Environmental Science & Technology

Article

pubs.acs.org/est

Differential Effects of High Atmospheric N and S Deposition on Bog Plant/Lichen Tissue and Porewater Chemistry across the Athabasca Oil Sands Region

R. Kelman Wieder,*[,†] Melanie A. Vile,[†,‡] Kimberli D. Scott,[†] Cara M. Albright,[†,§] Kelly J. McMillen,[‡] Dale H. Vitt,[⊥] and Mark E. Fenn[¶]

[†]Department of Biology, [‡]Department of Geography and the Environment, and [§]Department of Civil and Environmental Engineering, Villanova University, Villanova, Pennsylvania 19085, United States

[⊥]Department of Plant Biology, Southern Illinois University, Carbondale, Illinois 62901, United States

[¶]USDA Forest Service, Pacific Southwest Research Station, 4955 Canyon Crest Drive, Riverside, California 92507, United States

Supporting Information

ABSTRACT: Oil extraction and development activities in the Athabasca Oil Sands Region of northern Alberta, Canada, release NO_x, SO_x, and NH_y to the atmosphere, ultimately resulting in increasing N and S inputs to surrounding ecosystems through atmospheric deposition. Peatlands are a major feature of the northern Alberta landscape, with bogs covering 6−10% of the land area, and fens covering 21−53%. Bulk deposition of NH_4^+−N, NO_3^-−N, dissolved inorganic N (DIN), and SO_4^{2-}−S, was quantified using ion-exchange resin collectors deployed at 23 locations, over 1−6 years. The results reveal maximum N and S deposition of 9.3 and 12.0 kg ha^{-1} yr^{-1}, respectively, near the oil sands industrial center (the midpoint between the Syncrude and Suncor upgrader stacks), decreasing with distance to a background deposition of 0.9 and 1.1 kg ha^{-1} yr^{-1}, respectively. To assess potential influences of high N and S deposition on bogs, we quantified N and S concentrations in tissues of two *Sphagnum* species, two lichen species, and four vascular plant species, as well as surface porewater concentrations of H^+, NH_4^+−N, NO_3^-−N, SO_4^{2-}−S and dissolved organic N in 19 ombrotrophic bogs, distributed across a 3255 km^2 sampling area surrounding the oil sands industrial center. The two lichen species (*Evernia mesomorpha* and *Cladonia mitis*), two vascular plant species (*Rhododendron groenlandicum* and *Picea mariana*), and to a lesser extent one moss (*Sphagnum fuscum*), showed patterns of tissue N and S concentrations that were (1) highest near the oil sands industrial center and (2) positively correlated with bulk deposition of N or S. Concentrations of porewater H^+ and SO_4^{2-}−S, but not of NH_4^+−N, NO_3^-−N, DIN, or dissolved inorganic N, also were higher near the oil sands industrial center than at more distant locations. The oil sands region of northern Alberta is remote, with few roads, posing challenges to the monitoring of oil sands-related N and S deposition. Quantification of N and S concentrations in bog plant/lichen tissues and porewaters may serve as a monitoring tool to assess both the local intensity and the spatial extent of bulk N and S deposition, and as harbingers of potential shifts in ecosystem structure and function.

INTRODUCTION

Oil extraction and development activities in the Athabasca Oil Sands Region of northern Alberta, Canada, has led to increasing emissions of oxidized forms of N and S (notably NO_x and SO_2) from diesel-fueled trucks used in mining activity, from *in situ* extraction where the deposit is too deep to be recovered through surface mining, and from stack emissions related to upgrading the bitumen to synthetic crude oil.[1,2] These emissions ultimately lead to higher than background atmospheric N and S bulk deposition, with modeled and measured values exceeding 10 kg ha^{-1} yr^{-1} or higher near the oil sands industrial center (the midpoint between the Syncrude and Suncor upgrader stacks).[1,3,4] In addition, atmospheric reduced N concentrations (NH_y) are high in parts of the oil sands region,[5,6] although their sources of emission are not well characterized. Atmospheric NH_3 can be transferred to regional ecosystems through dry deposition or wet deposition, after conversion to ammonium salts in the atmosphere.[7]

Within the 140422 km^2 Oil Sands Administrative Area,[8] peatlands (bogs and fens) cover an estimated 29% of the land surface.[9] In contrast to minerotrophic fens, ombrotrophic bogs are hydrologically isolated from groundwater or surface water runoff and receive input of water and solutes from atmospheric deposition alone,[10] with the exception of N for which inputs may be strongly dominated by biological N_2 fixation.[11] As such,

Received: June 21, 2016
Revised: September 21, 2016
Accepted: October 20, 2016
Published: October 21, 2016

DOI: 10.1021/acs.est.6b03109
Environ. Sci. Technol. 2016, 50, 12630−12640

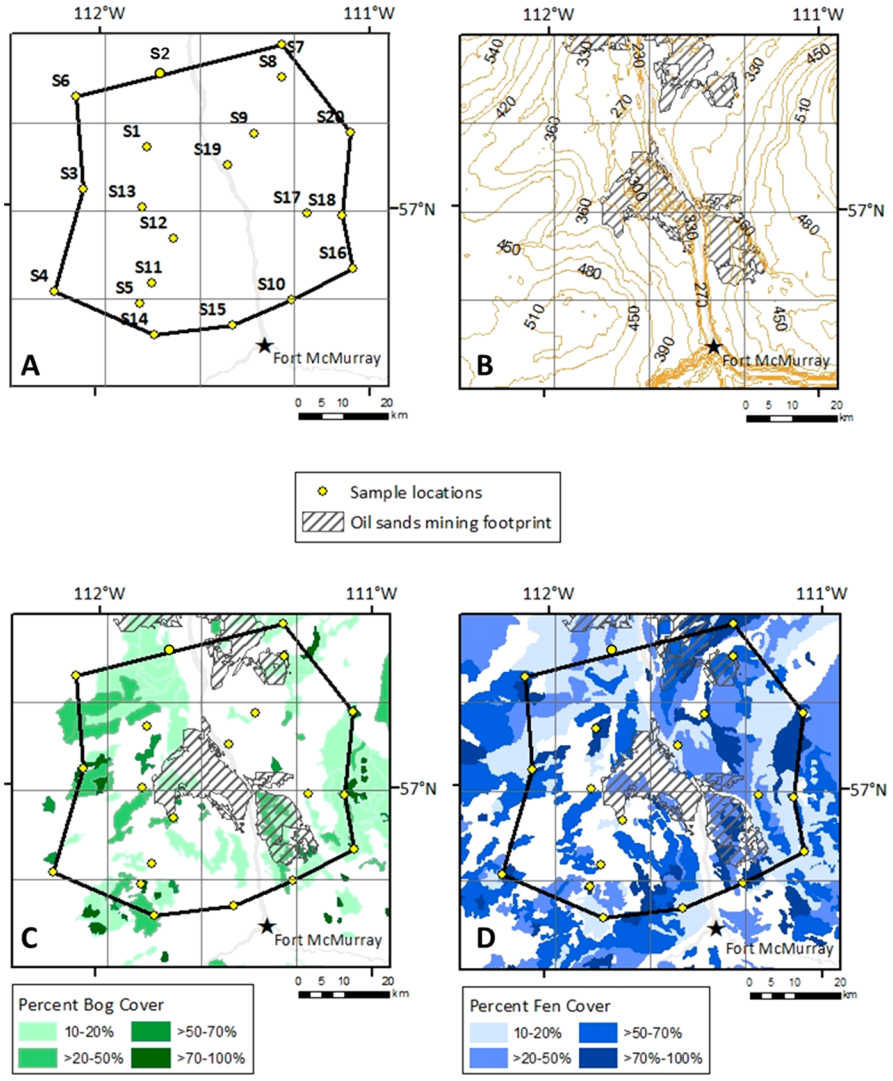

Figure 1. Location of the bog study sites north of Fort McMurray, Alberta, Canada, within the 80 km × 80 km grid used to select sites; boundary of the region used for inverse distance weighting analyses of N and S deposition, porewater chemistry, and plant tissue N and S concentrations determined by the outermost bog sites (A); topographic contours of the study area (B); bog percent cover (C); fen percent cover (D). The oil sands mining footprint is shown as the hatched area in panels B–D.

bogs not only may be especially susceptible to changes in atmospheric deposition of N and S, but also may have the potential to serve as monitors of the spatial extent and/or intensity of increasing N and S emissions.

