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Tracing industrial sulfur contributions to atmospheric sulfate deposition in the Athabasca oil sands region, Alberta, Canada

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ABSTRACT

Anthropogenic S emissions in the Athabasca oil sands region (AOSR) in Alberta, Canada, affect SO_4 deposition in close vicinity of industrial emitters. Between May 2008 and May 2009, SO_4-S deposition was monitored using open field bulk collectors at 15 sites and throughfall collectors at 14 sites at distances between 3 and 113 km from one of the major emission stacks in the AOSR. At forested plots >90 km from the operations, SO_4 deposition was ~1.4 kg SO_4-S ha^{-1} yr^{-1} for bulk deposition and ~3.3 kg SO_4-S ha^{-1} yr^{-1} for throughfall deposition. Throughfall SO_4 deposition rates in the AOSR exceeded bulk deposition rates at all sites by a factor of 2–3, indicating significant inputs of dry deposition especially under forest canopies. Both bulk and throughfall SO_4 deposition rates were elevated within 29 km distance of the industrial operations with deposition rates as high as 11.7 kg SO_4-S ha^{-1} yr^{-1} for bulk deposition and 39.2 kg SO_4-S ha^{-1} yr^{-1} for throughfall at industrial sites. Sulfur isotope ratio measurements of atmospheric SO_4 deposited in the AOSR revealed that at a few selected locations ^{34}S-depleted SO_4, likely derived from H_2S emissions from tailing ponds contributes to local atmospheric SO_4 deposition. In general, however, $\delta^{34}S$ values of SO_4 deposition at distant forested plots (>74 km) with low deposition rates were not isotopically different from $\delta^{34}S$ values at sites with high deposition rates in the AOSR and are, therefore, not suitable to determine industrial S contributions. However, O isotope ratios of atmospheric SO_4 in bulk and throughfall deposition in the AOSR showed a distinct trend of decreasing $\delta^{18}O$-SO_4 values with increasing SO_4 deposition rates allowing quantification of industrial contributions to atmospheric SO_4 deposition. Two-end-member mixing calculations revealed that open field bulk SO_4 deposition especially at industrial sites in close proximity (<29 km) to the operations is significantly (17–59%) affected by industrial S emissions and that throughfall generally contained 49–100% SO_4 of industrial origin. Hence, it is suggested that $\delta^{18}O$ values of SO_4 may constitute a suitable tracer for quantifying industrial contributions to atmospheric SO_4 deposition in the AOSR.

1. Introduction

Anthropogenic SO_2 emissions and subsequent SO_2 oxidation lead to the formation of H_2SO_4 in the atmosphere (Savarino et al., 2000). This H_2SO_4 dissociates to SO_4^{2-} and H^+, acidifying aquatic and terrestrial ecosystems (Doney et al., 2007). In the USA, the 1970 Clean Air Act and subsequent amendments were passed to regulate SO_2 and other industrial emissions into the atmosphere. This act and comparable legislation and programs in Europe and Canada have resulted in substantial decreases in industrial SO_2 emissions and consequently a decrease in atmospheric SO_4 deposition (Posch et al., 2003; Schöpp et al., 2003; Novák et al., 2007). The decrease in SO_4 deposition has resulted in reduced S fluxes in catchment exports from watersheds in the Northeastern USA and Europe (Posch et al., 2003; Mitchell et al., 2011; Miles et al., 2012).

In northeastern Alberta and northern Saskatchewan, Canada, the potential for acid deposition has been a concern for more than 30 years due to ongoing development in the Athabasca oil sands region (AOSR) (Shewchuk, 1982; Sandhu and Blower, 1986). The majority of anthropogenic S emitted in the AOSR is in the form of SO_2 (NPRI, 2011) which is subsequently oxidized to atmospheric SO_4 (Newman et al., 1991). Monitoring SO_4 in precipitation in the AOSR began in 1966 (Klemm, 1977) and was continued in subsequent years (Bertram et al., 1986). In 1980, S deposition rates in northeastern Alberta and northern Saskatchewan were believed to be near background levels (Shewchuk, 1982) and Sandhu and Blower (1986) reported that wet SO_4 deposition from 14 sites including urban centers in Alberta in 1982 averaged 3.2 kg SO_4-S ha^{-1} yr^{-1}. More recently, lower bulk SO_4 deposition rates in the AOSR were reported, averaging 1.14 ± 0.06 kg SO_4-S ha^{-1} yr^{-1} (Wieder et al., 2010), but no sampling sites within close proximity (<25 km) to the center of the oil sands operations were investigated. Monitoring SO_4 deposition is important because of its

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potential effect on terrestrial and aquatic ecosystems since some of the surrounding soils in the AOSR are acid sensitive (Shewchuk, 1982; Whitfield et al., 2010).

Previous research has shown that stable isotope techniques can be used successfully for tracing sources and cycling of S, particularly if anthropogenic emissions are isotopically distinct from background values (Krouse, 1977; Newman et al., 1991; Novák et al., 2001; Puig et al., 2008). The S isotopic composition of atmospheric SO_4 depends on the S sources. Potential S sources include sea spray with $\delta^{34}S$ values around +21‰ (Jamieson and Wadleigh, 2000) and marine aerosols with $\delta^{34}S \approx 17‰$ (Sanusi et al., 2006), biogenic emissions with $\delta^{34}S$ values usually lower than 0‰ (Wadleigh and Blake, 1999) such as H_2S from bacterial SO_4 reduction, soil-derived SO_4 (Nriagu et al., 1987), and S emitted from coal combustion (Puig et al., 2008), smelters and vehicle exhaust ($\delta^{34}S \approx 5‰$) (Norman et al., 2004, 2006). Nakai and Jensen (1967) found $\delta^{34}S$-SO_4 values in rain and snow from sites in Japan and the USA between +3.2‰ and +7.3‰ for industrial sites, and +12.3‰ to +19.0‰ for non-industrial sites, suggesting contributions of fuel S depleted in ^{34}S to atmospheric SO_4 deposition.

The O isotopic composition of atmospheric SO_4 depends on the oxidation pathway of emitted SO_2. In the atmosphere, the main homogeneous (gaseous) oxidation pathway of SO_2 is initiated by OH radicals and a third molecule (M) (Savarino et al., 2000):

$$SO_2 + OH + M \rightarrow HOSO_2 + M \quad (1)$$

$$HOSO_2 + O_2 \rightarrow SO_3 + HO_2 \quad (2)$$

$$SO_3 + H_2O + M \rightarrow H_2SO_4 \quad (3)$$

In the aqueous oxidation of SO_2 (e.g. in droplets), the oxidation pathways are (Newman et al., 1991):

$$SO_2 + H_2O \rightarrow H_2SO_3 \quad (4)$$

$$H_2SO_3 \rightarrow HSO_3^- + H^+ \quad (5)$$

$$HSO_3^- \rightarrow SO_3^{2-} + 2H^+ \quad (6)$$

The oxidation of SO_3^{2-} to SO_4^{2-} may then proceed via O_2 (with or without the presence of metal catalysts), H_2O_2 or O_3 (Newman et al., 1991; Savarino et al., 2000).

In the atmosphere, the O in SO_2 equilibrates rapidly with the O in water vapor and hence O isotope ratios of SO_2 cannot be used to identify sources of SO_2 directly (Holt et al., 1983). The O isotopic composition of atmospheric secondary SO_4 derived form SO_2 oxidation, therefore, depends partially on the isotopic composition of water or vapor (Holt et al., 1983). If liquid water is present, up to three out of four oxygens in the SO_4 molecule are derived from the water (Holt et al., 1981; Holt and Kumar, 1991). The remaining oxygen is either from O_2, H_2O_2 or O_3. Rainwater and snow in Alberta have an average $\delta^{18}O$ value of −18‰ (Peng et al., 2004) whereas atmospheric O_2 is more enriched in ^{18}O with a $\delta^{18}O$ value of +23.5‰ (Kroopnick and Craig, 1972). After oxidation of SO_2 to SO_4^{2-}, the O isotopic composition of atmospheric SO_4 is stable (Holt and Kumar, 1991; Jamieson and Wadleigh, 2000).

