

# Can plant or lichen natural abundance $^{15}\text{N}$ ratios indicate the influence of oil sands N emissions on bogs?

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## ABSTRACT

**Study region:** The 140,329 km<sup>2</sup> Athabasca Oil Sands Administrative Area (OSAA), which contains 8982 km<sup>2</sup> of bogs. Since the late 1970s, N emissions from oil sands development in the OSAA have steadily increased, reaching over 80,000 metric tonnes yr<sup>-1</sup> in 2017.

**Study focus:** If oil sands N emissions have distinct stable isotopic signatures, it may be possible to quantify the extent to which these emissions have affected N cycling in surrounding aquatic, wetland, and terrestrial ecosystems. To assess the potential for  $^{15}\text{N}$  as a tracer of oil sands N emissions, we measured natural abundance  $^{15}\text{N}$  ratios and tissue N concentrations in 10 plant or lichen species at 6 peatland sites at different distances from the oil sands region, collected on 17 sampling dates over three years (2009–2011).

**New hydrological insights:** To understand how the pressures of changing N and S deposition regimes and hydrologic disturbance interactively affect the region's wetlands, it is critical to understand how these pressures act individually. The epiphytic lichen, *Evernia mesomorpha*, was the only species that exhibited patterns that could be interpreted as being influenced by oil sands N emissions. The paucity of data on  $\delta^{15}\text{N}$  signatures of oil sands related N sources precludes definitive interpretations of  $\delta^{15}\text{N}$  in plant or lichen tissues with respect to oil sands N emissions.

## 1. Introduction

Associated with the development of the oil sands resource in northern Alberta are substantial emissions of NO<sub>x</sub> and SO<sub>2</sub> from upgrader stacks and mine fleets. NO<sub>x</sub> emissions have progressively increased over time, exceeding 80,000 metric tonnes in 2017; SO<sub>2</sub> emissions peaked in 2009 at over 120,000 metric tonnes (Davidson and Spink, 2018; Wieder et al., 2021). These emissions have led to high wet and dry deposition of N and S that generally decreases with increasing distance from oil sands operations (Fenn et al., 2015; Hsu et al., 2016; Wieder et al., 2016; Edgerton et al., 2020). Prior to the beginning of oil sands development in 1978, aquatic,

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terrestrial, and wetland ecosystems in the Athabasca Oil Sands Region had been receiving very low N and S in atmospheric deposition. Thus, considerable attention has been given to exploring how changing N, and to a lesser extent, S deposition regimes may be affecting the structure and function of the region's ecosystems.

Wetlands in the oil sands region also are affected by anthropogenic land disturbance, sometimes at a relatively local scale. Land disturbances may cause hydrologic alteration through groundwater and surface water withdrawals/releases, surface water diversions, vegetation removal, and road and seismic line construction (Volik et al., 2020; Chasmer et al., 2021; Ficken et al., 2021). To understand how the pressures of changing N and S deposition regimes and hydrologic disturbance interactively affect the region's wetlands (e.g. Gibson et al., 2021), it is critical to understand how these pressures act individually. Of the various wetland types in the oil sands region, bogs are likely to be the most sensitive to changing N and S regimes, given their acidic ombrotrophic nature (Wieder et al., 2020). For example, increasing N deposition to bogs stimulates shrub growth, with an attendant consequence of decreasing *Sphagnum* growth through either shading or competition with short-statured ericaceous shrubs, leading to a change in plant community composition (Wieder et al., 2020; Vitt et al., 2020). Increasing shrub cover and decreasing *Sphagnum* cover may alter evapotranspirational losses from bogs, which could further enhance shrub growth (e.g. Hirano et al., 2016). Should hydrologic alteration result in a lowering of bog water tables, N availability in the acrotelm may increase (Williams and Wheatley, 1988), which could affect  $\delta^{15}\text{N}$  values in leaves of bog species (e.g. Munir et al., 2017). If these responses were to occur in bogs in the oil sands region receiving elevated N deposition, it would be difficult to attribute increased N availability to hydrologic alteration versus N deposition. More generally, linking wetland ecosystem responses directly to oil sands development, however, often is a challenge, with several studies utilizing natural abundance  $^{15}\text{N}$  approaches to support such linkages.

If oil sands N emissions have distinct stable isotopic signatures, it may be possible to quantify the extent to which these emissions have affected N cycling in surrounding ecosystems. Despite scant data on the  $\delta^{15}\text{N}$  signatures from various oil sands sources (notably upgrader stack emissions, diesel-fueled heavy hauler exhaust), several studies have incorporated  $\delta^{15}\text{N}$  measurements into research directed toward identifying and quantifying oil sands N deposition effects on forest (Laxton et al., 2010; Jung et al., 2013; Proemse et al., 2016; Hemsley et al., 2019) and aquatic (Farwell et al., 2009; Curtis et al., 2010) ecosystems. Others have assessed the extent to which lichen (*Evernia mesomorpha*)  $\delta^{15}\text{N}$  signatures might be used as a proxy for oil sands N emissions (Proemse and Mayer, 2012; Proemse et al., 2013). Thus far, establishing linkages between oil sands N emissions and N cycling in the region's ecosystems based on  $\delta^{15}\text{N}$  signatures has been inconclusive.

