Atmospheric dry deposition of sulfur and nitrogen in the Athabasca Oil Sands Region, Alberta, Canada

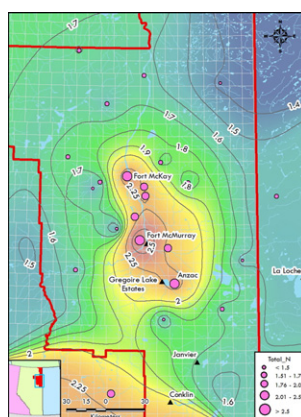Yu-Mei Hsu [a,*], Andrzej Bytnerowicz [b], Mark E. Fenn [b], Kevin E. Percy [a]

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HIGHLIGHTS

- NH_3, HNO_3, NO_2, and SO_2 concentrations were characterized by passive measurements.
- Dry deposition fluxes of N and S were estimated by a multi-layer model.
- Spatial distributions of N and S dry deposition in the AOSR were determined.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Due to the potential ecological effects on terrestrial and aquatic ecosystems from atmospheric deposition in the Athabasca Oil Sands Region (AOSR), Alberta, Canada, this study was implemented to estimate atmospheric nitrogen (N) and sulfur (S) inputs. Passive samplers were used to measure ambient concentrations of ammonia (NH_3), nitrogen dioxide (NO_2), nitric acid/nitrous acid (HNO_3/HONO), and sulfur dioxide (SO_2) in the AOSR. Concentrations of NO_2 and SO_2 in winter were higher than those in summer, while seasonal differences of NH_3 and HNO_3/HONO showed an opposite trend, with higher values in summer. Concentrations of NH_3, NO_2 and SO_2 were high close to the emission sources (oil sands operations and urban areas). NH_3 concentrations were also elevated in the southern portion of the domain indicating possible agricultural and urban emission sources to the southwest. HNO_3, an oxidation endpoint, showed wider ranges of concentrations and a larger spatial extent. Concentrations of NH_3, NO_2, HNO_3/HONO and SO_2 from passive measurements and their monthly deposition velocities calculated by a multi-layer inference model (MLM) were used to calculate dry deposition of N and S. NH_3 contributed the largest fraction of deposited N across the network, ranging between 0.70–1.25 kg N ha^{-1} yr^{-1}, HNO_3/HONO deposition ranged between 0.30–0.90 kg N ha^{-1} yr^{-1}, and NO_2 deposition between 0.03–0.70 kg N ha^{-1} yr^{-1}. During the modeled period, average dry deposition of the inorganic gaseous N species ranged between 1.03 and 2.85 kg N ha^{-1} yr^{-1} and SO_4-S deposition ranged between 0.26 and 2.04 kg ha^{-1} yr^{-1}. Comparisons with co-measured ion exchange resin throughfall data (8.51 kg S ha^{-1} yr^{-1}) indicate that modeled dry deposition

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combined with measured wet deposition (1.37 kg S ha^{-1} yr^{-1}) underestimated S deposition. Gas phase NH$_3$ (71%) and HNO$_3$ plus NO$_2$ (79%) dry deposition fluxes dominated the total deposition of NH$_4$-N and NO$_3$-N, respectively.

1. Introduction

Oil sands are a mixture of clay, sand, water and crude bitumen containing heavy molecular weight hydrocarbons used for production of asphalt, oil and various petroleum derivatives. Canada's Oil Sands in the Athabasca, Peace River and Cold Lake regions of Alberta, cover some 140,200 km^2 (Alberta Energy, 2011). Large-scale oil bitumen exploitation and processing in the Athabasca Oil Sands Region (AOSR) in northeastern Alberta has raised environmental concerns, partially due to the potential for eutrophication of terrestrial and aquatic ecosystems (Aherne and Shaw, 2010). In the AOSR, there are various emission sources including natural (e.g. forest fires and vegetation), oil sands operations (i.e. fixed, mobile, fugitive), and urban/transportation. Nitrogen oxide (NO$_x$), sulfur dioxide (SO$_2$), carbon monoxide and volatile organic compounds are the major criteria air contaminants emitted from the oil sands processes. According to the Canadian National Pollutant Release Inventory (NPRI), 2013 stack emissions of ammonia (NH$_3$), nitrogen oxides (NO$_x$) and SO$_2$ in the region were 4.4, 102 and 238 t d^{-1}, respectively (http://www.ec.gc.ca/inrp-npri/). However, NH$_3$ emissions may be underestimated in these inventories (Fenn et al., 2015). Facility reporting indicates stacks (main, flue-gas desulfurization) as the major SO$_2$ sources with NO$_x$ emission sources being split between stacks and area sources (i.e. mine-fleets) at ratios dependent upon process used.

