Spatial and temporal distribution of ambient nitric acid and ammonia in the Athabasca Oil Sands Region, Alberta

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ABSTRACT

Monthly average ambient concentrations of gaseous nitric acid (HNO3) and ammonia (NH3) were monitored at the Athabasca Oils Sands Region (AOSR), Alberta, Canada, between May 2005 and September 2008. Generally, concentrations of both pollutants were elevated and highly variable in space and time. The highest atmospheric concentrations occurred in the vicinity of the major mining and oil extraction activities of Fort Murray and Fort McKay. Maximum monthly average concentrations of HNO3 decreased from >6 µg m–3 in 2005 and 2006 to <4 µg m–3 in 2007 and 2008. While the HNO3 summer seasonal averages in 2005 and 2006 approached ~2 µg m–3 at some sites, in the subsequent summers and during winter seasons it rarely exceeded 1 µg m–3 and no clear differences between summer and winter occurred. Concentrations of NH3 were elevated during the entire study and frequently reached 6 µg m–3. Generally, NH3 stayed higher in summer than in winter; the summer seasonal averages often exceeded 4 µg m–3 while those for winter only on two occasions were above 3 µg m–3. In summer 2008, an expansion of the area with elevated NH3 levels was observed extending to remote locations. Ammonia is of a much higher concern from a perspective of possible biological effects, because of its potential for direct toxic effect on lichens and its contribution to the elevated N dry deposition with possible negative consequences for forests and other ecosystems.

Key words: air pollution, passive samplers, nitrogen deposition, boreal forests, potential phytotoxic effects, Canada

1. INTRODUCTION

The Athabasca Oil Sands Region (AOSR) is located in the north-eastern part of Alberta, Canada, and contains large deposits of oil in a form of naturally occurring heavy molecular weight hydrocarbons of high viscosity, called bitumen, which are mixed with clay, sand and water. The AOSR deposits are the largest of three major oil sands deposits in Alberta, along with the nearby Peace River and Cold Lake areas (Fig. 1). These three oil sand deposits lie beneath 141,000 km² of a sparsely populated boreal forest and muskeg, and contain 1.7 trillion barrels (270×10⁹ m³) of bitumen (Kean 2009). With modern non-conventional oil production technology at least 10% of these deposits were considered to be economically recoverable at the 2006 prices making Canada’s oil reserves the second largest in the World, after Saudi Arabia (Kunzig 2009). Since 2003, as a result of rapid increases of oil prices, the mining and extraction activities have been greatly expanded and new facilities are being planned-while the current production is 1.3 million barrels daily, it is projected to reach 3 million barrels (477,000 m³) per day by 2018 (Kean 2009).

The large scale of oil extraction operations at the AOSR is energy intensive and causes numerous environmental problems, among them emissions of greenhouse gases and toxic air pollutants (Charpentier et al. 2009). Major sources of air pollutants in the AOSR are associated with the open-pit mining, bitumen separation from sand and clay, steam assisted gravity drainage, cystic steam stimulation, upgrading and transformation of oil from bitumen into a high quality synthetic crude oil using variations of the Clark Hot Water Extraction method (Gu et al. 2002). Other important sources of air pollutants are exhausts from numerous trucks and other types of machinery used in mining and transportation of bitumen ore as well as emissions of vapours from the tailing ponds (Kelly et al. 2009). Air pollutants associated with health and environmental concerns in the AOSR are the criteria pollutants such as ozone (O3), sulphur dioxide (SO2), nitrogen oxides (NOₓ), as well as other pollutants such as nitric acid (HNO3), ammonia (NH3), carbon monoxide (CO), particulate matter measured as PM2.5 and PM10, and total hydrocarbons (THC). The Wood Buffalo Environmental Association (WBEA) has been responsible for ambient air quality monitoring in this area using both continuous monitors and passive samplers.

Ammonia and HNO3 are important components of reactive atmospheric nitrogen (N) and major drivers of atmospheric N dry deposition to forests and other ecosystems (Hanson & Lindberg 1991; Lovett 1994; Magnani et al. 2009). Nitric acid is a final product of oxidation of NOₓ emitted during fossil fuel combustion, forest fires, and other natural and anthropogenic processes (Finlayson-Pitts & Pitts 2000). Ammonia emissions are caused by agricultural activities,
biological decay processes, catalytic converters, the smouldering phase of fires, and other activities (Krupa 2003). Both $\text{HNO}_3$ and $\text{NH}_3$ are potentially phytotoxic at high ambient concentrations, and their toxicity may be enhanced at low temperatures when rates of the biochemical detoxification mechanisms in plants are low (Bytnerowicz et al. 1998). Recently developed passive samplers for $\text{HNO}_3$ and $\text{NH}_3$ are simple to use, inexpensive, do not require electricity or air conditioned shelters and can be used in remote locations (Krupa & Legge 2000). As such, passive samplers allow for an improved spatial coverage of the areas of interest providing data that can be used for generation of geostatistical maps of air pollutant distributions.

