Science of the Total Environment 711 (2020) 134737

Contents lists available at ScienceDirect

Science of the Total Environment

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

Atmospheric sulfur and nitrogen deposition in the Athabasca oil sands region is correlated with foliar nutrient levels and soil chemical properties

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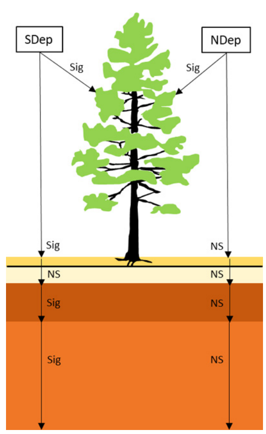
HIGHLIGHTS

- Sulfur deposition is correlated to increased foliar, LFH and soil sulfur.
- Nitrogen deposition is correlated to increased foliar nitrogen, but not LFH or soil.
- PAI correlated positively with LFH pH, potentially indicating model uncertainties.
- Calcium from fugitive dust was not related to the spatial pattern of pH in the topsoil layer.
- Dry ammonia deposition was positively correlated with LFH pH.

GRAPHICAL ABSTRACT

Significant (sig) and non-significant (NS) sulfur (SDep) and nitrogen (NDep) deposition, as determined by regression analysis on different jack pine receptors.



ARTICLE INFO

Article history:
Received 25 April 2019
Received in revised form 26 September 2019
Accepted 28 September 2019
Available online 31 October 2019

Keywords:
Industrial air pollutants
SO_2
NO_X
Inverse distance weighting
Spatial analysis
Forest health
Fugitive dust
Potential acid input

ABSTRACT

The oil extraction industry and human activity in north eastern Alberta has been growing steadily since the 1960's and is a source of air pollution. In the late 1990's the Wood Buffalo Environmental Association was established to monitor air quality for both public and environmental health. A primary environmental concern was soil acidification caused by sulfur (S) and nitrogen (N) deposition. A network of forest health monitoring (FHM) sites was established in dry jack pine ecosystems to serve as an early indicator of negative impacts. A sampling campaign was executed in 2011 and this study examines soil properties and foliar nutrients in the context of measured and modeled acid deposition. Total N (TN), SO_4^{2-}, pH, base cation to aluminum ratio (BC:Al), and base saturation (% BS) are reported for the organic layer (LFH) and 3 depths in the mineral soil, while foliar nutrients were analysed from current annual growth in jack pine needles. Atmospheric deposition of S, N, BC, and potential acid input (PAI) in the study area was recently provided by Edgerton et al. (2020) and soil and foliar chemistry was evaluated based on deposition estimates and measurements. Inverse distance weighting was used to examine spatial patterns and regression analysis was used to quantify relationships between variables. The results indicated that S deposition is spatially correlated with foliar SO_4^{2-} concentration, and LFH SO_4^{2-}, but not mineral topsoil (0–5 cm) SO_4^{2-}. Nitrogen deposition was spatially correlated with foliar N concentration, but not LFH or topsoil TN indicating potential uptake by the foliage or rapid uptake by roots in the LFH layer. High

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https://doi.org/10.1016/j.scitotenv.2019.134737
0048-9697/

BC deposition in the same areas with the highest potential acid inputs (PAI) did not correlate significantly with changes in soil pH. However, LFH pH was significantly related to dry NH_3 deposition, which has not been reported previously and requires further investigation.

1. Introduction

Negative effects of atmospheric S and N deposition from industrial and vehicular emissions have been of concern in areas around the globe with high population concentrations (Tian and Niu, 2015). Negative effects include soil acidification and N saturation (Binkley and Hogberg, 2016). Soil acidification occurs due to a reduction of acid-neutralizing capacity in soil or likewise and increase in base-neutralizing capacity which results in higher concentrations of H^+ in soil and subsequently a decrease in soil pH. Base cations can also be leached out of the soil through this process, resulting in further lowering of the pH. Nitrogen saturation occurs when there is a net export of N from an ecosystem, which is believed to only happen under human influence (Binkley and Hogberg, 2016).

Resource development in the Canadian north has the potential to impact ecosystem function and health (Maynard et al., 2014). Oil and gas development in northern Alberta has been increasing since the late 1960's (see introduction by Foster et al., 2019, this speciual issue). With an estimated 1.7 trillion barrels of oil, Canada's oil reserve is the third largest in the world after Saudi Arabia and Venezuela (Percy, 2013). The Alberta oil sands are located in three main reserves around the cities of Peace River, Cold Lake, and Fort McMurray, with the last being the largest and known as the Athabasca oil sands region (AOSR). Concern that extraction and upgrading of bitumen (viscous mixture of oil, sand, and water) was the source of many environmental pollutants, stimulated some research into air quality between the late 1960's and early 1990's. In 1997, the Wood Buffalo Environmental Association (WBEA) was created to monitor public and environmental health related to air quality in the AOSR. As described by Percy et al. (2012), natural ecosystems are the interface between climate, land, and water. They are in a constant disequilibrium due to the stochastic effects of disturbance (rapid process) and ecosystem growth (slow process). Both of these processes can be affected by air pollution, including acidifying agents and fugitive dust (Percy, 2013), all of which have the potential to negatively affect ecosystem processes.

Exceedances of critical loads for acidifying S and N deposition in the AOSR have been predicted based on modeled data (Makar et al., 2018), but to date measured values have not been published. For the purpose of ecosystem resilience, it has been suggested that the critical load for N deposition should be <6 kg N ha^{-1} $year^{-1}$ in boreal Sweden, as anything higher results in plant community shifts (Nordin et al., 2005). Most terrestrial ecosystems are believed to be N limited (Vitousek and Howarth, 1991), therefore additions of N should have a stimulatory affect to growth. Indeed, some research shows this, for example Binkley and Hogberg (2016) indicated that tree growth in Sweden increased annually under high deposition rates and understorey composition changed over a 20-year period. Research from temperate forests in North America indicated similar shifts, where 25 years of N deposition affected understorey plant community structure in west Virginia, leading to increased biomass and a shift to nitrophilic species (Gilliam et al., 2016). Sulfur emissions caused growth decline in Scots pine from 1930 to 1980, as indicated by dendrochronology records and reduced drought resistance (Savva and Berninger, 2010). And finally, long-term experimental additions of S and N acids to boreal forest plots caused changes to soil pH and plant community structure, along with increases in graminoid and some ericoid shrubs (Shevtsova and Neuvonen, 1997). Quantification of critical loads is needed for the AOSR as well as an indication of forest health.