Based on the Alberta Wetland Inventory (Halsey et al., 2003), bogs occupy 8982 km<sup>2</sup> within the 140,329 km<sup>2</sup> Athabasca Oil Sands Administrative Area (Wieder et al., 2016). Across the boreal zone, bogs generally have been regarded as N-limited, at least in pristine regions where N deposition has not been increased from anthropogenic activities (Aerts et al., 1992; Vitt, 2006). It now appears that at least for Alberta bogs, biological N<sub>2</sub>-fixation carried out mainly by methanotrophs in surface peat, is much more important than atmospheric deposition as a source of new N inputs to bogs and poor fens (Vile et al., 2013, 2014; Wieder et al., 2019, 2020). As a consequence, *Sphagnum* net primary production (NPP) in Alberta bogs and poor fens appears not to be N-limited while vascular plant NPP is N-limited (Wieder et al., 2019, 2020). Nonetheless, in the oil sands region, as N emissions from oil sands operations have changed and continue to change, if oil sands-related N emissions are accompanied by a change in  $\delta^{15}\text{N}$  signatures in wet and dry deposition, it may be possible that  $\delta^{15}\text{N}$  in lichen thalli, *Sphagnum capitula* (top 1-cm of plants), or leaves/needles of vascular plants, especially those representing current growth, in bogs could provide an indicator of the importance of oil sands N emissions and deposition to the region's bog ecosystems. With this in mind, over three growing seasons, we quantified  $\delta^{15}\text{N}$  in tissues of two lichen, two *Sphagnum*, and six vascular plant species in six bogs ranging from 11 to 251 km distant from the heart of the Athabasca oil sands operations in northern Alberta (taken as the midpoint between the Syncrude and Suncor upgrader stacks) as a preliminary study to assess which bog plant or lichen species, if any, might serve as a proxy for oil-sands derived N inputs. We expected that the lichens, *Cladonia mitis* and *Evernia mesomorpha* would be the most likely species to exhibit an  $^{15}\text{N}$  response given their reliance on wet and dry deposition as sources of N, followed by *Sphagnum* mosses given their position at the peat/atmosphere interface and lack of vascular tissues. Vascular plants should be the least likely to exhibit an  $^{15}\text{N}$  response given the efficient scavenging of atmospherically deposited N at the peat surface.

**Table 1**

Characteristics of the six bog study sites. Deposition values are means  $\pm$  standard errors (May 2009–October 2011), weighted by the number of days that ion exchange resin collectors were in the field between each sampling date (Wieder et al., 2016. Supplemental Material, Table S2). Site means with the same letter superscript do not differ significantly (ANOVA with collection date as a blocked effect; *a posteriori* comparisons using Tukey's Honestly Significant Difference test).

Parameter	Site					
	Mildred	JPH4	McKay	McMurray	Anzac	Utikuma
Latitude	56°55'49"N	57°6'45"N	57°13'41"N	56°37'37"N	56°28'8"N	55°59'9"N
Longitude	111°28'31"W	111°25'23"W	111°42'11"W	111°11'44"W	111°2'34"W	115°11'3"W
Distance from midpoint between Syncrude and Suncor stacks (km)	11	12	24	49	69	251
Annual NH <sub>4</sub> <sup>+</sup> -N deposition (kg N ha <sup>-1</sup> yr <sup>-1</sup> )	0.55 $\pm$ 0.04 <sup>ab</sup>	0.61 $\pm$ 0.05 <sup>a</sup>	0.51 $\pm$ 0.04 <sup>ab</sup>	0.70 $\pm$ 0.09 <sup>a</sup>	0.50 $\pm$ 0.05 <sup>ab</sup>	0.32 $\pm$ 0.03 <sup>b</sup>
Annual NO <sub>3</sub> <sup>-</sup> -N deposition (kg N ha <sup>-1</sup> yr <sup>-1</sup> )	0.94 $\pm$ 0.10 <sup>a</sup>	0.80 $\pm$ 0.10 <sup>ab</sup>	0.59 $\pm$ 0.06 <sup>b</sup>	0.60 $\pm$ 0.05 <sup>b</sup>	0.53 $\pm$ 0.03 <sup>b</sup>	0.22 $\pm$ 0.04 <sup>c</sup>
Annual DIN deposition (kg N ha <sup>-1</sup> yr <sup>-1</sup> )	1.50 $\pm$ 0.12 <sup>a</sup>	1.41 $\pm$ 0.13 <sup>ab</sup>	1.11 $\pm$ 0.09 <sup>ab</sup>	1.29 $\pm$ 0.11 <sup>ab</sup>	1.03 $\pm$ 0.05 <sup>b</sup>	0.54 $\pm$ 0.05 <sup>c</sup>
Annual SO <sub>4</sub> <sup>2-</sup> -S deposition (kg N ha <sup>-1</sup> yr <sup>-1</sup> )	6.30 $\pm$ 0.49 <sup>a</sup>	6.86 $\pm$ 0.82 <sup>a</sup>	5.12 $\pm$ 0.58 <sup>ab</sup>	3.55 $\pm$ 0.30 <sup>b</sup>	3.22 $\pm$ 0.24 <sup>b</sup>	0.96 $\pm$ 0.09 <sup>c</sup>

## 2. Materials and methods

Six peatlands were chosen for study (Table 1). Five are located in the Athabasca Oil Sands Region; the Utikuma site was chosen as a control (251 km from the oil sands industrial center), sufficiently distant from oil sands facilities to be unaffected by N and S emissions. Five of the sites (JPH4, McKay, McMurray, Anzac, Utikuma) are ombrotrophic bogs, with acidic porewaters, a nearly continuous cover of *Sphagnum* mosses (*S. fuscum* and *S. capillifolium* on hummocks, *S. angustifolium* in hollows), and an abundance of ericaceous shrubs (*Rhododendron groenlandicum*, *Vaccinium oxycoccos*, and *Vaccinium vitis-idaea*). One of the sites (Mildred) is best described as a mixed mire with minerogenous water affecting lawns and carpets (circumneutral pore water pH) and ombrogenous hummocks dominated by *S. fuscum* and, to a lesser extent, *S. capillifolium*. Detailed descriptions of the sites can be found in Wieder et al. (2016). In general, these six peatlands represent a gradient of decreasing annual deposition of  $\text{NO}_3^-$ -N, DIN, and  $\text{SO}_4^{2-}$ -S with increasing distance from oil sands operations (Table 1).