$\delta^{18}O$ values of SO_4 have been used to distinguish between primary SO_4 that is directly formed in the emission stack at high temperatures >450 °C, and secondary SO_4 that is formed by oxidation of SO_2 in the atmosphere. Primary sulfates formed in the presence of metal catalysts have been reported to have elevated $\delta^{18}O$-SO_4 values of +35‰ to +40‰ (Holt et al., 1982) compared to $\delta^{18}O$-SO_4 values of secondary sulfates ranging from ~0‰ to +20‰ (Holt and Kumar, 1991). More recently, Lee et al. (2002) investigated the S and O isotopic compositions of primary sulfates formed during high temperature combustion and observed low $\delta^{18}O$-SO_4 values between +5.5‰ and +10.5‰, suggesting that different oxidation mechanisms may lead to different $\delta^{18}O$-SO_4 values in the resulting SO_4.

The objective of this study was (a) to determine whether SO_4 derived from industrial S emissions is isotopically distinct from atmospheric SO_4 deposition at distant forested plots in the AOSR. If so, the goal was (b) to determine relative contributions of industrial S to SO_4 deposition in the AOSR by measurement of deposition rates and isotopic composition ($\delta^{34}S$, $\delta^{18}O$) of atmospheric SO_4 in open field bulk deposition and throughfall.

2. Study area

The Athabasca oil sands region (AOSR) in northeastern Alberta is Canada's largest oil sand deposit (Fig. 1). Its bitumen constitutes a major unconventional oil resource and there has been an expansion of mining operations (open pit mining) and of *in situ* oil recovery projects (e.g. steam-assisted gravity drainage) in the AOSR over the last decade. Following the separation of the bitumen from sand and fines, upgrading is necessary to convert bitumen to synthetic crude oil. Both open pit mining operated by heavy haulers and the bitumen upgrading facilities release S-bearing compounds into the atmosphere. While there is no estimate on the contribution of vehicle exhaust to S emissions in the AOSR, SO_2 stack emissions of all oil sand operators in the AOSR were estimated at 100,908 t for the year 2010 (NPRI, 2011). There has also been concern over H_2S emissions from tailing ponds due to S-reducing bacteria that convert SO_4-S to H_2S. Sulfide emissions from tailing ponds were, however, suggested to be limited due to the high solubility and oxidation of sulfide in surface waters (Ramos-Padrón et al., 2011).

The Athabasca oil sands operations are surrounded by a mixture of peatlands and upland forests composed of jack pine, spruce and aspen (Whitfield et al., 2009), and some of the forest soils are known to be acid-sensitive (Whitfield et al., 2010).

Annual precipitation in Fort McMurray (airport station) is 455.5 mm and the mean annual temperature is 0.7 °C (30-year average (1971–2000), Environment Canada, 2011). Lowest average monthly precipitation rates are reported for January (0.5 mm) and highest average monthly precipitation rates occur in July (81.3 mm). Monthly precipitation rates in 2007 were generally lower than reported 30-year averages, whereas monthly precipitation rates in 2008 indicated a wet summer with 156.5 mm of precipitation during August alone (Environment Canada, 2011). The prevailing wind direction is dependent on season (Government of Alberta, 2011) and it was suggested that terrain may affect wind direction and hence plume distributions in the AOSR, even at sites well above average ground level (Leahey and Hansen, 1982). However, Sandhu and Blower (1986) reported that the prevailing winds at the surface and at 1100 m height in the AOSR are from the West and NW. Acid-forming emissions from the AOSR may, therefore, predominantly affect regions east and SE of the AOSR including potentially some of the western portions of the neighboring province of Saskatchewan.

3. Methods

3.1. Sample collection

Atmospheric S species enter the environment as dry deposition or as wet deposition. Sixteen jack pine sites established by the Terrestrial Environmental Effects Monitoring (TEEM) group of the Wood Buffalo Environmental Association (WBEA) were selected based on a set of site selection criteria (AMEC, 2001) for monitoring of acid inputs and effects. At a subset of these sites open field bulk deposition (wet deposition + dry deposition) and throughfall deposition (bulk deposition under tree canopy) was collected between April 2007 and May 2009. One of the major stacks in the AOSR near Fort McMurray (57.0479875°N, 111.615502°W) was used as a

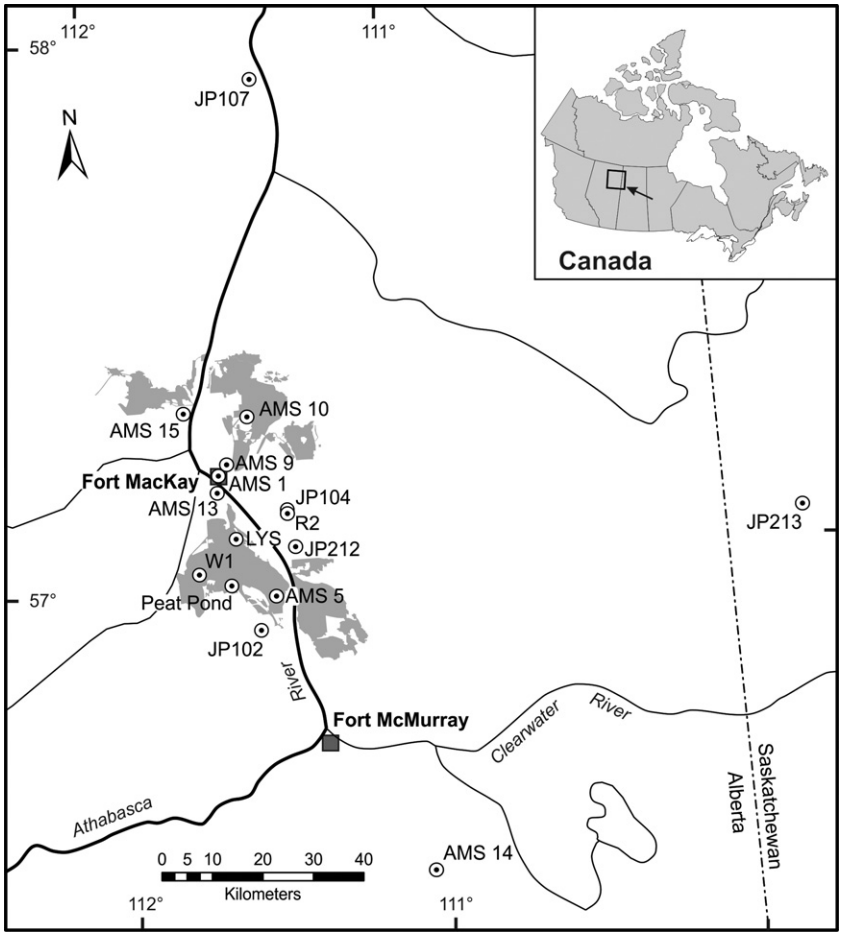

Fig. 1. The Athabasca oil sands region in northeastern Alberta, Canada, showing the sulfate deposition sampling sites (circles) and towns (black boxes). The gray shaded areas are open pit mining sites as of 2008.

central marker point for the industrial emissions. Distances between the stack and the sampling sites vary between 3 and 113 km. However, this stack is not the only source of anthropogenic S emissions as there are several other stationary, mobile and fugitive emission sources in the AOSR. Also the town of Fort McMurray is rapidly developing and expanding, creating a nearby urban emission source. Four of the sampling sites have existed since April 2007 (JP102, JP212, JP213 and JP107), and twelve additional sites were established in May 2008 (AMS 1, AMS 5, AMS 9, AMS 10, AMS 13, AMS 14, AMS 15, LYS, JP104, W1, Peat Pond, R2) (Fig. 1). The sites AMS 5, AMS 9, AMS 10, AMS 15, LYS, W1 and Peat Pond are located on land leased by industry and will, therefore, be referred to as industrial sites. AMS 1 (Fort MacKay) and AMS 14 (Anzac) are located in small communities and will be called community sites. The sites JP104, JP102, JP212, JP213, JP107 and R2 are forest health plots at upland forest sites.

