Science of the Total Environment 849 (2022) 157684

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Are bog plant/lichen tissue concentrations of Ca, Mg, K, and P affected by fugitive dust released from oil sands development in the Fort McMurray region of Alberta?

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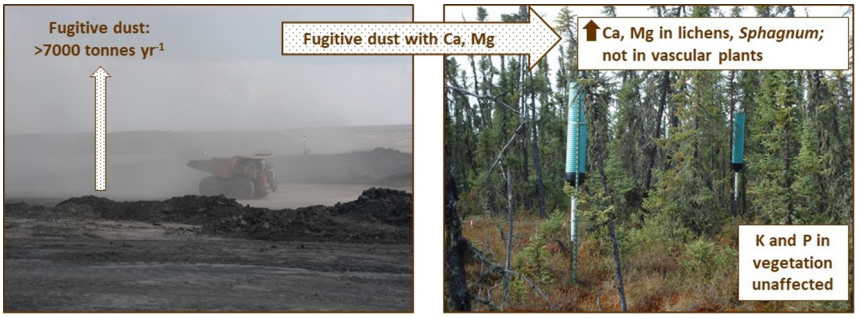
HIGHLIGHTS

- Oil sands operations release over 7000 t of fugitive dust per year.
- Ca^{2+} and Mg^{2+} deposition decreases with distance from oil sands operations.
- Lichen and *Sphagnum* Ca and Mg concentrations increase with distance from the oil sands.
- Fugitive dust increases Ca and Mg loads to bogs in the oil sands region.
- K and P deposition and in lichen/plant tissues are not related to oil sands.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Jan Vymazal

Keywords:
Base cations
Bog
Dust
Oil sands
Phosphorus
Vegetation

ABSTRACT

Bogs are ombrotrophic, relying solely on atmospheric deposition for new inputs of elements. Increased element deposition through anthropogenic activities has the potential to alter nutrient availability, and hence ecosystem function, in bogs. Further, because of efficient element retention, bogs may function as effective monitors of element deposition. To assess the potential effects of particulate fugitive dust from oil sands development in Alberta, Canada, we quantified plant/lichen tissue Ca, Mg, K, and P concentrations in 6 bogs ranging from 12 to 77 km from the oil sands industrial center. Deposition of Ca and Mg, but not K or P, quantified using ion exchange resin collectors, to bogs decreased with distance from the oil sands industrial center. Concentrations of Ca and Mg, but not K or P, in tissues of lichens (*Cladonia mitis*, *Evernia mesomorpha*) and *Sphagnum* (*S. capillifolium*, *S. fuscum*) decreased with distance from the oil sands industrial center. Tissue Ca concentrations were positively correlated with growing season Ca and Mg deposition in all species except *Vaccinium oxycoccos*, *Rhododendron groenlandicum*, and *Picea mariana*; leaf Mg concentrations were positively correlated with growing season Mg deposition for all species except *P. mariana*. Tissue concentrations of K and P were not correlated with growing season K and P deposition. For each species, receptor modeling identified two distinct sources, one dominated by Ca and Mg, presumed to represent particulate fugitive dust from oil sands activities, and a second dominated by K and P, which may reflect tight internal cycling and upward translocation of K and P in peat and/or K and P deposition as particulates generated in wildfires. Increasing Ca^{2+} and Mg^{2+} deposition may acidify bog porewaters through cation exchange in peat.

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http://dx.doi.org/10.1016/j.scitotenv.2022.157684
Received 5 April 2022; Received in revised form 23 July 2022; Accepted 24 July 2022
Available online 31 July 2022

1. Introduction

Associated with oil sands development in northern Alberta, Canada, is the release of NO_x and SO_2 into the atmosphere, from both upgrader stacks and diesel-fueled mine fleets (Davidson and Spink, 2018; Wieder et al., 2021a). These emissions ultimately are returned to regional ecosystems in both wet and dry nitrogen (N) and sulfur (S) deposition, which generally decrease with distance from oil sands facilities (cf. Fenn et al., 2015; Wieder et al., 2016a, 2016b; Hsu et al., 2016; Edgerton et al., 2020). Several studies have shown that N and/or S concentrations in lichens (*Evernia mesomorpha, Hypogymnia physodes, Cladonia mitis*; Addison and Puckett, 1980; Davies, 2012; Laxton et al., 2010; Wieder et al., 2016a, 2021a; Graney et al., 2017; Landis et al., 2019a), *Sphagnum* moss capitula, and leaves of several bog-dwelling vascular plant species (Wieder et al., 2016a, 2021a) reflect spatial patterns in N and S deposition in the oil sands region. In Alberta bogs, increasing N deposition above historically low background levels (<2 kg N ha^{-1} yr^{-1}) stimulates the growth of some bog vascular plant species and appears to be causally related to changing plant species composition, and in particular increasing vascular plant cover and decreasing *Sphagnum* cover (Wieder et al., 2019; Vitt et al., 2020).

In addition to gaseous N and S emissions, oil sands development generates considerable quantities of aeolian particulate matter, or fugitive dust, from sources such as dry tailings sand, gravel roads, quarries, and stockpiles of soil, overburden, coke, and sulfur, with small emissions from heavy hauler fleets (Landis et al., 2012; Wang et al., 2015). In 2017 through 2020, dust emissions ($PM_{2.5}$ and $PM_{10-2.5}$) from oil sands *in situ* development in Alberta averaged 740 and 0.5 metric tonnes, respectively, and from oil sands mining, extraction, and upgrading in Alberta averaged 3602 and 2862 metric tonnes, respectively (Fig. 1). Transition metals and polycyclic aromatic hydrocarbons (PAHs) are associated with oil sands fugitive dust, spurring considerable effort to characterize temporal and spatial patterns in fugitive dust deposition, source apportionment, and receptor modeling (e.g., Larsen and Baker, 2003; Shotyk et al., 2014, 2016; Wang et al., 2015; Mullan-Boudreau et al., 2017; Phillips-Smith et al., 2017; Harner et al., 2018; Landis et al., 2019b; Gopalapillai et al., 2019; Schuster et al., 2019; Stachiw et al., 2019).

Compared to N, S, metals, and PAHs, far less attention has been paid to the potential effects of oil sands-derived base cation (Ca^{2+}, Mg^{2+}, K^+, Na^+) or phosphorus (P) deposition on forest and peatland ecosystems in the oil sands region. Like N and S, deposition of Ca^{2+}, Mg^{2+}, and K^+ appears to decrease with increasing distance from oil sands facilities (Fenn et al., 2015; Wieder et al., 2016b; Edgerton et al., 2020). Spring-time snowpack concentrations of total P, but not of bioavailable P, were elevated near the main area of oil sands industrial activity (Summers et al., 2016). However, anionic ortho-P deposition, assessed using ion exchange resin collectors, did not decrease with increasing distance from oil sands industrial operations (Wieder et al., 2016b). We are not aware of any study that has examined whether increased base cation and/or P deposition affects peatlands, and especially bogs, in the oil sands region.

By their ombrotrophic nature, bogs receive inputs of new Ca, Mg, K, and P solely from atmospheric deposition. Atmospherically deposited base cations are effectively retained in bogs through high cation exchange capacity and low base saturation of peat, but also by uptake and storage in woody biomass (Urban et al., 1995). In general, there is little evidence to suggest that plant net primary (NPP) production in bogs is base cation limited, although under high N deposition, P and/or K limitation may develop (Gunnarsson and Rydin, 2000; Aerts et al., 1992; Verhoeven et al., 1996; Hoosbeek et al., 2002; Bragazza et al., 2004; Wang and Moore, 2014).

