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Assessing Forest Health in the Athabasca Oil Sands Region

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Final Report

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Chapter 3: Wet and dry deposition in the AOSR collected by ion exchange resin samplers

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3.1 Introduction

Atmospheric deposition of nitrogen (N), sulfur (S), and base cations was measured across the network of jack pine sites using ion exchange resin (IER) collectors as described in Fenn *et al.* 2015. Deposition was measured in forest clearings (bulk deposition) and under jack pine canopies (throughfall). Bulk deposition consists primarily of wet deposition, with a minor dry deposition component that collects onto the funnel collectors during dry periods. Throughfall deposition refers to the hydrologic flux of ions and other compounds washed from the tree canopies by precipitation or snowmelt and deposited in solution to the forest floor (Parker, 1983). Measurement of nutrient deposition in throughfall is a widely used method for estimating atmospheric deposition inputs to forest ecosystems (Bleeker *et al.*, 2003; Thimonier, 1998).

A passive sampling method for measuring bulk deposition in forest clearings or throughfall deposition based on the deployment of ion exchange resin (IER) columns connected to a sampler funnel has been successively used in many field studies (Fenn and Poth, 2004; Root *et al.*, 2013). The IER sampling method is very useful for deposition monitoring in remote regions because of the infrequent sampling requirements.

The objective of this study was to measure atmospheric deposition levels and to characterize spatial gradients and seasonal trends of deposition to the forest surrounding and downwind of the major industrial zone in the AOSR. A major question to be addressed by this research was to describe the spatial extent of the zone of influence resulting from atmospheric emissions of N and S from the industrial processes within the AOSR. Base cation deposition was also measured for one year, allowing a comparison of atmospheric inputs to the forest of acidifying N and S deposition versus acid-neutralizing base cation deposition. It is important to quantify base cation deposition in the AOSR because of their potential to neutralize the acidifying potential of N and S deposition. Nitrogen deposition also has the potential to cause eutrophication or other N-excess effects.

3.2 Methods

Throughfall and bulk precipitation samples were collected with “passive” throughfall collectors based on a mixed bed (cation and anion resin) ion exchange resin (IER) column (Fenn and Poth, 2004; Fenn *et al.*, 2009). Precipitation or throughfall samples are collected by a polyethylene funnel or snow tube and channeled through the resin column, where ions are retained by the ion exchange resin. The major advantage of the IER method is that sample collection continues in the field without the need for repeated field trips to collect liquid samples or the need for

repeated sample analyses from each collector. This is highly advantageous in the AOSR study region where many sites are only accessible by helicopter. Deposition samples were collected seasonally. The IER columns for the summer exposures were installed in May and changed out in October. Winter exposures were from October to May.

The IER columns were prepared by pouring 25 grams of the ion exchange resin beads into PVC tubes (20 cm in length and 1.25 cm I.D.) as aqueous slurry and then further rinsed with distilled water. After the field exposure periods the IER columns were extracted with 75 ml of 1*N* KI, followed by a second extraction with 75 ml of 1*N* KI. Nitrate and sulfate concentrations in the column extracts were analyzed by ion chromatography (Dionex DX-1600, Sunnyvale, CA) using a procedure modified from Simkin *et al.* (2004). Ammonium concentrations in the KI extracts were determined colorimetrically (Technicon TRAACS autoanalyser). Samples designated for base cation analysis received an additional extraction of 200 ml KCl. The KI and KCl extracts were proportionately combined and analyzed for Ca, Mg and Na by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Atmospheric deposition fluxes were determined by extrapolating from the area of the collector opening and the amounts of inorganic N and S or base cations that were extracted from the IER columns (Fenn and Poth, 2004; Fenn *et al.*, 2009, 2015). Spatial patterns of deposition amounts with increasing distance from the industrial center of the oil sands were determined by plotting deposition fluxes versus distance and curve fitting this relationship.

IER deposition maps were created using inverse distance weighting (IDW) with a smoothing option, using 21 data points, except for base cations in which case the smoothed IDW was performed using 19 data points. Base cation deposition was not sampled at all 21 sites where N and S were sampled. Because base cation deposition was not sampled at all the same sites in winter 2009 and summer 2010, base cation deposition was estimated for some sites. The seasonal DIN+S distance regression was used to estimate the missing winter 2009 or summer 2010 base cation deposition in throughfall. The annual value was then the sum of the estimated and the actual data. If both winter and summer throughfall base cation data were missing (e.g. Peat Pond and W1 sites), the seasonal estimates were summed to obtain an annual estimate. For the eight sites with data for both the summer and winter seasons, the actual (not estimated) data were used (Fenn *et al.*, 2015).