Previously, we reported that at five bog sites in the oil sands region over a six year period (2009–2014), growth of *Sphagnum fuscum*, the dominant peat-forming moss, increased with proximity to the oil sands industrial center, but was more related to growing season precipitation and atmospheric Ca^{2+} and Mg^{2+} deposition than to N or S deposition.[4] Accumulation of N and S in peat also increased with proximity to the oil sands industrial center[4]. At these bog sites, several lichen, vascular plant, and moss species exhibited decreasing tissue C:N and C:S ratios with proximity to the oil sands industrial center.[12]

To complement long-term monitoring of individual bog sites, a one-time synoptic survey of 19 bogs, ranging from 6 to 43 km from the oil sands industrial center, was conducted in 2013. Results from this survey revealed that concentrations of certain metals in *S. fuscum* increased with proximity to the oil sands.[13] These patterns were attributed not to upgrader stack emissions, but to spatial patterns of dust deposition, originating from the open pit oil sands mines, gravel roads, quarries, and stockpiles of mining overburden and coke, a byproduct of the upgrading process.[13] Here we extend the findings from the synoptic survey to assess whether bog plant/lichen tissue and/or porewater chemistry reflect the spatial distribution of atmospheric N and S deposition resulting from oil sands development.

MATERIALS AND METHODS

To achieve a regional coverage of bog sites, we established a square 80 × 80 km grid (16 cells, 20 × 20 km each), centered on the midpoint between the Syncrude and Suncor upgrader stacks. In each of the 16 grid cells, we identified at least two candidate bog sites, each helicopter accessible only, from Google Earth imagery. Over a two day period (July 6–7 2013), we successfully deployed teams to 20 of these candidate bog sites, which were spatially well distributed across the grid (Figure 1A). The bog sites are the same as those for which Shotyk et al.[13] reported metal concentrations in *Sphagnum* moss. Site locations (latitude, longitude) are reported in Shotyk et al.[13]

DOI: 10.1021/acs.est.6b03109
Environ. Sci. Technol. 2016, 50, 12630–12640

At each site, we collected five replicate samples of mosses (*Sphagnum fuscum* and *S. capillifolium*, top 2 cm of plants), lichens (*Cladonia mitis* and *Evernia mesomorpha*, top 5 cm of *C. mitis*, whole thalli of *E. mesomorpha*), ericaceous shrubs (*Rhododendron groenlandicum*, top three leaves from individual shoots, all current year's growth; *Vaccinium oxycoccos*, aboveground portions of plants; *Vaccinium vitis-idaea*, top 3−5 leaves from individual plants), and *Picea mariana* (current year's needles). In the laboratory, samples tissues were cleaned to remove any material not of the target species; leaves were separated from stems of *V. oxycoccos* and the stems discarded. Plant/lichen tissues were oven-dried (65 °C), ground in a Wiley mill, and analyzed for total N and S concentrations (Leco TruSpec N, S analyzer). Coefficients of variation for N and S measurements averaged 1.0 and 3.1%, respectively. On average, mean measured N and S concentrations were within 2.2 and 5.4% of certified values, respectively (Table S1).

In addition, at each site, we collected five replicate water samples from the top of the bog water table, by manually excavating an approximate 10 cm diameter hole through the surface peat to the depth where saturated conditions prevailed. Water was collected into 125 mL acid-washed, Nalgene sample bottles. As is typical for Alberta bogs in midsummer, bog water tables were at least 30 cm from the peat surface. Collected water samples were filtered (Whatman 41 filter paper) and analyzed for NH_4^+−N (phenate method, Seal AA3 AutoAnalyzer), NO_3^-−N and SO_4^{2-}−S (DIONEX ion chromatograph), and total dissolved N (TDN; Shimadzu TC/TN analyzer, with prefiltration through 0.45 μm syringe filters). Dissolved organic N (DON) was calculated as the difference between TDN and DIN (DIN, dissolved inorganic N equals NH_4^+−N + NO_3^-−N).

Maps of peatland distribution within the 6400 km^2 coarse sampling grid, and the 3255 km^2 sampling area (the polygon determined by the bog sites farthest from the grid center) were prepared using ArcGIS (v. 10.3). The extent of disturbance directly related to oil sands surface mining activity until 2008, namely, the oil sands mining footprint, is from Global Forest Watch Canada.[14] A topographic map of the 6400 km^2 km coarse sampling grid was created by calculating hillshade from a digital elevation model (LIDAR15 DEM from AltaLIS; http://www.altalis.com/products/terrain/lidar15_dem.html) and application of the contour tool in ArcGIS (v. 10.3). Bog and fen coverage within the Oil Sands Administrative Area, the 6400 km^2 coarse sampling grid, and the 3255 km^2 sampling area bounded by the outermost bog locations was determined using the shape files and percentage coverage information in the Alberta Wetland Inventory.[15] Contour plots of bog plant/lichen tissue N and S concentrations and of bog porewater chemical constituents were prepared using inverse distance weighting and a smoothing factor of 0.2 in ArcGIS (v. 10.3).

We also constructed contour plots for atmospheric deposition of NH_4^+−N, NO_3^-−N, DIN, and SO_4^{2-}−S across the 3255 km^2 sampling region using inverse distance weighting and a smoothing factor of 0.2 in ArcGIS (v. 10.3). Sources of N and S bulk deposition are based on ion-exchange resin collectors that were placed in the open in jack pine forests (for data from 2008 to 2012;[3] Fenn, unpublished data from 2012 to 2015), in peat bogs,[4,16] and at the Sand Hill Fen restoration project near the Syncrude Canada main facility (Vitt, Pers. comm.); we used only sites that were within or less than 40 km outside of the polygon defined by the outermost bog sampling sites (Table S2). Bulk deposition quantified using ion-exchange resin collectors includes wet deposition with a possibly small amount of dry deposition.[17] Correlations between atmospheric deposition, plant/lichen tissue chemistry, and porewater chemistry variables were determined using two approaches. Region-wide correlation coefficients were determined using the band collection statistics tool in ArcGIS (v. 10.3) after using the resample tool to adjust the raster data sets to equivalent dimensions. These correlation coefficients are comparable to Pearson's correlation coefficients in that potential values range from −1 to 1, but the spatial autocorrelation of individual variables violates the assumption of independence of values for each of the pair of variables for which the correlation is examined. As such, p values associated with the correlation coefficients are not reported in ArcGIS. We also calculated site-scale Pearson's correlations between predicted values for NH_4^+−N, NO_3^-−N, DIN, and SO_4^{2-}−S deposition at each bog sampling site (from the inverse distance weighting analyses) and the species-specific plant/lichen tissue chemistry or pore water chemistry variables at each site, reporting both correlation coefficients (r) and p values.

RESULTS AND DISCUSSION

Peatland Distribution in the Oil Sands Region. On the basis of the Alberta Wetland Inventory,[15] we determined that the 140329 km^2 Oil Sands Administrative Area (OSAA)[8] contains 8962 km^2 of bogs and 29083 km^2 of fens. These values are similar to those of Lee and Cheng,[9] who reported that 29% of the OSAA is covered by peatlands. Within the 6400 km^2 coarse sampling grid, bogs covered 643 km^2 and fens covered 2804 km^2. Further, within the 3255 km^2 sampling area, 239 km^2 was occupied by bogs and 931 km^2 by fens (Figure 1C,D). Raine et al.[18] reported that within the 22774 km^2 surface-mineable oil sands area, bogs and wooded poor fens covered an estimated 1873 km^2; graminoid, shrubby, and wooded fens covered 12 164 km^2. While the coverage of bogs and fens on the landscape differs depending on where the assessment occurs, peatlands are a major feature of the northern Alberta landscape, with bogs covering 6−10% of the land and fens covering 21−53%.

Atmospheric N and S Deposition. Across all years and across the 23 bog and open jack pine sites where ion-exchange resin collectors were deployed, NH_4^+−N, NO_3^-−N, DIN and SO_4^{2-}−S deposition averaged 1.70, 0.95, and 2.65, and 5.67 kg ha^{-1} yr^{-1}, with significant positive correlations between all four parameters (Table 1). On average, the ratio of NH_4^+−N to NO_3^-−N in deposition was 1.9, similar to the ratio reported by Fenn et al.[3] for ion-exchange resin collectors placed in the open in jack pine sites.