The rapidly growing bitumen mining, oil recovery and processing, as well as the spatial expansion of the oil sands exploitation area have increased the emissions of air pollutants in the AOSR. Consequently, there has been a growing concern that ambient concentrations of air pollutants could increase to the levels which can have negative effects on ecosystems. This concern has resulted in a need for more extensive monitoring of the key air pollutants, including $\text{HNO}_3$ and $\text{NH}_3$. Since these two pollutants are important components of atmospheric dry N deposition, they may potentially have negative impacts on forests, wetlands and lakes in the AOSR. These effects may be numerous and complex, including acidification of lakes and streams, contamination of water with nitrate ($\text{NO}_3^-$) and ammonium ($\text{NH}_4^+$), eutrophication of bogs, fens and meadows, changing composition of the vegetation community, direct toxic effects of pollutants on lichen communities, and many others (Fenn et al. 2003; U.S. EPA 2009).

The main objective of this study was to characterize the spatial and temporal distribution of $\text{HNO}_3$ and $\text{NH}_3$ in the AOSR from a perspective of their potential biological effects. The secondary objective was to provide information needed for future optimization of the air pollution monitoring network.
2. METHODS

2.1. Passive samplers

A network of passive samplers was established for monitoring integrated, month-long, concentrations of HNO$_3$ and NH$_3$. The initial network developed in 2005 consisted of the passive sampler sites collocated with 14 ambient air quality monitoring stations and 11 remote forest health assessment sites. Gradually the network grew to 37 sites in 2008 (Fig. 2a, b), and in September 2008 covered the area of about 320 by 160 km (~51,000 km$^2$). There were three major groups of monitoring sites: 'local', where the passive samplers were collocated with the continuous monitoring equipment; 'remote' at the forest research sites, and 'lakes' at the limnological research sites. At the 'remote' sites samplers were located above forest canopy at about 10 m from the ground on towers specially designed for passive samplers. At all other sites the samplers were placed on wooden posts about 2 m above the ground level. In summer 2008 at the remote site B213, in addition to the regular samplers positioned above the forest canopy, samplers were also placed beneath the canopy at 0.5, 1 m and 2 m above the ground to evaluate vertical distribution of the pollutants. Three replicate HNO$_3$ samplers of the USDA Forest Service design (Bytnierowicz et al. 2005) were used at each monitoring site. In these samplers, ambient air passes through a Teflon membrane and gaseous HNO$_3$ is absorbed on a Nylasorb nylon filter as nitrate (NO$_3^-$). Nylon filters from the samplers were extracted in nano-pure water, and NO$_3^-$ concentrations in filter extracts were analyzed by ion chromatography (Dionex ICS 2000 LCD). Average ambient HNO$_3$ concentrations were calculated using calibration curves developed by comparing the passive samplers against the collocated annular denuder systems (Koutrakis et al. 1993). In the field trials performed in Riverside, California, the samplers showed high accuracy (relative standard deviation of three replicate readings of ~5%). Passive samplers of the Ogawa design (Roadman et al. 2003) were used for NH$_3$ monitoring with two replicate filters coated with citric acid. Ammonia reacts with citric acid on the filters producing ammonium citrate. After water extraction, NH$_4^+$ concentrations in filter extracts were determined colourimetrically on a TRAACS 2000 Autoanalyzer, and ambient NH$_3$ concentrations were calculated based on a comparison of passive samplers against the collocated annular denuder systems (Koutrakis et al. 1993). The accuracy of the samplers tested during field trials performed in Riverside, California, was high (relative standard deviation of four replicate readings ~4%). In this paper we report results for the period May 1$^{st}$, 2005 through to September 30$^{th}$, 2008. Both HNO$_3$ and NH$_3$ passive samplers were changed every month between May 1$^{st}$ through October 31$^{st}$, and every 2 months between November 1 and April 30. Four blank HNO$_3$ filters and four blank NH$_3$ filters were used for each exposure period. Blank samples were kept in closed containers located in chemical laboratory of the US Forest Service, Riverside, California. For the entire study, the average relative standard deviation values for the HNO$_3$ and NH$_3$ field-exposed samplers were 12.9% and 12.6%, respectively.
2.2. Geostatistical analysis