Deposition of  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N, DIN ( $\text{NH}_4^+$ -N +  $\text{NO}_3^-$ -N) and  $\text{SO}_4^{2-}$ -S was determined using field-deployed ion exchange resin collectors, 5 in the open and 5 beneath black spruce trees with 2 control collectors capped at each end at each site; resin tubes were replaced in May or June and October (see Wieder et al., 2016 for details).

At each site, we established 5 large representative “plots,” spatially distributed across the peatland. On each sampling date, from each plot at each site, with gloved hands, we collected 5 replicate samples, one from each plot, of *Evernia mesomorpha* (whole thalli), *Cladonia mitis* (top 2–2.5 cm of thalli; we did not distinguish between ssp. *arbuscula* and ssp. *mitis*), *Sphagnum capillifolium* and *Sphagnum fuscum* (about 100 cm<sup>2</sup> of surface moss; ~3 cm deep), *Rhododendron groenlandicum* and *Vaccinium vitis-idaea* (the topmost 3–5 leaves), *Vaccinium oxycoccos* (aboveground leaves and stems), *Rubus chamaemorus* and *Maianthemum trifolium* (leaves), and *Picea mariana* (apical shoots of current year’s growth). There were five collections in 2009 (except for JPH4 which was not established as a site until 2010), and 6 collections in both 2010 and 2011, all between late May and early October.

In the laboratory, samples were cleaned to remove any debris. The topmost 1-cm of *Cladonia mitis* was separated from lower portions of the lichen thalli and retained for analysis. Leaves/needles were separated from stems of *Vaccinium oxycoccos* and *Picea mariana*, with the leaves/needles retained for analysis. For the two *Sphagnum* species, capitula (the top 1-cm of plants) were retained for analysis. Dried samples (at 60 °C) were ground in a Wiley Mini-mill and subsamples were sent to the Southern Illinois University-Carbondale Stable Isotope Facility for  $^{15}\text{N}$  analysis on a Thermo Electron Delta V Plus Isotope Ratio Mass Spectrometer. Values are reported as parts per thousand (‰) relative to atmospheric  $\text{N}_2$  as:

**Table 2**

Mean  $\delta^{15}\text{N}$  values (‰), N concentrations ( $\text{mg g}^{-1}$ )  $\pm$  standard errors, and number of samples (*n*) for 10 species at the six bog study sites. For each species, means with the same letter superscript do not differ significantly ( $p < 0.0042$ ; ANOVA with site as a main factor and collection date a blocked effect; *a posteriori* means comparisons using Tukey’s Honestly Significant Difference test). nd indicates no data.