There is ample evidence that oil sands development is affecting the N and S chemistry of atmospheric deposition in the oil sands region, while base cation and P deposition have received comparatively less attention. Here, we report tissue Ca, Mg, K, and P concentrations in eight plant/lichen species at six bog sites situated at different distances from oil sands industrial operations. If oil sands-generated fugitive dust contains Ca, Mg, K, and P and affects plant/lichen tissue chemistry, we would hypothesize that: 1) Ca, Mg, K, and P deposition should decrease with distance from the center of oil sands industrial development, 2) Ca, Mg, K, and P

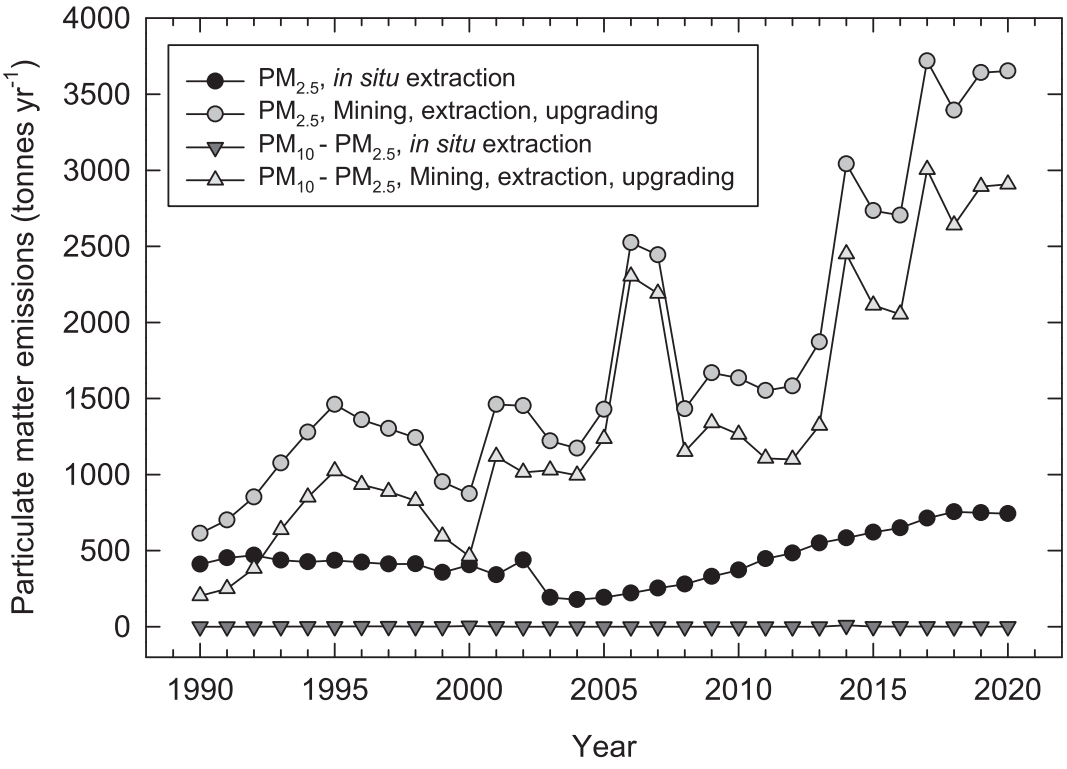

Fig. 1. Annual emissions of Particulate Matter <2.5 μm in diameter ($PM_{2.5}$) and between 10 and 2.5 μm in diameter (PM_{10}-$PM_{2.5}$) from oil sands *in situ* extraction and from oil sands mining, extraction, and upgrading in Alberta.
Source: Environment Canada (https://pollution-waste.canada.ca/air-emission-inventory/).

concentrations in plant/lichen tissues should not only to differ between bog sites, but also decrease with distance from the center of oil sands industrial development; and 3) Ca, Mg, K, and P concentrations in plant/lichen tissues should be positively correlated with growing season Ca, Mg, K, and P deposition, respectively (cf. Wieder et al., 2021a, 2021b). To further understand possible linkages between element deposition and concentrations in plant/lichen tissues, we applied the PCA-MLR (principal component-multiple linear regression) receptor modeling approach to identify sources of Ca, Mg, K, and P to the region's bogs.

2. Methods

2.1. Study sites

Sampling occurred at six bogs ranging from 12 to 77 km from the oil sands industrial center, defined as the midpoint between the Syncrude and Suncor upgrader stacks (JPH4, 57°06′45”N; 111°25′23”W, 12 km; McKay, 57°13′41”N, 111°42′11”W, 24 km; Kearl, 57°19′04”N, 111°13′07”W, 32 km; McMurray, 56°37′37”N, 111°11′44”W, 49 km; Anzac, 56°28′08”N, 111°02′34”W, 69 km; Horse Creek, 56°19′46”N, 111°35′22”W, 77 km). Vegetation is similar at all sites and is typical of Alberta bogs (Belland and Vitt, 1995). The peat surface has a nearly continuous cover of *Sphagnum* mosses (mainly *S. fuscum*, with lesser abundance of *S. capillifolium*, *S. magellanicum*, *S. angustifolium*), an ericaceous shrub layer (*Rhododendron (Ledum) groenlandicum*, *Chamaedaphne calyculata*, *Kalmia polifolia*, *Vaccinium oxycoccos*, *Vaccinium vitis-idaea*), scattered forbs (*Maianthemum (Smilacina) trifolium* and *Rubus chamaemorus*), and an open tree canopy of *Picea mariana*. The epiphytic lichen *Evernia mesomorpha* is abundant on *Picea mariana* branches, and the terricolous lichen, *Cladonia* (*Cladina*) *mitis*, occurs in scattered patches on the peat surface (Vitt et al., 2020). All of the sites are ombrotrophic bogs with pH values in porewater at the top of the water table between 3.8 and 4.7 (Wieder et al., 2021b).

2.2. Ca, Mg, K, and P deposition

At each site, we placed five ion exchange resin (IER) collectors beneath *Picea mariana* canopies (capturing throughfall) and five tubes in the open; two field-deployed resin tubes capped at each end served as blank controls. Resin tubes were replaced in May or June and October over the period from October 2017 through October 2019. Laboratory extraction and analysis followed Wieder et al. (2016b). Data for K deposition are from IER collectors deployed at the bog sites by the Wood Buffalo Environmental Association (https://wbea.org/network-and-data/integrated-data-search/).

Ion exchange resin collectors capture soluble ionic forms of elements, but extract solutions could include elements deposited as particulate matter that dissolves into ionic components upon contact with resins and/or during extraction of resins in the laboratory. Here we refer to deposition of elements without their ionic charges, recognizing most of what is recovered was deposited as soluble ions in precipitation.

2.3. Plant/lichen sampling and analysis

At each site, we collected five replicate samples of each of eight species on three dates in 2018 and in 2019 (June 8–11, July 8–12, August 2–4, 2018; June 7–9, July 9–11, August 2–5, 2019). The five replicate samples were collected, one from each of five different areas within each big separated by at least 20 m. We collected whole thalli of the lichens *Evernia mesomorpha* Nyl. and *Cladonia mitis* Sandst., ~100 cm^2 samples of *Sphagnum capillifolium* (Ehrh.) Hedw. and *Sphagnum fuscum* Klinggräff (in the laboratory, capitula separated from stems and retained for analysis), the topmost 3–5 leaves of *Rhododendron groenlandicum* (Oeder) Kron & Judd and *Vaccinium vitis-idea* (L.), aboveground *Vaccinium oxycoccos* (L.) (in the laboratory, leaves separated from stems and retained for analysis), and apical shoots of *Picea mariana* (Mill.) Britton (current year's growth; in the laboratory, needles separated from stems and retained for analysis). Samples were cleaned to remove debris, oven-dried (60 °C), and ground in a Wiley micromill, generally yielding 2–10 g of dried ground material. One subsample from each replicate was analyzed for Ca, Mg, K, and P in one of two laboratories. At Villanova University, samples were microwave digested (0.25–0.5 g tissue, 10 mL of 68–70 % HNO_3, 15-minute digestion at 200 °C in a Mars 6 digestor). Digest solutions were filtered (Whatman 541 filter paper) and Ca, Mg, K, and P concentrations determined on an Agilent ICP-MS; standards were prepared from dilutions of Agilent Environmental Standard 5183–4688 for Ca, Mg, and Na and Standard 519–8499 for P. Samples not analyzed at Villanova University were sent to QC Analytical, LeClair, Iowa, where they were digested following EPA Method 200.7 (0.5 g tissue, 3 mL 50 % HNO_3, 2 mL 50 % HCl, 3 mL distilled, deionized water, heating on a hot block at 95 °C for 30 min) and analyzed by ICP-OES. For all elements, measured concentrations at either Villanova University or QC Analytical did not differ significantly from NIST or LECO certified concentrations (Table S1).

2.4. Statistical analyses

Given that sampling occurred over time, for element deposition at each site and for tissue concentrations in each species at each site, we assessed potential first-order temporal autocorrelation using the Durbin-Watson test (PROC AUTOREG, SAS v. 9.4).

Because element concentration data for each species were not normally distributed, site differences were assessed using the nonparametric Friedman's test (blocking on sampling date); *a posteriori* site comparisons were made using Tukey's Honestly Significant Difference test (SAS, v. 9.4; Pereira et al., 2015). Exponential regressions of element concentrations in a species (mg g^{-1}) as a function of distance from the midpoint between the Syncrude and Suncor upgrader stacks (km) were fit to tissue Ca, Mg, K, or P concentrations using PROC NLIN (SAS, v. 9.4) and the equation:

$$\textit{Concentration in plant or lichen tissue}\ (mg\ g^{-1}) = A + B \times e^{(-1 \times C \times Distance)}, \quad (1)$$

where A and B are constants (mg g^{-1}) and C is an exponential decay constant (km^{-1}). For significant nonlinear regressions, we report pseudo-R^2 values, calculated as 1 - the ratio of the error sum of squares to the corrected total sum of squares (Lindquist et al., 1994).