The mandate of the WBEA Terrestrial Environmental Effects Monitoring (TEEM) program is to examine forest health by: 1) detecting pollution, 2) quantifying pollution, and 3) understanding how pollution affects ecosystem processes and resilience (Percy et al., 2012). Therefore, given that the TEEM program has spent the last 20 years achieving mandate 1 and 2, the goal for recent work was to initiate the execution of mandate 3, where the specific research objectives were to: 1) examine the spatial distribution of S and N deposition and determine if it is similar to that of ecosystem receptors, including soil surface layers (LFH, 0–5, 5–15, and 15–30 cm mineral soil) and foliar tissue, 2) investigate if a causal relationship can be established between S and N deposition and the ecosystem receptors, including soil surface layers (LFH, 0–5 cm, 5–15 cm, and 15–30 mineral soil) and foliar tissue, and 3) examine if a correlative relationship exists for S and N deposition and changes to soil acidity. A companion paper will further investigate mandate 3 by examining the response of vegetation to air pollution (Bartels et al., 2019).

2. Materials and methods

2.1. Study area

Jack pine ecosystems on coarse textured soils represent a significant proportion of the landscape in the AOSR and have been shown to be susceptible to negative impacts of acid deposition, as discussed in Foster et al. (2019). Soils of the jack pine ecosystems monitored in this study were classified as Eluviated Dystric Brunisols (Table 1) following the Canadian System of Soil Classification (SCWG, 1998) and would be classified as Umbrisols following the FAO World Reference Base for Soil Resources (IUSS, 2006), or Inceptisols (Dystrocryepts) following the USDA soil taxonomy (USDA, 1975). The genesis of Brunisols is associated with perhumdid to semiarid moisture and mesic to arctic temperature regimes (Turchenek and Lindsay, 1982). Brunisolic soils are rapidly to imperfectly drained mineral soils; characterized by a brownish Bm horizon, which result from hydrolysis or in situ oxidation, leading to changes in color, composition, and structure allowing for differentiation from A and C horizons (Turchenek and Lindsay, 1982). Processes that lead to the diagnostic horizons of Podzols have not been substantially expressed in the Brunisols in this area, but they are likely transitioning to these soils. Analysis of soil texture of all sites revealed that they are dominated by sand contents of 80% or greater throughout the profile, except for sites 1007, 2013, and 3003 where more fine textured horizons were identified. Brunisolic soils in the study area support xeric to subxeric and nutrient-poor type a ecosites (Beckingham and Archibald, 1996), which are characterized by Jack Pine (*Pinus banksiana*), Bearberry (*Arctostaphylos uva-ursi*), Bog Cranberry (*Vaccinium vitis-idaea*), Blueberry (*Vaccinium myrtilloides*), Twin-flower (*Linnaea borealis*), Sand Heather (*Hudsonia tomentosa*), Wild Lily-of-the-valley (*Liliaceae Maianthemum dilatatum*), Schreber's Moss (*Pleurozium schreberi*), Awned Hair-cap (*Polytrichum*), and Reindeer Lichen (*Cladina rangiferina*). Forest stands typical for those ecosites are generally open canopied

Table 1
Generalized profile description for soils of the jack pine ecosystems described in this study. Soils were classified as Eluviated Dystric Brunisols.

Horizon	Depth (cm)	Description
LFH	2–0	Lichen/needle litter
Ae	0–5	Grayish brown (10YR 5/2); fine sand; single grain; loose; few, fine to medium, horizontal roots; no coarse fragments; wavy boundary, pH (0.01 M $CaCl_2$) <5.5
Bm1	5–35	Yellowish brown (10YR 5/8); fine sand; single grain; loose; very few; fine to medium, horizontal roots; no coarse fragments, pH (0.01 M $CaCl_2$) <5.5
Bm2	35–50	Brownish-yellow (10 YR 6/6); fine sand; single grain; loose; no roots; no coarse fragments, pH (0.01 M $CaCl_2$) <5.5
BC	50–120	Light yellowish brown (10YR 6/4); fine sand; single grain; loose; very few, fine to medium, horizontal roots; no coarse fragments, pH (0.01 M $CaCl_2$) <5.5
C	120–150+	Light yellowish brown (10 YR 6/4); few, fine, prominent red (2.5 YR 4/8) mottles; fine sand; single grain; loose; no roots; no coarse fragments, pH (0.01 M $CaCl_2$) <5.5

and are characterized by a lichen-covered forest floor (Beckingham and Archibald, 1996). In 1998, sites of the 1000 series were established in line with the forest health monitoring (FHM) program established in the AOSR by WBEA to monitor acid deposition in this ecosystem. Between 2001 and 2004, sites of the 2000 series were added to increase the monitoring footprint, and in 2011 and 2012, sites of the 3000 series were added (see Table 2 for a complete list and Foster et al. 2019 for more details).

2.2. Atmospheric deposition

Data for atmospheric deposition was provided by Edgerton et al. (2020) who applied a hybrid approach to estimate sulfur (S), nitrogen (N) and base cations (BC) deposition, and from these data, a derived estimate of potential acid input (PAI), to FHM sites. Detailed information on the methods used and estimates are available in Edgerton et al. (2020).

2.3. Sample collection and analysis

Soil samples were collected from subplots of the 4 10x10 m plots that were established for sample collection by the TEEM program of WBEA (Foster et al., 2019). Samples were collected following the program specific requirements (Kalra and Maynard, 1991; Foster et al., 2019). Briefly, soils were collected by depths (LFH, 0–5 cm, 5–15 cm, and 15–30 cm mineral soil) from the side of small soil pits, from 4 subplots in each of 4 plots, per site. Soil samples were transferred to plastic bags and stored at either 4 °C or −20 °C (for N analysis) until they could be analyzed. Foliar samples were collected from current annual growth, and frozen until being dried at 70 °C for 24 h. Total S and N in soil and tissue samples were analysed by dry combustion (Kalra and Maynard, 1991). Foliar SO_4-S was measured following hydriodic acid digestion (Johnson and Nishita, 1952). Soil pH was measured in 0.01 M $CaCl_2$ at a ratio of 4:1 for LFH and 2:1 for mineral soil (Kalra and Maynard, 1991). The base cation to aluminium (BC:Al) ratio was calculated based on cation extraction with 1.0 M NH_4Cl sloution, which were then analyzed by ICP-OES (Kalra and Maynard, 1991).

2.4. Rationale for analysis of a subset of sites

Six of the FH monitoring sites were affected by wildfire in 2011 before data collection (Table 2). A major wildfire complex, known as the Richardson fire, started in early May of 2011 and burned 576,000 ha of jack pine dominated forest (Pinno et al., 2013). Soil physical, chemical, mineralogical, and biological conditions can be affected by forest fires, with the magnitude of effect related to the fire intensity and severity (Certini, 2005). Soil total N in some stands can be reduced by 25% directly following fire (Kutiel and Naveh, 1987). Both, S and N are volatilized during fire (DeBano, 1990) and re-deposited locally and regionally. Soil pH has been demonstrated to significantly increase following fire (Murphy et al., 2006). Hence, inclusion of recently burned sites would have affected the signal to noise ratio for deposition data, and foliar and soil chemical parameters. For that reason, sites affected by fire were excluded from analysis.