Nitrogen dioxide is produced during oxidation of NO emitted during combustion processes, including fossil fuel combustion, forest fires, and other natural and anthropogenic processes (Finlayson-Pitts and Pitts, 2000). Nitric acid (HNO$_3$) is a final product of complex photochemical reactions between NO, NO$_2$, O· and OH·. NH$_3$ emissions result from agricultural activities, biological decay processes, catalytic converters, smoldering phase of fires, from flue gas desulfurization systems (Wang et al., 2012). NH$_3$, NO$_2$ and HNO$_3$ are important components of reactive atmospheric nitrogen (N$_r$) and major drivers of atmospheric nitrogen (N) dry deposition to forests and other ecosystems (Bytnerowicz and Fenn, 1996; Hanson and Lindberg, 1991). Sulfur dioxide may be released during natural processes (e.g., volcanic emissions) and from anthropogenic activities such as combustion of fossil fuels, refining and smelting of sulfide ores, and other industrial processes (Seinfeld and Pandis, 2006). Through stomatal uptake, it is an important source of S deposition to vegetation including forest ecosystems (Fowler et al., 1989).

The Wood Buffalo Environmental Association (WBEA; www.wbea.org) is a multi-stakeholder, not-for-profit organization responsible for monitoring air quality in the AOSR. Outside of the Athabasca River Valley in the boreal forest, WBEA has used passive sampling techniques since 2000 to measure ambient concentrations of selected air pollutants for providing estimates of air pollutant exposure to forests and other vegetation. Passive samplers are simple to use, inexpensive, do not require electricity or air conditioned shelters and thus can be used in remote locations (Bytnerowicz et al., 2005; Krupa and Legge, 2000). As such, passive samplers allow for a spatial coverage of the areas of interest providing data that can be used for the generation of geostatistical maps of air pollutants. The information gathered helps to better understand atmospheric composition and distribution of air pollutants, atmospheric dry deposition of N (NH$_3$, HNO$_3$, and NO$_2$) and S (SO$_2$), as well as regional imports and exports.

In this study, ambient concentrations of selected inorganic N and S gaseous species and their dry deposition amounts have been determined to elicit an improved understanding of potential effects of gaseous phase N and S on the terrestrial ecosystems of the AOSR.

2. Methods

2.1. Monitoring network

WBEA operates a regional monitoring program focused in part on assessing whether or not emissions of acidifying and eutrophyting compounds are having adverse effects on the terrestrial environment in the AOSR. This program is well described in Percy (2013). A passive sampler network was established in the region to characterize the spatial distribution of pollutants and their deposition by using geostatistical methods. Coordinates and a detailed map of all AOSR monitoring sites, including those for the ion exchange resin (IER) deposition determinations is also shown in Supplementary information (SI) Table S1 and Fig. S1.

2.2. NH$_3$, HNO$_3$/HONO, NO$_2$ and SO$_2$ passive measurements

Passive samplers to monitor NH$_3$, HNO$_3$ with nitrous acid (HONO), NO$_2$ and SO$_2$ were exposed to ambient air on towers above the tree canopy or on posts at a height of 2 m above ground level in the industrial areas of the AOSR and at 2 m above bog surfaces. Passive samplers were collected every month in summer (from April to September) and every two months in winter (from October to March). Ambient NH$_3$ and HNO$_3$/HONO concentrations were monitored near the mining and industrial operations and in remote areas of the AOSR from 2005 until 2013. The monitoring network for NH$_3$ and HNO$_3$/HONO consisted of 25 sites in 2005, gradually grew to 38 sites in 2009 and was reduced to 26 sites for 2010–2013. The passive sampling program for NO$_2$ and SO$_2$ concentrations have been initiated in 1999 at 11 sites, gradually increased to 15 sites in 2005 and to 23 sites in August 2008.

Passive samplers of the Ogawa design (Ogawa & Co. USA, Inc.) (Roadman et al., 2003) were used for NH$_3$ monitoring with two replicate filters coated with citric acid. Three replicate HNO$_3$/HONO samplers of the US Department of Agriculture Forest Service (USDA FS) design (Bytnerowicz et al., 2016; Bytnerowicz et al., 2005) were used at each monitoring site. In these samplers, ambient air passes through a Teflon membrane and both HNO$_3$ and HONO species are absorbed on a Nylasorb nylon filter as nitrate (NO$_3^-$). After sampling, exposed samplers of HNO$_3$/HONO and NH$_3$ were shipped to the USDA FS chemical laboratory in Riverside, California for sample analysis. Both NH$_3$ and HNO$_3$/HONO samples were extracted by de-ionized (DI) water and analyzed using a TRAACS 2000 autoanalyzer for ammonium (NH$_4^+$) and an ion chromatography system (ICS, Dionex ICS 2000 LCD, Dionex Corp., now Thermo Fisher Scientific Inc.) for NO$_3^-$. Ambient NH$_3$ and HNO$_3$/HONO concentrations were calculated based on a comparison of passive samplers against the collocated honeycomb denuder systems (Koutrakis et al., 1993). In field trials performed in Riverside, California, the samplers showed high accuracy (relative standard deviation of three replicate readings of ~5%)(Bytnerowicz et al., 2010).

The all-season SO$_2$ passive sampling system (SPSS) (Tang et al., 1997), and NO$_2$ passive sampling system (NPSS) (Tang et al., 1999) were installed at the network locations to estimate SO$_2$ and NO$_2$ concentrations, respectively (Hsu, 2013). After collection, SO$_2$ and NO$_2$ samples were extracted in DI water and analyzed by an ICS (DX-120,