Table 1. Pearson's Correlation Coefficients (above diagonal) and Associated p Values (below Diagonal) between Atmospheric Deposition Variables from the 23 Sites Where Ion Exchange Resin Collectors Were Deployed for Periods of 1 to 6 Years (n = 85; See Table S2 for Deposition Values)

	deposition (kg ha^{-1} yr^{-1})			
deposition (kg ha^{-1} yr^{-1})	NH_4^+−N	NO_3^-−N	DIN	SO_4^{2-}−S
NH_4^+−N		0.691	0.983	0.341
NO_3^-−N	<0.0001		0.811	0.545
DIN	<0.0001	<0.0001		0.413
SO_4^{2-}−S	0.0014	<0.0001	<0.0001	

DOI: 10.1021/acs.est.6b03109
Environ. Sci. Technol. 2016, 50, 12630−12640

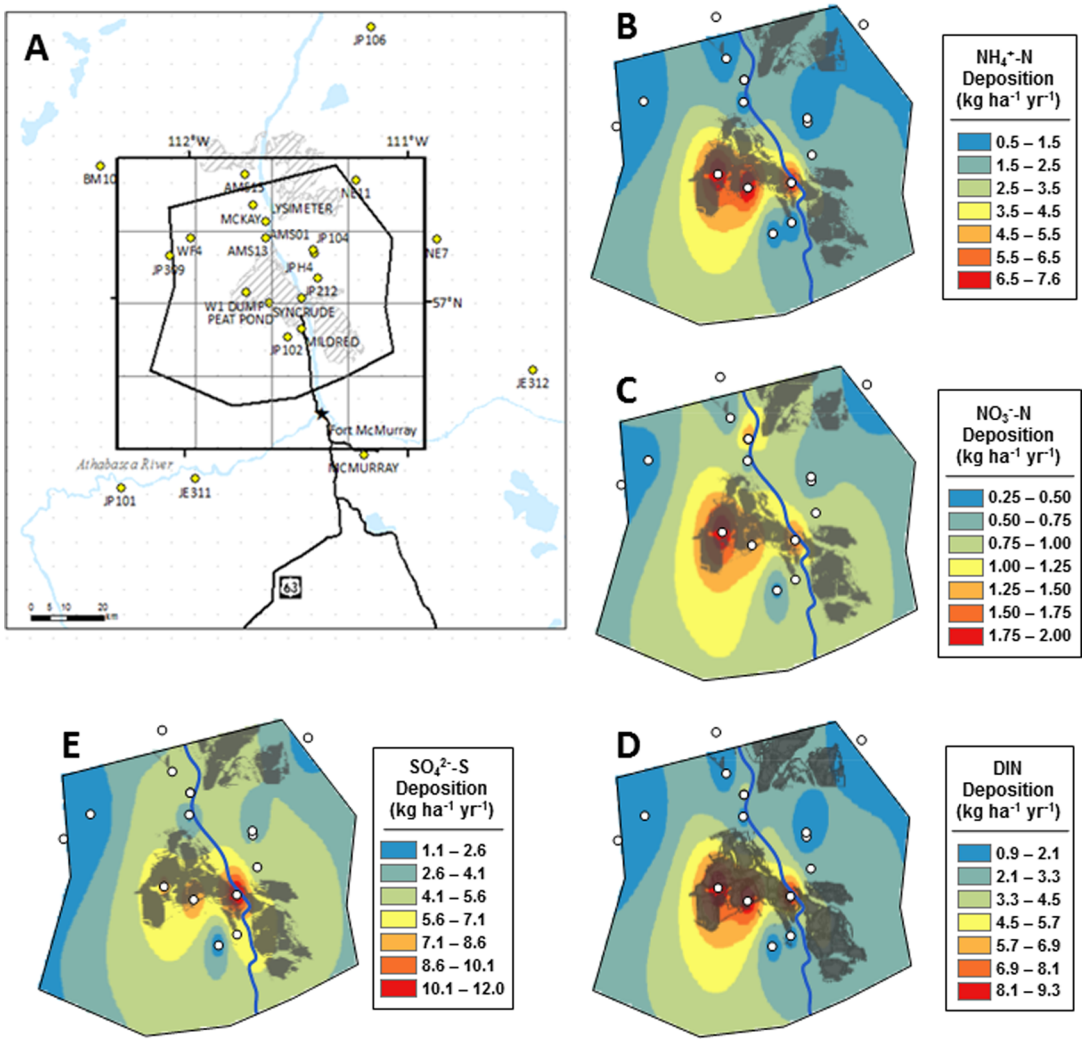

Figure 2. Location of the 23 sites where atmospheric N and S deposition has been quantified using ion-exchange resin collectors, within the 6400 km^2 coarse sampling grid and the 3255 km^2 bog sampling area (A). The spatial distribution of atmospheric NH_4^+–N (B), NO_3^-–N (C), DIN (D), and SO_4^{2-}–S (E) deposition within the 3255 km^2 bog sampling area, with selected ion-exchange resin collector site locations, the oil sands mining area footprint (gray-shaded area), and the Athabasca River, running south to north.

All four parameters exhibited markedly higher deposition with proximity to the oil sands industrial center (Figure 2). Similarly, for ion-exchange resin collectors placed in the open in jack pine forest stands between 2008 and 2011, Fenn et al.[3] reported maximum values for NH_4^+–N, NO_3^-–N, DIN and SO_4^{2-}–S deposition of 2.8, 1.6, 4.4, and 6.8 kg ha^{-1} yr^{-1}, respectively, at 3 km from the oil sands industrial center, decreasing to background values (at 113–129 km from the oil sands industrial center) of 0.8, 1.0, 1.2, and 1.1 kg ha^{-1} yr^{-1}, respectively. Considerably higher deposition values were obtained for throughfall collectors in jack pine forest stands than for collectors placed in the open, especially at sites close to the oil sands industrial center.[3] In contrast, for bogs in the oil sands region, where the black spruce trees occur in a patchy distribution of scattered clumps of a few trees and overall canopy cover is 30–50%, SO_4^{2-}–S deposition, but not NH_4^+–N, NO_3^-–N, or DIN deposition, was higher in throughfall than for open collectors.[4]

Plant/Lichen Tissue N and S Concentrations. Across all 19 bog sites, for *Evernia mesomorpha*, site mean N and S concentrations averaged 6.96 and 0.84 mg g^{-1}, respectively, while for *Cladonia mitis*, site mean N and S concentrations averaged 4.27 and 0.51 mg g^{-1}, respectively (Tables S3, S4). In upland jack pine forests of the Athabasca Oil Sands Region, Laxton et al.[19] reported ranges of N and S concentrations for *E. mesomorpha* of 5.8–9.0 and 0.8–1.3, respectively, and strong positive correlations between lichen N concentrations and both NO_2 and SO_2 (but not NH_3 or HNO_3) concentrations in air. An earlier study in the oil sands region reported gradients in *E. mesomorpha* S concentrations with maximum value in excess of 3 mg g^{-1} at sites closest to the Suncor upgrader stack.[20] *Cladonia mitis* is listed as an indicator species for SO_2 and acid rain across Canada.[21] However, after determining that the ground-dwelling *C. mitis* accumulated atmospherically deposited elements to a lesser extent than arboreal *E. mesomorpha*, collection of *C. mitis* was discontinued as a part of the Wood Buffalo Environmental Association's Lichen Monitoring Program in 2005.[22] Along a suspected pollution gradient in northern Minnesota, ground-dwelling *Cladonia rangiferina* had lower concentrations of S than arboreal lichens (*E. mesomorpha*, *Hypogymnia physodes*, *Parmelia sulcata*).[23] Similarly, we found lower concentrations of N and S in ground-dwelling *C. mitis* than in arboreal *E. mesomorpha*.