Pollutant distribution maps were developed with the Geostatistical Analyst, extension of ArcGIS software (ESRI, Redlands, CA). The Geostatistical Analyst uses values measured at sample points at different locations in the landscape and interpolates them into a continuous surface. The spatial distribution of NH₃ and HNO₃ were based on averages of 6 monthly pollutant concentrations at 37 sites using an inverse distance weighting method (Johnston et al. 2001). The uncertainty of prediction, called the prediction standard error map, was calculated using simple kriging with a ‘normal score’ transformation type. The numerical values were calculated to represent two standard deviations, or the 95% confidence level (Chiles & Delfiner 1999). With this, 95% of the time the true value of the prediction (represented by the map of prediction) is within the interval formed by the predicted value ± the relevant prediction standard error. Levels of uncertainty are shown as shades starting from light (lowest uncertainty of prediction) to dark (highest uncertainty).

3. RESULTS

3.1. Pollutant levels and distribution

Nitric acid concentrations expressed as monthly averages during the entire study between May 2005 and September 2008, were highly variable both spatially and temporally (Fig. 3, Tab. 1). The highest concentrations exceeding 7 µg m⁻³ in July 2005 occurred at site AMS 10T and 6.5 µg m⁻³ at site PH2 in April 2006; since then the HNO₃ concentrations were <4 µg m⁻³. No clear trends of seasonal patterns were observed, in some years the summer values were higher (2005 and 2006) while in other (2007 and 2008) the winter levels were higher (Fig. 3, Tab. 1). Measurement performed on a vertical gradient at Site B213 in summer 2008 showed that HNO₃ at 0.5 and 1 m above the ground was much lower (0.18 and 0.13 µg m⁻³, respectively) than at 2 m above the ground and above the canopy (0.44 and 0.45 µg m⁻³, respectively). The 2007/2008 winter and 2008 summer data were chosen as the examples of HNO₃ spatial distribution (Fig. 4a, b). The geostatistical maps pre-
sent on these figures show slightly higher HNO₃ values in winter compared to summer with the highest levels, in the centre of the bitumen exploitation and oil processing area near Fort McMurray and Fort McKay.

Monthly average NH₃ concentrations were also highly variable in time and space (Fig. 3, Tab. 2). The highest NH₃ value ~9 µg m⁻³ occurred at site AMS 2 in August 2005, and occasional peaks >6 µg m⁻³ occurred in various locations throughout the monitoring period. Ammonia measurements on a vertical gradient showed that at 0.5, 1 and 2 m above the ground concentrations were higher (1.74; 1.81, and 1.96 µg m⁻³, respectively) than above the forest canopy (1.39 µg m⁻³). During the entire study the NH₃ levels were higher in summer than in winter (Fig. 3, Tab. 2). This is clearly seen on the maps presenting NH₃ distribution in winter 2007/2008 and summer 2008 (Figs 4c, d). Similarly as for HNO₃, the highest NH₃ concentrations occurred in the vicinity of Fort McMurray and Fort McKay. There was a trend of increasing NH₃ concentrations in remote locations far away from the main oil exploitation activities; while the 2007 average concentration for those sites was 1.24 µg m⁻³, for the 2008 summer it increased to 1.57 µg m⁻³ (Tab. 2).

3.2. Uncertainty of prediction

The uncertainty of prediction is described by the prediction standard error maps for both pollutants during winter 2007/2008 and summer 2008 (HNO₃ in Figs 5a, b and NH₃ in Figs 5c, d). These maps correspond with maps of spatial distribution of HNO₃ (Figs 4a, b) and NH₃ (Figs 4c, d). In winter, the average prediction standard error for HNO₃ for the entire area was ±0.32-0.34 µg m⁻³, while the lowest uncertainty was in the centre of the monitoring area and near individual monitoring sites. It was determined that relatively high levels of uncertainty existed around the central part of the monitoring activities within a radius of 25-35 km W and NW of Fort McKay and in a radius of ~30 km W and E of Fort McMurray (Fig. 5a). In
In winter, the average prediction standard error for NH₃ concentration was ±0.87–0.90 µg m⁻³ over the entire area, which was lower than in summer at ±0.16–0.18 µg m⁻³ with most of the monitoring area showing low levels of uncertainty. However, the area near Fort McMurray showed high levels of uncertainty up to ±0.23–0.31 µg m⁻³ (Fig. 5b). In winter, the average prediction standard error for NH₃ was ±0.57–0.58 µg m⁻³ with lower levels of uncertainty near the individual sites and with relatively high levels of uncertainty up to ±0.99–1.22 µg m⁻³ in the centre of the monitoring area in the vicinity of Fort McKay and Fort McMurray (Fig. 5c). In summer, the average prediction error for the entire area was ±0.87–0.90 µg m⁻³. Contrary to the winter values, the central, industrial area near Fort McKay and Fort McMurray had relatively low levels of uncertainty in summer (Fig. 5d).