3.3 Results

Atmospheric deposition of N, S and base cations all showed a similar pattern of rapidly decreasing values with distance from the industrial center, particularly in throughfall (Fig. 3.1). Throughfall deposition of S and N (NH_4-N + NO_3-N) decreased from maximum values of 24 and 22 kg $ha^{-1}yr^{-1}$ at 3 km from the emissions sources to predicted values of 11 and 3 kg $ha^{-1}yr^{-1}$ at 20 km from the industrial center–a decrease of 56% and 88%, respectively. Nitrogen in throughfall was already reduced by 75% at only 10.5 km from the industrial center. In contrast, moderately elevated fluxes of S in throughfall extended further away from the emissions sources than N deposition, with S deposition in throughfall reduced by 80% at 84 km from the industrial center (Fig. 3.1).

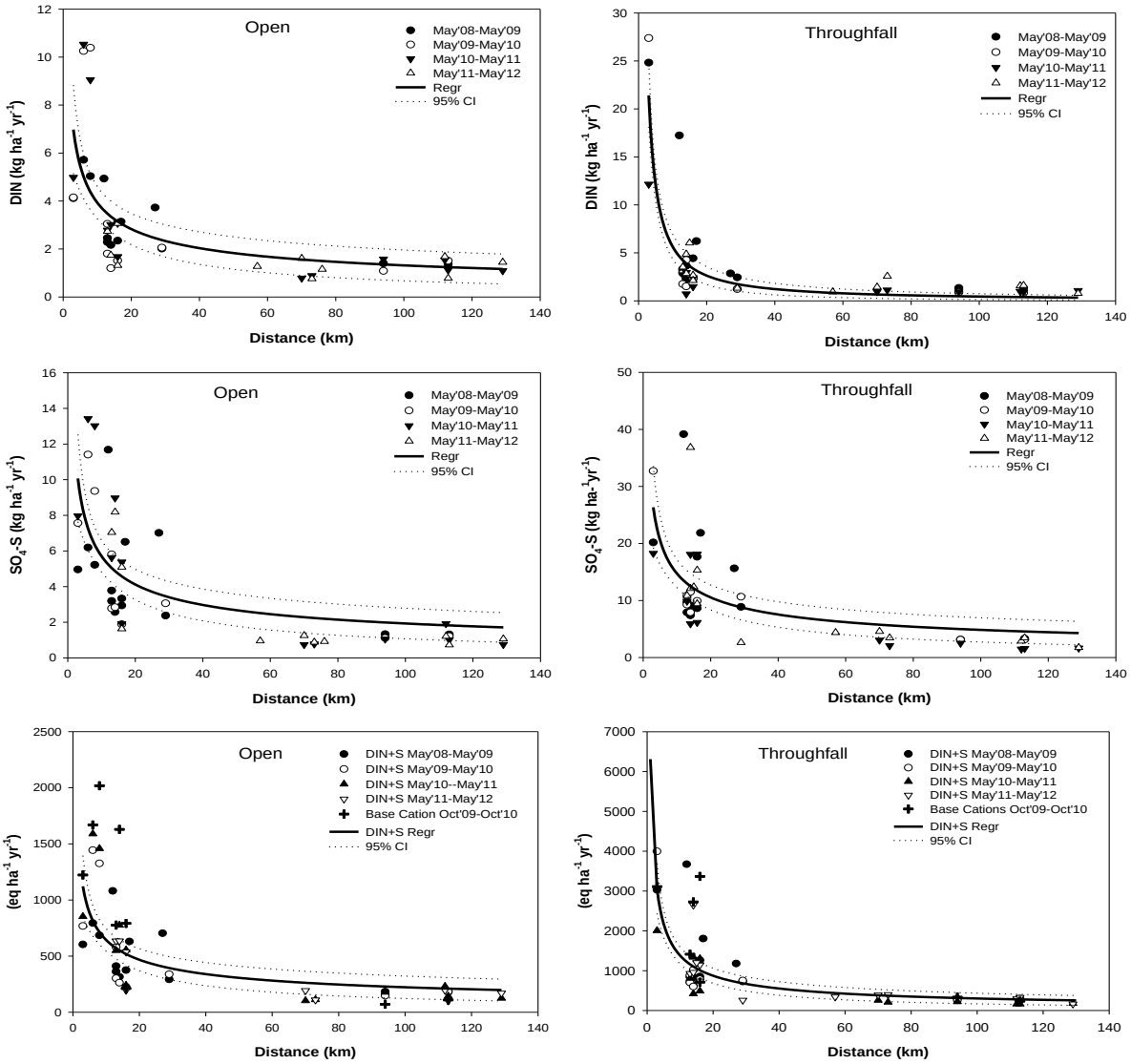

Figure 3. 1 Deposition (kg $ha^{-1}yr^{-1}$) of dissolved inorganic N (DIN; sum of NO_3-N + NH_4-N) and SO_4^- in forest clearings and in throughfall versus distance from the industrial center of the Athabasca Oil Sands Region. Also shown are four years of DIN + SO_4-S deposition (eq $ha^{-1}yr^{-1}$) in forest clearings and in throughfall versus distance. On these latter two graphs, data points (as + symbols) are shown (but not a separate regression line) for one year of base cation deposition (Na + Mg + Ca).