Table 2
Forest health sites with coordinates used in the spatial analysis and details on which sites were removed after being affected by wildfire.

FHM Site ID	Latitude	Longitude	Site affected by fire in 2011	Wildfire ID
1001	56.53897	−112.27495		
1002	56.90962	−111.54072		
1003	57.42482	−111.58980	Yes	Alberta Wildfire MWF010-2011
1004	57.11902	−111.42542		
1006	57.66158	−111.16735	Yes	Alberta Wildfire MWF007-2011
1007	57.89043	−111.43529	Yes	Alberta Wildfire MWF007-2011
1008	56.70515	−109.92699		
1009	57.54103	−111.09348	Yes	Alberta Wildfire MWF007-2011
2001	57.03207	−113.73552		
2005	57.83751	−110.44880	Yes	Alberta Wildfire MWF007-2011
2010	56.27350	−110.44858		
2012	57.05369	−111.40916		
2013	57.04999	−109.74986	Yes	SK Wildfire C115005-2011
3003	56.83357	−111.10785		
3004	57.05360	−111.37590		
3007	57.35931	−111.02264		
3008	57.10188	−112.07542		
3010	56.69278	−111.79445		
3011	56.82992	−110.43277		
3012	56.66140	−110.06596		
3013	57.10678	−112.05982		
3015	56.35326	−110.11850		
3016	56.53897	−112.27495		
Total sites affected in 2011: 6; Sites not affected: 17				

See Foster et al. (2019) for full details on site characteristics.

2.5. Statistical analysis

Inverse Distance Weighting (IDW) was used for spatial interpolation of measured parameters and provided deposition estimates. Interpolated values in IDW are based on values at proximal locations and are weighted based on distance. Only the fundamental assumption that nearby points are more closely related than distant points is used to derive values for interpolated locations in creating IDW maps. ArcGIS 10.5 (Environmental Systems Research Institute, Redlands, CA) was used to produce the IDW output.

Linear regression was conducted to explore relationships between atmospheric inputs and scalar responses of foliar, LFH, and topsoil elemental concentrations and changes in acidity. Regression models were plotted in R v3.4.4 (The R Foundation for Statistical Computing) using the ggplot2 and ggpmisc package. The coefficient of determination (R^2) for model fit and the P-value for each linear model were reported. In all cases, the assumptions for parametric statistics, including normality, independence, and homogeneity of variance, were checked and met, and statistical significance was assigned at an alpha of 0.05.

The data used in this study are available upon request from the WBEA data storage administrator (https://wbea.org/deposition/wbea-terrestrial-monitoring/).

3. Results

3.1. Sulfur deposition and effects on foliar and soil chemistry

Spatial interpolation of SDep to the AOSR sampling domain revealed an area of elevated deposition north of 57-degree latitude and east of −111.5-degree longitude (Fig. 1), in the core of industrial activity north of Fort McMurray. Analysis of foliar and LFH SO_4^{2-} concentration demonstrated increased SO_4^{2-} values in the respective area with higher SDep data. Soil 0–5 cm concentrations, however, did not show increased measurements in the area with higher SDep. North of 57-degree latitude and east of −114-degree longitude no measurable increase in soil or needle sulfur were found (Fig. 1).

A significant positive, relationship (R^2 = 0.42, P-value = 0.005) for SDep and foliar SO_4^{2-} concentration was identified (Fig. 2a). Regression analysis for SDep and LFH SO_4^{2-} concentration also revealed a significant, positive relationship (R^2 = 0.46, P-value = 0.029) between both parameters (Fig. 2b). No significant relationship between SDep and topsoil (0–5 cm) SO_4^{2-} concentration was detected (R^2 = 0.026, P-value = 0.55) (Fig. 2c). However, at 5–15 cm a significant positive relationship (R^2 = 0.38, P-value = 0.01) was detected (Fig. 2d) and there was strong, but insignificant, trend at 15–30 cm depth as well (R^2 = 0.21, P-value = 0.07) (Fig. 2e).

3.2. Nitrogen deposition and effects on foliar and soil chemistry

Spatial interpolation of NDep to the AOSR sampling domain showed an area of increased deposition north of 57-degree latitude and east of −111.5-degree longitude (Fig. 3). Foliar total N concentration was significantly, and positively, correlated with NDep (R^2 = 0.24, P-Value = 0.04) (Fig. 2f). There was no relationship between NDep and total N in LFH or in soil 0–30 cm (Fig. 2g–j).

3.3. Effects of deposition on soil pH

Spatial interpolation of PAI and base cation deposition based on FHM monitoring data indicated higher levels for both parameters north of 57-degree latitude and east of −111.5-degree longitude (Fig. 4), but these were not centered on the same spot. The analysis of LFH pH found higher values for the same area north of 57-degree latitude and east of −111.5-degree longitude (Fig. 4). The pH of LFH did not match the spatial pattern of PAI or base cations with highest pH south of 57-degree latitude and west of −111.5-degree longitude, and lowest pH north of 56.5-degree latitude and east of −110-degrees longitude (Fig. 4). For topsoil (0–5 cm) pH no correlation was evident with estimates of PAI or base cation deposition (Fig. 4). Topsoil pH (0–5 cm) was predicted to be higher east of −111-degree longitude, while to the west pH values were predicted to decrease (Fig. 4). Ammonia (NH_3) dry deposition was predicted to be highest south of 57° latitude and east of −110.5°longitude (Fig. 4).

PAI exhibited no significant negative relationship with soil pH values in the study area. For LFH data, a significant positive relationship of increasing pH with increasing PAI was observed (LFH R^2 = 0.23, P-value = 0.05), although the relationship barely met the significance threshold (Fig. 5a). No significant relationship between mineral soil pH and PAI was found (0–5 cm R^2 = 0.03, P-value = 0.49; 5–15 cm R^2 = 0.009, P-value = 0.73; 15–30 cm R^2 = 0.000056, P-value = 0.98) (Fig. 5b–d). Base cation deposition was not significantly associated with the pH of LFH or mineral soil (0–5 cm) at the study sites (LFH R^2 = 0.01, P-value = 0.70; 0–5 cm R^2 = 0.08, P-value = 0.27) (Fig. 5e, f), but a significant negative relationship existed between base cation deposition and pH in mineral soil 5–15 cm depth (R^2 = 0.35, P-value = 0.017; Fig. 5g) and 15–30 cm depth (R^2 = 0.32, P-value = 0.021; Fig. 5h).