We calculated the quantities of Ca, Mg, K, and P in the annual new growth of *S. fuscum* by multiplying element concentrations in capitula by annual net primary production measured at each of the sites in 2018 and 2019 (Vitt et al., 2020).

We carried out receptor modeling using Principal Components Analysis with Multiple Linear Regression (PCA-MLR) (Landis et al., 2012) with varimax rotation using plant/lichen tissue Ca, Mg, K, and P concentration data for each species at all sites (Factor Analysis in JMP, v. 15.0). Identified factors with eigenvalues >1 were retained. However, subsequent to identifying only one significant factor, if the significance test that one factor was sufficient was rejected, we retained a second factor, even if its eigenvalue was <1. In no cases were three factors identified. For each species, after varimax factors were determined, we quantified percent contribution of each element to each varimax factor using stepwise multiple linear regression, with varimax factor scores as the independent variables and plant/lichen tissue concentrations of Ca, Mg, K, and P as dependent variables (Larsen and Baker, 2003; Landis et al., 2012; Salim et al., 2019).

3. Results

3.1. Ca, Mg, K, and P deposition

There was no temporal autocorrelation for Ca, Mg, K, of P deposition at any of the six bog sites (Table S2). Across all sites and sampling dates, Ca, Mg, and P deposition in the open was 1.8 ± 0.2, 0.7 ± 0.05, and 0.13 ± 0.01 kg ha^{-1} yr^{-1}, respectively; Ca, Mg, K, and P in throughfall was 3.1 ± 0.3, 2.3 ± 0.3, 2.2 ± 0.0.5, 0.2 ± 0.04 kg ha^{-1} yr^{-1}, respectively. Averaged over the two years and over open or throughfall placement, Ca

and Mg deposition generally decreased with distance from oil sands operations, with highest values at JPH4 or McKay and lowest values at Anzac or Horse Creek (Fig. 2). While there were site differences in P deposition among sites, there was no evidence of a pattern related to distance from oil sands operations. Deposition of Ca and Mg, but not P, was significantly lower in IER collectors placed in the open than in those placed beneath black spruce (throughfall). Deposition of K differed among sites, but did not exhibit a pattern of decreasing with distance from oil sands operations.

For all four elements, deposition did not decrease exponentially with distance from the oil sands industrial center (Fig. 3). While Ca and Mg deposition decreased linearly with distance from the oil sands industrial center, R^2 values were quite low (0.10 and 0.03, respectively). Neither K nor P deposition exhibited clear trends with distance. Ca and Mg deposition were notably high at the McKay site, K deposition was notably high at the McMurray site, and P deposition was notably high at the Anzac site (Figs. 1 and 2).

3.2. Plant/lichen Ca, Mg, K, and P concentrations

In general, plant/lichen element concentrations did not exhibit temporal autocorrelation (Table S3). For nearly all elements and species, there were significant differences in median Ca, Mg, K, or P tissue concentrations between at least two sites ($p \leq 0.0042$), the lone exception being P concentrations in *S. capillifolium*, for which there were no significant differences among sites (Table 1; means ± standard errors in Table S4). For the two lichen species, *C. mitis* and *E. mesomorpha*, and for the two *Sphagnum* species, *S. capillifolium* and *S. fuscum*, tissue concentrations of Ca and Mg decreased exponentially with distance from the midpoint between the Syncrude and Suncor upgrader stacks, a reference point for the oil sands industrial center (Fig. 4). The only other instances where tissue element concentrations decreased exponentially with distance were for K in *V. oxycoccos* leaves and P in *C. mitis* thalli (Fig. 5); regressions were significant, but with low

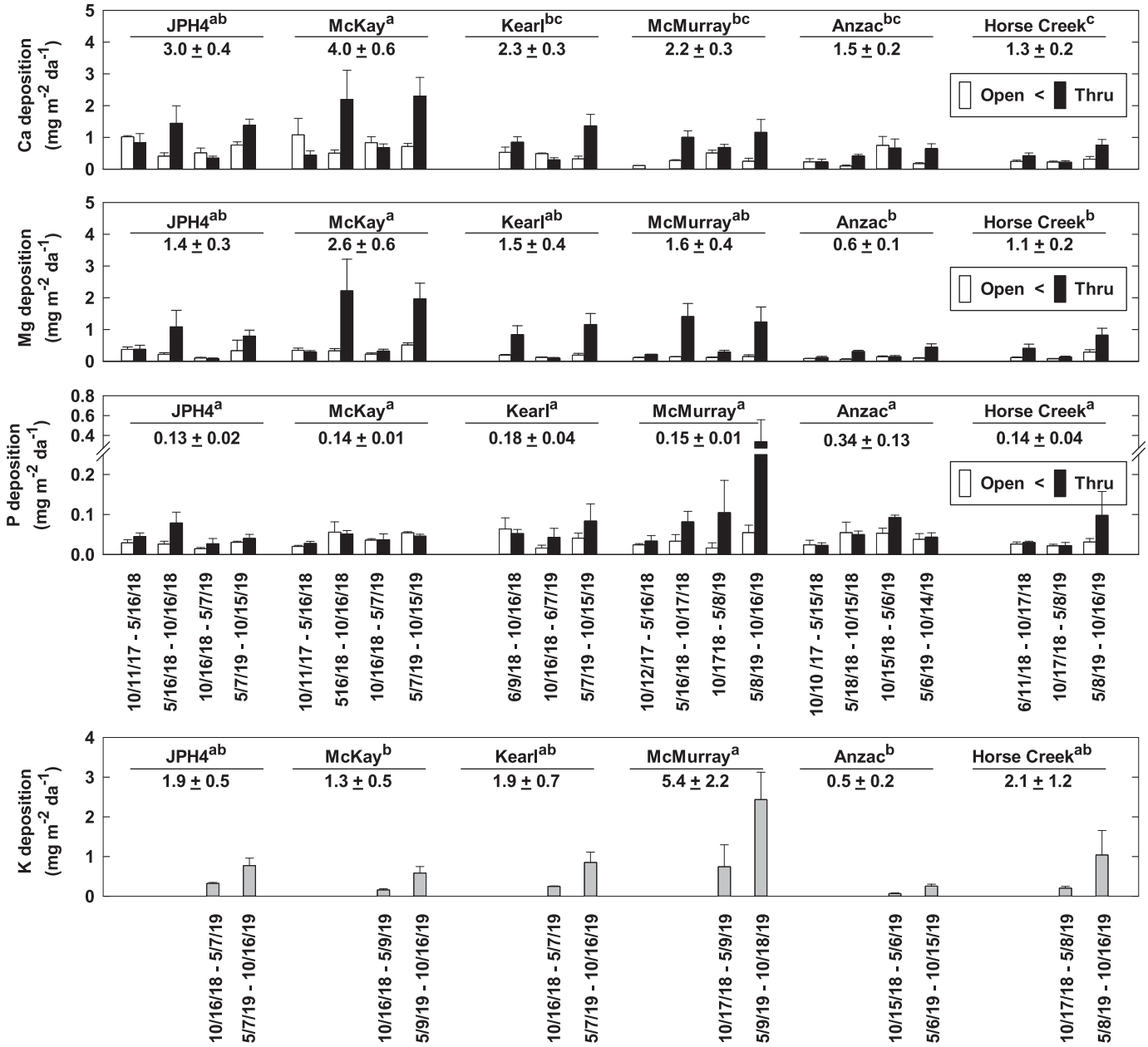

Fig. 2. Element deposition of at the six bog sites as determined using ion exchange resin collectors. Values are means + one standard error; $n = 5$ for Ca, Mg, and P, $n = 2$ for K. Data for K deposition are from the Wood Buffalo Environmental Association (https://wbea.org/network-and-data/integrated-data-search/). Site labels with the same letter superscript do not differ significantly (ANOVA, with collection date as a blocked effect). Numbers beneath site labels are deposition in kg ha^{-1} yr^{-1}).