Sulfate in bulk deposition was sampled using an ion exchange resin (PVC tubes containing ion exchange beads) method (Fenn and Poth, 2004). At each of the 16 sites, four open field bulk deposition samplers were installed in clearings in the boreal forest. In addition, eight throughfall samplers were mounted on trees in nearby jack pine forest stands (Fenn and Ross, 2010). Resins were exposed for approximately half-year periods. The results from the following four sampling periods are presented: April 2007 to September 2007 (“summer 2007”) and October 2007 to May 2008 (“winter 2007/2008”) for four different sites (JP107, JP102, JP212, JP213), and May 2008 to October 2008 (“summer 2008”) and October 2008 to May 2009 (“winter 2008/2009”) for all 16 sites.

3.2. Concentration analyses and deposition rates

In the laboratory, the ion exchange resins were quantitatively eluted with 1 N KI and SO_4^{2-} concentrations and deposition rates were determined at the USDA Forest Service Laboratory in Riverside (California, USA). Sub-samples of the eluted solutions were subsequently shipped to the University of Calgary (Alberta, Canada) for isotopic analyses of SO_4 (δ^{34}S-SO_4 ($n = 294$) and δ^{18}O-SO_4, ($n = 328$)). Samples with concentrations which were too low or contamination problems, e.g. due to bird droppings, were excluded from isotopic analyses.

3.3. Isotope analyses

Sulfur and O isotope ratios (δ^{34}S, δ^{18}O) of SO_4 were determined on $BaSO_4$ precipitated from the samples. Barium chloride solution (10%) was added in excess and the resulting $BaSO_4$ precipitate was filtered, rinsed with deionized water, and dried. For the determination of δ^{34}S values, approximately 250 μg of $BaSO_4$ precipitate were weighed into tin cups. Niobium pentoxide was added to enhance the thermal decomposition of the samples that were analyzed using SO_2 gas via continuous flow-isotope ratio mass spectrometry (EA-CF-IRMS), using a Carlo Erba NA 1500 elemental analyzer (EA) interfaced to a VG PRISM II mass spectrometer (Giesemann et al., 1994). δ^{18}O values of SO_4 were determined on CO generated by pyrolysis of $BaSO_4$ in the presence of graphite at a temperature of 1450 °C (Kornexl et al., 1999). Isotope ratios are reported in the internationally accepted δ notation (δ^{34}S, δ^{18}O) defined as

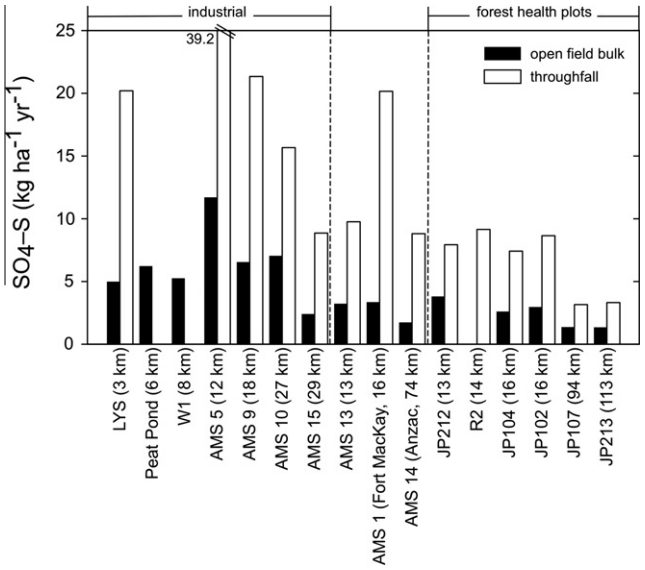

Fig. 2. Yearly deposition rates (May 2008 to May 2009) for SO_4-S in open field bulk deposition and throughfall.

$$\delta_{\text{sample}}\ (‰) = \left[\left(R_{\text{sample}}/R_{\text{standard}}\right) - 1\right] * 1000 \tag{7}$$

where R is the $^{34}S/^{32}S$ or $^{18}O/^{16}O$ ratio of the sample and a standard respectively. $\delta^{18}O$ values are reported relative to Vienna Standard Mean Ocean Water (VSMOW) and $\delta^{34}S$ relative to Vienna Canyon Diablo Troilite (V-CDT). For $\delta^{34}S$ and $\delta^{18}O$ analyses the reference materials NBS 127 ($\delta^{34}S = +21.1‰$, $\delta^{18}O = +8.7 \pm 0.2‰$), IAEA S05 ($\delta^{34}S = +0.49 \pm 0.11‰$, $\delta^{18}O = +12.0 \pm 0.2‰$) and IAEA S06 ($\delta^{34}S = -34.05 \pm 0.08‰$, $\delta^{18}O = -11.2 \pm 0.2‰$) were used resulting in precisions of ±0.3‰ and ±0.5‰ for $\delta^{34}S$ and $\delta^{18}O$ values of SO_4, respectively (Coplen et al., 2002).

Average $\delta^{34}S$ and $\delta^{18}O$ values of atmospheric SO_4 from bulk deposition and throughfall samplers were determined by calculating deposition-weighted means ($\bar{x}$) per site and sampling period according to:

$$\bar{x} = \frac{\sum_{i=1}^{n} w_i x_i}{\sum_{i=1}^{n} w_i} \tag{8}$$

where w_i is the deposition rate and x_i the isotope ratio of the sample i.

4. Results

4.1. Sulfate deposition rates

Annual deposition rates for the sixteen sampling sites monitored from May 2008 to May 2009 were calculated by adding the summer 2008 to the winter 2008/2009 deposition rates (Fig. 2). The annual SO_4-S deposition rates varied between 1.4 and 11.7 kg SO_4-S ha^{-1} yr^{-1} for bulk deposition, and between 3.2 and 39.2 kg SO_4-S ha^{-1} yr^{-1} for throughfall deposition. The SO_4-S deposition rates were lowest at forest health plots farthest distant from the oil sands operations. The two most distant forest plots JP107 and JP213 located 94 km north and 113 km east of the industrial operations, respectively, had annual SO_4 deposition rates in bulk deposition of ~1.4 kg SO_4-S ha^{-1} yr^{-1} and ~3.3 kg SO_4-S ha^{-1} yr^{-1} in throughfall. Annual SO_4 deposition rates in bulk deposition exceeded 5 kg SO_4-S ha^{-1} yr^{-1} only at industrial sites (LYS, W1, Peat Pond, AMS 5, AMS 9, AMS 10, see Fig. 1). However, annual throughfall SO_4 deposition rates were as high as 39.2 kg SO_4-S ha^{-1} yr^{-1} for site AMS 5 and were higher than 7.4 kg SO_4-S ha^{-1} yr^{-1} for all sites except the two most distant forest plots (JP107 and JP213). The industrial site AMS 5 (Fig. 1), also had the highest annual bulk deposition rate (11.7 kg SO_4-S ha^{-1} yr^{-1}, Fig. 2). Annual throughfall SO_4 deposition rates exceeded the corresponding bulk deposition rates at all sites. Annual throughfall deposition rates were about twice as high as the corresponding bulk deposition rates at distant forested plots (>90 km), and about three times as high at sites located at a distance of <90 km from the industrial operations.