Species		Site					
		Mildred	JPH4	McKay	McMurray	Anzac	Utikuma
<i>Cladonia mitis</i>	$\delta^{15}\text{N}$ (‰)	$-3.6 \pm 0.2^{\text{ab}}$	$-3.7 \pm 0.1^{\text{ab}}$	$-3.5 \pm 0.1^{\text{ab}}$	$-4.0 \pm 0.2^{\text{bc}}$	$-4.5 \pm 0.1^{\text{c}}$	$-3.2 \pm 0.1^{\text{a}}$
	N ( $\text{mg g}^{-1}$ )	$5.7 \pm 0.1^{\text{a}}$	$5.4 \pm 0.2^{\text{ab}}$	$5.1 \pm 0.1^{\text{abc}}$	$4.9 \pm 0.1^{\text{bc}}$	$4.7 \pm 0.1^{\text{c}}$	$4.9 \pm 0.1^{\text{c}}$
	<i>n</i>	66	54	73	70	76	39
<i>Evernia mesomorpha</i>	$\delta^{15}\text{N}$ (‰)	$-7.0 \pm 0.1^{\text{d}}$	$-5.9 \pm 0.1^{\text{c}}$	$-5.9 \pm 0.1^{\text{c}}$	$-5.6 \pm 0.1^{\text{c}}$	$-5.0 \pm 0.1^{\text{b}}$	$-4.5 \pm 0.1^{\text{a}}$
	N ( $\text{mg g}^{-1}$ )	$11.2 \pm 0.1^{\text{a}}$	$9.7 \pm 0.1^{\text{b}}$	$8.9 \pm 0.1^{\text{c}}$	$8.2 \pm 0.1^{\text{d}}$	$8.8 \pm 0.1^{\text{c}}$	$6.4 \pm 0.1^{\text{e}}$
	<i>n</i>	73	55	74	69	75	39
<i>Sphagnum capillifolium</i>	$\delta^{15}\text{N}$ (‰)	$-4.1 \pm 0.2^{\text{ab}}$	$-3.7 \pm 0.1^{\text{a}}$	$-3.8 \pm 0.2^{\text{a}}$	$-4.2 \pm 0.1^{\text{abc}}$	$-4.9 \pm 0.2^{\text{c}}$	$-4.7 \pm 0.2^{\text{bc}}$
	N ( $\text{mg g}^{-1}$ )	$13.0 \pm 0.3^{\text{a}}$	$13.0 \pm 0.0^{\text{a}}$	$13.4 \pm 0.3^{\text{a}}$	$12.7 \pm 0.2^{\text{ab}}$	$12.9 \pm 0.2^{\text{a}}$	$11.7 \pm 0.2^{\text{b}}$
	<i>n</i>	67	43	59	64	58	31
<i>Sphagnum fuscum</i>	$\delta^{15}\text{N}$ (‰)	$-3.9 \pm 0.2^{\text{ab}}$	$-3.7 \pm 0.1^{\text{a}}$	$-3.9 \pm 0.2^{\text{abc}}$	$-4.4 \pm 0.1^{\text{bcd}}$	$-4.6 \pm 0.1^{\text{d}}$	$-4.5 \pm 0.2^{\text{cd}}$
	N ( $\text{mg g}^{-1}$ )	$12.2 \pm 0.2^{\text{a}}$	$12.0 \pm 0.2^{\text{a}}$	$12.0 \pm 0.2^{\text{a}}$	$11.8 \pm 0.2^{\text{a}}$	$11.6 \pm 0.2^{\text{a}}$	$11.6 \pm 0.2^{\text{a}}$
	<i>n</i>	68	51	64	65	68	34
<i>Vaccinium oxycoccos</i>	$\delta^{15}\text{N}$ (‰)	$-7.1 \pm 0.1^{\text{a}}$	$-7.6 \pm 0.1^{\text{ab}}$	$-7.9 \pm 0.1^{\text{bc}}$	$-8.3 \pm 0.1^{\text{cd}}$	$-8.7 \pm 0.1^{\text{c}}$	$-7.4 \pm 0.2^{\text{a}}$
	N ( $\text{mg g}^{-1}$ )	$13.0 \pm 0.2^{\text{a}}$	$12.4 \pm 0.2^{\text{ab}}$	$11.4 \pm 0.2^{\text{bcd}}$	$11.0 \pm 0.2^{\text{cd}}$	$10.7 \pm 0.2^{\text{d}}$	$11.9 \pm 0.3^{\text{bc}}$
	<i>n</i>	75	53	76	76	67	39
<i>Vaccinium vitis-idaea</i>	$\delta^{15}\text{N}$ (‰)	$-6.5 \pm 0.1^{\text{c}}$	$-4.7 \pm 0.1^{\text{b}}$	$-5.2 \pm 0.1^{\text{c}}$	$-5.9 \pm 0.1^{\text{d}}$	$-5.9 \pm 0.1^{\text{d}}$	$-3.1 \pm 0.2^{\text{a}}$
	N ( $\text{mg g}^{-1}$ )	$11.3 \pm 0.4^{\text{a}}$	$11.6 \pm 0.3^{\text{a}}$	$10.9 \pm 0.2^{\text{ab}}$	$10.1 \pm 0.2^{\text{b}}$	$10.8 \pm 0.1^{\text{ab}}$	$11.4 \pm 0.3^{\text{a}}$
	<i>n</i>	70	48	62	66	67	37
<i>Rhododendron groenlandicum</i>	$\delta^{15}\text{N}$ (‰)	$-4.9 \pm 0.2^{\text{c}}$	$-3.1 \pm 0.2^{\text{b}}$	$-3.5 \pm 0.1^{\text{b}}$	$-4.5 \pm 0.1^{\text{c}}$	$-3.3 \pm 0.1^{\text{b}}$	$-1.1 \pm 0.2^{\text{a}}$
	N ( $\text{mg g}^{-1}$ )	$16.3 \pm 0.4^{\text{ab}}$	$18.7 \pm 0.8^{\text{a}}$	$17.8 \pm 0.6^{\text{ab}}$	$17.1 \pm 0.6^{\text{ab}}$	$17.9 \pm 0.0^{\text{ab}}$	$16.2 \pm 0.4^{\text{b}}$
	<i>n</i>	73	44	68	73	71	26
<i>Picea mariana</i>	$\delta^{15}\text{N}$ (‰)	$-8.9 \pm 0.2^{\text{a}}$	$-10.1 \pm 0.1^{\text{b}}$	$-10.5 \pm 0.1^{\text{bc}}$	$-11.9 \pm 0.2^{\text{d}}$	$-10.7 \pm 0.1^{\text{c}}$	$-10.1 \pm 0.2^{\text{b}}$
	N ( $\text{mg g}^{-1}$ )	$8.1 \pm 0.3^{\text{a}}$	$10.1 \pm 0.6^{\text{a}}$	$9.0 \pm 0.6^{\text{a}}$	$8.8 \pm 0.3^{\text{a}}$	$9.9 \pm 0.6^{\text{a}}$	$9.9 \pm 0.9^{\text{a}}$
	<i>n</i>	71	55	74	70	71	35
<i>Rubus chamaemorus</i>	$\delta^{15}\text{N}$ (‰)	$3.2 \pm 0.5^{\text{a}}$	$-0.4 \pm 0.2^{\text{d}}$	$0.6 \pm 0.1^{\text{cd}}$	$1.2 \pm 0.4^{\text{bc}}$	$-2.7 \pm 0.2^{\text{e}}$	$2.1 \pm 0.4^{\text{ab}}$
	N ( $\text{mg g}^{-1}$ )	$28.0 \pm 1.1^{\text{ab}}$	$30.3 \pm 0.7^{\text{a}}$	$26.0 \pm 0.7^{\text{bc}}$	$22.9 \pm 0.8^{\text{c}}$	$28.5 \pm 0.9^{\text{ab}}$	$23.6 \pm 1.4^{\text{c}}$
	<i>n</i>	34	40	55	55	55	14
<i>Maianthemum trifolium</i>	$\delta^{15}\text{N}$ (‰)	$3.9 \pm 0.3^{\text{a}}$	$3.2 \pm 0.2^{\text{a}}$	$2.8 \pm 0.2^{\text{a}}$	$2.4 \pm 0.5^{\text{a}}$	$2.0 \pm 0.2^{\text{a}}$	nd
	N ( $\text{mg g}^{-1}$ )	$30.4 \pm 1.3^{\text{a}}$	$35.6 \pm 4.4^{\text{a}}$	$34.3 \pm 1.1^{\text{a}}$	$31.3 \pm 0.9^{\text{a}}$	$35.9 \pm 1.9^{\text{a}}$	
	<i>n</i>	32	6	58	46	15	