PAI was not significantly related to the BC:Al ratio in LFH or any mineral soil depth (LFH R^2 = 0.05, P-value = 0.41; 0–5 cm R^2 = 0.03, P-value = 0.53; 5–15 cm R^2 = 0.01, P-value = 0.70; 15–30 cm R^2 = 0.003, P-value = 0.83) and neither was base cation deposition (LFH R^2 = 0.02, P-value = 0.61; 0–5 cm R^2 = 0.03, P-value = 0.53; 5–15 cm R^2 = 0.01, P-value = 0.70; 15–30 cm R^2 = 0.003, P-value = 0.83) . Similarly, base saturation showed no significant relationship with PAI in any soil layer (LFH R^2 = 0.05, p = 0.40; 0–5 cm R^2 = 0.04, P-value = 0.48; 5–15 cm R^2 = 0.00003, P-value = 0.95; 15–30 cm R^2 = 0.16, P-value = 0.13). For the LFH layer a significant positive effect of BC deposition on %BS was identified (R^2 = 0.27, P-value = 0.04) but not for mineral soil (0–5 cm R^2 = 0.02, P-value = 0.57; 5–15 cm R^2 = 0.1, P-value = 0.23; 15–30 cm R^2 = 0.1, P-value = 0.22). Even though %BS significantly increased with deposition, no significant relationship between BC deposition and LFH pH was detected (R^2 = 0.01, P-value = 0.67). However, a significant positive relationship (R^2 = 0.29, P-value = 0.033) was detected for NH_3 dry deposition and LFH pH (Fig. 6). NH_3 deposition had no significant association with the pH of any mineral soil depth (0–5 cm R^2 = 0.03, P-value = 0.53; 5–15 cm R^2 = 0.01, P-value = 0.70; 15–30 cm R^2 = 0.003, P-value = 0.83).

4. Discussion

4.1. Sulfur deposition and effects on foliar and soil chemistry

Spatially interpolated values for SDep (Edgerton et al., 2020) were found to be consistent with measured patterns of foliar and LFH SO_4^{2-} concentration at the FHM sites. This observation was confirmed by linear regression indicating that atmospheric deposition is significantly related to both foliar and LFH SO_4^{2-} concentrations. The analysis of upper mineral soil (0–5 cm) did not reveal a significant relationship with predicted SDep, suggesting that other processes are affecting this pattern, like plant uptake as suggested by Bartels et al. (2019). There were significant positive relationships between SDep and soil SO_4^{2-} concentration in both the 5–15 cm and 15–30 cm soil layers, indicating that excess SO_4^{2-} was retained in deeper layers. These soils are on their way to becoming Podzols with Bf and Bfh horizons, so it is possible that the excess S was retained at depth on the accumulating iron oxides (f) or organic matter (h). In forest ecosystems S is a macronutrient that can limit tree seedling growth (Ericsson, 1995). Deposition of SO_2 and elemental S dust resulted in a fertilizer effect with greater apical growth of *Pinus contorta* × *Pinus banksiana* over a period of 3 years when compared to unaffected control treatments (Mayo et al., 1992). Elevated SO_4^{2-} concentrations in foliage and LFH in areas with higher deposition, but no corresponding increase in mineral topsoil may indicate that SO_4^{2-} currently is utilized by vegetation, contributing to the fertilizer effect that Bartels et al. (2019) observed on these sites. However, increases in foliar SO_4^{2-} concentrations in *Pinus banksiana* in our study could also be related to increased foliar absorption of SO_2, which can contribute to S supply for plant nutrition (Linzon et al., 1979).

A consistent elevated input of S into jack pine ecosystems may be cause for concern, as excess S can negatively impact plant metabolism and can affect dry weight accumulation, yield, and delay of flowering (Rennenberg, 1984). For that reason, we sug-

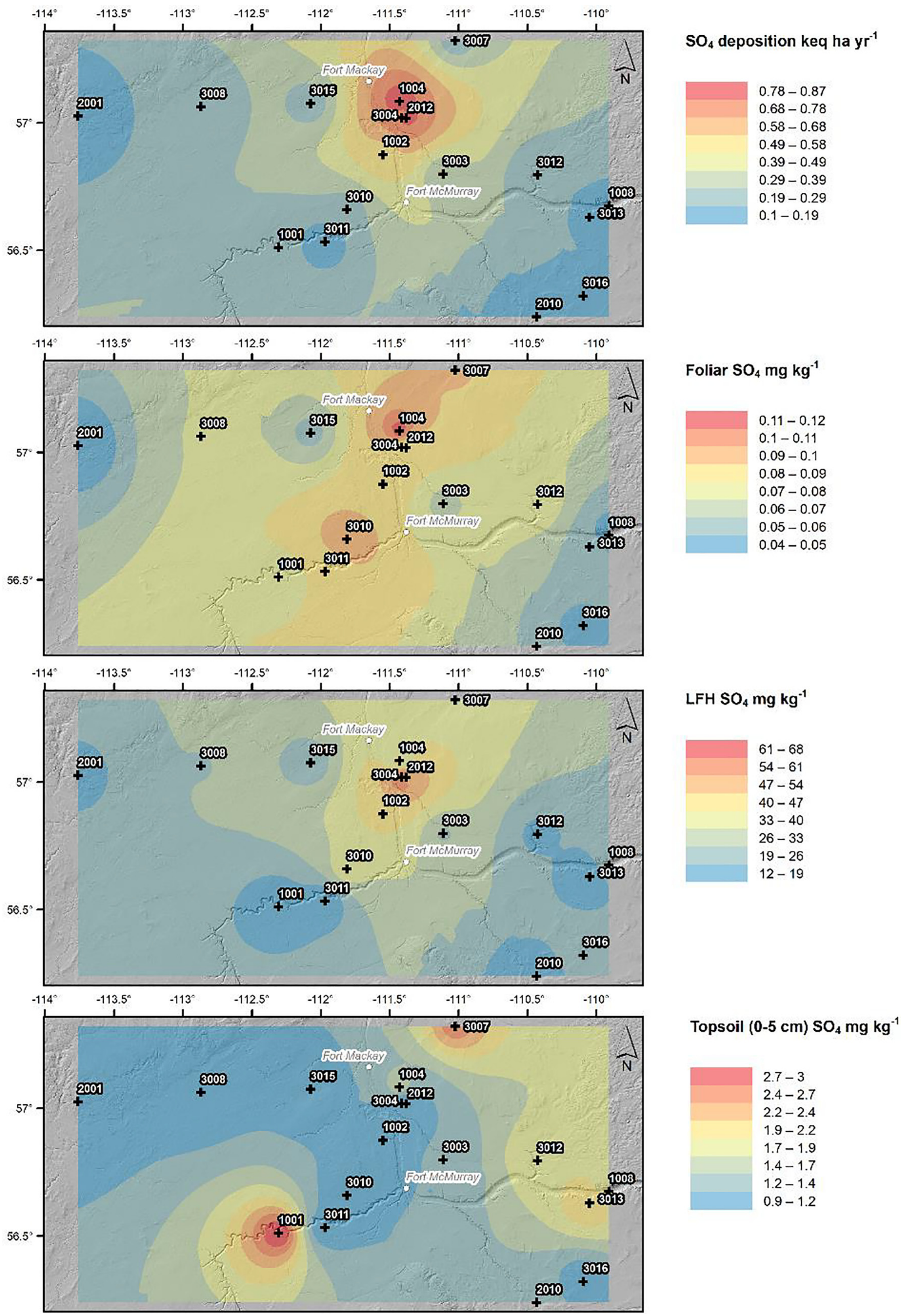

Fig. 1. Inverse distance weighting interpolation for SO_4 deposition and SO_4 concentration in *Pinus banksiana* foliage, LFH, and topsoil (0–5 cm depth).