Sulfate deposition rates were influenced by the amount of precipitation during the sampling period and varied considerably between the sampling periods. Fig. 3 shows the variability of SO_4 deposition rates with sampling period for the four sampling sites that were monitored since April 2007 (JP212, JP102, JP107 and JP213). Summer bulk and throughfall SO_4 deposition rates were typically higher compared to winter deposition rates. The highest bulk and throughfall SO_4 deposition rates for all four sites were observed during summer 2008. Summer 2008 was extremely wet with more than 150 mm of precipitation during the month of August, twice as high as in August 2007.

4.2. Sulfur isotope ratios of atmospheric sulfate

Site averaged, SO_4-S deposition weighted S isotope ratios of SO_4 in bulk deposition and throughfall are shown in Fig. 4a with respect to distance from the industrial operations. Average $\delta^{34}S$ values of SO_4 in bulk deposition varied between −3.9‰ and +5.9‰. Average $\delta^{34}S$ values of SO_4 in throughfall were higher, ranging from +3.6‰ to +7.1‰. Average $\delta^{34}S$ values <2‰ were only observed in open field samplers at industrial sites W1, Peat Pond, and AMS 5,

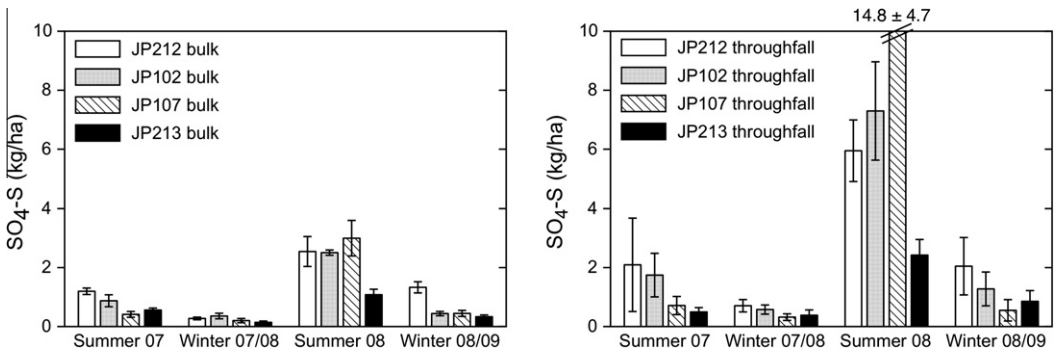

Fig. 3. SO_4-S deposition rates for bulk deposition (left) and throughfall (right) for the four sampling periods. Deposition rates were highest during summer 2008 when highest precipitation amounts were observed.

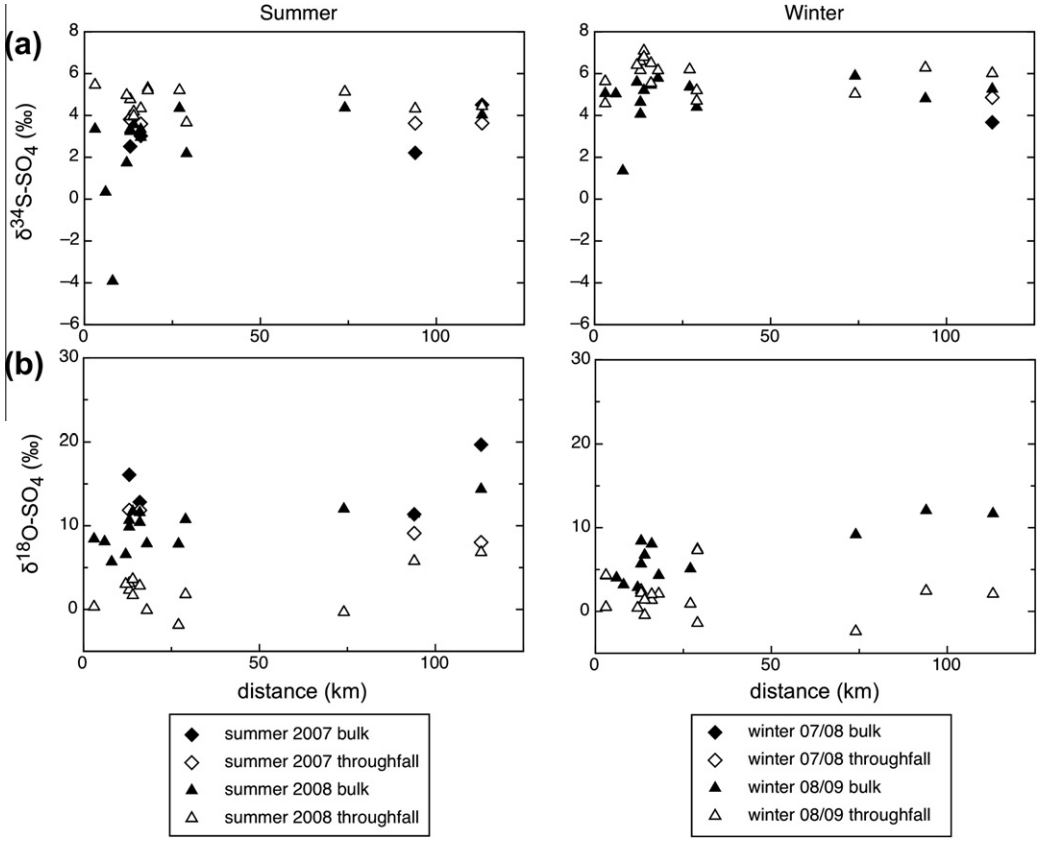

Fig. 4. SO_4-S deposition weighted site averaged $\delta^{34}S$ (a) and $\delta^{18}O$ values (b) of sulfate in bulk deposition and throughfall versus distance from the emission stack for summer (left) and winter sampling periods (right).

during the summer, except for the site W1 which also had a $\delta^{34}S$ value <2‰ in the winter. All three sites are in close proximity to tailing ponds. Aside from those sites, there is no trend of $\delta^{34}S$ with distance, regardless of the season. However, Fig. 4a shows that sites closer (<29 km) to the oil sands operations have a wider range of $\delta^{34}S$ values (−3.9‰ to 5.5‰ during summer and 1.4–7.1‰ during winter). In contrast, sites at >74 km distance have a rather constant $\delta^{34}S$ value of 4.1‰ for SO_4 deposition during summer and 5.2‰ during winter. On average, winter bulk and throughfall $\delta^{34}S$ values of SO_4 were around 1.5‰ higher than those of summer bulk deposition and throughfall.

4.3. Oxygen isotope ratios of atmospheric sulfate

Fig. 4b shows SO_4-S deposition weighted site averages of the O isotope ratios of atmospheric SO_4 deposition in the AOSR with distance from the industrial operations. Average $\delta^{18}O$-SO_4 values in bulk deposition varied between 3.2‰ and +19.7‰. Average $\delta^{18}O$-SO_4 values in throughfall were lower, ranging between −2.4‰ and +11.9‰. Summer $\delta^{18}O$-SO_4 values ranged from −1.9‰ to 19.7‰ and were higher than winter $\delta^{18}O$-SO_4 values, ranging from −2.4‰ to 12.1‰.