Annual deposition of NH_4-N in throughfall across the monitoring sites in the AOSR ranged widely from 0.8 – 14.7 kg ha^{-1} compared to a range of 0.3 – 6.7 kg ha^{-1} for throughfall NO_3-N. Deposition of SO_4-S in throughfall ranged also range widely from 2.5 – 23.7 kg ha^{-1} yr^{-1}. Deposition of NH_4-N, NO_3-N and SO_4-S in bulk precipitation (in open, canopy-free areas) across the network ranged from 0.8 – 2.8, 0.4 – 1.6 and 1.0 – 6.8 kg ha^{-1} yr^{-1}, respectively. The sum of measured base cation (Na, Mg and Ca) inputs in bulk deposition and throughfall were generally similar to or greater than inputs of acidic deposition in the form of DIN + S (Fig. 3.1). In bulk deposition, Ca was by far the most prevalent cation (57-80% of the total), followed by Mg (14-34%), and lastly Na (4-20%).

The average NH_4-N:NO_3-N ratios for annual bulk deposition and throughfall, considering all years and sampling locations were 1.8 and 2.0, respectively, indicating that over the monitoring network deposition of NH_4-N was approximately double that of NO_3-N (Fig. 3.2). The highest NH_4-N: NO_3-N ratios in bulk deposition during summer were found at the Peat Pond and W1 sites located 6 and 8 km. from the industrial center; winter ratios at these sites were also among the highest. However ratios in bulk deposition in winter only occasionally exceeded 2.0.

