A multi-isotope approach for estimating industrial contributions to atmospheric nitrogen deposition in the Athabasca oil sands region in Alberta, Canada

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A B S T R A C T

Industrial nitrogen (N) emissions in the Athabasca oil sands region (AOSR), Alberta, Canada, affect nitrate (NO_3) and ammonium (NH_4) deposition rates in close vicinity of industrial emitters. NO_3–N and NH_4–N open field and throughfall deposition rates were determined at various sites between 3 km and 113 km distance to the main oil sand operations between May 2008 and May 2009. NO_3 and NH_4 were analyzed for $\delta^{15}N$–NO_3, $\delta^{18}O$–NO_3, $\Delta^{17}O$–NO_3 and $\delta^{15}N$–NH_4. Marked differences in the $\delta^{18}O$ and $\Delta^{17}O$ values between industrial emissions and background deposition allowed for the estimation of minimum industrial contributions to atmospheric NO_3 deposition. $\delta^{15}N$–NH_4 values also allowed for estimates of industrial contributions to atmospheric NH_4 deposition. Results revealed that particularly sites within ~30 km radius from the main oil sands developments are significantly affected by industrial contributions to atmospheric NO_3 and NH_4 deposition.

1. Introduction

The Athabasca oil sands in northeastern Alberta, Canada, constitute an enormous heavy oil resource that is becoming increasingly important for the Canadian economy as the availability of conventional fossil fuel reserves continues to decline. This unconventional oil resource has experienced an unprecedented expansion of mining projects (open pit mining) and in-situ operations (e.g. steam-assisted gravity drainage) over the last decade. The bitumen is extracted from the mined oil sand and upgraded to synthetic crude oil while removing excess nitrogen and sulfur. Both mining and upgrading of bitumen are accompanied by significant industrial nitrogen (N) emissions, including stack emissions, vehicle emissions from heavy haulers operating in the open pit mines and other off- and on-road vehicles, among others. NO_x (nitrogen oxides) emissions have increased by 29% in Western Canada between 1985 and 2000 contrasting with declines observed in Eastern Canada (Schindler et al., 2006). The potential consequences of elevated N

emissions are diverse, including acid deposition and eutrophication of terrestrial and aquatic ecosystems (Galloway et al., 2008; Gruber and Galloway, 2008). Acid deposition, soil acidification and the potential of N saturation are particularly of concern in the typically N-limited boreal forest ecosystems of the Athabasca oil sands region (AOSR) (Laxton et al., 2012; Jung and Chang, 2012; Jung et al., 2011; Cheng et al., 2011; Ok et al., 2007; Whitfield et al., 2009; Wieder et al., 2010). Hence, monitoring of atmospheric N deposition and a better understanding of nitrogen transport from industrial sources to sinks in terrestrial and aquatic ecosystems are crucial for a thorough assessment of environmental effects of elevated nitrogen emissions and deposition in the AOSR.

Nitrogen isotope ratios have been successfully used in some case studies of the atmospheric N cycle determining the sources and fate of anthropogenic atmospheric nitrogen (e.g. Elliott et al., 2007; Nanus et al., 2008). However, the usefulness of nitrogen isotope ratios to trace N emissions is often limited due to significant variability observed for $\delta^{15}N$ values of atmospheric nitrate (NO_3) and ammonium (NH_4) (Freyer, 1991; Garten, 1992; Hastings et al., 2004), wide ranges of nitrogen isotope ratios observed for potential NO_x sources, and possible isotope fractionation during nitrogen conversion reactions (Moore, 1977; Ammann et al., 1999; Pearson