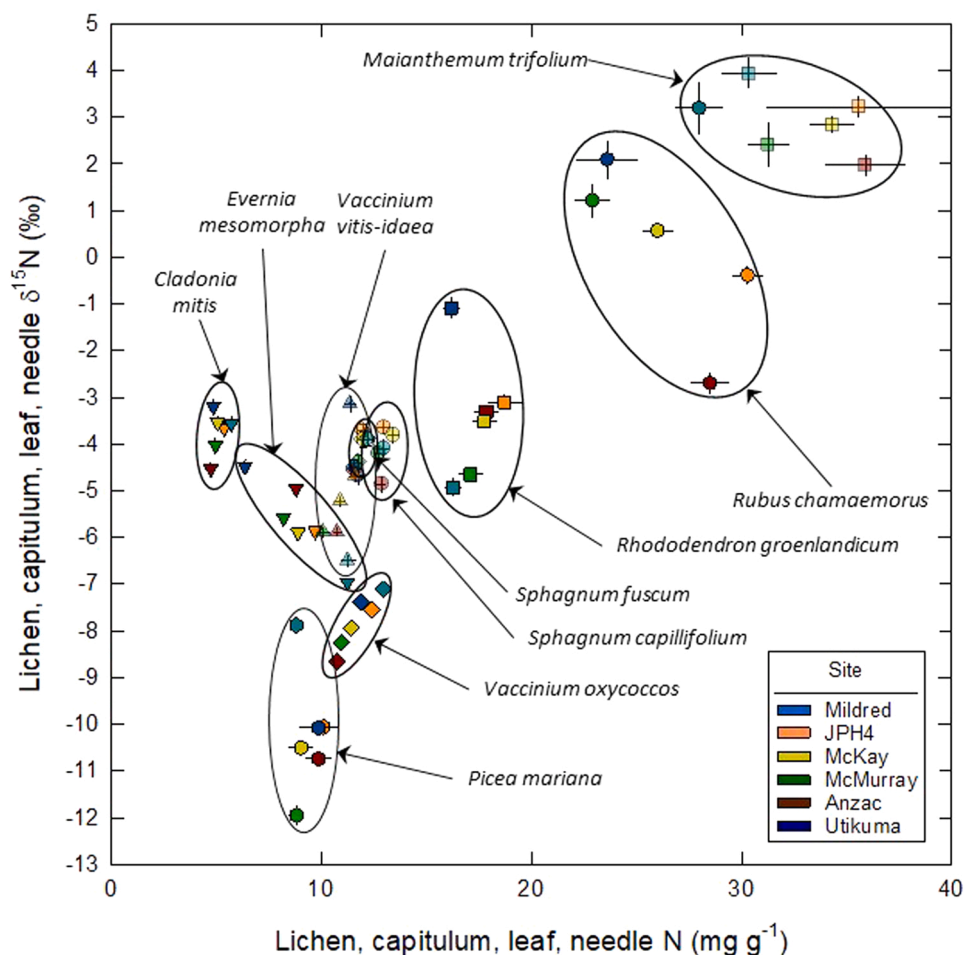
$$\delta^{15}\text{N} = \frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}} - (^{15}\text{N}/^{14}\text{N})_{\text{standard}}}{(^{15}\text{N}/^{14}\text{N})_{\text{standard}}} \times 1000.$$

Samples values were corrected using international reference standards USGA 40 and USGS 41. The analytical long-term standard deviation for  $\delta^{15}\text{N}$  is 0.2‰.

