation response. Given the potential widespread impact of dust emissions in the region it is suggested that future work should focus on establishing the biogeochemical mechanisms that link possible plant community changes to atmospheric deposition. This should further be expanded to other prominent ecosystems that dominate the regions close to the mines (bogs and poor fens) for emissions emanating from industrial activities in the region to be properly managed.

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