gest monitoring *P. banksiana* phenology on study sites, as the forest health effects of excess S, have not been evaluated to date in the AOSR. A previous study from the AOSR that evaluated jack pine foliar nutrients based on distance from industrial source could only establish a weakly significant increase of total S, as well as total N, Ca, B, Zn, and Fe, (Proemse et al., 2016), but did not

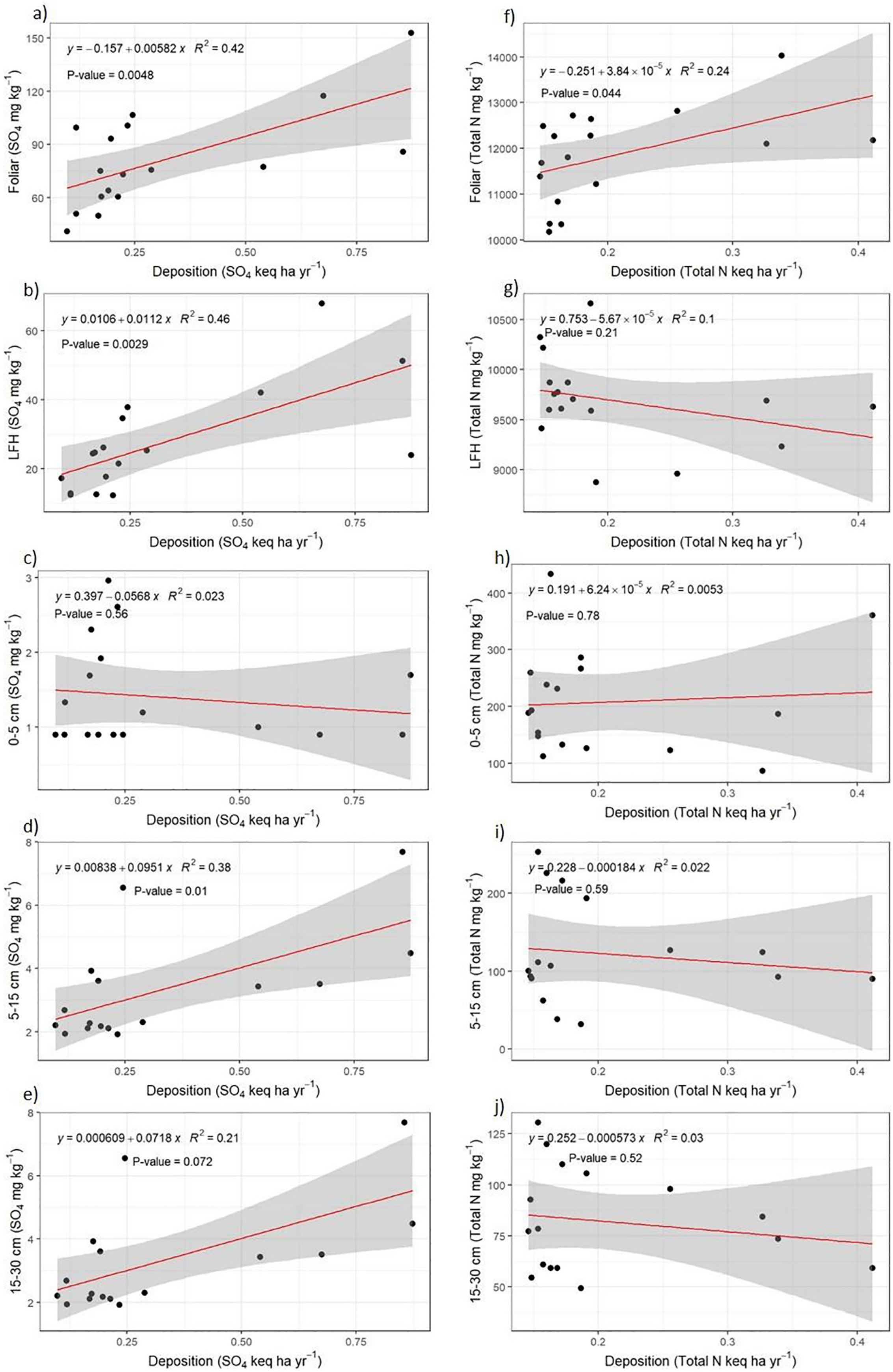

Fig. 2. Linear regression for modelled potential SO_4 deposition vs. SO_4 concentration in current annual growth a), LFH b), 0–5 cm c), 5–15 cm d), and 15–30 cm e); for modelled total N deposition and total N concentration in current annual growth f), LFH g), 0–5 cm h), 5–15 cm i), 15–30 cm j). Grey band represents the standard error of the regression.