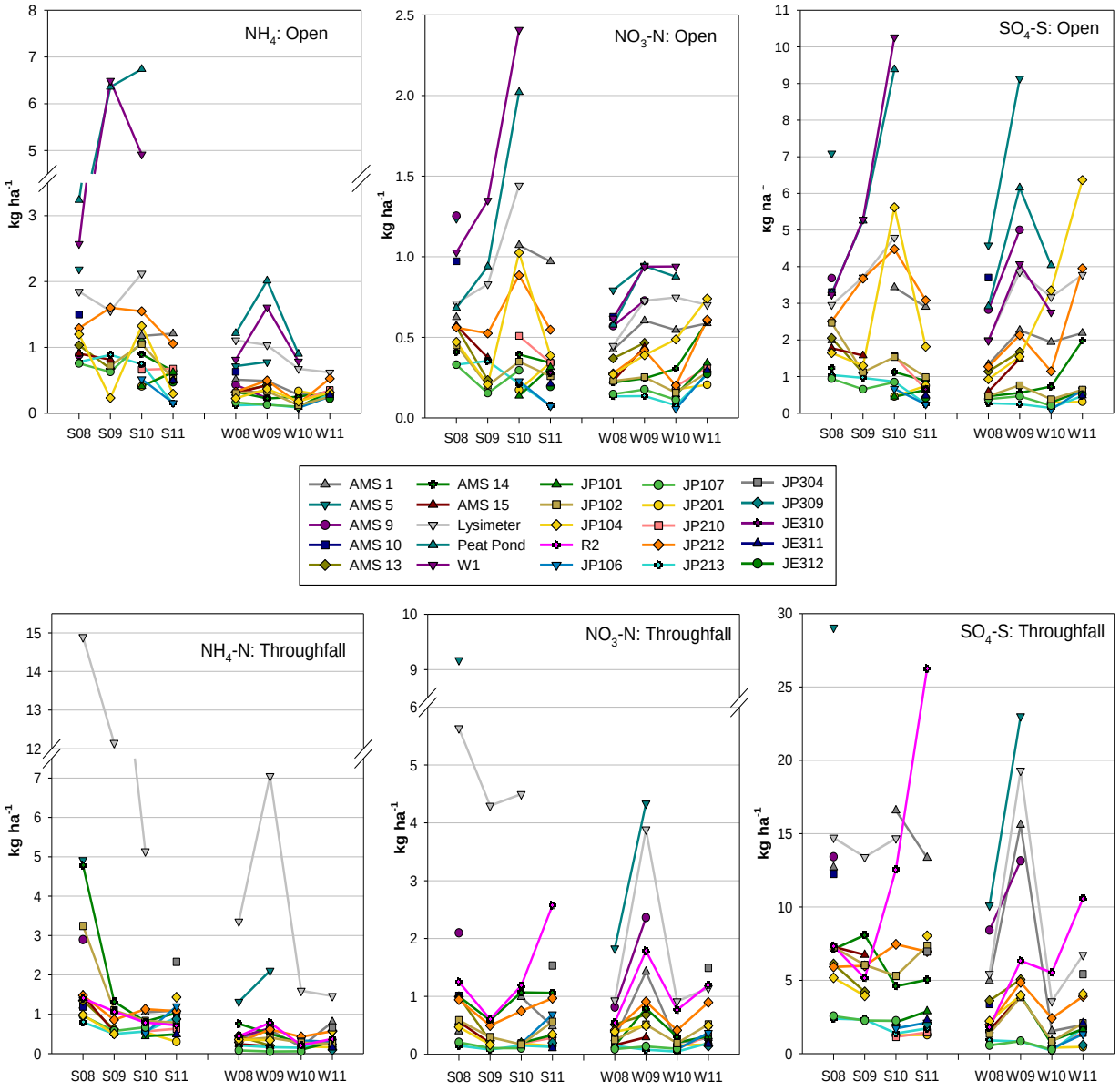

Figure 3. 2 Temporal patterns of summer and winter deposition of NH_4-N, NO_3-N and SO_4- S in (a) forest clearings (open) and (b) throughfall under jack pine in the Athabasca Oil Sands Region.

The IER deposition maps illustrate the rapid drop-off of NH_4-N, NO_3-N and their sum (DIN; Figs. 3.3) with distance from the industrial center, which is near the Lysimeter site shown on the maps. Sulfate deposition shows a larger footprint (Fig. 3.4), although sites with >12 kg S ha^{-1} yr^{-1} are generally restricted to a zone within approximately 30 km of the Lysimeter site. Of particular interest is a comparison of the deposition maps showing the combined deposition of DIN and SO_4-S and base cation deposition (Fig. 3.4). It can readily be seen that estimated base cation deposition is greater than the sum of DIN + SO_4-S deposition throughout the study region. However, it should be emphasized that this data set may be substandard as the base cation deposition values in throughfall are for only one year (Oct 2009 to October 2010) and base cation data were not collected at as many sites as for N and S. Estimated values, based on distance/deposition relationships (see Fig. 3.1) were used to provide missing data base cation throughfall deposition for some combinations of monitoring sites and seasons (summer or winter).