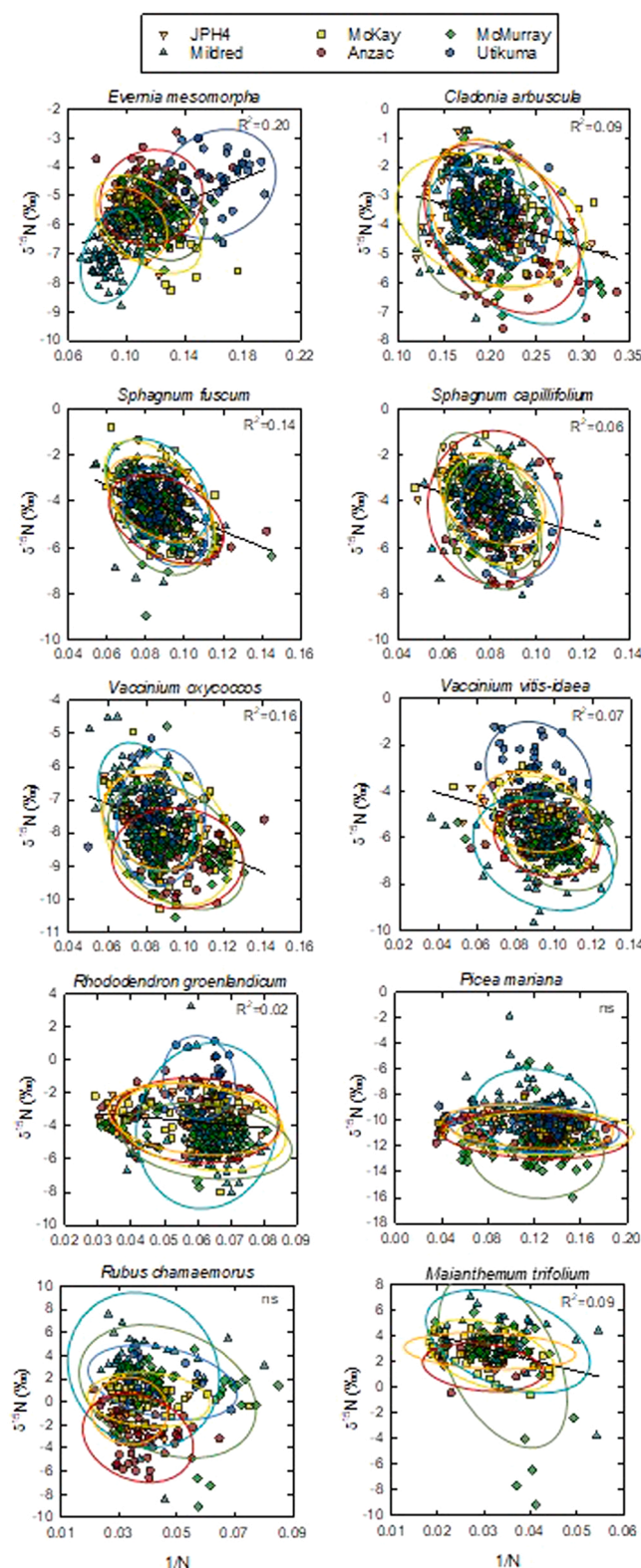
Nitrogen concentrations in lichen/plant material were determined on a Leco TruSpec® CN analyzer. Standard curves for N were constructed using differing quantities (0.1–0.2 g) of standard reference materials (NIST 1547 peach leaves, NIST 1632b coal, Leco 1018 tobacco leaves). All standard curves had  $R^2$  values > 0.999. Analyses with 0.2 g of samples had limits of detection of  $0.3 \text{ mg g}^{-1}$ ; analyses of standard reference materials not used to construct standard curves produced N concentrations within 1.5% of certified values (cf. Wieder et al., 2016).

### 3. Results and discussion

Overall,  $\delta^{15}\text{N}$  values of the 10 bog plant or lichen species examined in this study (Table 2) are comparable to those found in other bog studies (Table S1). We characterized the 10 species examined as one of five types: lichens (*Evernia mesomorpha*, *Cladonia mitis*), bryophytes (*Sphagnum capillifolium*, *Sphagnum fuscum*), nonmycorrhizal (*Rubus chamaemorus*, *Maianthemum trifolium*), ericoid mycorrhizal (*Rhododendron groenlandicum*, *Vaccinium oxycoccos*, *Vaccinium vitis-idaea*), and ectomycorrhizal (*Picea mariana*). Averaged across all sites and collection dates, mean  $\delta^{15}\text{N}$  values for each of five plant or lichen types were significantly different from all other types: nonmycorrhizal ( $1.3 \pm 0.1\text{‰}$ ,  $n = 447$ ), bryophytes ( $-4.2 \pm 0.1\text{‰}$ ,  $n = 698$ ), lichens ( $-4.8 \pm 0.1\text{‰}$ ,  $n = 764$ ), ericoid mycorrhizal ( $-5.7 \pm 0.1\text{‰}$ ,  $n = 1107$ ), and ectomycorrhizal ( $-10.4 \pm 0.1\text{‰}$ ,  $n = 385$ ). The trend of vascular plant foliar  $\delta^{15}\text{N}$  values of nonmycorrhizal > arbuscular mycorrhizal > ericoid mycorrhizal > ectomycorrhizal has been related to differences in the distances from the roots that different types of mycorrhizae can explore, different enzymatic capabilities to access different forms of N, and the extent



**Fig. 1.** Lichen, *Sphagnum* capitulum, leaf and needle  $\delta^{15}\text{N}$  (‰) as a function of tissue N concentration for the 10 plant or lichen species. Values are means, averaged across all sampling dates,  $\pm$  standard errors, for each of the bog sites. Ellipses do not denote statistical groupings, but are hand drawn to identify individual species.



**Fig. 2.** Keeling plots of lichen/*Sphagnum*/leaf/needle  $\delta^{15}\text{N}$  (‰) as a function of the inverse of tissue N concentrations,  $1/\text{N}$  ( $\text{g mg}^{-1} \text{N}$ ), with 90% confidence ellipses for each site. Where regressions were significant ( $p < 0.05$ ), the regression line is plotted and the  $R^2$  value is shown.



to which different mycorrhizal groups preferentially retain  $^{15}\text{N}$  while preferentially transferring  $^{14}\text{N}$  to the host plant (Michelsen et al., 1998; Emmerton et al., 2001; Craine et al., 2015).