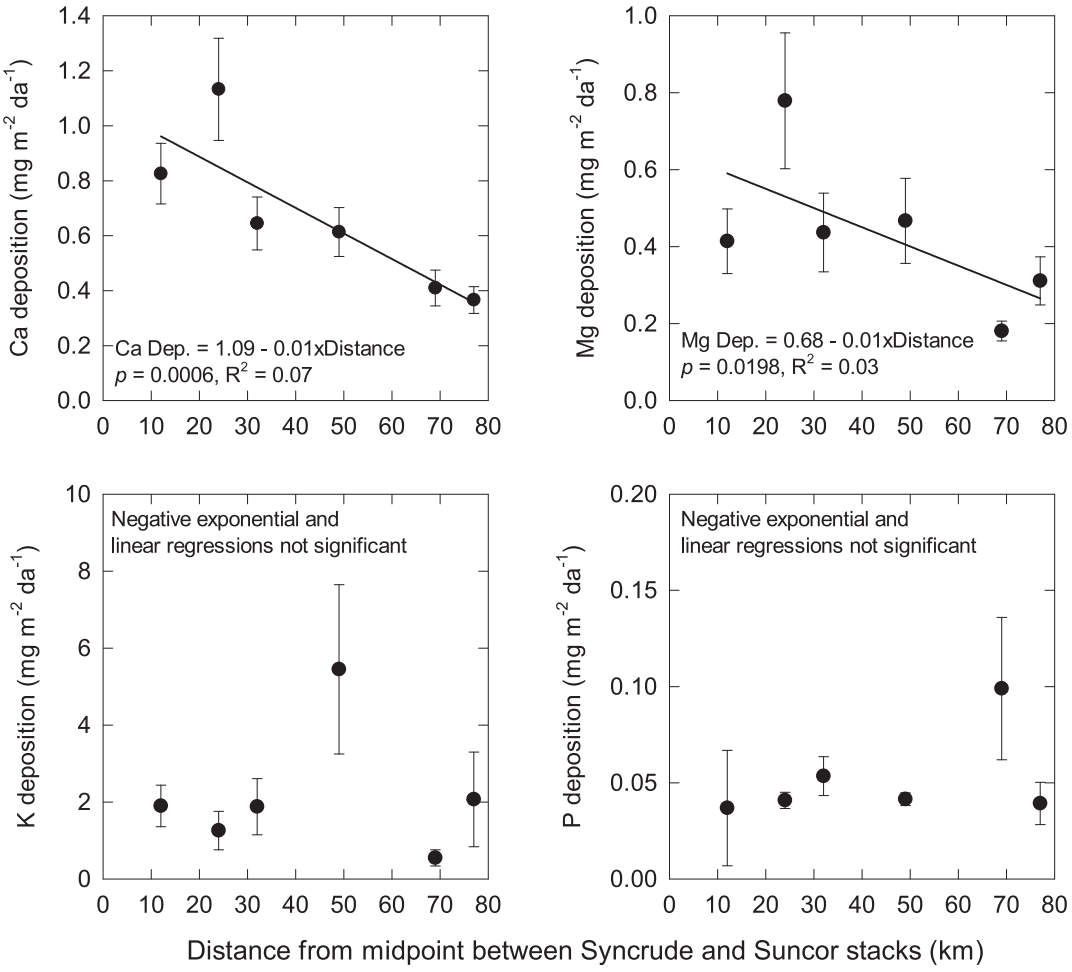

Fig. 3. Deposition of Ca, Mg, K, and from IER collectors. Values are means ± standard errors averaged across all IER collection dates, weighted by the number of days that IER collectors were deployed in the field. Negative exponential regressions did not converge or were not significant. Significant linear regressions are shown.

pseudo-R^2 values (pseudo-R^2 ≤ 0.10) (regression parameters are in Table S5).

Plant/lichen tissue Ca concentrations were positively correlated with growing season Ca deposition for all species except *V. oxycoccos*, *R. groenlandicum*, and *P. mariana*; tissue Mg concentrations were positively correlated with growing season Mg deposition for all species except *P. mariana* (Table 2). Tissue K or P concentrations were not significantly correlated with growing season deposition for any of the plant/lichen species (Table 2).

Receptor modeling identified two factors for each plant/lichen species; the two factors combined explained between 63 % (*V. oxycoccos*) and 91 % (*V. vitis-idaea* and *R. groenlandicum*) of overall variability in plant element concentrations (Tables S6-S13). Communalities, the proportion of tissue Ca, Mg, K, or P concentration variance that can be explained by the two factors, ranged from 0.43 to 1.00, and in general were quite high; 20 of the 32 species/element combinations had communalities ≥0.80. Across all species, one factor was dominated by Ca and Mg and the other factor was dominated by K and P (Fig. 6).

4. Discussion

4.1. Ca, Mg, K, and P deposition

Averaged across all sites and IER collection dates, Ca, Mg, and P deposition are lower than reported in Wieder et al. (2016b) from 2009 to 2014 (10.0, 3.3, and 0.2 kg ha^{-1} yr^{-1}, respectively). Some of these differences may be related to changes in sites where IER collectors were deployed. One of our previous sites (Mildred, 56°55'49" N, 111°28'31" W) was 11 km from the midpoint between the Syncrude and Suncor upgrader stacks and had relatively high Ca and Mg deposition, but the site burned in a 2016 Fort McMurray wildfire so we discontinued monitoring at the Mildred site. We began monitoring at two new sites, Kearl and Horse Creek (32 and 77 km from the midpoint between the Syncrude and Suncor upgrader stacks, respectively) in 2018, and the low Ca and Mg deposition at these sites lowered the overall mean deposition values as compared with deposition values in Wieder et al. (2016b).

Based on IER collectors deployed at 25 jack pine (*Pinus banksiana*) sites in the oil sands region, Fenn et al. (2015) reported that base cation (Ca^{2+} + Mg^{2+} + Na^{+}) deposition decreased exponentially with distance from the oil sands industrial center, but this paper did not separate out the relative importance of each cation (P deposition was not reported). We did not observe an exponential decrease in Ca, Mg, K, or P deposition with distance from the oil sands industrial center (Fig. 3), a pattern that would support the premise that oil sands activities are a major source of fugitive dust that affects Ca, Mg, K and P deposition regionally. However, the absence of such a pattern does not necessarily indicate that fugitive dust from oil sands development is not important. It may be the case that there are other local sources of airborne particulate matter that override a potential oil sands influence. For example, comparing Ca, Mg, and P deposition at JPH4, McKay, McMurray, and Anzac from 2009 to 2014 (Wieder et al., 2016b) with deposition for 2018–2019 reported here, we found no significant difference between the two sampling periods for Ca and Mg deposition at McKay, McMurray, or Anzac, but significantly lower Ca and Mg deposition at JPH4 for 2018–2019 than for the prior period (mean Ca and Mg

Table 1
Element concentrations (mg g^{-1} dry mass) in 8 plant/lichen tissues. Values are medians, n = 28–30 except for *Sphagnum capillifolium* where n = 12–15 (insufficient sample for analysis in 2018). For each element and species, medians with the same letter superscript do not differ significantly (Friedman's test, blocking on sampling date, with a posteriori site comparisons using Tukey's Honestly significant difference test; SAS, v. 9.4; Pereira et al., 2015). Means and standard errors are provided in Table S4.