DOI: 10.1021/acs.est.6b03109
Environ. Sci. Technol. 2016, 50, 12630–12640

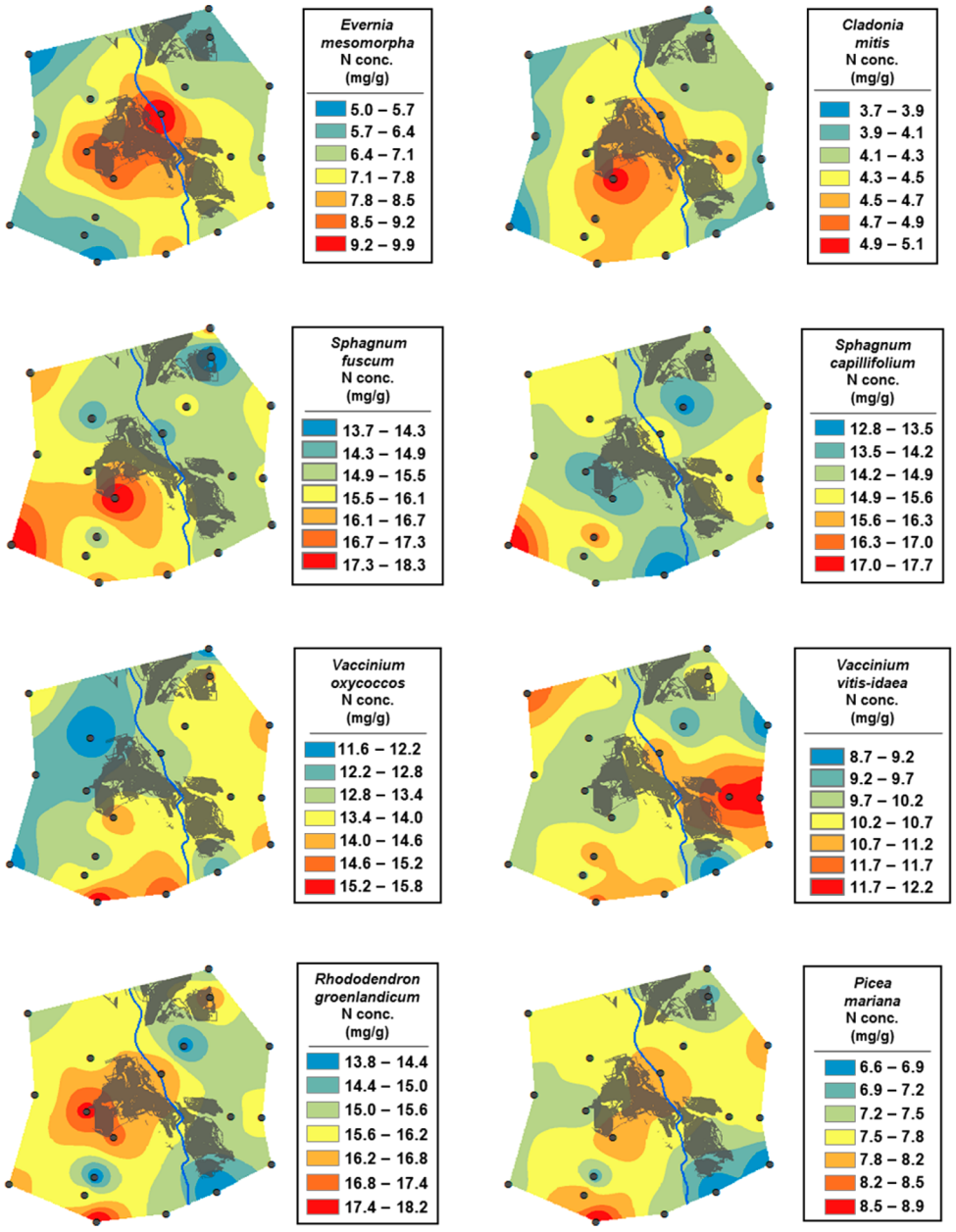

Figure 3. Spatial distribution of N concentrations in plant/lichen tissues; bog sampling locations, the oil sands mining area footprint, and the Athabasca River, running south to north, are shown.

Traditional analysis of variance approaches revealed significant site differences in both N and S concentrations for *E. mesomorpha* and *C. mitis* (Tables S3, S4). More importantly, both lichen species exhibited distinctive patterns of high N and S concentrations near the oil sands industrial center, decreasing with distance (Figures 3, 4). Across the 3255 km^2 sampling area, for both lichen species, tissue N concentrations exhibited positive region-wide and site-scale correlations with NH_4^+–N, NO_3^-–N and DIN deposition (Table 2) and tissue S concentrations exhibited positive region-wide and site-scale correlations with SO_4^{2-}–S deposition (Table 3), Region-wide and site-scale correlation coefficients between N or S deposition and N or S concentrations in lichen tissues were higher than for any of the moss or vascular plant species. These high correlations are not surprising given that lichen tissue chemistry has long been recognized as an indicator of atmospheric nutrient concentrations and/or deposition.[24,25] Across the oil sands region, both *E. mesomorpha* and *C. mitis* have potential as biomonitors of N and S inputs to bog ecosystems via bulk deposition.

In bogs of northern Alberta, *Sphagnum fuscum* and *S. capillifolium* are dominant hummock and peat-forming species. We had expected that N concentrations in these species would exhibit spatial patterns in N concentrations reflecting gradients in N input via bulk deposition. Along a broad N deposition gradient across European sites, N concentrations of apical portions of *Sphagnum* species were about 7 mg g^{-1} at N deposition below 13 kg N ha^{-1} yr^{-1}, increasing to 12 mg g^{-1} at N deposition between 13 and 18 kg N ha^{-1} yr^{-1}, and remaining constant at 12 mg g^{-1} at N deposition above 18 kg N ha^{-1} yr^{-1}.[26] Similarly, as atmospheric N deposition increased along another European gradient ranging from 0.6 to 20 kg N ha^{-1} yr^{-1}, N concentrations in *Sphagnum* increased from 6 to 13 mg g^{-1}.[27] Along a central European gradient spanning higher N

DOI: 10.1021/acs.est.6b03109
Environ. Sci. Technol. 2016, 50, 12630–12640

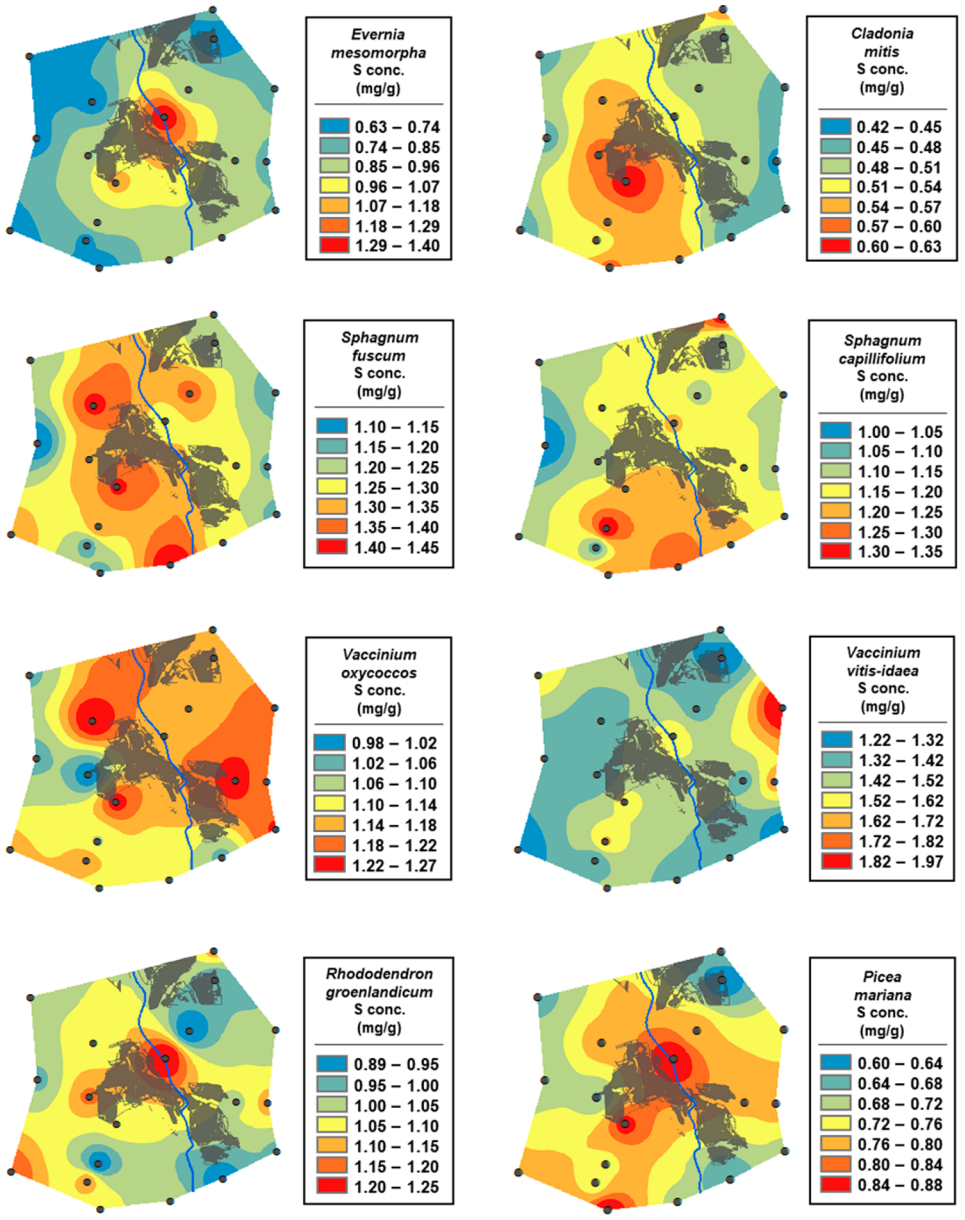

Figure 4. Spatial distribution of S concentrations in plant/lichen tissues; bog sampling locations, the oil sands mining area footprint, and the Athabasca River, running south to north, are shown.

deposition values (ranging from 10 to 21.3 kg N ha^{-1} yr^{-1}), *Sphagnum* N concentrations increased from 13 to 14.6 mg g^{-1}, although the relationship was not significant (p = 0.08).[28]

Our results, however, are not consistent with the pattern obtained across European N deposition gradients. At low N deposition locations in the oil sands region, *S. fuscum* and *S. capillifolium* N concentrations were higher than would be expected based on European studies. Site mean N concentrations for *S. fuscum* averaged 15.8 mg g^{-1}, ranging from 13.7 to 18.3 mg g^{-1}, and for *S. capillifolium* they averaged 14.8 mg g^{-1}, ranging from 12.8 to 17.6 mg g^{-1} (Table S3). Both *Sphagnum* species exhibited significant site differences in N concentration (Tables S3), as well as spatial variation in N concentration (Figure 3). However, N concentrations in *S. fuscum* exhibited positive region-wide correlations, and non-significant site-scale correlations, with NH_4^+–N, NO_3^-–N, or DIN deposition; *S. capillifolium* N concentrations were not positively correlated with N deposition at the regional or site scale (Table 2).