The separation of the five plant or lichen types is even more pronounced when tissue  $\delta^{15}\text{N}$  values are plotted as a function of tissue N concentrations (Fig. 1). The nonmycorrhizal species, *Rubus chamaemorus* and *Maianthemum trifolium*, had the highest leaf  $\delta^{15}\text{N}$  values and N concentrations. The high  $\delta^{15}\text{N}$  values for these species are likely the result of their non-mycorrhizal status, deep aerenchymatous roots allowing for N acquisition from deep peat, and the general pattern of increasing  $\delta^{15}\text{N}$  of bog peat with depth (Kohzu et al., 2003; Blodau et al., 2006; Hobbie et al., 2017; Drollinger et al., 2019). The lichen and *Sphagnum* species cluster together, differing more in N concentrations than in  $\delta^{15}\text{N}$  values, and ericoid mycorrhizal species are more similar to each other than to the ectomycorrhizal *Picea mariana* (Fig. 1).

The key question, though, is whether for any of these 10 species, the within-species between-site variability in  $\delta^{15}\text{N}$  values reflects the influence of oil sands N emissions. We used the approach of Proemse and Mayer (2012), plotting plant or lichen  $\delta^{15}\text{N}$  values as a function of the inverse of the N concentration in tissues for each species across all bog sites to evaluate whether plant or lichen tissue N and  $^{15}\text{N}$  chemistry could be explained as the mixing of two or more sources of N. Such mixing would be reflected by a significant linear regression and by the six bog sites being arrayed along distance from oil sands operations. The only species that clearly exhibited such patterns was the epiphytic lichen *Evernia mesomorpha*, suggesting background  $\delta^{15}\text{N}$  values of about  $-4.0\text{‰}$  at remote sites presumably reflecting wet and dry deposition unaffected by oil sands emissions, and possible oil sands sources with more negative  $\delta^{15}\text{N}$  values (Fig. 2). This result is in contrast to the findings of Proemse and Mayer (2012), who analyzed 32 *Evernia mesomorpha* samples collected from 24 sites ranging from 3 to 113 km from oil sands operations. While N concentrations increased with proximity to the oil sands, 30 of the 32 samples had  $\delta^{15}\text{N}$  values ( $-5.3 \pm 1.0\text{‰}$ ) similar to pristine atmospheric  $\text{NO}_3^-$  and  $\text{NH}_4^+$  deposition, unaffected by oil sands development. Duplicate samples from the site closest to oil sands operations, however, had  $\delta^{15}\text{N}$  values of  $+11.6$  and  $+9.8\text{‰}$ , suggesting an oil sands N source with a very positive  $\delta^{15}\text{N}$  signature.

For the terricolous lichen, *Cladonia mitis*, N concentrations increased with proximity to oil sands operations (Table 1, Wieder et al., 2021), but there was no clear evidence of an oil-sands related  $^{15}\text{N}$  influence (Fig. 2). Although the regression in Fig. 2 was significant, the  $R^2$  value was low and the six bog sites were not clearly arrayed according to distance from oil sands facilities. The contrasting patterns of *Evernia mesomorpha* and *Cladonia mitis* are consistent with the concept that epiphytic lichens may be more responsive to varying N inputs than terricolous lichens (Graney et al., 2017; Watmough et al., 2019).

Both *Sphagnum* species exhibited an increase in  $\delta^{15}\text{N}$  with increasing capitulum N concentrations (Fig. 2). The two *Sphagnum* species behaved similarly, with background  $\delta^{15}\text{N}$  values of about  $-4.5\text{‰}$  that became more positive with proximity to oil sands operations (Fig. 2). However, the  $R^2$  values for the *Sphagnum* regressions in Fig. 2 were quite low and despite significant site differences in both  $\delta^{15}\text{N}$  and capitulum N concentrations (Table 1), the six bog sites are not clearly separated in Fig. 2. Delgado et al. (2013) reported that mosses, thought to rely entirely on atmospheric N, can vary by up to  $8\text{‰}$  within a narrow geographic region, underscoring the complications of  $\delta^{15}\text{N}$  interpretations. Along a European N bulk deposition gradient ranging from  $0.8$  to  $20 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , N concentrations in *Sphagnum* capitula increased logarithmically, with no significant change in  $\delta^{15}\text{N}$  values (Bragazza et al., 2005). Along an eastern Canadian N deposition gradient ranging from  $1.3$  to  $10.6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , with increasing N deposition, *Sphagnum* N concentrations increased while  $\delta^{15}\text{N}$  values became more negative ( $-1$  to  $-6\text{‰}$ ) (Živković et al., 2017), in contrast to our result that as N concentrations increased,  $\delta^{15}\text{N}$  values became more positive. We cannot definitively conclude that the  $\delta^{15}\text{N}$  patterns in the two *Sphagnum* species (Fig. 2) reflect an oil sands N source.

Four of the six vascular plant species exhibited significant regressions, albeit with low  $R^2$  values, and none of these species showed a clear separation of sites with distance from oil sands facilities (Fig. 2). For these vascular plant species, either atmospheric deposition does not provide the major source of N for plant uptake, or the  $\delta^{15}\text{N}$  signatures of oil sands emissions are not sufficiently distinct to be reflected in leaf/needle  $\delta^{15}\text{N}$  values.