Element	Species	Site					
		JPH4	McKay	Kearl	McMurray	Anzac	Horse Creek
Ca	*Cladonia mitis*	1400 ^{a}	1300 ^{a}	1000 ^{b}	1000 ^{b}	980 ^{b}	935 ^{b}
	Evernia mesomorpha	13,193 ^{a}	9503 ^{b}	3102 ^{c}	1822 ^{e}	1100 ^{f}	2800 ^{d}
	Sphagnum capillifolium	5300 ^{a}	4600 $^{a-c}$	4700 ^{ab}	4100 ^{c}	2500 ^{d}	4150 ^{bc}
	Sphagnum fuscum	5400 ^{a}	4600 ^{a}	3700 ^{b}	3300 ^{bc}	2550 ^{d}	3200 ^{cd}
	Vaccinium oxycoccos	12,000 ^{a}	11,000 ^{a}	11,000 ^{a}	11,000 ^{b}	10,116 ^{b}	12,058 ^{a}
	Vaccinium vitis-idaea	5400 ^{ab}	5600 ^{a}	5650 ^{a}	5350 ^{a}	4600 ^{c}	4800 ^{bc}
	Rhododendron groenlandicum	4075 ^{bc}	4292 ^{a}	4248 ^{ab}	5084 ^{a}	3290 ^{bc}	2851 ^{c}
	Picea mariana	2312 ^{ab}	2100 ^{ab}	2350 ^{a}	2177 ^{bc}	1843 ^{c}	1750 ^{c}
Mg	*Cladonia mitis*	470 ^{a}	440 ^{a}	280 ^{b}	300 ^{b}	275 ^{b}	290 ^{b}
	Evernia mesomorpha	496 ^{a}	544 ^{a}	345 ^{c}	440 ^{b}	290 ^{d}	310 ^{cd}
	Sphagnum capillifolium	1100 ^{b}	1050 ^{a}	1100 ^{b}	1050 ^{b}	620 ^{c}	1150 ^{b}
	Sphagnum fuscum	1100 ^{b}	1400 ^{a}	955 ^{c}	800 ^{c}	520 ^{d}	930 ^{c}
	Vaccinium oxycoccos	2000 ^{a}	2200 ^{a}	2000 ^{a}	2000 ^{a}	1689 ^{b}	2080 ^{a}
	Vaccinium vitis-idaea	1600 ^{b}	1800 ^{a}	1850 ^{a}	1700 ^{ab}	1300 ^{c}	1300 ^{c}
	Rhododendron groenlandicum	1300 ^{b}	1487 ^{a}	1388 ^{a}	1553 ^{a}	789 ^{c}	845 ^{c}
	Picea mariana	804 ^{c}	810 ^{bc}	1069 ^{a}	963 ^{ab}	811 ^{bc}	838 ^{bc}
K	*Cladonia mitis*	1900 ^{a}	1800 ^{a}	1300 ^{bc}	1450 ^{b}	1700 ^{a}	1150 ^{c}
	Evernia mesomorpha	2400 ^{a}	2346 ^{a}	2052 ^{b}	2399 ^{a}	1900 ^{bc}	1800 ^{c}
	Sphagnum capillifolium	4900 ^{ab}	3950 ^{ab}	4600 ^{ab}	3950 ^{b}	5300 ^{a}	4950 ^{a}
	Sphagnum fuscum	4700 ^{bc}	5500 ^{a}	5100 ^{ab}	4900 ^{bc}	4450 ^{c}	4400 ^{c}
	Vaccinium oxycoccos	5000 ^{a}	5150 ^{a}	4450 ^{b}	5100 ^{a}	4800 ^{ab}	2100 ^{ab}
	Vaccinium vitis-idaea	4200 ^{a}	4350 ^{s}	3450 ^{c}	3750 ^{bc}	4200 ^{ab}	3800 ^{bc}
	Rhododendron groenlandicum	6650 ^{a}	7097 ^{a}	7110 ^{ab}	5350 ^{cd}	4400 ^{c}	4514 ^{d}
	Picea mariana	8429 ^{b}	8900 ^{a}	8500 ^{ab}	7950 ^{c}	8350 ^{ab}	8978 ^{b}
P	*Cladonia mitis*	610 ^{a}	730 ^{a}	510 ^{b}	500 ^{b}	670 ^{a}	465 ^{b}
	Evernia mesomorpha	560 ^{a}	400 ^{bc}	365 ^{cd}	430 ^{b}	496 ^{a}	355 ^{d}
	Sphagnum capillifolium	880 ^{a}	835 ^{a}	920 ^{a}	835 ^{a}	1100 ^{a}	940 ^{a}
	Sphagnum fuscum	750 $^{a-c}$	890 ^{a}	820 ^{a}	675 ^{c}	795 ^{ab}	700 ^{bc}
	Vaccinium oxycoccos	1000 ^{ab}	1100 ^{a}	990 ^{ab}	875 ^{c}	1157 ^{a}	984 ^{b}
	Vaccinium vitis-idaea	820 ^{ab}	935 ^{a}	815 ^{b}	750 ^{b}	970 ^{a}	820 ^{a}
	Rhododendron groenlandicum	1707 ^{a}	1700 ^{a}	1611 ^{a}	1222 ^{b}	1275 ^{b}	1253 ^{b}
	Picea mariana	1545 ^{a}	1565 ^{a}	1371 ^{b}	1200 ^{c}	1605 ^{a}	1503 ^{b}

deposition from IER collectors from 2010 to 2014 of 3.1 and 1.3, respectively; mean Ca and Mg deposition from IER collectors from 2018 to 2019 of 0.8 and 0.4, respectively). Construction of the East Athabasca Highway was completed in 2009, and the road remained unpaved through 2015. The JPH4 site is ~100 m south of the East Athabasca Highway. It is likely that the paving of the East Athabasca Highway reduced fugitive dust deposition from this road to the JPH4 site. Particulate emissions, whether oil sands related or not, may have more of an effect locally (over short distances) than regionally (over longer distances).

4.2. Plant/lichen Ca, Mg, K, and P concentrations

4.2.1. Cladonia mitis and Evernia mesomorpha

Each of the two lichens examined in this study is an association between an ascomycete fungus and a non-N_2-fixing green algal species, most commonly in the genus *Trebouxia* (Piercey-Normore, 2004, 2006). Neither *C. mitis* nor *E. mesomorpha* has a cyanbacterial N_2-fixing symbiont. Lichens in general have widely been used in biomonitoring assessments, as they lack protective tissues (e.g., waxy cuticles of vascular plant leaves) so that they readily absorb elements delivered via wet and dry atmospheric deposition (Giordani, 2019; Abas, 2021). Lichens in general can accumulate elements by particulate trapping, by dissolution of trapped particles on the lichen surfaces and retention of newly formed cations through cation exchange, by retaining cations in precipitation via cation exchange, or by intracellular uptake (Nieboer et al., 1978). Anions, including $H_2PO_4^-$, can be assimilated into lichen biomass through active transport against an electrochemical gradient (Nieboer et al., 1978).

Our findings are consistent with oil sands-derived Ca and Mg being deposited to the region's bogs, where lichens accumulate Ca and Mg (Ca and Mg deposition decreases linearly, but not exponentially, with distance from the oil sands industrial center, Fig. 3; lichen tissue Ca and Mg concentrations decrease exponentially with distance from the oil sands industrial center, Table 1, Fig. 4; lichen Ca and Mg concentrations are significantly correlated with Ca and Mg deposition, Table 2). Atmospherically deposited Ca^{2+} and Mg^{2+} may be retained on lichen cation exchange sites (Puckett et al., 1973). Lichens also can accumulate Ca and Mg when deposited as dust (Gallo et al., 2014). Although lichen Ca concentrations were much higher than those in Table 1, and the lichen species were not *C. mitis* or *E. mesomorpha*, Lucadamo et al. (2015) and Bačkor et al. (2017) demonstrated that high Ca concentrations in lichen tissues can have adverse ecophysiological effects. We note that with increasing proximity to oil sands operations, *E. mesomorpha* on the branches of black spruce trees becomes smaller (our observation), and less luxuriant (Addison and Puckett, 1980); this may be a direct effect of exposure to SO_2, however (Addison and Puckett, 1980; Laxton et al., 2010; Davies, 2012), rather than related to Ca deposition.

Although there are site differences in K and P concentrations in *C. mitis* and *E. mesomorpha* (Table 1), the only instance where K or P tissue concentrations decreased exponentially with distance from the oil sands industrial center was for P in *C. mitis* (Fig. 5). While the negative exponential regression was significant, the pseudo-R^2 value was quite low (0.10). Further, K and P concentrations in the two lichen species were not correlated with K or P deposition, respectively (Table 2). These findings suggest that if regional variation in lichen P or K concentrations is related to oil sands development, other factors acting on a site level may override an oil sands influence.

4.2.2. Sphagnum capillifolium and Sphagnum fuscum

Our findings are consistent with oil sands-derived Ca and Mg being deposited to the region's bogs, where *Sphagnum* species accumulate Ca and Mg (Ca and Mg deposition decreased with distance from the oil sands industrial center, Fig. 2; *Sphagnum* capitulum Ca and Mg concentrations