For northern Alberta bogs, by far the dominant source of new N to support the growth of *Sphagnum* species (including *S. fuscum* and *S. capillifolium*) is microbial N_2-fixation occurring in the apical portions of the mosses, not atmospheric NH_4^+–N and NO_3^-–N deposition.[11] While increasing N deposition likely leads to lowered N_2-fixation, overall N supply to growing *Sphagnum* from deposition and N_2-fixation combined may not be affected. As such, contrary to our initial expectation, N concentrations in *Sphagnum* appear to be uninfluenced by regional patterns in N bulk deposition and hence do not offer potential as a tool for monitoring either the intensity or spatial pattern of N deposition in the oil sands region.

We also expected that the two *Sphagnum* species would reflect spatial patterning in S concentration that would be reflective of regional oil sands-related SO_4^{2-}–S bulk deposition gradients. Along a Finnish S deposition gradient of 5.1–9.9 kg

DOI: 10.1021/acs.est.6b03109
Environ. Sci. Technol. 2016, 50, 12630–12640

Table 2. Correlations between Inorganic N Deposition (kg ha^{-1} yr^{-1}), Plant/Lichen Tissue N Concentrations (mg g^{-1}), and Porewater N Concentrations (mg L^{-1})[a]

	region-wide correlation coefficients			site-scale Pearson's correlation coefficients and associated p values		
	NH_4^+–N deposition	NO_3^-–N deposition	DIN deposition	NH_4^+–N deposition	NO_3^-–N deposition	DIN Deposition
Evernia mesomorpha N	0.569	0.615	0.583	0.461	0.497	0.470
				<0.0001	<0.0001	<0.0001
Cladina mitis N	0.712	0.711	0.719	0.442	0.448	0.445
				<0.0001	<0.0001	<0.0001
Sphagnum fuscum N	0.380	0.245	0.360	0.150	0.091	0.138
				0.1508	0.3842	0.1865
Sphagnum capillifolium N	−0.163	−0.201	−0.171	−0.078	−0.108	−0.083
				0.4873	0.3356	0.4560
Vaccinium oxycoccos N	0.052	−0.018	0.040	0.043	0.041	0.042
				0.6821	0.6957	0.6984
Vaccinium vitis-idaea N	−0.034	−0.059	−0.039	−0.047	−0.068	−0.051
				0.6583	0.5189	0.6336
Rhododendron groenlandicum N	0.497	0.427	0.490	0.303	0.254	0.295
				0.0034	0.0146	0.0043
Picea mariana N	0.344	0.290	0.338	0.254	0.214	0.247
				0.0136	0.0378	0.0165
porewater NH_4^+–N	0.101	0.099	0.102	0.111	0.104	0.112
				0.3190	0.3520	0.3179
porewater NO_3^-–N	0.113	0.033	0.100	0.114	0.068	0.105
				0.3072	0.5465	0.3456
porewater DIN	0.114	0.101	0.113	0.120	0.105	0.118
				0.2847	0.3485	0.2899
porewater DON	−0.021	−0.054	−0.026	−0.136	−0.206	−0.148
				0.0568	0.0822	0.2159
porewater H^+	0.182	0.323	0.208	0.234	0.346	0.257
				0.0343	0.00014	0.0196

[a]Region-wide correlation coefficients were determined between two raster data sets using the band collection statistics tool in ArcGIS (v. 10.3; p values not provided) (columns 2–4). Site-scale Pearson's correlation coefficients (r) and associated p values also were obtained between estimated N deposition at each of the 19 bog sampling locations (from inverse distance weighting; Figure 2) and plant/lichen tissue N concentrations or porewater chemistry variables measured at each of the 19 bog sampling locations (columns 5–7).

ha^{-1} yr^{-1}, *S. fuscum* S concentrations increased linearly from about 0.97 to 1.15 mg g^{-1}, with site mean S concentrations ranging from 0.92 to 1.60 mg g^{-1}.[29] For our Alberta bogs, site mean S concentrations for *S. fuscum* averaged 1.27 mg g^{-1}, ranging from 1.10 to 1.45 mg g^{-1}, and for *S. capillifolium*, they averaged 1.27 mg g^{-1}, ranging from 1.01 to 1.34 mg g^{-1}. Both species exhibited significant site differences (Table S4) as well as spatial variation across the 3255 km^2 sampling area (Figure 4) While both *Sphagnum* species exhibited positive region-wide correlations with SO_4^{2-}–S deposition, site-scale correlations were significant for *S. fuscum*, but not for *S. capillifolium* (Table 3). The moderately high region-wide correlation, but non-significant site-scale correlation, obtained for *S. capillifolium* represents the only instance for which the two correlation approaches led to inconsistent results. Thus, S concentrations in *S. fuscum*, but not in *S. capillifolium*, may be of potential use for monitoring the intensity and/or spatial distribution of SO_4^{2-}–S deposition in the oil sands region.

Among the general vascular plant responses as N deposition increases above background levels is an increase in foliar N concentration, although this response may not persist at high N deposition.[30] Although S concentrations in vascular plant tissues may increase with proximity to known SO_2 sources, whether this response is sufficiently consistent to warrant its use as a biomonitor of SO_2 exposure or SO_4^{2-}–S deposition remains uncertain.[31] We quantified N and S concentrations in first-year leaves/needles of four commonly occurring vascular plant species that differ notably with respect to rooting depth in the peat.

Vaccinium oxycoccos and *Vaccinium vitis-idaea* are ecologically similar in many respects. Both are ericaceous, evergreen, and mycorrhizal. *Vaccinium oxycoccos* is a very small, prostrate, trailing shrub, with a very shallow, highly branched, hair-like root system that generally penetrates only a few centimeters into the peat column.[32,33] *Vaccinium vitis-idaea* also is a dwarf shrub with hair-like adventitious roots arising from creeping stems and rhizomes.[34,35] At our Alberta bog sites, *V. vitis-idaea* roots penetrate only a few cm into the peat column. Both *R. groenlandicum* and *P. mariana* are evergreen and mycorrhizal, with thicker roots than the *Vaccinium* species that penetrate well into the peat column above the minimum water table level.[36,37] Given differences in rooting depth, we expected that atmospherically deposited soluble N and S would be more accessible to the shallow rooted *Vaccinium* species than to either *R. groenlandicum* or *P. mariana*.

We observed site differences in leaf N concentrations for all four vascular species (Table S3). For leaves/needles of *V. oxycoccos*, *V. vitis-idaea*, *R. groenlandicum*, and *P. mariana*, site mean N concentration ranges were 11.6–15.2, 8.7–12.1, 13.8–18.1, and 6.6–8.9 mg g^{-1}, respectively. Although all four species exhibited spatial variation in leaf/needle N concentrations (Figure 3), positive and/or significant correlations between N

DOI: 10.1021/acs.est.6b03109
Environ. Sci. Technol. 2016, 50, 12630–12640

Table 3. Correlations between Inorganic SO_4^{2-}−S Deposition (kg ha^{-1} yr^{-1}), Plant/Lichen Tissue S Concentrations (mg g^{-1}), and Porewater SO_4^{2-}−S (mg L^{-1})[a]

	region-wide correlation coefficients	site-scale Pearson's correlation coefficients and associated p values
Evernia mesomorpha S	0.708	0.604
		<0.0001
Cladina mitis S	0.428	0.383
		0.0001
Sphagnum fuscum S	0.457	0.298
		0.0037
Sphagnum capillifolium S	0.554	0.082
		0.4714
Vaccinium oxycoccos S	0.242	0.103
		0.3223
Vaccinium vitis-idaea S	0.171	0.158
		0.1368
Rhododendron groenlandicum S	0.275	0.090
		0.3919
Picea mariana S	0.470	0.321
		0.0016
porewater SO_4^{2-}−S	0.337	0.331
		0.0024
porewater H^+	0.437	0.387
		0.0003

[a]Region-wide correlation coefficients were determined between two raster data sets using the band collection statistics tool in ArcGIS (v. 10.3; p values not provided) (column 2). Site-scale Pearson's correlation coefficients (r) and associated p values also were obtained between estimated SO_4^{2-}−S deposition at each of the 19 bog sampling locations (from inverse distance weighting; Figure 2) and plant/lichen tissue S concentrations or porewater chemistry variables measured at each of the 19 bog sampling locations (column 3).

deposition and leaf N concentrations were obtained for *R. groenlandicum* and *Picea mariana*, but not for the two *Vaccinium* species (Table 2).

For *V. oxycoccos*, *V. vitis-idaea*, *R. groenlandicum*, and *P. mariana* site mean leaf/needle S concentration ranges were 0.98−1.27, 1.22−1.97, 0.89−1.28, and 0.60−0.89 mg g^{-1}, respectively, with significant site differences in leaf/needle S concentrations for three of the four vascular species (no site effect for *V. oxycoccos*; Table S4). All four species exhibited spatial variation in leaf S concentrations (Figure 4); however, positive and/or significant correlations between SO_4^{2-}−S deposition and leaf S concentrations were obtained only for *Picea mariana* (Table 3).