et al., 2000). As a consequence, $\delta^{15}N$ values of atmospheric nitrate and ammonium can vary from $<-15‰$ to $>+15‰$ (Kendall et al., 2007). It is also possible to determine the oxygen isotope ratios ($^{18}O/^{16}O$, $^{17}O/^{16}O$) of atmospheric nitrate, which have been shown to be enriched in both ^{18}O and ^{17}O due to reactions involving ozone (O_3) that is anomalously enriched in the heavy oxygen isotopes (Durka et al., 1994; Kendall et al., 2007; Michalski et al., 2003). Oxygen-17 contents are typically expressed as $\Delta^{17}O$ ($\Delta^{17}O = \delta^{17}O - 0.52*\delta^{18}O$) in per mil (‰). Recently, $\Delta^{17}O$ of stack emitted nitrate in $PM_{2.5}$ from one of the oil sands facilities has been reported to be near 0‰ (Proemse et al., 2012a) and therefore this nitrate is distinct from atmospheric nitrate with $\Delta^{17}O$ values that typically range between 20 and $\sim31‰$ (Michalski et al., 2003), providing a potential tracer for industrial nitrate emissions. $\delta^{18}O$ values of nitrate in $PM_{2.5}$ emitted from industrial point sources have also been shown to have low values ($\sim18‰$) (Proemse et al., 2012a) compared to $\delta^{18}O$ values of atmospheric nitrate ($\sim60–\sim95‰$) (Kendall et al., 2007). Hence $\delta^{18}O$ and $\Delta^{17}O$ values of nitrate in atmospheric deposition are not only capable of revealing oxidation pathways of nitrogen compounds in the atmosphere (Michalski et al., 2003; Morin et al., 2008; Savarino et al., 2007), but may possibly also fingerprint sources of nitrate. However, no studies of the isotopic composition of nitrogen compounds in atmospheric deposition have been reported for Western Canada or the Athabasca oil sands region in particular. To fill this knowledge gap, atmospheric nitrate and ammonium were collected in open field and throughfall deposition samplers located at various distances from industrial emission sources in the AOSR for two years (2007–2009). The objectives of this study were: 1) to test whether stable isotope techniques ($\delta^{18}O$, $\Delta^{17}O$, $\delta^{15}N$) have the potential to trace industrial contributions to atmospheric nitrogen deposition in the vicinity of industrial emitters in the AOSR, and if so, 2) to quantify N contributions from industrial emission sources to NO_3 and NH_4 deposition in the Athabasca oil sands region.

2. Materials and methods

2.1. Study area

The Athabasca oil sands region is the largest of three oil sand reservoirs in Alberta, Canada (Peace River, Cold Lake, Athabasca). These oil sands operations are surrounded by a mixture of peatlands and upland forest ecosystems including jack pine, spruce and aspen. The upland forests often grow on an eluviated Dystric Brunisol consisting mostly of sand (Soil Classification Working Group, 1998). Annual precipitation in Fort McMurray (Fig. 1) is 455.5 mm and the mean annual temperature is 0.7 °C (30-year-average (1971–2000), Environment Canada, 2011). Precipitation rates are typically highest during the summer months. The prevailing wind direction is from the West and Northwest (Sandhu and Blower, 1986), but varies with season (Government of Alberta, 2011) and terrain (Leahey and Hansen, 1982).

Sixteen sampling sites established by the Terrestrial Environmental Effects Monitoring (TEEM) group of the Wood Buffalo Environmental Association (WBEA) were selected based on numerous site selection criteria (AMEC, 2001) for collection of open field bulk deposition (wet deposition + dry deposition) and throughfall deposition (bulk deposition underneath tree canopy) between April 2007 and May 2009. In areas where dry deposition constitutes a major component of atmospheric deposition, throughfall deposition rates are a better indicator of atmospheric N input and availability in an ecosystem because it contains dry deposition scavenged by the tree canopy. A major emission stack from one of the oil sands operators near Fort McMurray (57.0479875 °N, 111.615502 °W) was used as a central marker point and distances from marker to sampling sites vary between 3 and 113 km. However, this site is not the only source of industrial N emissions as there are several other oil sand processing plants and open pit mines in the AOSR that are associated with stack and vehicle emissions (e.g. from heavy haulers among others). The expanding town of Fort McMurray and the frequent forest fires in northeastern Alberta (Larsen, 1997) represent other potential sources of atmospheric N in the region.

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. AMS 14 is also close

to an in-situ operation including a bitumen upgrader. The sites JP104, JP102, JP212, JP213, JP107 and R2 are forest health plots at upland forest sites.

2.2. Sample collection and concentration analyses

Nitrate (NO_3^-) and ammonium (NH_4^+) in bulk deposition were sampled using an ion exchange resin (PVC tubes containing ion exchange resin beads) method (Fenn and Poth, 2004; Fenn et al., 2009). 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 jack pine trees (Fenn and Ross, 2010). Resins were typically exposed for approximately half-year periods. The results from the following 4 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.