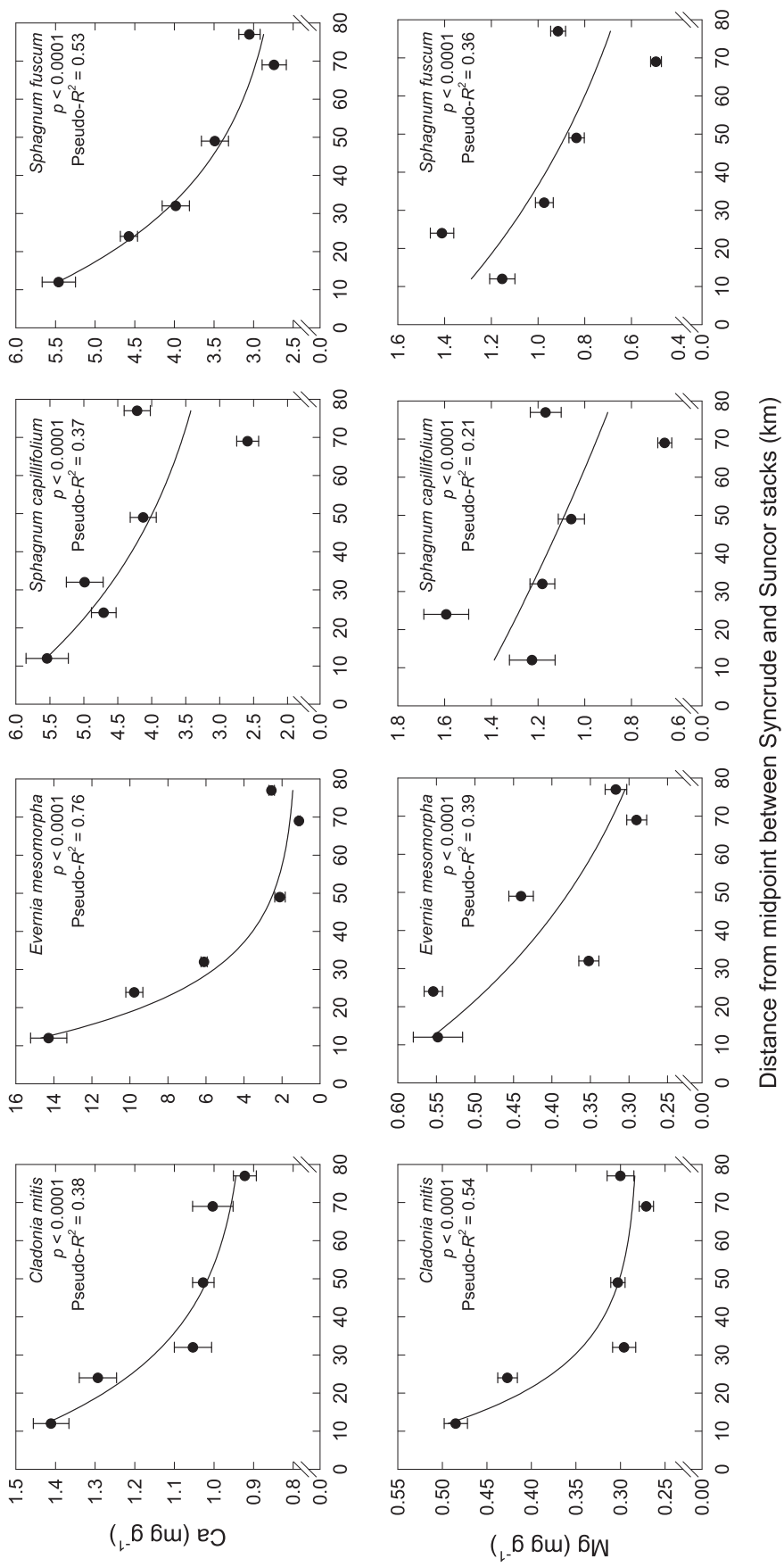

Fig. 4. Negative exponential fits of Ca and Mg concentrations in thalli of *Cladonia mitis* and *Evernia mesomorpha*, and in capitula of *Sphagnum capillifolium* and *Sphagnum fuscum* as a function of distance from the midpoint between the Syncrude and Suncor upgrader stacks. Plotted values are means ± standard errors, averaged across all collection dates. Equation parameters are provided in Table S3.

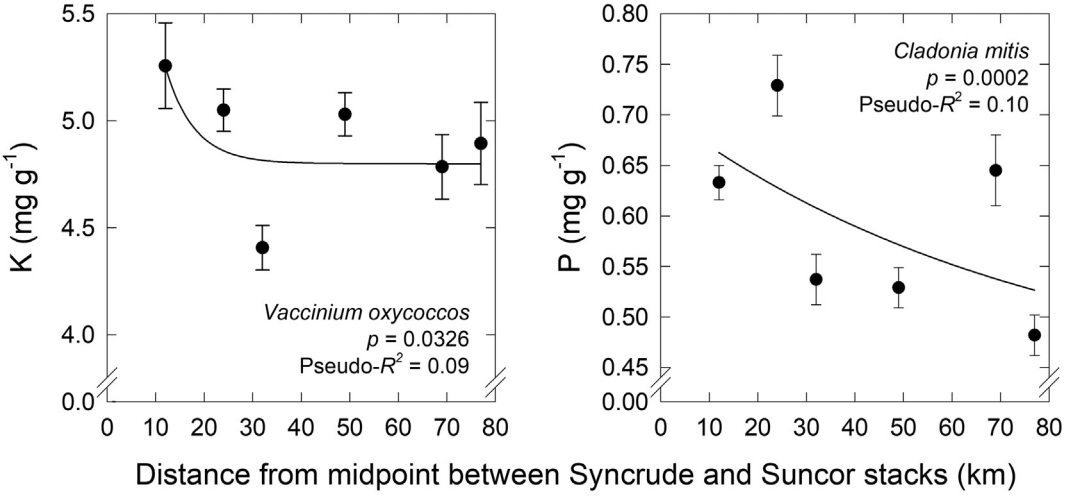

Fig. 5. Negative exponential fits of Mg and K concentrations in *Vaccinium oxycoccos* leaves and P concentrations in *Cladonia mitis* thalli, as a function of distance from the midpoint between the Syncrude and Suncor upgrader stacks. Plotted values are means ± standard errors, averaged across all collection dates. Equation parameters are provided in Table S3.

decreased exponentially with distance from the oil sands industrial center, Table 1, Fig. 4; *Sphagnum* capitulum Ca and Mg concentrations were significantly correlated with Ca and Mg deposition, Table 2). We assume that IER collectors capture ionic Ca^{2+} and Mg^{2+}, but not particulate Ca and Mg, although it is possible that some particulate Ca and Mg deposited to IER collectors may dissolve, with the Ca^{2+} and Mg^{2+} produced retained on the resin. As with lichens, particulate Ca and Mg deposited onto *Sphagnum* plants may dissolve, creating Ca^{2+} and Mg^{2+} that could be taken up into growing *Sphagnum* or could be abiotically retained on peat surfaces by cation exchange. Therefore, it is likely that a substantial component of the high Ca and Mg concentrations in *Sphagnum* capitula close to the oil sands industrial center is more the result of accumulation of Ca^{2+} and Mg^{2+} retention via cation exchange than the result of moss uptake to support growth (cf. Malmer, 1988).

If Ca^{2+} and Mg^{2+} in deposition are effectively retained in the *Sphagnum* layer, we would expect that the quantities of Ca and Mg in new growth of *Sphagnum* would be equal to the quantities in deposition. This was generally the case for Mg, while the quantities of Ca in new *S. fuscum* growth considerably exceeded Ca in deposition (Fig. 7). Mullan-Boudreau et al. (2017) reported annual accumulation through *Sphagnum* growth of Ca and P in bogs in the oil sands region of 199–832 and 40–200 mg m^{-2} yr^{-1}, respectively, values that are somewhat higher than those in Fig. 7. However, Mullan-Boudreau et al. (2017) apparently assumed that the visibly green upper portions of *Sphagnum* plants represent one year's growth, which may or may not be the case. Possible sources of this Ca to support annual growth of *Sphagnum* (and other species) could be dry deposition or uptake of Ca^{2+} produced by decomposition of litter and/or peat. A consequence of binding of Ca^{2+} and Mg^{2+} to cation exchange sites on *Sphagnum* would be the exchange for H^+, which would be released into the peat porewater (cf. Clymo, 1963, 1964, 1984; Kooijman and Bakker, 1994). Such acidification would not result from the release of Ca^{2+} into solution dissolution of $CaCO_3$ in particulate limestone dust, as in general, the other dissolution products would consume H^+ at rates equivalent rates of Ca^{2+} production. A synoptic survey of 23 bogs across the oil sands region indicated that bog porewater at the top of the water table was more acidic at sites near the oil sands industrial center than at sites farther away (Wieder et al., 2016a). Deposition of Ca- and Mg-containing fugitive dust from oil sands development could also contribute to higher concentrations of Ca and Mg in *Sphagnum* capitula if the Ca/Mg containing molecules in particulate dust (other than $CaCO_3$ or $MgCO_3$ in limestone) would dissolve upon encountering the acidic conditions of bog porewater so that Ca^{2+} and Mg^{2+} would bind to cation exchange sites. Beyond potential acidification of bogs, we know of no evidence that increasing Ca and/or Mg deposition or availability has negative consequences for *Sphagnum* ecophysiology or bogs generally.

Unlike Ca^{2+} and Mg^{2+}, which accumulate mainly on *Sphagnum* cation exchange sites, K and P accumulate mainly intracellularly in *Sphagnum* (Hemond, 1980; Malmer, 1988). Although K^+ does bind to cation exchange sites on *Sphagnum* surfaces, its competitivity is lower than for Ca^{2+} or Mg^{2+} (Breuer and Melzer, 1990). Capitulum exchangeable: intracellular ratios for Ca^{2+}, Mg^{2+}, and K^+ were 3.4 and 0.4, 0.06, respectively for *Sphagnum fuscum* and 2.6, 0.4, and 0.4, respectively, for *Sphagnum capillifolium* (Hájek and Adamec, 2009), reflecting a strong cation exchange role for Ca^{2+} and a strong intracellular role for K^+ in *Sphagnum*.