5. Discussion

5.1. Sulfate deposition rates

Sulfate deposition rates at the two most distant forest plots (94 and 113 km) were lower compared to sites at ⩽74 km distance to the industrial operations. Annual bulk deposition rates at the two distant sites were ∼1.4 kg SO_4-S ha^{-1} yr^{-1}, and annual throughfall deposition rates were ∼3.3 kg SO_4-S ha^{-1} yr^{-1}. These observed bulk deposition rates are similar to those reported by Wieder et al. (2010) who found that SO_4 deposition rates in the AOSR were on average 1.14 ± 0.06 kg SO_4-S ha^{-1} yr^{-1} between 2005 and 2008. The deposition sampling sites of their study were ∼26–150 km distant from the oil sand operations. In the present study, elevated bulk SO_4-S deposition rates were found within 27 km distance, and elevated throughfall SO_4-S deposition rates within 74 km from the industrial operations, particularly at industrial sites (Fig. 2). For these sites, annual bulk deposition rates ranged from 2.6 to 11.7 kg SO_4-S ha^{-1} yr^{-1}, and annual throughfall deposition rates varied from 7.4 to 39.2 kg SO_4-S ha^{-1} yr^{-1} (Fig. 2). The SO_4 deposition rates at the two most distant sites in the AOSR are relatively low compared to SO_4 deposition rates reported for other regions especially in northeastern parts of the USA or in Central Europe (Novák et al., 2001, 2007; Likens et al., 2002). However, SO_4 deposition rates at some industrial sites in the oil sand operations exceed recent SO_4 deposition rates reported for North America and Europe that are generally decreasing as a result of SO_2 emission reductions (Lynch et al., 2000; Novák et al., 2001; Van Der Swaluw et al., 2011).

To reduce industrial SO_2 emissions in the AOSR, flue gas desulfurization systems (FGD) are employed by some operators. In one of these systems, flue gas exiting the bitumen upgraders enters a spray tower where it is contacted with a dilute slurry of $(NH_4)_2SO_4$ and ammonia NH_3. In the spray tower, the injected NH_3 reacts with SO_2 from the flue gas to form $(NH_4)_2SO_4$ particles. Sulfate in $PM_{2.5}$ emitted from a FGD stack in the AOSR is in the form of $(NH_4)_2SO_4$ (Proemse et al., 2012). For any $(NH_4)_2SO_4$ particles, either directly emitted or formed in the atmosphere, a molar ratio of 1.14 is

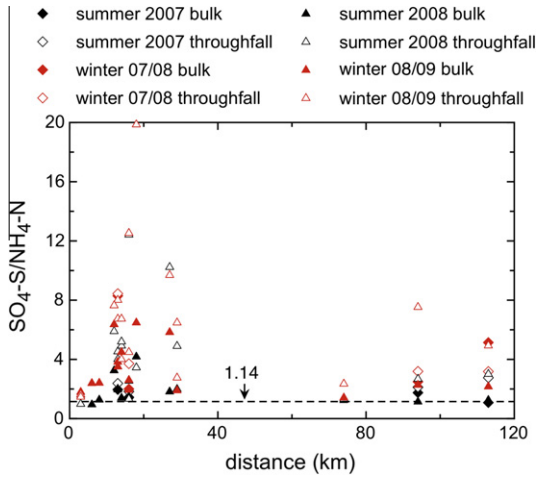

Fig. 5. Sulfate-S to ammonium-N deposition rate ratios versus distance. Ammonium sulfate particles would plot on the dotted line representing a molar ratio of 1.14.

expected for $[SO_4\text{-}S]/[NH_4\text{-}N]$ indicating whether $(NH_4)_2SO_4$ particles are dominant in atmospheric deposition. Calculating these ratios from SO_4 and NH_4 deposition data (Proemse and Mayer, in press) in the AOSR showed that SO_4 deposition generally exceeds NH_4 deposition (Fig. 5). This indicates that an additional S source adds to SO_4 depositing in the AOSR (Fig. 5). Sulfur dioxide emitted from stacks with or without FGD systems and subsequent oxidation to SO_4^{2-} is likely responsible for most of the elevated SO_4 deposition in close proximity to the oil sand operations. Dry deposition is the primary driver of atmospheric S deposition in the AOSR indicated by throughfall deposition rates exceeding bulk deposition rates at all sites. Higher throughfall SO_4-S deposition rates during the wetter summer periods compared to winter are due to greater wash off of the accumulated dry deposition from the tree canopies.

5.2. Sulfur isotopic composition of atmospheric sulfate deposition

Deposition-weighted and site-averaged $\delta^{34}S$ values in atmospheric SO_4 in bulk deposition and throughfall varied between −3.9‰ and +7.1‰. Fig. 6a shows the individual $\delta^{34}S$ values plotted versus SO_4 deposition rates. $\delta^{34}S$ values of atmospheric SO_4 samples were relatively constant at high SO_4-S deposition rates (>10 kg ha^{-1}). The average $\delta^{34}S$ value for samples with deposition rates > 10 kg ha^{-1} (only throughfall samples) is 5.0 ± 0.6‰ during summer (n = 25) and 6.2 ± 0.5‰ during winter (n = 5). Proemse et al. (2012) reported isotopic compositions of different S-containing materials in the AOSR that are potential sources of S for industrial SO_2 emissions. Total S in bitumen and untreated oil sand material had $\delta^{34}S$ values of 4.3 ± 0.3‰ and 6.5 ± 0.4‰, respectively. Elemental S from a S storage block and total S in coke are both upgrading by-products and had $\delta^{34}S$ values of 5.3 ± 0.5‰ and 3.9 ± 0.2‰, respectively. Different potential source materials for industrial S emissions are, therefore, not isotopically distinct, and have $\delta^{34}S$ values in a similar range as atmospheric SO_4 samples with high SO_4 deposition rates.

Plotting the $\delta^{34}S$ values of atmospheric SO_4 deposition in the AOSR versus the inverse SO_4 deposition rates (1/(SO_4-S)) may help to reveal the sources of atmospheric SO_4 (Krouse, 1980). The highest $\delta^{34}S$-SO_4 values associated with low inverse deposition ratios (=high SO_4 deposition rate) are 5.9‰ during summer 2008 and 8.2‰ during winter 2008/09 (Fig. 7a). Proemse et al. (2012) reported elevated $\delta^{34}S$-SO_4 values of industrial emitted SO_4 found in $PM_{2.5}$ in two stacks at a large upgrader site in the AOSR of 7.3 ± 0.3‰ (stack A) and 9.4 ± 2.0‰ (stack B). This indicates that industrial $PM_{2.5}$ emissions from these stacks may contribute to the observed elevated $\delta^{34}S$-SO_4 values. However, further isotopic characterization of other mobile and stationary S emission sources in the AOSR is necessary to evaluate whether other particle and gas emissions are also associated with slightly elevated $\delta^{34}S$-SO_4 values. The lowest $\delta^{34}S$-SO_4 values associated with low inverse deposition ratios (=high SO_4 deposition rate) were −4.0‰ during summer and 0.9‰ during winter indicating an additional SO_4 source depleted in ^{34}S. Particularly summer $\delta^{34}S$-SO_4 values at the industrial sites W1 (site average −3.9‰) and Peat Pond (site average +0.3‰) show evidence for a contribution of SO_4 from a ^{34}S depleted source. Both sites are in close proximity to tailing ponds, suggesting H_2S emissions from the ponds with low $\delta^{34}S$ values are a local source of atmospheric S especially during summer. The production of H_2S via SO_4-reducing bacteria in SO_4^{2-} rich tailing ponds water associated with oil extraction processes has been reported recently (Ramos-Padrón et al., 2011). A prevalence of fermenters and SO_4-reducing bacteria was recently found in a settling basin in the AOSR (Penner and Foght, 2010), and bacterial SO_4 reduction is also known to take place in one of the tailing ponds (Ramos-Padrón et al., 2011). Bacterial SO_4 reduction is associated with large S isotope fractionation, resulting in ^{34}S depleted H_2S (Canfield, 2001). The S isotopic composition is not expected to change markedly during oxidation of H_2S to SO_2 and SO_4^{2-} (Newman et al., 1991; Sanusi et al., 2006). The low $\delta^{34}S$ values observed for atmospheric SO_4 collected at sites close to the tailing ponds suggest that H_2S was oxidized to SO_4^{2-} that subsequently contributed to local SO_4 deposition. It has been suggested that sulfide produced via bacterial SO_4 reduction mostly remains in the ponds due to mineral precipitation and oxidation at the pond surface, although migration of H_2S formed in deeper pond layers to upper pond layers was deemed possible (Ramos-Padrón et al., 2011). The present data suggest that some reduced S gases are released from the tailing ponds into the atmosphere but that they are rapidly re-deposited on industrial sites after oxidation to SO_4. As a result of the relatively short residence time of H_2S in the atmosphere of only 1 day (Brimblecombe et al., 1989) $\delta^{34}S$ values of atmospheric SO_4 deposition collected at more distant (>12 km) industrial and community sites and forested plots do not show evidence of ^{34}S depleted SO_4 (Fig. 4a and b).