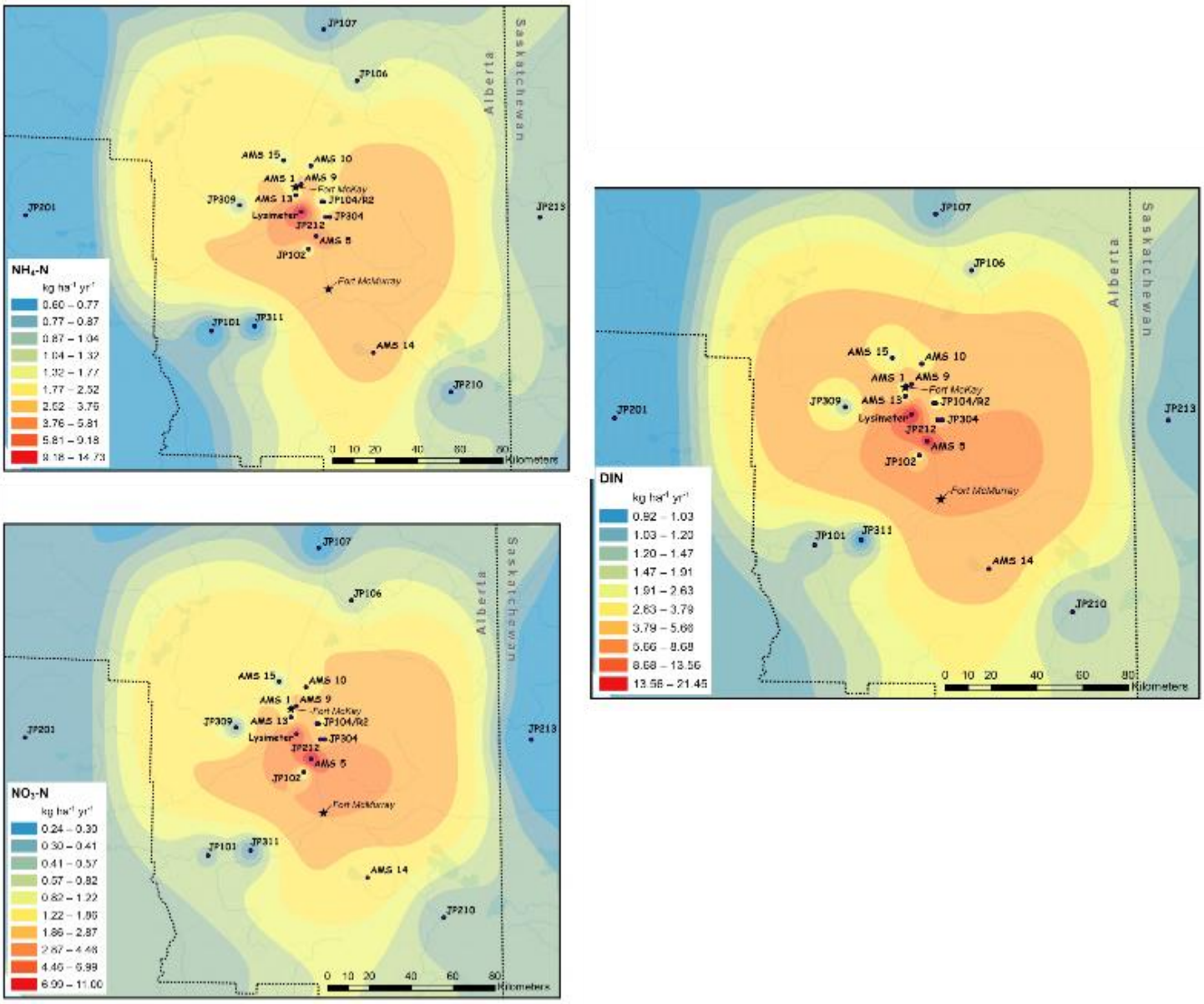

Figure 3. 3 Dissolved inorganic nitrogen (DIN; sum of NO_3-N and NH_4-N), NH_4-N, and NO_3-N deposition (kg ha^{-1} yr^{-1}) in the AOSR. Maps were developed from ion exchange resin (IER) data collected from October 2008 to October 2012 from 21 monitoring sites using inverse distance weighting.