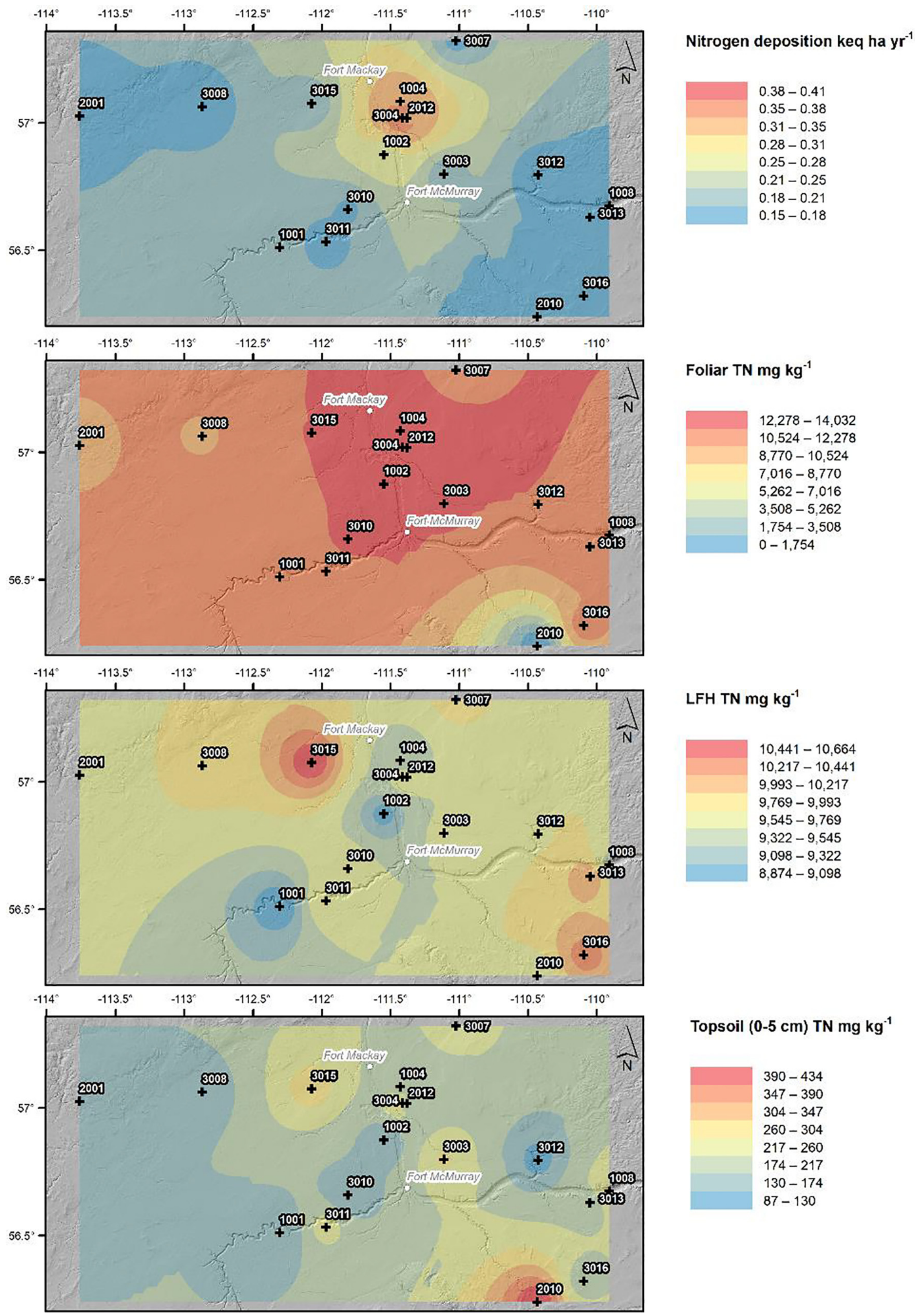

Fig. 3. Inverse distance weighting interpolation for total N deposition and total N concentration in *Pinus banksiana* foliage, LFH, and topsoil (0–5 cm depth).

measure deposition or forest health. In other pine forests in Canada, increased levels of S in the soil have been shown to negatively affect some macroinvertebrates (Cárcamo et al., 1998). Hence, an evaluation of the impacts of S deposition on soil biology is recommended for the FHM sites evaluated by the TEEM program.

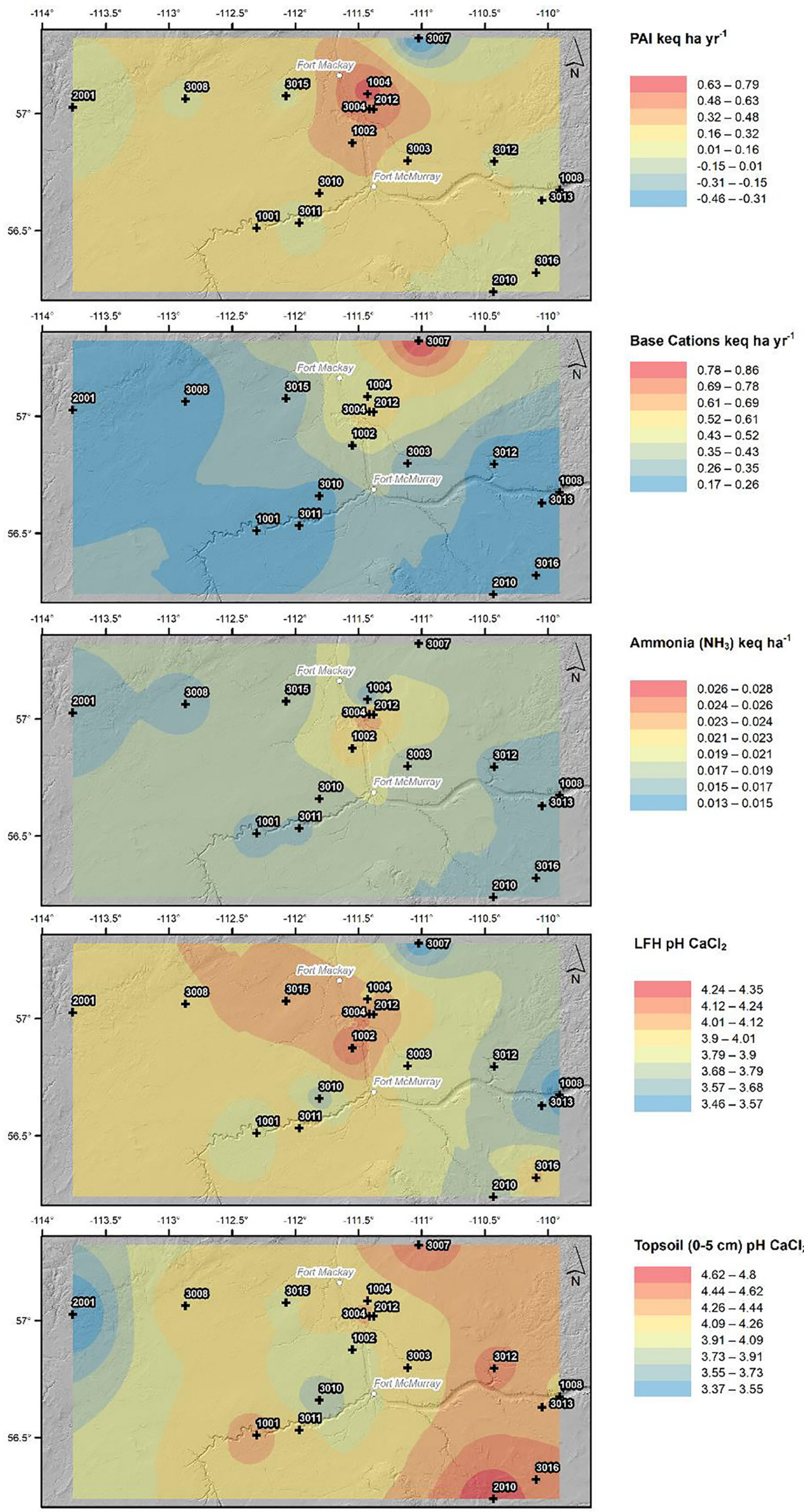

Fig. 4. Inverse distance weighting interpolation for potential acid input (PAI), base cation deposition, NH_3 deposition, and pH as measured in $CaCl_2$ for LFH, and topsoil (0–5 cm depth).