It is evident that $\delta^{34}S$ values of samples associated with low deposition rates (high 1/(SO_4-S) values) were quite constant (Fig. 7a and b). Samples with SO_4-S deposition rates <1.4 kg SO_4-S ha^{-1} (corresponding to 1/(SO_4-S) of ~0.75) had an average $\delta^{34}S$ value of 4.3 ± 0.3‰ during summer and 5.4 ± 0.7‰ during winter (Fig. 7a and b), indicating that the $\delta^{34}S$ value of long-range atmospheric SO_4 bulk deposition and throughfall is ~5‰. A similar $\delta^{34}S$ value of ~4‰ has been reported for long-range atmospheric SO_4 in eastern Canada (Jamieson and Wadleigh, 2000). In the AOSR, $\delta^{34}S$ values for atmospheric SO_4 at deposition rates <1.4 kg SO_4-S ha^{-1} (~5‰) are identical to average $\delta^{34}S$ values at high deposition rates >10 kg SO_4-S ha^{-1} (~5‰). The S isotopic composition of atmospheric SO_4 deposition in the AOSR can, therefore, not be used to distinguish industrial derived SO_4 from long-range background SO_4 deposition.

5.3. Oxygen isotopic composition of atmospheric sulfate

The highest deposition-weighted and site-averaged $\delta^{18}O$ value of SO_4 in atmospheric bulk deposition of 19.7‰ (Fig. 4b) was observed during summer 2007 at the most distant site JP213 (113 km). High $\delta^{18}O$-SO_4 values (>10‰) are associated with low SO_4-S deposition rates (Fig. 6b). Jamieson and Wadleigh (2000) reported similar elevated $\delta^{18}O$-SO_4 values of +15‰ for long-range transported SO_4 in eastern Canada. With increasing SO_4-S

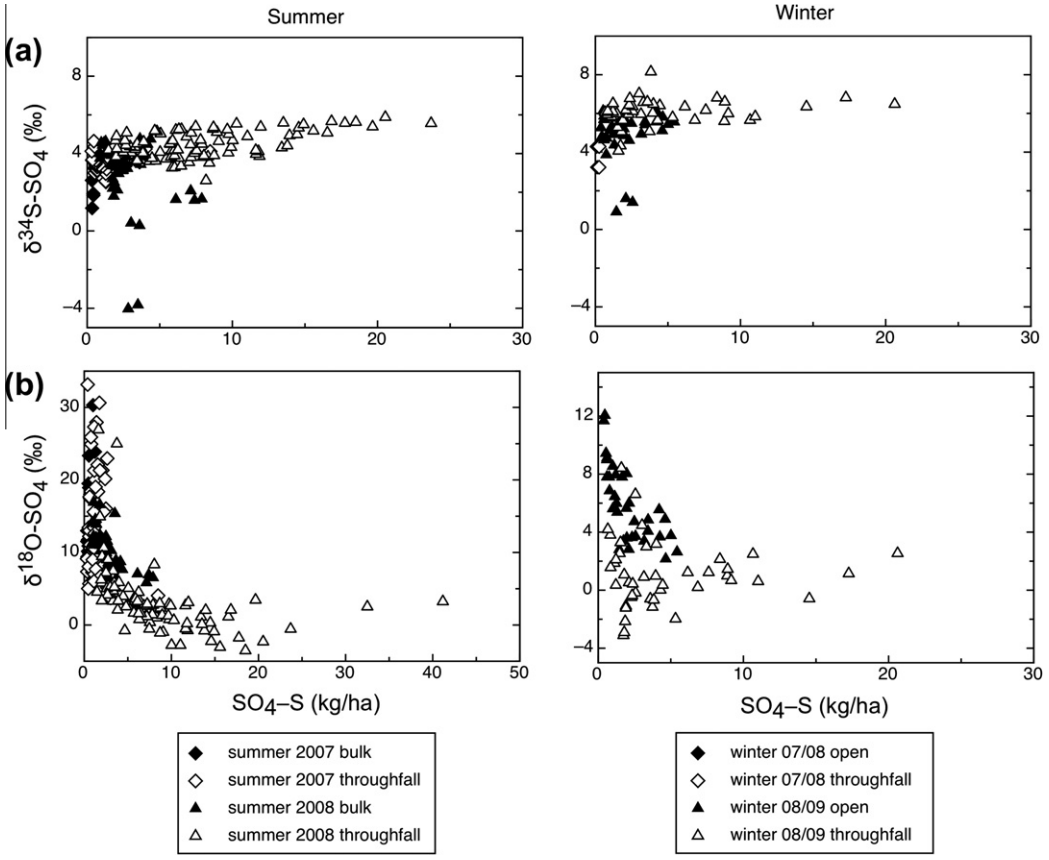

Fig. 6. $\delta^{34}S$ (a) and $\delta^{18}O$ values (b) of atmospheric sulfate versus deposition rates for summer (left) and winter sampling periods (right).

deposition rates, there is a trend towards lower $\delta^{18}O$-SO_4 values for both summer and winter periods (Fig. 6b). Fig. 7b shows the $\delta^{18}O$-SO_4 values versus the inverse atmospheric SO_4 deposition rates for summer and winter sampling periods. The majority of the $\delta^{18}O$-SO_4 values plot on a mixing line constrained by two end members representative for different SO_4 sources: atmospheric SO_4 at low deposition rates (corresponding to 1/(SO_4-S) of >0.75, Fig. 7a and b) associated with high $\delta^{18}O$-SO_4 values and industrial derived SO_4 with $\delta^{18}O$-SO_4 values near 0‰ associated with high deposition rates (low 1/(SO_4-S), Fig. 7b). Atmospheric SO_4 in open field bulk and throughfall samples at low deposition rates had average $\delta^{18}O$ values of 12.9 ± 1.9‰ during summer and 6.4 ± 3.3‰ during winter. Fig. 7b also indicates a trend to even higher $\delta^{18}O$-SO_4 values at low deposition rates (r^2 = 0.55 in summer, r^2 = 0.43 in winter). Since water and water vapor $\delta^{18}O$ values vary with season (e.g. Peng et al., 2004), $\delta^{18}O$ values of atmospheric SO_4 tend to be lower in winter compared to summer (Jamieson and Wadleigh, 1999; Novák et al., 2001).