When we began sampling of the bog sites in 2009, the only data on the  $\delta^{15}\text{N}$  signatures of oil sands N emissions were for  $\text{PM}_{2.5}$  emissions from two upgrader stacks in the oil sands region;  $\delta^{15}\text{N}\text{-NH}_4^+$  values ranged from  $-4.5$ – $20.1\text{‰}$ , while  $\delta^{15}\text{N}\text{-NO}_3^-$  values ranged from  $9.4\text{‰}$  to  $17.9\text{‰}$  (Proemse et al., 2012). Subsequently, Proemse et al. (2013) reported a wide range of  $\delta^{15}\text{N}$  values for wet atmospheric deposition of  $\text{NH}_4^+$  ( $-6.3$  to  $11.3\text{‰}$ ) and  $\text{NO}_3^-$  ( $-4.9$  to  $6.3\text{‰}$ ). Somewhat different results were reported by Hemsley et al. (2019): wet atmospheric deposition of  $\delta^{15}\text{N}\text{-NH}_4^+$  of  $9.6 \pm 1.2\text{‰}$  and  $\delta^{15}\text{N}\text{-NO}_3^-$  of  $-1.8 \pm 2.7\text{‰}$ . There is evidence for considerable  $\text{NH}_3$  deposition in the oil sands region, originating from the oil sands bitumen upgrading processes,  $\text{NH}_3$  emissions from tailings ponds, and volatilization of  $\text{NH}_3$  from urea fertilizer used in land reclamation (Bytnerowicz et al., 2010), although the relative magnitude of these sources has not been well established. Tailings pond  $\delta^{15}\text{N}\text{-NH}_4^+$  values are quite positive ( $28.8 \pm 2.5\text{‰}$ ), and urea used as a fertilizer in land reclamation has a  $\delta^{15}\text{N}$  of  $-0.33\text{‰}$  (Hemsley et al., 2019). Any  $\text{NH}_3$  volatilized from tailings ponds or from land to which urea has been applied would be enriched in  $^{14}\text{N}$  relative to their sources due to the high fractionation associated with the conversion of  $\text{NH}_4^+$  to  $\text{NH}_3$  (Nömmik et al., 1994).

Two major sources of N emissions from oil sands operations, for which there are no data, are N gases from upgrader stacks and N in exhaust from diesel-fueled mine fleets. The major fuel used in upgrading bitumen is natural gas. Walters et al. (2015a) report  $\delta^{15}\text{N}\text{-NO}_x$  from natural gas combustion sources of  $-16.5 \pm 1.7\text{‰}$ . The  $\delta^{15}\text{N}\text{-NO}_x$  values of diesel-truck exhaust have ranged from  $-12.0$  to  $-23.3\text{‰}$  (Heaton, 1990; Walters et al., 2015b). It is likely that the  $\delta^{15}\text{N}\text{-NO}_x$  signatures of upgrader stack and diesel-fueled trucks in the oil sands region are quite negative. We note that even with improved data on the  $^{15}\text{N}$  signatures of N emissions from various sources oil sands, once N compounds are emitted, N compounds participate in a diverse set of atmospheric chemical reactions often with isotope fractionation (cf. Elliott et al., 2019; Liu et al., 2020), complicating efforts to relate  $^{15}\text{N}$  in plant or lichen tissues to oil sands N emissions.

#### 4. Conclusions

While  $\delta^{15}\text{N}$  values can be an effective tool to trace anthropogenic N emissions (e.g., Heaton, 1986, Pearson et al., 2000, Pardo et al., 2007, Elliott et al., 2007, Xiao et al., 2011), a prerequisite is that the anthropogenic N source has a  $\delta^{15}\text{N}$  signature that is distinct from background values. Even if this prerequisite is met, plant tissue  $\delta^{15}\text{N}$  interpretations are not necessarily straightforward given the wide variation in signatures of atmospheric sources, multiple fractionating processes in the soil, variation across both spatial and temporal gradients (Craine et al., 2015), and N fractionation associated with atmospheric chemical reactions (Elliott et al., 2019; Liu et al., 2020). Of the 10 bog plant or lichen species examined in this study, *Evernia mesomorpha* has the highest potential for use as a bio-monitor of oil sands N emissions through  $\delta^{15}\text{N}$  values. The increasingly negative  $\delta^{15}\text{N}$  values for *Evernia mesomorpha* with increasing proximity to oil sands operations (Table 3, Figs. 1,2) may well reflect an oil sands influence with an  $\delta^{15}\text{N}$  signature of about  $-7\text{‰}$ . However, the scarcity of data on  $\delta^{15}\text{N}$  values for potential oil sands N sources, and the variability that exists in this scarce data set, preclude definitive interpretations.

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#### CRediT authorship contribution statement

**R. Kelman Wieder:** Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Writing – original draft, Visualization, Supervision, Project administration, Funding acquisition. **Melanie A. Vile:** Conceptualization, Methodology, Investigation, Data curation, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Dale H. Vitt:** Conceptualization, Methodology, Investigation, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Kimberli D. Scott:** Methodology, Investigation, Resources, Data curation, Writing – review & editing, Supervision, Project administration. **Bin Xu:** Methodology, Investigation, Data curation. **James C. Quinn:** Methodology, Investigation, Resources, Data curation, Supervision. **Cara M. Albright:** Methodology, Investigation, Resources, Data curation, Supervision.

#### 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.

#### Availability of Data and Material

Data are available through the Environmental Data Initiative (<https://doi.org/10.6073/pasta/043c6ebb2e2294ab96f0bdcaff10601e>).

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.ejrh.2022.101030](https://doi.org/10.1016/j.ejrh.2022.101030).

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