Our results are not consistent with our initial expectation that leaf/needle N and/or S concentration responses to variation in N and/or deposition would be greater in shallow-rooted vascular plant species than in deeper-rooted species. Factors other than rooting depth may play roles in determining leaf/needle N and S responses to N deposition. The four vascular plant species included in our work are mycorrhizal (ericoid for *V. oxycoccos*, *V. vitis-idaea*, *R. groenlandicum*; ectomycorrhizal for *P. mariana*), and hence it may be that mycorrhizally mediated DON uptake dominates over DIN root uptake.[38] The dominance of DON over DIN as a source of N would dampen any potential direct influence of high NH_4^+−N or NO_3^-−N deposition on plant N nutrition and leaf/needle N concentrations. Moreover, plants in the oil sands region are exposed to gaseous forms of N and S, especially near the industrial center.[5,39] At our bog sites, *P. mariana* plants may be as tall as 8 m and *R. groenlandicum* plants are 30−50 cm tall, plants of the two *Vaccinium* species are only 1−3 cm tall. Plant height, and hence exposure to gaseous N and S compounds, may explain in part why spatial patterns in leaf/needle N and/or S concentrations for *R. groenlandicum* and *P. mariana* seem to reflect an oil sands influence more so than for *V. oxycoccos* or *V. vitis-idaea*. While N and S concentrations in plant tissues might be expected to depend to some extent on regional wind patterns as well, prevailing wind direction in the oil sands region varies seasonally.[40] Available data are insufficient to determine whether prevailing wind patterns affect N and/or S concentrations in plant tissues.

Porewater N and S Concentrations. Porewater concentrations of NH_4^+−N, NO_3^-−N, and SO_4^{2-}−S at our study sites (Table S5) were within the range of values reported for North American bogs (NH_4^+−N: 8−1789 μg L^{-1}; NO_3^-−N: 5−384 μg L^{-1}; SO_4^{2-}−S: 10−3667 μg L^{-1}).[41] We obtained no significant differences between sites for porewater NH_4^+−N, NO_3^-−N, or DIN concentrations and significantly higher porewater DON concentrations at five sites (S6, S7, S13, S15) that were not located near the oil sands industrial center (Table S5). While porewater NH_4^+−N, NO_3^-−N, DIN, and DON concentrations all exhibited spatial variation (Figure 5), correlations between porewater N and bulk N deposition were low and/or nonsignificant at both the regional and site scales (Table 2).

When N deposition to peatland ecosystems increases to the point where N input exceeds the capacity for N uptake and retention, dissolved inorganic N can leach downward through the unsaturated upper soil/peat, resulting in higher than background concentrations in receiving streams and/or peatland porewater.[26] For six European bogs along an atmospheric N deposition gradient of 2−20 kg ha^{-1} yr^{-1}, DON constituted 61−82% of total dissolved porewater N, and porewater concentrations of both DIN and DON increased with increasing N deposition.[27] We acknowledge that bogs along this European deposition gradient have been exposed to high levels of N deposition over a much longer time frame than bogs in the oil sands region, and that the 2−20 kg ha^{-1} yr^{-1} European N deposition gradient is wider than the 0.9−9.3 kg ha^{-1} yr^{-1} N deposition gradient across the oil sands region. Nonetheless, we find no evidence that N deposition affects bog porewater N concentrations across the oil sands region.

Porewater SO_4^{2-}−S concentrations were significantly higher at two sites (S15 and S19; Table S5), contributing to a spatial pattern of higher porewater SO_4^{2-}−S concentrations oriented along the Athabasca River valley (Figure 5). In contrast to N, correlations between porewater SO_4^{2-}−S and bulk SO_4^{2-}−S deposition were positive and/or significant at both the regional and site scales (Table 3).

Along deposition gradients, bogs have been shown to retain 59−75% of atmospherically deposited SO_4^{2-}−S in peat.[4,42] Retention of S appears to be mediated by microbial sulfate reduction, producing reduced carbon-bonded S endproducts.[43−45] While microbial sulfate reduction increases with chronic exposure to high levels of atmospheric S deposition (up to 75 kg ha^{-1} yr^{-1}),[46] short-term experimental addition of SO_4^{2-}−S to an Alberta bog (for two years at 25 kg ha^{-1} yr^{-1}) did not stimulate microbial sulfate reduction rates, but did result in an increase in porewater SO_4^{2-}−S.[45] Thus, our finding

DOI: 10.1021/acs.est.6b03109
Environ. Sci. Technol. 2016, 50, 12630−12640

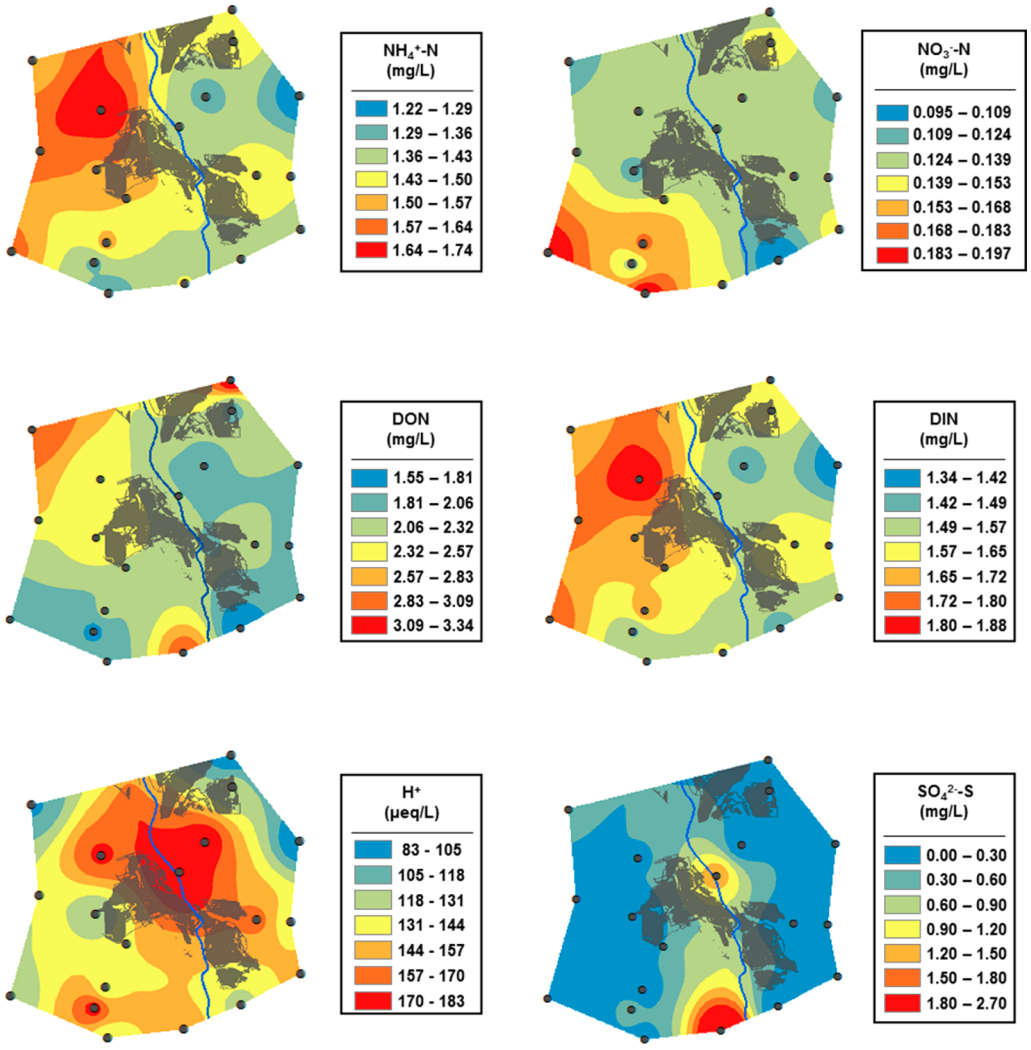

Figure 5. Spatial distribution of porewater NH_4^+−N, NO_3^-−N, DON, DIN, H^+, and SO_4^{2-}−S for samples collected from the top of the bogwater table; bog sampling locations, the oil sands mining area footprint, and the Athabasca River, running south to north, are shown.

that bog porewater SO_4^{2-}−S concentrations are correlated with bulk SO_4^{2-}−S deposition is consistent with prior research.