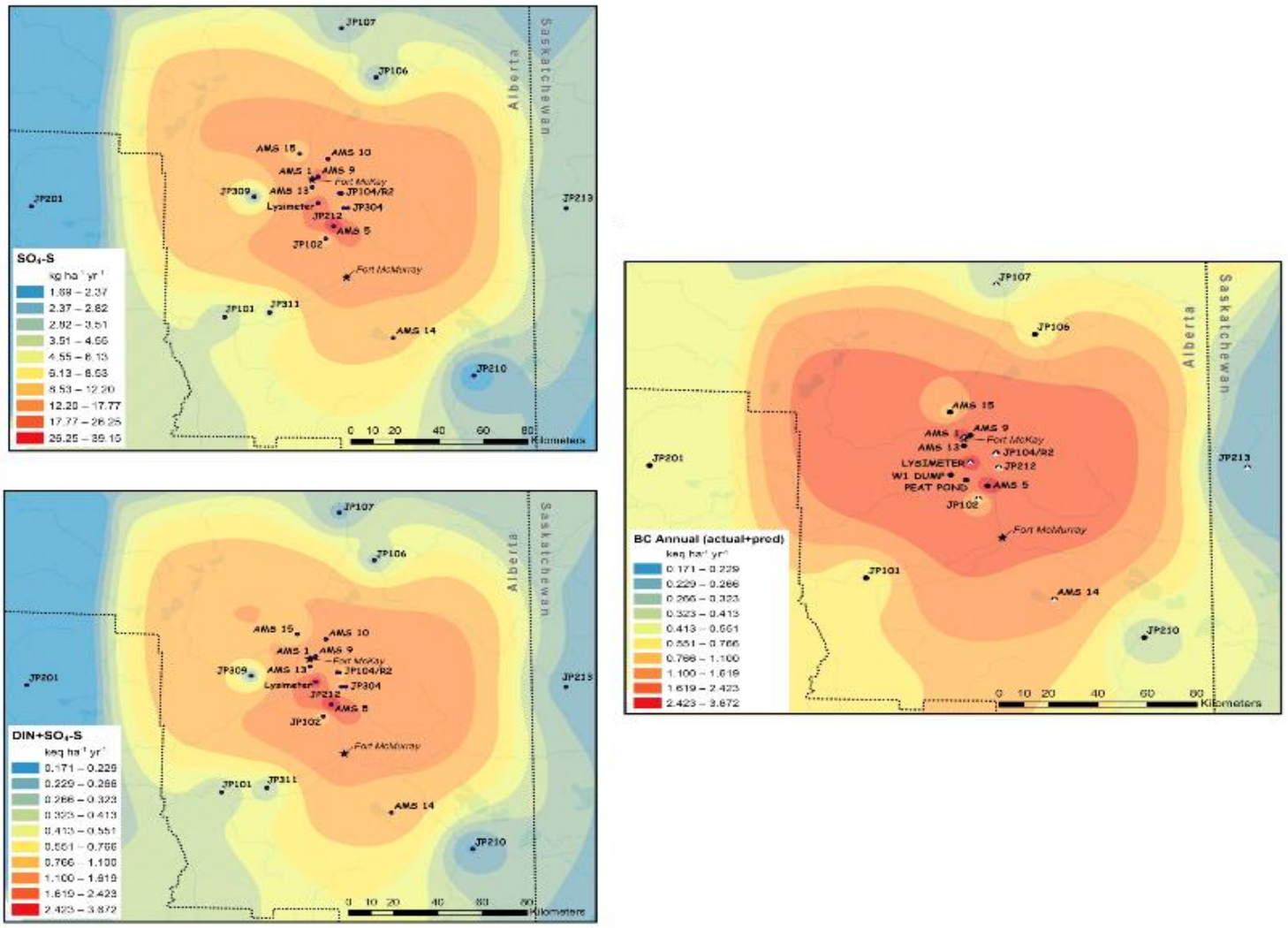

Figure 3. 4 Maps of SO_4-S deposition in kg ha^{-1} yr^{-1} and DIN+ SO_4-S and sum of base cations in keq ha^{-1} yr^{-1} in the AOSR.

3.4 Discussion

Deposition in throughfall of NO_3-N and NH_4-N were reduced by 80 and 91% at 20 km from the industrial center demonstrating the rapid drop-off with distance from the source area. In contrast throughfall deposition of base cations and SO_4-S only decreased by 72 and 56% at 20 km and by 75% at 25 and 53 km, illustrating the larger footprint of SO_4-S, and to a lesser degree, of base cation deposition in the AOSR.

Historical emphasis on N monitoring, modeling and effects in the AOSR has focused almost exclusively on oxidized forms of N as evidenced by N and S deposition modeling work that includes only NO_x and SO_x (Davies, 2012). However, our deposition data clearly show that atmospheric inputs of N in reduced forms are greater than oxidized forms. Atmospheric concentrations of gaseous NO_y and NH_3 in the AOSR are enhanced; however, much of the

reduced N input in the region is likely in particulate form as evidenced by stack emissions (Wang *et al.*, 2012; Watson *et al.*, 2011) and the steeply declining patterns of deposition with distance from the source zone.