In the laboratory, the ion exchange resins were quantitatively eluted with 1N KI (Simkin et al., 2004). Nitrate concentrations in the KI extracts were analyzed using ion chromatography and NH_4 concentrations were determined colorimetrically, and deposition rates for the exposure periods were determined at the USDA Forest Service Laboratory, Riverside (California, USA). Annual deposition rates for the year May 2008 to May 2009 were calculated by adding summer 2008 deposition rates to winter 2008/2009 deposition rates. Sub-samples of the eluted solutions were subsequently shipped to the University of Calgary (Alberta, Canada) for isotopic analyses of nitrate ($\delta^{15}N-NO_3$ and $\delta^{18}O-NO_3$, $n = 455$) and ammonium ($\delta^{15}N-NH_4$, $n = 134$). $\Delta^{17}O$ of nitrate was analyzed on 30 sub-samples at the University of Washington in Seattle (WA, USA).

2.3. Isotope analyses

Nitrogen isotope ratios ($\delta^{15}N$) and oxygen isotope ratios ($\delta^{18}O$) of nitrate were analyzed by isotope ratio mass spectrometry (IRMS) using N_2O gas generated via the bacterial denitrification method (Sigman et al., 2001; Casciotti et al., 2002). Results are reported in the internationally accepted δ notation defined as

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

where R is the $^{15}N/^{14}N$ or $^{18}O/^{16}O$ ratio of the sample and a standard respectively. $\delta^{15}N$ values are reported relative to AIR and $\delta^{18}O$ relative to Vienna Standard Mean Ocean Water (VSMOW). The international reference materials IAEA KNO$_3$ and USGS 34, and in-house laboratory standards were used to ensure accuracy and long-term external precisions of $\pm0.5‰$ and $\pm1.0‰$ for $\delta^{15}N$ and $\delta^{18}O$ values of nitrate, respectively.

$\Delta^{17}O-NO_3$ values were determined using a modified bacterial denitrification method (Kaiser et al., 2007). $\Delta^{17}O-NO_3$ is reported as the deviation of $\delta^{17}O$ from the mass dependent relationship ($\delta^{17}O = 0.52*\delta^{18}O$) and expressed as $\Delta^{17}O$ ($\Delta^{17}O = \delta^{17}O - 0.52*\delta^{18}O$). Each sample was analyzed in duplicate. The long-term external precision based on measurements of USGS 32, USGS 34, USGS 35, IAEA KNO$_3$ and sample replicates was 0.6‰.

$\delta^{15}N$ of ammonium (NH_4^+) was measured using the ammonium diffusion method (Sebilo et al., 2004). The international reference material IAEA-N-2, an in-house standard, and a blank were included in each sample set to assure accuracy. $\delta^{15}N-NH_4$ values were determined using an elemental analyzer interfaced with an isotope ratio mass spectrometer (IRMS). Accuracy and precisions of $\delta^{15}N$ values of ammonium samples were ensured using the reference materials USGS 40 and USGS 41 and the external precision of $\delta^{15}N-NH_4$ values using the ammonium diffusion method was $\pm0.6‰$.

For each collection period, N-deposition weighted mean values for samples from several collectors at one site were calculated for $\delta^{15}N-NH_4$, $\delta^{15}N-NO_3$ and $\delta^{18}O-NO_3$ in open field deposition and throughfall, but it was not possible to calculate averages for $\Delta^{17}O$ values due to the low number of measurements ($n = 30$). Both N-deposition weighted sample averages and the non-deposition weighted individual measurements are reported here. Average $\delta^{15}N$ and $\delta^{18}O$ values of atmospheric nitrate and ammonium from open field deposition and throughfall samplers were determined by calculating deposition-weighted means ($\bar{x}$) per site and sampling period according to

$$\bar{x} = \frac{\sum_{i=1}^{n} w_i x_i}{\sum_{i=1}^{n} w_i} \tag{2}$$

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

3. Results

3.1. Ammonium deposition rates

Yearly ammonium (NH_4-N) deposition rates for the sixteen sampling sites monitored between May 2008 and May 2009 varied