We also have demonstrated a pattern of higher porewater H^+ concentration near the oil sands industrial center than at more distant locations (Figure 5). We cannot correlate this pattern with regional or site-scale H^+ deposition, as ion-exchange resin collectors do not allow for the quantification of H^+ deposition. Nonetheless, bog porewater H^+ concentrations were positively and/or significantly correlated with NH_4^+−N, NO_3^--N, DIN, and SO_4^{2-}-S deposition (Tables 2,3). While deposition of H^+ associated with strong acid anions could contribute directly to bog porewater acidification, we note that base cation deposition in the oil sands region also is high near the industrial center.[3,4,47] The displacement of H^+ from *Sphagnum* peat cation exchange sites by atmospherically deposited base cations also could contribute indirectly to bog porewater acidification.[48−50] Such an effect would be in contrast to jack pine (*Pinus banksiana*) stands on sandy, nutrient deficient upland soils in the oil sands region, where base cation deposition may moderate soil acidification.[47]

Implications. When oil sands development began in the 1960s, it was expected that it would supplement, but not displace conventional crude oil (IOSI, http://www.iosi.ualberta.ca/en/OilSands.aspx). However, the 21st century has seen synthetic crude oil and nonupgraded bitumen (produced from oil sands) production in Alberta surpass conventional oil production.[51] Oil sands production is expected to increase considerably over the coming decades,[52] with potential implications for regional ecosystems. Over the period from 2003 to 2008, oil sands related SO_2 emissions ranged from 274 to 314 tons per day with no clear increase over time, while NO_x emissions increased from 148 to 200 tons per day, with an air quality footprint that was concentrated within 20 km of the major emission sources.[1] Monitoring of air quality on a regional basis is difficult given the remote nature of the Oil Sands Administrative Area, much of which is not road accessible. Ultimately, NO_x, SO_x, and NH_y emissions result in wet and dry N and S depositional inputs to regional ecosystems. While past monitoring efforts have focused on oxidized gaseous and/or soluble forms of N and S, our finding that bulk NH_4^+-N deposition averages 1.9 times that of NO_3^--N deposition confirms the finding of Fenn et al.[3] and suggests a need to include reduced N compounds in future monitoring efforts.

Here we have characterized regional variation in bulk (consisting mostly of wet) deposition of N and S, and have documented correlations with tissue concentrations of N and S for some, but not all, plant/lichen species. We acknowledge that high N and S deposition in the oil sands area is spatially

DOI: 10.1021/acs.est.6b03109
Environ. Sci. Technol. 2016, 50, 12630−12640

restricted, has been occurring over a much shorter time period than in parts of eastern North America or Europe, and is less intense, in terms of annual deposition in kg ha^{-1} yr^{-1}, than in parts of eastern North America or Europe. Nonetheless, we have shown that high N and S deposition may be associated with altered N and S tissue concentrations in certain plant/lichen species, suggesting early biogeochemical responses to a changing atmospheric deposition regime that are indicative of changes in bog ecosystem function. As such, future monitoring efforts in the oil sands region could serve two complementary purposes. First, given the remoteness and lack of roads across much of the oil sands area, periodic monitoring that quantifies N and/or S concentrations in bog-inhabiting *E. mesomorpha*, *C. mitis*, *P. mariana*, *R. groenlandicum*, and *S. fuscum* may provide insights into future changes in both the local intensity and the spatial extent of N and S deposition across the region. Second, as N and S deposition increases in both local intensity and spatial extent, information on how plant/lichen tissue N and S concentrations change into the future will provide insights into the bog biogeochemical responses to the changing atmospheric deposition regime.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b03109.

Precision and accuracy of plant/lichen tissue N and S measurements; locations (latitude, longitude) of the 23 sites where atmospheric bulk deposition has been quantified using ion exchange resins and deposition of NH_4^+−N, NO_3^-−N, DIN, and SO_4^{2-}−S (kg ha^{-1} yr^{-1}) for each year of measurement; mean (±standard error) tissue N and S concentrations for each of the 20 synoptic sampling locations for each of the plant/lichen species, with ANOVA results; mean (±standard error) porewater concentrations of H^+, NH_4^+−N, NO_3^-−N, DIN, DON, and SO_4^{2-}−S at the top of the water table for each of the 20 synoptic sampling locations, with ANOVA results (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 610-519-4856; fax: 610-519-6200; e-mail: kelman.wieder@villanova.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by a grant to MAV and RKW from the Wood Buffalo Environmental Association, Fort McMurray, Alberta, Canada (Agreement No. T105-13). Support from the Wood Buffalo Environmental Association, Fort McMurray, Alberta, Canada to MEF (Cooperative Agreements 06-CO-11272172-030, 11-CO-11272172-041, 16-CO-11272139-036) funded the collection and analysis of ion-exchange resin data from the jack pine forest sites. Support from Syncrude Canada (Agreement 4410032979) to DHV funded the collection and analysis of ion-exchange resin data for the Syncrude Sand Hill Fen site. We thank Hope Fillingim, Jeremy Graham, Natalie Kashi, Jacqueline Popma, Mikah Schlesinger, Julia Stuart, Nathan Thorp, Anita Uche, Toby Warren, and Brian Whitehouse for field assistance.

■ REFERENCES

(1) Davies, M. J. E. Air Quality Modeling in the Athabasca Oil Sands Region. In *Alberta Oil Sands: Energy, Industry and the Environment; Developments in Environmental Science*; Percy, K. E., Ed.; Elsevier: Oxford, 2012; Vol. *11*, pp 267−309.

(2) Wang, X. L.; Watson, J. G.; Chow, J. C.; Kohl, S. D.; Chen, L.-W. A.; Sodeman, D. A.; Legge, A. H.; Percy, K. E. Measurement of real-world stack emissions with a dilution sampling system. In *Alberta Oil Sands: Energy, Industry and the Environment; Developments in Environmental Science*; Percy, K. E., Ed.; Elsevier: Oxford, 2012; Vol. *11*; pp 171−192.

(3) Fenn, M. E.; Bytnerowicz, A.; Schilling, S. L.; Ross, C. S. Atmospheric deposition of nitrogen, sulfur and base cations in jack pine stands in the Athabasca Oil Sands Region, Alberta, Canada. *Environ. Pollut.* **2015**, *196*, 497−510.

(4) Wieder, R. K.; Vile, M. A.; Albright, C. M.; Scott, K. D.; Vitt, D. H.; Quinn, J. C.; Burke-Scoll, M. Effects of altered atmospheric nutrient deposition from Alberta oil sands development on *Sphagnum fuscum* growth and C, N, and S accumulation in peat. *Biogeochemistry* **2016**, *129*, 1−19.

(5) Bytnerowicz, A.; Fraczek, W.; Schilling, S.; Alexander, D. Spatial and temporal distribution of ambient nitric acid and ammonia in the Athabasca Oil Sands Region, Alberta. *J. Limnol.* **2010**, *69* (Suppl. 1), 11−21.

(6) Hsu, Y.-M.; Bytnerowicz, A.; Fenn, M. E.; Percy, K. E. Atmospheric dry deposition of sulfur and nitrogen in the Athabasca Oil Sands Region, Alberta, Canada. *Sci. Total Environ.* **2016**, *568*, 285−296.

(7) Krupa, S. V. Effects of atmospheric ammonia (NH_3) on terrestrial vegetation: A review. *Environ. Pollut.* **2003**, *124*, 179−221.

(8) ERCB. *Declaration of oil sands areas to facilitate orderly leasing and stable regulation. Informational Letter IL 84-7*; Energy Resources Conservation Board: Calgary, Alberta. 1984.

(9) Lee, P.; Cheng, R. *Bitumen and Biocarbon: Land Use Conversions and Loss of Biological Carbon due to Bitumen Operations in the Boreal Forests of Alberta, Canada*; Global Forest Watch Canada: Edmonton, Alberta, Canada, 2009.

(10) Vitt, D. H. Functional characteristics and indicators of boreal peatlands. In *Boreal Peatland Ecosystems*; Wieder, R. K., Vitt, D. H., Eds.; Springer-Verlag: Berlin, 2006; pp 9−24.

(11) Vile, M. A.; Wieder, R. K.; Živkovic, T.; Scott, K. D.; Vitt, D. H.; Hartsock, J. A.; Iosue, C. L.; Quinn, J. C.; Petix, M.; Fillingim, H.; Popma, J. M. A.; Dynarski, K. A.; Jackman, T. R.; Albright, C. M.; Wykoff, D. D. N_2-fixation by methanotrophs sustains carbon and nitrogen accumulation in peatlands. *Biogeochemistry* **2014**, *121*, 317−328.

(12) Vile, M. A.; Wieder, R. K.; Vitt, D. H. *Development of Monitoring Protocols for Nitrogen-sensitive Bog Ecosystems, including further Development of Lichen Monitoring Tools—2009−2013; Final Report*; Wood Buffalo Environmental Association: Fort McMurray, Alberta, Canada, 2013.

(13) Shotyk, W.; Belland, R.; Duke, J.; Kempter, H.; Krachler, M.; Noernberg, T.; Pelletier, R.; Vile, M.; Wieder, K.; Zaccone, C.; Zhang, S. *Sphagnum* mosses from twenty-one ombrotrophic bogs in the Athabasca Bituminous Sands region fail to reveal significant atmospheric contamination of "heavy metals. *Environ. Sci. Technol.* **2014**, *48*, 12603−12611.

(14) Global Forest Watch Canada. *Oil Sands Surface Mining Activity in Alberta, Canada up to 2008*; Global Forest Watch Canada, 2008; https://databasin.org/datasets/ca774c8d651a46a1949bdbdb408a2561.

(15) Halsey, L. A.; Vitt, D. H.; Beilman, D.; Crow, S.; Mehelcic, S.; Wells, R. *Alberta Wetland Inventory Classification System*, version 2.0; Alberta Sustainable Resource Development: Edmonton, Alberta, Canada, 2003; https://www.arcgis.com/home/item.html?id=80cc26491bd545589ac72b003d4cc5c9).