Although deposition of NH_4-N is on average double that of NO_3-N deposition in the AOSR, emissions inventories of the National Pollutant Release Inventory (NPRI, 2010, 2011) report that NH_3 emissions from stationary sources were only 3% as large as NO_2 emissions in 2010 and 2011. Furthermore, the NPRI inventory does not include NO_x emissions from mobile sources, which in 2008 made up 40% of the anthropogenic NO_x emissions in the AOSR (Davies, 2012). The discrepancy between the reported dominance of NO_x emissions and deposition data showing that NH_4-N deposition is double that of NO_3-N deposition is apparently due to unreported elevated emissions of particulate NH_4 and likely also because of underestimates in reported NH_3 emissions. Emissions of particulate matter mass is reported in the emissions inventory (NPRI, 2010, 2011), but chemical characterization of particulate matter emissions is not.

In summary, publicly available N emissions data for the AOSR are inadequate to address quantitatively what sources and processes are responsible for the observed atmospheric deposition in throughfall and bulk deposition. However, it is clear that emissions and atmospheric deposition of reduced forms of N (NH_3 and NH_4^+) are much greater than previous understanding and available emissions inventories indicate.

3.4.1 Potential Ecological Effects of Air Pollution in the AOSR

Concentrations of N in foliage of *P. banksiana* (jack pine) and in the lichen species *Evernia mesomorpha* and *Hypogymnia physodes* were positively correlated with atmospheric concentrations of NO_2 (Laxton *et al.*, 2010), indicating that N deposition in the AOSR enriches the N status of vegetation and lichens (Davies, 2012) in the more polluted portions of the AOSR. Likewise, a 2004 survey of the TEEM plots revealed that S concentrations in foliage of jack pine (total S and inorganic S) and of the forest floor, and both N and S levels in lichen tissue, increased with increasing atmospheric deposition (C.E. Jones & Associates Ltd., 2007). Further work is needed to evaluate possible biological responses to this N and S enrichment and its spatial extent. These findings suggest that the areas of highest potential risk of N and S deposition effects are limited to within 20-30 km of the main industrial zone of the AOSR—and possibly even a smaller zone for N effects.

Although soils in jack pine stands are naturally acidic with low base cation saturation, the consensus of previous studies in the AOSR is that there is limited potential for acidification of soils or lakes under current conditions (Hazewinkel *et al.*, 2008; Jung *et al.*, 2013; Whitfield *et al.*, 2009; Watmough, this report). A field study at four forest sites in the AOSR found that soil pH increased from 2005 to 2010. The authors proposed that likely mechanisms for the soil pH increase were decreased H^+ input as a result of decreasing S deposition and increased base cation deposition (Jung *et al.*, 2013). The results of our study also indicate that base cation deposition closely tracks acidic deposition in the form of N and S deposition. Watmough *et al.* (2014)

concluded that despite extremely low soil base cation weathering rates in the region, the risk of soil acidification is mitigated to a large extent by high base cation deposition as shown in Fig. 4.1.

3.5 Conclusions

As noted previously for other pollutants, throughfall deposition of NO_3-N and NH_4-N decreased exponentially within a 20-25 km zone surrounding the industrial center (Fenn *et al.*, 2015). At a distance of 20 km from the industrial center N deposition decreased by 88%, while S and base cations decreased by 56 and 72% respectively, showing a greater footprint. Deposition of NH_4-N in the AOSR was on average double that of NO_3-N. Higher deposition of reduced forms of N compared to oxidized forms had not previously been well documented except for data showing elevated atmospheric concentrations of NH_3 in the AOSR (Bytnerowicz *et al.*, 2010a,b). More studies are needed to better understand the emissions sources and chemical forms of reduced N that contribute to NH_4-N deposition in the region.

Results of this study support the hypothesis that eutrophication effects to sensitive organisms such as epiphytic lichens may be of greater concern than acidification because acidic deposition is matched by equivalent amounts of buffering base cation deposition (Watmough *et al.*, 2014). However, the zone at risk of excess N effects is limited in size as indicated by the steep decrease in N deposition with distance from the source areas.

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