Sphagnum cell walls have negligible anion exchange capacity (Clymo, 1963), so P deposited in ionic form in precipitation, or in particulate form that creates anionic P through dissolution, is retained almost exclusively by plant uptake. For K and P, the annual demand to support new growth of. *fuscum* ranged from 7.7 (Anzac) to 10.0 (McKay) kg ha^{-1} yr^{-1} for K and from 1.2 (Horse Creek) to 1.6 (McKay) kg ha^{-1} yr^{-1} for P (cf. Fig. 7). Averaged across all sites, collection dates, and open versus throughfall collectors, mean K and P deposition is 2.2 and 0.2 kg ha^{-1} yr^{-1}. Clearly, annual wet deposition of K and P, quantified using IER

Table 2
Pearson correlations between growing season deposition of an element (mg m^{-2} da^{-1}; determined from ion exchange resin collectors) and concentrations of that element in plant or lichen tissues. Correlations were performed on mean element deposition and mean element concentration at each site in each year ($n = 12$, except for *S. capillifolium* where $n = 6$). Significant ($p \leq 0.10$) one-sided correlations and associated p values are highlighted in bold, italic text.

Species		Element			
		Ca	Mg	K	P
Cladonia mitis	*r*	***0.688***	***0.493***	−0.646	−0.420
	p	***0.007***	***0.052***	0.918	0.913
Evernia mesomorpha	*r*	***0.751***	***0.717***	−0.578	−0.274
	p	***0.002***	***0.004***	0.776	0.816
Sphagnum capillifolium	*r*	***0.649***	***0.912***	−0.891	−0.787
	p	***0.081***	***0.006***	0.992	0.978
Sphagnum fuscum	*r*	***0.776***	***0.810***	−0.906	−0.864
	p	***0.002***	***0.001***	0.994	>0.999
Vaccinium oxycoccos	*r*	0.191	***0.665***	−0.669	−0.859
	p	0.276	***0.009***	0.927	>0.999
Vaccinium vitis-idaea	*r*	***0.630***	***0.581***	−0.980	−0.882
	p	***0.014***	***0.024***	0.999	>0.999
Rhododendron groenlandicum	*r*	0.382	***0.652***	−0.611	−0.842
	p	0.110	***0.011***	0.902	>0.999
Picea mariana	*r*	0.151	−0.035	−0.603	−0.901
	p	0.320	0.543	0.897	>0.999

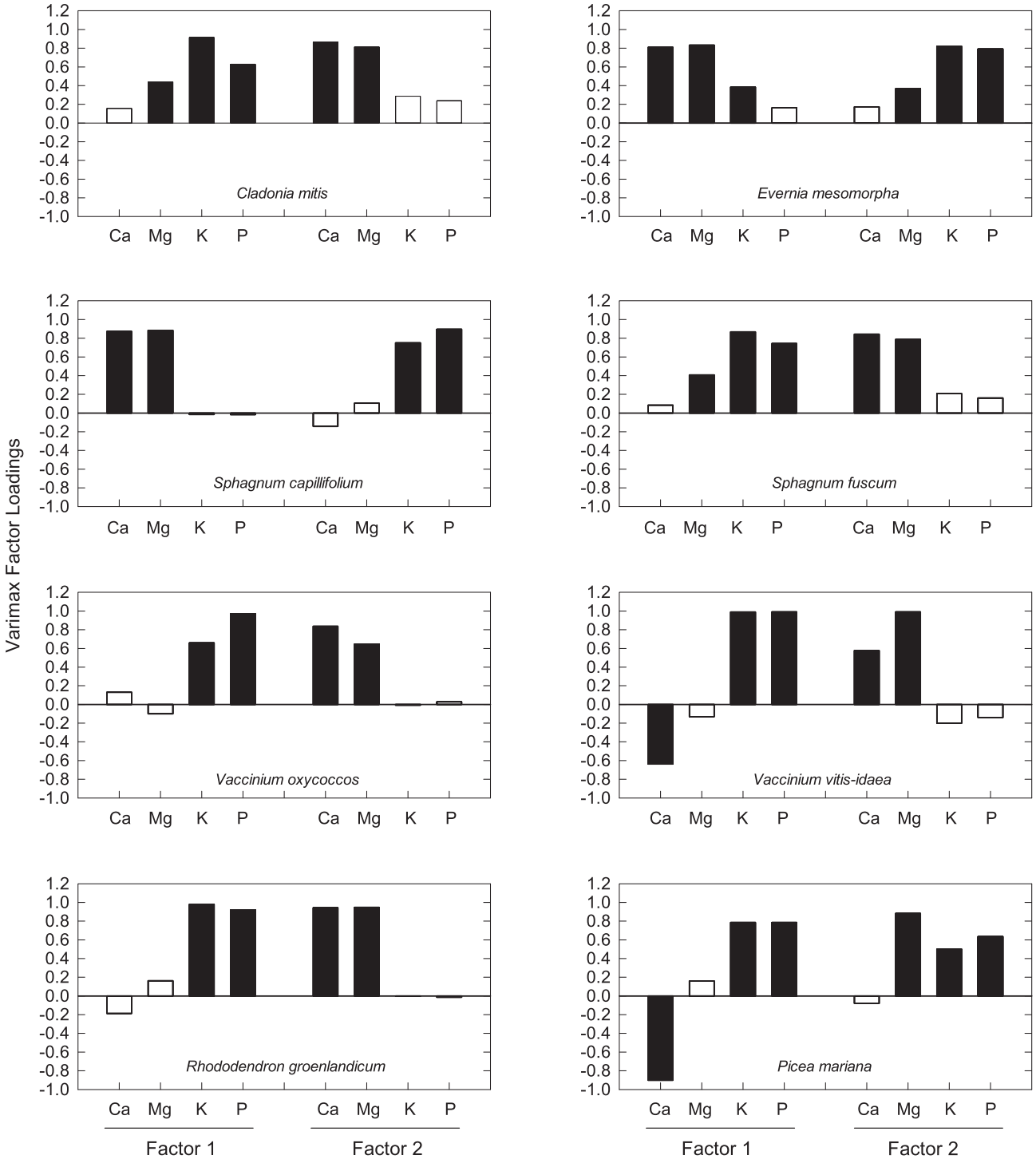

Fig. 6. Varimax factor loadings for the two identified factors for each of the eight plant/lichen species.

collectors, is a minor contributor to the annual K and P economy of *Sphagnum,* even if wet deposition is multiplied by 2 as a rough estimate of dry deposition. Much of the P required for new *Sphagnum* growth may come from upward translocation within plants to the capitulum (Rydin and Clymo, 1989), which is consistent with P concentrations in *Sphagnum* capitula being considerably higher than in *Sphagnum* stems (Malmer, 1988; Živkovič et al., 2017). Upward translocation of K in *Sphagnum* may occur as well, as evidenced by upward translocation of ^{137}Cs derived from the Chernobyl accident in *Sphagnum* (Gerdol et al., 1994; Rosén et al., 2009), and surface peat being highly enriched in K relative to deeper peat (Malmer, 1988; Shotyk et al., 1990). As with the two lichen species, K and P concentrations in *Sphagnum* capitula do not appear to be influenced by K and P deposition.

4.2.3. Vaccinium oxycoccos, Vaccinium vitis-idaea, Rhododendron groenlandicum, and Picea mariana

For each species and each element, there were differences in leaf concentrations among sites (Table 1), but in no instances did leaf element concentrations decrease exponentially with distance from oil sands operations. Leaf Ca concentrations in *V. vitis-idaea* were correlated with growing season Ca deposition, leaf Mg concentrations in the two *Vaccinium* species and in *R. groenlandicum* were correlated with growing season Mg deposition