(16) Wieder, R. K.; Vitt, D. H.; Burke-Scoll, M.; Scott, K. D.; House, M.; Vile, M. A. Nitrogen and sulphur deposition and the growth of

DOI: 10.1021/acs.est.6b03109
Environ. Sci. Technol. 2016, 50, 12630−12640

Sphagnum fuscum in bogs of the Athabasca Oil Sands Region, Alberta. *J. Limnol.* **2010**, *69* (Suppl. 1), 161−170.
(17) Simkin, S. M.; Lewis, D. N.; Weathers, K. C.; Lovett, G. M.; Schwarz, K. Determination of sulfate, nitrate, and chloride in throughfall using ion-exchange resins. *Water, Air, Soil Pollut.* **2004**, *153*, 344−353.
(18) Raine, M.; Mackenzie, I.; Gilchrist, I. Terrestrial Vegetation, Wetlands and Forest Resources Baseline, Appendix B. *CNRL Horizon Project Environmental Impact Assessment*; Report no. 012−2220; Golder Associates: Calgary, Alberta, 2002; Vol. 6.
(19) Laxton, D. L.; Watmough, S. A.; Aherne, J.; Straker, J. An assessment of nitrogen saturation in *Pinus banksiana* plots in the Athabasca Oil Sands Region, Alberta. *J. Limnol.* **2010**, *69* (Suppl. 1), 171−180.
(20) Addison, P. A.; Puckett, K. J. Deposition of atmospheric pollutants as measured by lichen element content in the Athabasca oil sands area. *Can. J. Bot.* **1980**, *58*, 2323−2334.
(21) Thormann, M. N. Lichens as indicators of forest health in Canada. *For. Chron.* **2006**, *82*, 335−343.
(22) WBEA. *Wood Buffalo Environmental Association 2004 Annual Report*; Wood Buffalo Environmental Association: Fort McMurray, Alberta, Canada, 2004.
(23) Bennett, J. P.; Wetmore, C. M. Chemical element concentrations in four lichens on a transect entering Voyageurs National Park. *Environ. Exp. Bot.* **1997**, *37*, 173−185.
(24) Herzig, R.; Liebendorfer, U. M.; Ammann, K.; Cuecheva, M.; Landolt, W. Passive biomonitoring with lichens as part of an integrated biological measuring system for monitoring air pollution in Switzerland. *Int. J. Environ. Anal. Chem.* **1989**, *35*, 43−57.
(25) Root, H. T.; Geiser, L. H.; Fenn, M. E.; Jovan, S.; Hutten, M. A.; Ahuja, S.; Dillman, K.; Schirokauer, D.; Berryman, S.; McMurray, J. A. A simple tool for estimating throughfall nitrogen deposition in forests of western North America using lichens. *For. Ecol. Manage.* **2013**, *306*, 1−8.
(26) Lamers, L. P. M.; Bobbink, R.; Roelofs, J. G. M. Natural nitrogen filter fails in raised bogs. *Global Change Biol.* **2000**, *6*, 583−586.
(27) Bragazza, L.; Limpens, J. Dissolved organic nitrogen dominates in European bogs under increasing nitrogen deposition. *Global Biogeochem. Cycles* **2004**, *18*, GB4018.
(28) Jiroušek, M.; Hajek, M.; Bragazza, L. Nutrient stoichiometry in *Sphagnum* along a nitrogen deposition gradient in highly polluted region of Central-East Europe. *Environ. Pollut.* **2011**, *159*, 585−590.
(29) Pakarinen, P. Regional variation of sulphur concentrations in *Sphagnum* mosses and *Cladonia* lichens in Finnish bogs. *Ann. Bot. Fenn.* **1981**, *18*, 275−279.
(30) Aber, J. D.; Nadelhoffer, K. J.; Steudler, P.; Melillo, J. M. Nitrogen saturation in northern forest ecosystems. *BioScience* **1989**, *39*, 378−386.
(31) Reimann, C.; Koller, F.; Frengstad, B.; Kashulina, G.; Niskavaara, H.; Engelmaier, P. Total sulphur in leaves of several plant species from nine catchments within a 1,500,000 km^2 area in northern Europe: local vs. regional variability. *Geochem.: Explor., Environ., Anal.* **2003**, *3*, 205−215.
(32) Warming, E. The structure and biology of arctic flowering plants. I. Ericinae. I. Morphology and biology. *Medd. Groenland.* **1908**, *36*, 1−71.
(33) Malmer, N.; Svensson, B.; Wallen, B. Interactions between *Sphagnum* mosses and field layer vascular plants in the development of peat-forming systems. *Folia Geobot. Phytotax.* **1994**, *29*, 483−496.
(34) Smith, D. W. Ecological studies of *Vaccinium* species in Alberta. *Can. J. Plant Sci.* **1962**, *42*, 82−90.
(35) Hall, I. V.; Shay, J. M. The biological flora of Canada. 3. *Vaccinium vitis-idaea* L. var. *minus* Lodd. Supplementary account. *Can. Field Nat.* **1981**, *95*, 434−464.
(36) Malloch, D.; Malloch, B. The mycorrhizal status of boreal plants: species from northeastern Ontario. *Can. J. Bot.* **1981**, *59*, 2167−2172.
(37) Viereck, L. A.; Johnston, W. F. Picea mariana. In *Silvics of North America. Vol. 1. USDA Forest Service Agric. Handbook 654*; Burns, R. M., Honkala, B. H., Eds.; U.S. Department of Agriculture: Washington, DC, 1990; pp 227−237.
(38) Lipson, D.; Nasholm, T. The unexpected versatility of plants: Organic nitrogen use and availability in terrestrial ecosystems. *Oecologia* **2001**, *128*, 305−316.
(39) Percy, K. E.; Hansen, M. C.; Dann, T. Air quality in the Athabasca Oil Sands Region 2011. In *Alberta Oil Sands: Energy, Industry and the Environment; Developments in Environmental Science*; Percy, K. E., Ed.; Elsevier: Oxford, 2012; Vol. *11*; pp 47−91.
(40) Alberta Agriculture and Forestry, Wind Speed and Prevailing Direction 1971−2000. http://www1.agric.gov.ab.ca/$department/deptdocs.nsf/all/sag7019 (accessed 30 April 2016).
(41) Bourbonniere, R. A. Review of water chemistry research in natural and disturbed peatlands. *Can. Water Resour. J.* **2009**, *34*, 393−414.
(42) Moore, T.; Blodau, C.; Turunen, J.; Roulet, N.; Richard, P. J. H. Patterns of nitrogen and sulfur accumulation and retention in ombrotrophic bogs, eastern Canada. *Glob. Change Biol.* **2004**, *11*, 356−367.
(43) Wieder, R. K.; Lang, G. E. Cycling of inorganic and organic sulfur in peat from Bog Run Bog, West Virginia. *Biogeochemistry* **1988**, *5*, 221−242.
(44) Wieder, R. K.; Yavitt, J. B.; Lang, G. E. Methane production and sulfate reduction in two Appalachian peatlands. *Biogeochemistry* **1990**, *10*, 81−104.
(45) Vile, M. A.; Bridgham, S. D.; Wieder, R. K. Response of anaerobic carbon mineralization rates to sulfate amendments in a boreal peatland. *Ecol. Appl.* **2003a**, *13*, 720−734.
(46) Vile, M. A.; Bridgham, S. D.; Wieder, R. K.; Novak, M. Atmospheric sulfur deposition alters pathways of gaseous carbon production in peatlands. *Glob. Biogeochem. Cycles* **2003b**, *17*, 1966.
(47) Watmough, S. A.; Whitfield, C. J.; Fenn, M. E. The importance of base cation deposition for preventing soil acidification in the Athabasca Oil Sands Region of Canada. *Sci. Total Environ.* **2014**, *493*, 1−11.
(48) Clymo, R. S. Ion exchange in *Sphagnum* and its relation to bog ecology. *Ecol. Stud.* **1963**, *27*, 309−324.
(49) Clymo, R. S. Control of cation concentrations, and in particular of pH in *Sphagnum*-dominated communities. In *Chemical Environment in the Aquatic Habitat*; Golterman, H. L., Clymo, R. S., Eds.; Amsterdam, North Holland, 1967; pp 273−284.
(50) Clymo, R. S. *Sphagnum*-dominated peat-bog: A naturally acid ecosystem. *Philos. Trans. R. Soc., B* **1984**, *305*, 487−499.
(51) ERCB. *Alberta's energy reserves 2009 and supply/demand outlook 2010−2019. Report ST98−2010*; Energy Resources Conservation Board: Calgary, Alberta, 2010.
(52) CAPP. *Crude oil: Forecasts, Markets & Transportation*; Canadian Association of Petroleum Producers: Calgary, Alberta, Canada, 2015.

DOI: 10.1021/acs.est.6b03109
Environ. Sci. Technol. 2016, 50, 12630−12640