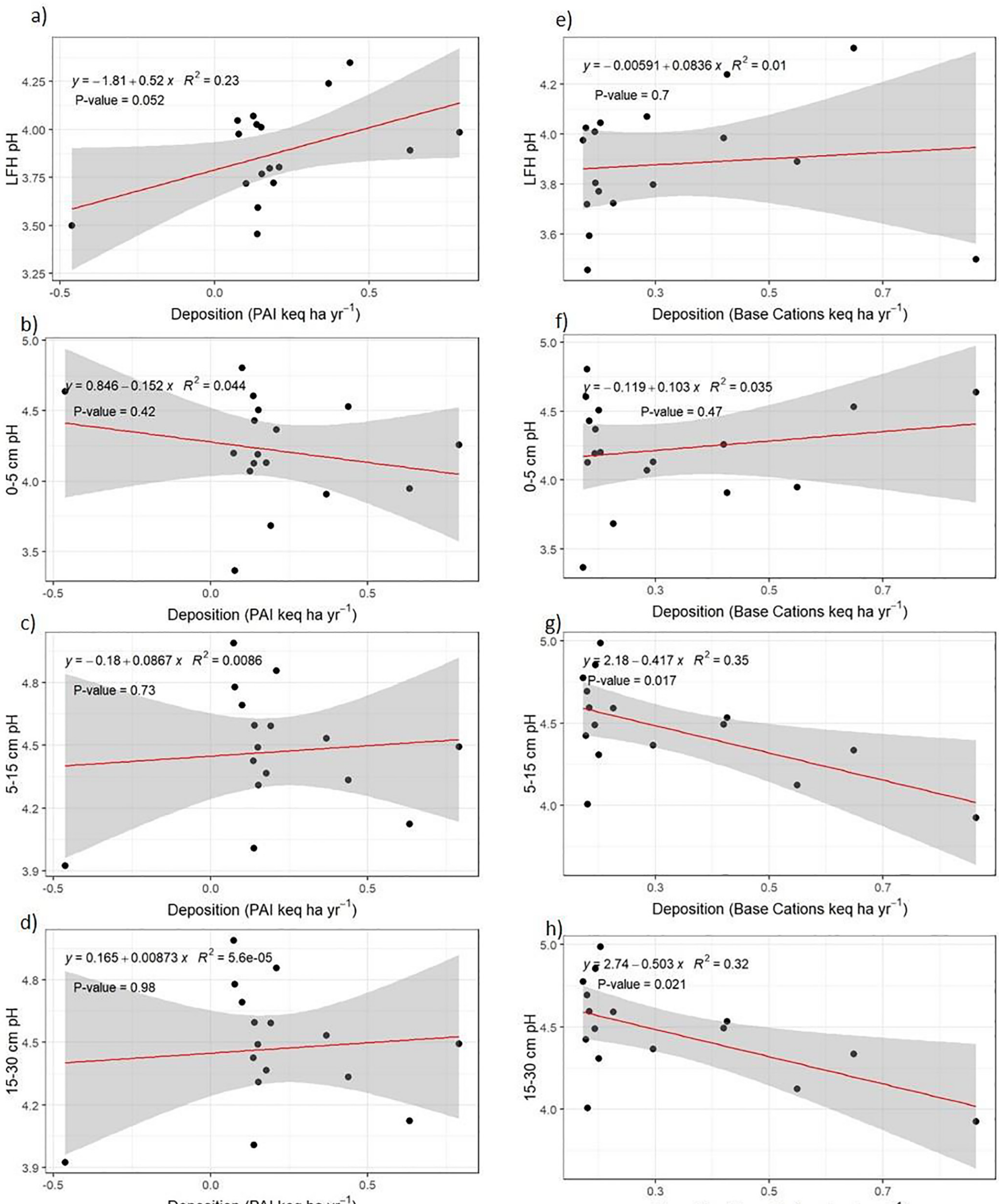

Fig. 5. Linear regression for potential acid input (PAI) and pH in $CaCl_2$ of LFH a), 0–5 cm b), 5–15 cm c), and 15–30 cm d); for modelled base cation deposition pH in $CaCl_2$ of LFH e), 0–5 cm f), 5–15 cm g), 15–30 cm h). Grey band represents the standard error of the regression.

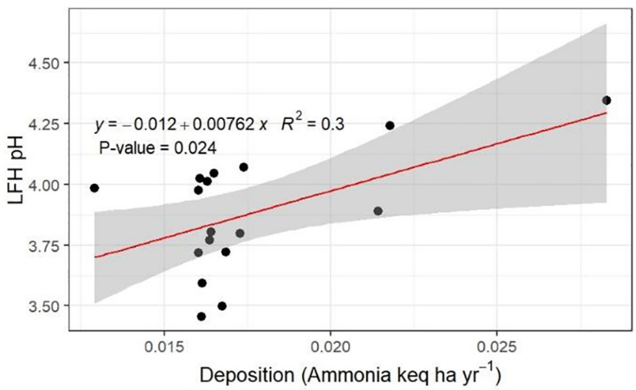

Fig. 6. Linear regression for ammonia deposition (NH_3) and pH in $CaCl_2$ for LFH. Grey band represents the standard error of the regression.

4.2. Nitrogen deposition and effects on foliar and soil chemistry

Spatially interpolated NDep showed a relationship with measured hotspots of foliar N concentrations, but not for LFH or any mineral soil depth, potentially indicating strong N uptake by Jack pine foliage and understorey vegetation. The spatially observed correlation of foliage and Ndep was shown by linear regression, which indicated a strong positive relationship between both parameters. It has been suggested that foliar NO_3^- uptake from the atmosphere can contribute a significant proportion of N to plant metabolism, particularly under N limiting conditions (Vallano and Sparks, 2008). Contrary to foliar uptake where N is directly available to plants, the addition of N to the soil surface may result in incorporation of N into soil organic matter (Sparks, 2009). When N is deposited to soil it is highly reactive and can undergo a number of different physio-chemical processes, including (i) volatilize back to the atmosphere as gas due to denitrification or NH_3 bi-directional exchange, (ii) be immobilized into microbial or vegetative biomass, or (iii) be leached into soil groundwater (Sparks, 2009). Jack pine stands evaluated during this study show no evidence for incorporation of N in LFH or topsoil, so likely not leaching. Higher N availability in soil can lead to increased herbaceous cover that adversely affects the establishment of woody seedlings (Davis et al., 1999). N accumulation in ecosystems is a main driver for changes in species composition (Bobbink et al., 2010). Both of these have been observed at the FHM sites of this study as both plant community structure has changed and overall growth of different functional groups has increased, possibly due to increased NDep (Bartels et al., 2019).