Sulfate in $PM_{2.5}$ emitted from two stacks at a large upgrader facility in the AOSR had $\delta^{18}O$ values as high as 18.9 ± 2.9‰ (Proemse et al., 2012). However, Fig. 5 indicates that particulate $(NH_4)_2SO_4$ emitted from stacks is not the main source of atmospheric SO_4 deposition in the AOSR. In fact, atmospheric SO_4 at high deposition rates is associated with low $\delta^{18}O$-SO_4 values (Fig. 7b). Both trendlines in Fig. 7b intersect the *y*-axis at a $\delta^{18}O$ value of ~0.6‰, which is indicative of SO_4 derived from industrial SO_2 emissions.

During bitumen extraction, significant amounts of hot water are used for bitumen processing (Masliyah et al., 2004). The processing water is partially withdrawn from the Athabasca River which has $\delta^{18}O$ values around −18‰ (Gue et al., 2011). Rainwater in Alberta is also depleted in ^{18}O with average $\delta^{18}O$–H_2O values around −18‰ (Peng et al., 2004). The observed low $\delta^{18}O$ values in atmospheric SO_4 at high deposition rates are likely caused by the oxidation of SO_2 to SO_4^{2-} via water (droplets) and water vapor as shown in equations 4–6. This appears to be the dominant oxidation pathway for industrially emitted SO_2 in close proximity to the oil sand operations resulting in characteristically low $\delta^{18}O$ values for the generated SO_4^{2-} of industrial origin.

5.4. Quantification of industrial contributions to atmospheric sulfate deposition

Atmospheric SO_4 at high deposition rates had markedly lower $\delta^{18}O$ values compared to atmospheric SO_4 associated with deposition rates that were lower than 1.4 kg SO_4-S ha^{-1}. If the O isotopic composition of industrially derived SO_4 (stationary or mobile sources) and atmospheric background SO_4 deposition are known and different, a two-end-member mixing analysis can be applied to determine industrial contributions to atmospheric SO_4 deposition at various sites in the AOSR. The fraction *f* of industrial derived SO_4 contributing to the total atmospheric SO_4 deposition can be resolved by applying a two-end-member mixing model:

$$\delta^{18}O_M = f\delta^{18}O_{IND} + (1-f)\delta^{18}O_{BGRD} \quad (9)$$

yielding

$$f = (\delta^{18}O_M - \delta^{18}O_{BGRD})/(\delta^{18}O_{IND} - \delta^{18}O_{BGRD})(0 < f < 1) \quad (10)$$

where $\delta^{18}O_M$ is the O isotope ratio of SO_4 of the mixture (site averaged deposition weighted values), $\delta^{18}O_{IND}$ and $\delta^{18}O_{BGRD}$ the O isotope ratios of the SO_4 derived from industrial SO_2 emissions and

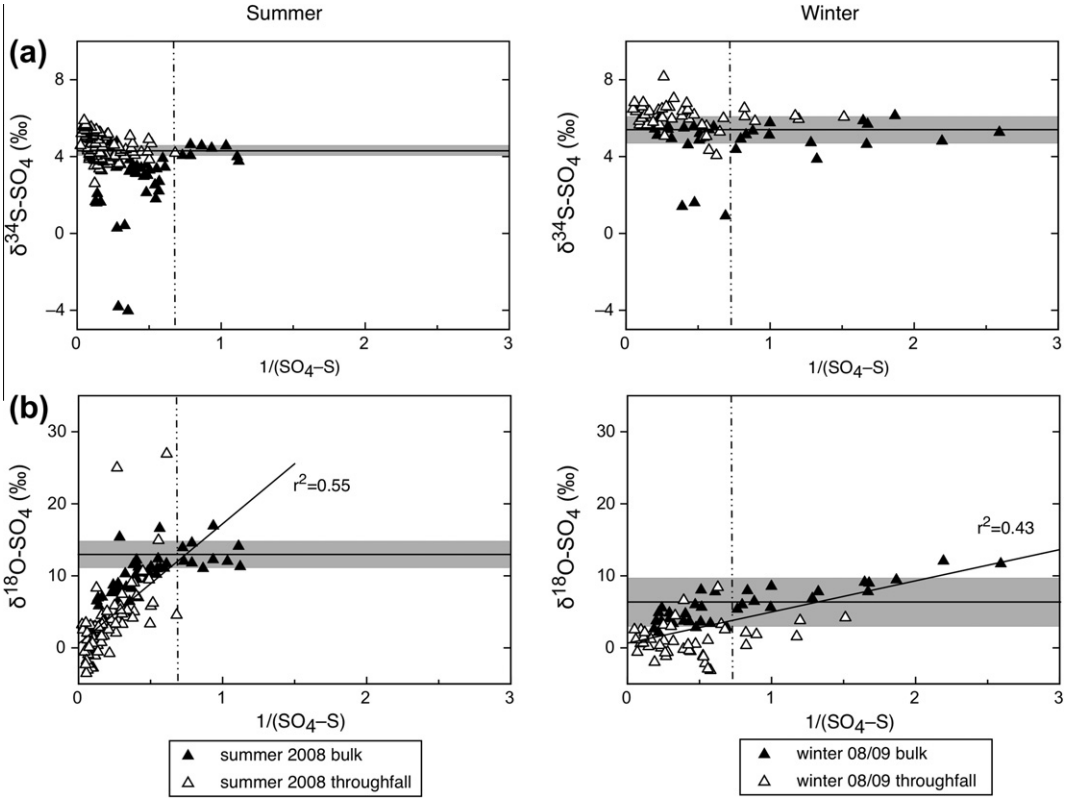

Fig. 7. δ^{34}S-SO_4 (a) and δ^{18}O-SO_4 values (b) versus the inverse SO_4-S deposition rate (in 1/(kg ha^{-1})) during summer (left) and winter (right) periods. The dotted lines indicate where the quite constant δ^{34}S values at low sulfate deposition rates (high 1/(SO_4-S) values) typically varying within 1‰ changed to more variable δ^{34}S values at high sulfate deposition rates (low 1/(SO_4-S). The horizontal lines in (a) indicate mean δ^{34}S values and their standard deviations (gray shaded area) for background sulfate deposition samples plotting to the right of the dotted line. The trendlines in (b) show mixing of sulfate from two sources, background and industrial emissions.

of the background atmospheric SO_4, respectively. Industrial derived SO_4 is characterized by a δ^{18}O value of ~0.6‰ (*y*-intercept in Fig. 7b). Background atmospheric SO_4 at low deposition rates of <1.4 kg S ha^{-1} (Fig. 7a) had an average δ^{18}O value of 12.9 ± 1.9‰ during summer 2008. However, there was a trend towards higher δ^{18}O-SO_4 values with lower SO_4 deposition rates (Fig. 7b), indicating that background SO_4 not derived from local industrial activities may have higher δ^{18}O values than the chosen average value of 12.9 ± 1.9‰. Using the average δ^{18}O value for background SO_4 deposition rates according to Fig. 7a, therefore, results in an underestimation of industrial SO_4 contributions to atmospheric deposition. Because most of the annual SO_4 deposition between May 2008 and May 2009 occurred during the summer sampling period, calculations were only conducted for summer 2008. Industrial contributions to SO_4 bulk deposition in summer 2008 ranged from 0% to 59%. Fig. 8a shows the spatial distribution of these results for bulk SO_4 deposition during summer 2008. The map reveals that bulk deposition at industrial sites (W1 (59%), AMS5 (51%), Peat Pond (39%), LYS (36%), AMS 9 (41%) and AMS 10 (41%)) is affected by minimum industrial SO_4 contributions between 25% and 59%. The overall error for these lower-bound estimates is approximately ±20% based on calculations applying the highest deposition weighted site averaged δ^{18}O value of summer 2008 (14.4‰) for $\delta^{18}O_{BGRD}$ instead of the average δ^{18}O value of background SO_4 deposition samples. Lower-bound estimates of industrial contributions to bulk SO_4 deposition at the community sites AMS 1 and AMS 14 were estimated to be 20% and 7%, respectively. Forest health plots appeared to receive less than 25% of their bulk SO_4 deposition from industrially derived SO_4 (JP212 (25%), JP104 (10%), JP102 (11%), JP107 (12%), JP213 (0%)).