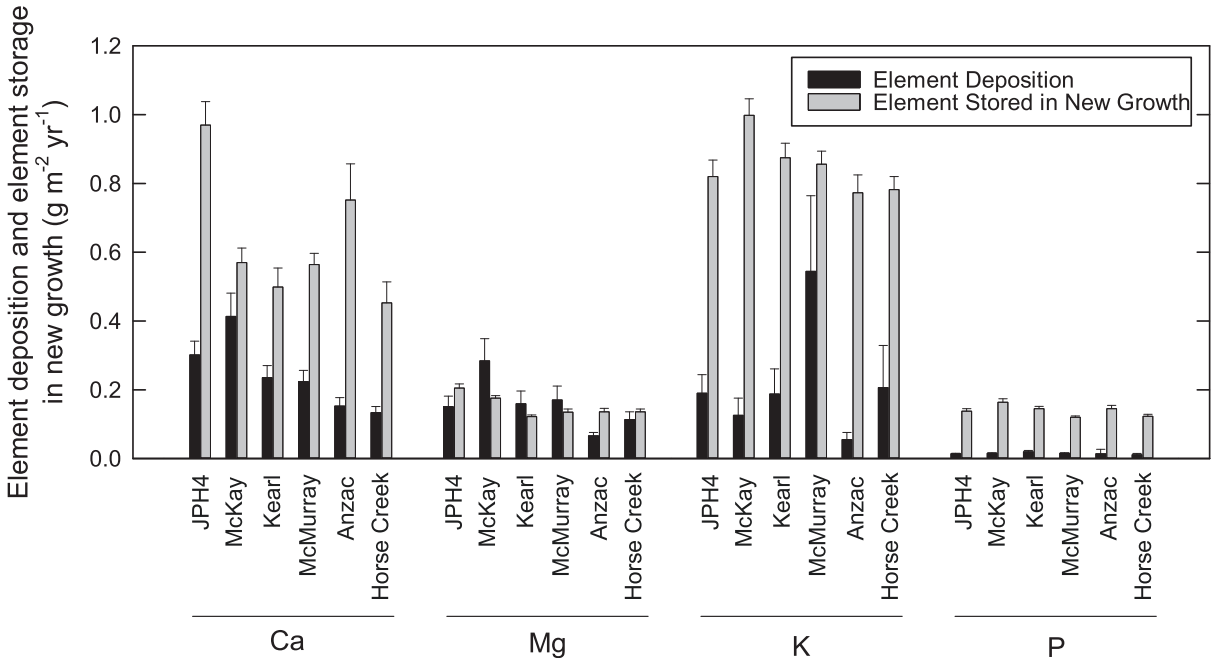

Fig. 7. Deposition of Ca, Mg, K, and P, determined using ion exchange resin collectors, and the quantities of Ca, Mg, K, and P in annual growth of *Sphagnum fuscum* at each of the six bog sites. Values are means + one standard error, averaged across 2018 and 2019.

(Table 2), observations that are consistent with the hypothesis that leaf Ca and Mg concentrations are influenced by oil sands-derived wet and/or dry Ca and/or Mg deposition. In no instance were leaf concentrations correlated with K or P deposition.

It is likely that demands of Ca, Mg, K, and P to support NPP of vascular plants are largely met by internal recycling of these elements within the peat acrotelm. The high cation exchange capacity and low base saturation of living *Sphagnum* and of *Sphagnum*-derived peat efficiently scavenge and retain atmospherically deposited Ca^{2+}, Mg^{2+}, and K^{+}, along with particulate C, Mg, and K that may dissolve in surface peat, such that these elements do not move downward through the upper peat layers where they could be taken up by vascular plants. Similarly, atmospherically deposited P may be effectively retained through uptake of growing *Sphagnum* mosses. The effective retention of Ca, Mg, K, and P in the topmost peat ensures that porewater concentrations of these elements are maintained at quite low levels. Most vascular plant species in Alberta bogs are mycorrhizal, including the four species examined in this study (*V. oxycoccos, V. vitis-idaea*, and *R. groenlandicum* host ericoid mycorrhizae; *P. mariana* hosts ectomycorrhizae). These mycorrhizal associations facilitate element uptake from bog water with low element concentrations (e.g., Liu et al., 2020) and hence may be critical to the Ca, Mg, K, and P economies of these vascular plant species.

4.2.4. What are the sources of Ca, Mg, K, and P to bogs in the oil sands region?

Receptor modeling gave remarkably similar results for each of the 8 lichen/plant species, identifying two factors – one dominated by Ca and Mg, and the other dominated by K and P. The PCA-MLR approach is based on plant tissue element concentrations and does not incorporate distance from oil sands operations as a variable. We interpret the Ca and Mg factor as indicative of fugitive dust deposition onto bogs not only from haul roads on oil sands mine sites, typically constructed with limestone rock, with high Ca and Mg concentrations (Ca, 27.8 mg g^{-1}; Mg, 6.3 mg g^{-1}; Landis et al., 2012), but from other gravel roads throughout the oil sands region, and/or fugitive dust from the Hammerstone Limestone Quarry, the major source of crushed limestone in the oil sands region. Other potential sources of Ca- and Mg- containing fugitive dust in the oil sands region, include releases from overburden (Ca, 1303 μg g^{-1}; Mg, 1004 μg g^{-1}), tailings sand (Ca, 355 μg g^{-1}; Mg, 129 μg g^{-1}) and heavy hauler fleets (Ca, 9914 μg g^{-1}; Mg, 62 μg g^{-1}), and main upgrader stacks (Ca, 411 μg g^{-1}; Mg, 90 μg g^{-1}) (Landis et al., 2012). We interpret the K- and P-dominated factor as indicative of internal recycling of these elements within bogs, with a strong upward translocation to the surface peat layers, and/or dry deposition to lichens with dissolution and uptake rather than immobilization on exchange sites on lichen cell walls. Of course, upward translocation of K and P should have no effect on K and P concentrations in the arboreal lichen *E. mesomorpha*. It is possible that the K- and P-dominated factor identified through PCA-MLR could represent K and P deposition from biomass burning. Wildfires are common in the oil sands region and $PM_{2.5}$ emissions, enriched in K and P, from wildfire in smoke can travel considerable distances (Landis et al., 2012, 2019b). Deposition of K- and P-enriched $PM_{2.5}$ onto bogs could affect K and P tissue concentrations in lichens, mosses, and vascular plants, and could also contribute to high concentrations of K and P in surface peat. Nonetheless, this K- and P-dominated factor appears to be unrelated to oil sands activities.

5. Conclusions

Three patterns support the hypothesis that Ca- and Mg-containing fugitive dust from oil sands operations affects bog plants/lichens. First, Ca and Mg deposition decrease with increasing distance from the oil sands industrial center. Second, tissue concentrations of Ca and Mg in the two lichen species (*C. mitis* and *E. mesomorpha*) and in the two *Sphagnum* species (*S. capillifolium* and *S. fuscum*) decrease exponentially with increasing distance from the oil sands industrial center. Third, tissue Ca concentrations in *E. mesomorpha* and *S. capillifolium* and tissue Mg concentrations in the two lichen species and the two *Sphagnum* species are positively correlated with growing season Ca and Mg deposition. Beyond acidification of bog porewaters, mediated by the binding of deposited Ca^{2+} and Mg^{2+} to cation exchange sites on *Sphagnum* cell walls, there appear to be no detrimental effects of Ca and Mg deposition to bog plant/lichen species. In contrast to lichens and *Sphagnum*, there is no evidence to indicate that regionally elevated Ca and Mg deposition affects vascular plant species in bogs. Although there are site differences in K and P deposition, there is no evidence to support the hypothesis that K- and P-containing fugitive dust from oil sands operations affects bog plants/lichens. Receptor modeling indicated two sources of Ca, Mg, K, and P. One source is dominated by Ca and Mg

and is most likely linked to deposition of oil sands-derived fugitive dust. The other source is dominated by K and P, reflecting strong internal cycling and upward translocation of K and P in surface peat, and/or K and P deposition from particulates generated in wildfires.

CRediT authorship contribution statement

R. Kelman Wieder: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization, Supervision, Project administration, Funding acquisition. **Kimberli D. Scott:** Methodology, Validation, Investigation, Resources, Data curation, Writing – review & editing, Supervision, Project administration. **Melanie A. Vile:** Conceptualization, Methodology, Investigation, Writing – review & editing, Project administration, Funding acquisition. **Caitlyn Herron:** Investigation, Data curation, Writing – review & editing.

Data availability

Link is provided, but this data set is not yet viewable. The AOSR bog plant and lichen tissue element concentration data are available at the Environmental Data Initiative: https://doi.org/10.6073/pasta/043c6ebb2e2294ab96f0bdcaff10601e. Data set has been submitted, but Kimberli Scott, who handles this for our group is on vacation through August 3. Our group is firmly committed to making our data publicly available.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was supported by the Oil Sands Monitoring Program and is a contribution to the Program (Grant # 18GRAEM07 and amendments to MAV and RKW), but does not necessarily reflect the position of the Program. We thank Jeremy Hartsock for the photograph used in the graphical abstract. This work received funding from the Villanova University Falvey Memorial Library Scholarship Open Access Reserve (SOAR) Fund. K deposition data were from the Wood Buffalo Environmental Association (WBEA), Fort McMurray, Alberta, Canada (https://wwbea.org/network-and-data/integrated-data-search/). The content and opinions expressed by the authors do not necessarily reflect the views of the WBEA, its affiliates, directors, officers, employees, agents or its membership.

Land acknowledgement

We acknowledge the traditional, unceded territories of the Cree, Denendeh (Dënësųłinë Nëné), Michif Piyii (Métis), Beaver, Beaver Lake Cree, Bigstone Cree, and Woodland Cree First Nations on which our research sites lie. We acknowledge the systems of oppression that have historically dispossessed indigenous people of their lands and rights. We are ever vigilant that as researchers, we are but transient and humble visitors to these lands.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.157684.

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