In the boreal biome, N bioavailability is considered to be limiting for forest growth (Sponseller et al., 2016). Increased biomass accumulation might currently buffer inputs of N into jack pine ecosystems. Research that evaluated the fate of nutrients in *P. banksiana* suggested that 71–89% of elements taken up by trees are returned to the soil either by litter fall or leaf wash (Foster and Morrison, 1976), however these needles can remain on the tree for 20 years which may result in a lag perod for elevated LFH toatl N. Given that no increase in LFH total N with increased deposition was detected in our study, two more possibilities exist, i) N is potentially being volatilized directly on the needle surface (Sparks, 2009), or ii) the demand for N is so high that it is taken up by plants immeadiately (Maynard et al, 2014).

Two primary concerns associated with S and N deposition are soil acidification and plant community changes through ecosystem eutrophication (Gilliam et al., 2016). The results from this study suggest that soil acidification is not occurring (discussed below). In a companion paper in this special issue, Bartels et al. (2019) show an increase in tree growth and a shift in plant community structure on these same sites, suggesting a fertilization effect of deposition. Continued monitoring is therefore necessary to follow this process, and determine if saturation occurs and we begin to see ecosystem level eutrophication with drastic shifts in below-ground processes and effects on adjacent ecosystems through ground water movement. Given how many sites are outside of the standard error of the regression (Figs. 2 and 5), we also recommend adding more sites to the FHM network to account for this uncertainty.

4.3. Effects of deposition on soil pH

LFH and mineral soil showed no evidence of pH responses to PAI. An apparent non-significant positive effect of estimated PAI and LFH pH was observed or compounds included in the PAI formula may react differently in nutrient limited boreal forest ecosystems than anticipated. Acidifying compounds such as NH_3 and NH_4^+ are likely directly taken up by vegetation, which could explain increased foliar concentration observed in this study, resulting in no H^+ release into soil. In boreal jack pine stands the majority of fine roots are found above the mineral soil in the LFH layer (Steele, 1997) and this may lead to an immediate uptake of N compounds in the LFH layer leading to no measurable effect in all soil layers. Nitrogen is a main mineral nutrient that represents about 2% of plant dry matter and N deficiency is often an important limitation for plant growth (Miller and Cramer 2005). Nitrogen that is bound in vegetation and subsequently in complex organic structures that are resistant to decay are a rate limiting factor for N cycling of forest ecosystems (Sponseller et al., 2016). Hence, the fate of NH_3 and NH_4^+ in nutrient limited boreal forest ecosystems should be monitored closely, to better understand the fate of both compounds and associated effects on soil acidification. Eventually, tracking trials for N isotopes should be established to understand the fate of deposited N better in jack pine ecosystems in the AOSR. Additionally, a more sensitive soil nutrient test like Plant-Root Simulator probes (PRS™) should be permanently employed to allow for an evaluation of the fate of NH_4^+ and NO_3^- at a higher resolution. Measurements for NO_3^- in soil samples were consistently below detection limit (data not shown). In this study, we additionally detected a significant positive association of dry NH_3 deposition on LFH pH, which may be related to the release of OH^- when converted to NH_4^+. Nitrification of NH_3 or NH_4^+ to NO_3^- typically would release H^+ ions, and for that reason is considered acidifying. Ammonia has been demonstrated to be capable of increasing soil pH in the LFH layer for decomposing fruitbodies of macrofungi in a closed laboratory setting (Ingelög and Nohrstedt 1993), but this may not be relevant for aerated field soils. Given the potential phytotoxic effect of NH_3 on vegetation of jack pine ecosystems (Bytnerowicz et al., 2010), further analysis of deposition of this molecule is merited. Spatial models have demonstrated changes in vegetation structure due to wildfire emissions and subsequent changes in soil pH (Das Gupta and Pinno, 2018), it is conceivable that negative effects of industrial NH_3 deposition may also be already occurring in jack pine ecosystems and potentially be reflected in those spatial models.

Additionally, increased deposition of base cations might have interacted with changes in LFH pH. However, an evaluation of BC deposition associated with fugitive dust also showed no significant relationship with pH in regression analysis. An evaluation of spatially resolved estimated BC deposition plots suggests increased inputs in areas with higher topsoil (0–5 cm) pH, but further refinement of estimated input data may be necessary to evaluate the effects of PAI on soil pH. SDep and NDep have been linked to increases in soil acidification and can lead to conditions that can reduce plant biodiversity (Bowman et al., 2008); however, we found no significant relationship between atmospheric inputs of S and N with soil pH (data not shown). Acid inputs are potentially being buffered by fugitive dust with high BC content, although the data presented here does not show clear patterns that this is the case. Effects of acid deposition on soil pH might be balanced by BC deposition which is associated with increased amounts of fugitive dust emitted by mining operations (Landis et al., 2012; Landis et al., 2017b; Wang et al., 2015). However, our study demonstrated no significant relationship between BC deposition and pH. Future work should focus on overall buffering capacity of soils in relation to predicted long term inputs and should consider the uptake of S and N by vegetation and associated fixation in complex organic structures.

A commonly used indicator of the potentially adverse effects of acid deposition on forest soils is the base cation to aluminum ratio (BC:Al ratio) (Løkke et al., 1996; van Schöll et al., 2004). In our study, no significant relationship between PAI and changes in the BC:Al ratio was detected. Van Schöll et al. (2004) suggested that the BC:Al ratio as an indicator for acid deposition was never evaluated properly and the absolute concentrations of Al in the soil solution may be a more appropriate indicator.

5. Conclusions

Our findings indicate that SDep is correlated with elevated S in foliar tissue, the organic layer of soils (LFH), and 5–30 cm in mineral soil in the AOSR, while NDep is only correlated with elevated N in foliar tissue. The vegetation companion paper to this suggests that this is having a possible fertilising effect on tree growth and causing a shift in understorey community structure. However, based on a lack of significant relationship with PAI and soil pH, we find no evidence that acidic critical loads have been reached; however, close attention should be paid to effects of increased SO_4 concentration in mineral soil. Future studies should evaluate critical loads in jack pine ecosystems in targeted fertilizer trials and investigate the fate of N and S compounds. Such a study could also be used for an evaluation of deposition on changes in soil pH. This lack of a relationship was hypothesized to result from fugitive dust containing Ca (Landis et al., 2017b), but no significant relationship between Ca deposition and soil pH was observed. We hypothesize that the effect of soil acidification may be mediated N fixation in plants and dry matter. The PAI model may need to be adjusted to account for ecosystem N fixation and effects on nitrification as well as Ca^{2+} and SO_4^{2-} sources to predict potential effects on pH more efficiently.

Declaration of Competing Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Acknowledgements

Funding for this work was provided via the Wood Buffalo Environmental Association (WBEA) through the Oil Sands Monitoring Program (OSM). The content and opinions expressed by the author in this document do not necessarily reflect the views of the Wood Buffalo Environmental Association (WBEA) or of the WBEA membership. A special thank you to all the WBEA field technicians responsible for high quality data collection and preservation over the years. We would also like to thank Ken Foster and Matt Landis for insightful additions and comments on the manuscript.

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