Dry deposition is a major contributor to atmospheric S deposition in the AOSR resulting in elevated throughfall SO_4 deposition. Therefore, calculations estimating industrial contributions to throughfall SO_4 deposition were also conducted for summer 2008 using the same δ^{18}O value (12.9 ± 1.9‰) for background SO_4 deposition. Industrial contributions to SO_4 deposition in throughfall in the AOSR ranged from 49% to 100% (Fig. 8b) and were higher than industrial contributions to open field bulk SO_4 deposition (Fig. 8a). Highest industrial SO_4 contributions were calculated for throughfall at industrial sites (LYS (100%), AMS 9 (100%), AMS 10 (100%), AMS 15 (90%), AMS 5 (80%)) and the community site AMS 14 (100%). Industrial contributions to throughfall SO_4 at AMS 13 were estimated at 79%, and throughfall in forest health plots received between 49% and 91% SO_4 of industrial origin (R2 (91%), JP104 (76%), JP102 (82%), JP107 (58%), JP212 (86%), JP213 (49%)). These results emphasize the importance of dry deposition as a major contributor to S deposition in the AOSR and suggest that the majority of throughfall SO_4 deposited within 74 km of the operation is of industrial origin.

6. Conclusions

Atmospheric throughfall SO_4 deposition rates in the AOSR are low at forested plots farthest distant from the oil sand operations (94 and 113 km, ~3.3 kg SO_4-S ha^{-1} yr^{-1}) compared to industrial sites close to the operations. Annual bulk deposition rates of SO_4 at the same distant forested sites were around 1.4 kg SO_4-S ha^{-1} yr^{-1}. Both bulk and throughfall SO_4 deposition rates were elevated within ~29 km distance to the industrial operations, particularly at

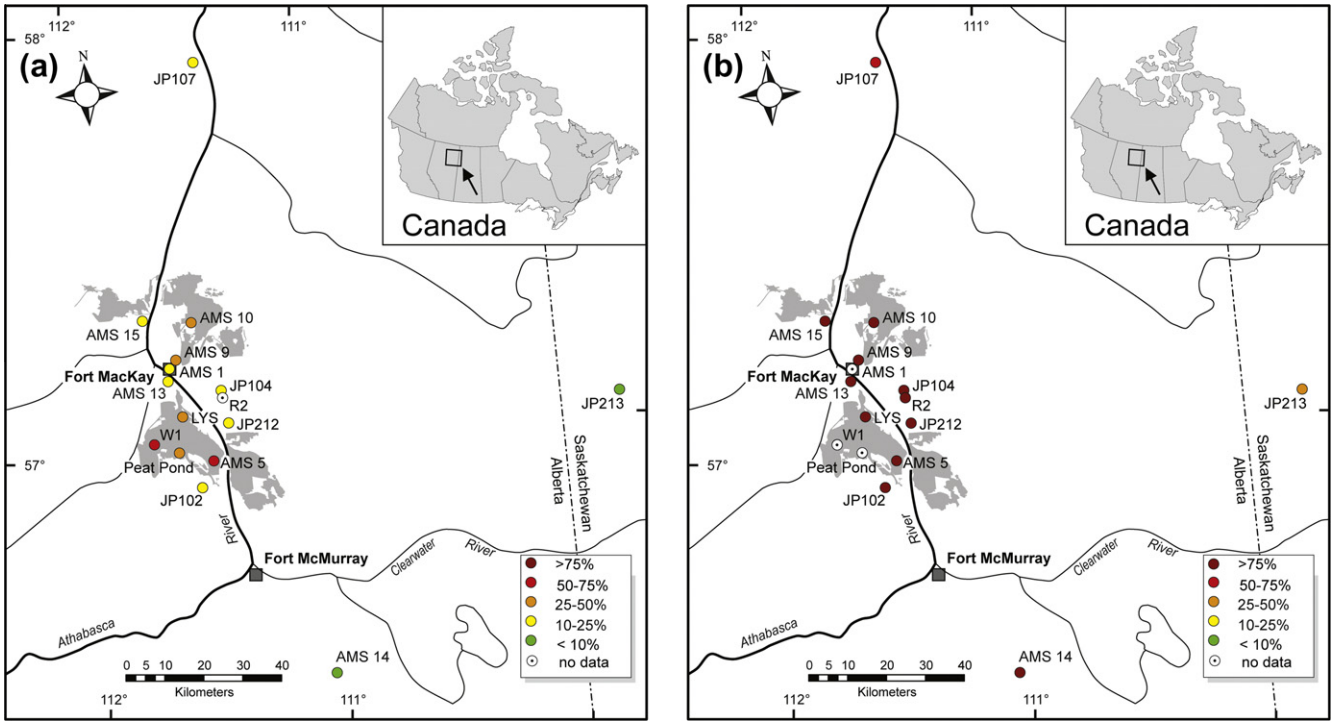

Fig. 8. Results of the two-end-member mixing analysis using $\delta^{18}O$ values of atmospheric sulfate in open field bulk deposition (a) and in throughfall deposition (b) in summer 2008, showing lower-bound estimates of industrial contributions to sulfate deposition (in %) in the AOSR.

industrial sites. More sampling sites between 29 and 74 km from the industrial operations are, however, required in future studies to more conclusively locate the boundary separating areas with elevated SO_4 deposition rates from those primarily only receiving long-range SO_4 deposition. Highest SO_4 deposition rates were observed at industrial sites. Throughfall deposition rates exceeded bulk deposition rates at all sites, indicating that dry deposition scavenged by the tree canopy is a dominant contributor to atmospheric S deposition. Sulfur isotope ratio measurements of atmospheric SO_4 deposited in the AOSR revealed that $\delta^{34}S$ values of SO_4 in long-range deposition was not markedly different from $\delta^{34}S$ values at high deposition rates in close proximity to the industrial emissions. $\delta^{34}S$ values, therefore, cannot be used to distinguish between SO_4 from long-range transport and local industrial S emissions. However, $\delta^{34}S$ values revealed that SO_4 derived from H_2S emissions from tailing ponds depleted in ^{34}S contributes to local atmospheric SO_4 deposition especially at the industrial sites W1 and Peat Pond.

$\delta^{18}O$ values of atmospheric SO_4 in bulk and throughfall deposition in the AOSR showed a distinct trend with deposition rates. $\delta^{18}O$ values of SO_4 at high deposition rates were more than 10‰ different from background SO_4 $\delta^{18}O$ values, providing an excellent tracer of industrial derived SO_4. Two end-member mixing calculations revealed that open field bulk SO_4 deposition at sites in close proximity (<27 km) to the industrial operations, particularly at industrial sites, is significantly affected by S of industrial origin. Lower-bound estimates of industrial S contributions to bulk deposition ranged from 0% to 59%. Dry deposition is a major contributor to atmospheric S deposition in the AOSR and industrial sources contributed between 49% and 100% to SO_4 deposition in throughfall at the investigated sites.

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