4. DISCUSSION

Industrial activities related to the oil extraction and upgrading produce numerous air pollutants. Ammonia emissions can result from various sources such as aqueous mixture of floating agent containing NH₃ used for separating and recovering bitumen from tar; second stage of upgrading of bitumen, called hydro treating, in which N is removed as NH₃; from tailing ponds which are contaminated with NH₃ (WSE 2005). Additionally, emissions from trucks and other heavy equipment in the area produce elevated concentrations of NOₓ, which undergo complex photochemical reactions with methane and other volatile organic compounds producing gaseous HNO₃ (Seinfeld & Pandis 1998).

Nitric acid concentrations during most of the study were elevated compared with the Alberta background concentration of 0.31 µg m⁻³ (Legge & Krupa 1989). The highest recorded values ~6–7 µg m⁻³ are comparable with the concentrations occurring on the western slopes of Sequoia & Kings Canyon National Park in the Sierra Nevada, California (Bytnerowicz et al. 2002), and are much lower than those in the highly polluted areas in southern California (Bytnerowicz et al. 1999a).

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Fig. 4. Spatial distribution of HNO$_3$ and NH$_3$ concentrations in the Athabasca Oils Sands Region in 2008: (a) HNO$_3$ in winter 2007/2008; (b) HNO$_3$ in summer 2008; (c) NH$_3$ in winter 2007/2008; (d) NH$_3$ in summer 2008.
Fig. 5. Uncertainty analysis for HNO$_3$ and NH$_3$ distribution on the AOSR monitoring network expressed as the prediction error: (a) HNO$_3$ in winter 2007/2008; (b) HNO$_3$ in summer 2008 (c) NH$_3$ in winter 2007/2008; (d) NH$_3$ in summer 2008.
Low summer-season levels of HNO$_3$ concentrations, which in many locations were close to the background values, could be partially caused by high atmospheric deposition of the pollutant during high physiological activity of vegetation (Hanson & Lindberg 1991), and also possibly by titration of HNO$_3$ by NH$_3$ and formation of the aerosol NH$_4$NO$_3$ (Finlayson-Pitts & Pitts 2000).

Highly elevated NH$_3$ concentrations occurred during the entire study in numerous monitoring sites and significantly exceeded the long-term background mean concentration for Alberta of 0.26 µg m$^{-3}$ (Krupa 2003), the value higher than 0.14 µg m$^{-3}$ measured at the remote Niwot Ridge site of the Rocky Mountains in Colorado (Langford & Fehsenfeld 1992). The highest recorded values of 6-9 µg m$^{-3}$ are higher than the long-term means for the agricultural areas of Alberta (Krupa 2003). These values are similar to the concentrations recorded in Sequoia & Kings Canyon National Park downwind of the intensive agricultural activities of the California Central Valley (Bytnerowicz et al. 2002), or in Boulder, Colorado also affected by the agricultural emissions (Langford & Fehsenfeld 1992). The high values reported from the western United States correspond well with the annual averages in the United Kingdom reaching 8 µg m$^{-3}$ (Sutton et al. 2009). At present, it is not clear what potential sources of the elevated and increasing NH$_3$ concentrations, especially in the remote sites, could be. The most obvious reason can simply be an expansion of the area of oil exploitation activities and higher intensity of its processing. This could lead to the increasing emissions from a variety of sources such as spills from the stack-installed SO$_2$ scrubbers (Srivastava et al. 2004), emissions from the waste management activities and tailing ponds, emissions from the in situ oil exploitation or those associated with catalytic converters on mine fleet trucks. High levels of NH$_3$ in remote areas could be caused by various phenomena such as biological decay, emissions from the smouldering phase of forest fires, volatilization of fertilizers from the nearby agricultural lands, etc. (Krupa 2003).

Summer season measurements on a vertical gradient under the forest canopy showed different distribution patterns for the two pollutants. Nitric acid levels above the canopy and at 2 m above the ground were similar and much higher than at 0.5 and 1 m above the ground. This seems to be an indication of the HNO$_3$ deposition to ground vegetation and soils at forest floor. On the contrary, NH$_3$ levels were higher underneath forest canopy than above it. This could indicate NH$_3$ emissions from ground vegetation and soils. Clearly, a better understanding of a vertical distribution of various air pollutants within forest canopies, in forest openings, and in open areas such as bogs and fens in the AOSR is needed. This may help in improving monitoring networks and calculations of fluxes of air pollutants to different landscape categories.

Generally, the performance of the passive samplers during the study was satisfactory. However, some modifications of the monitoring procedures should be considered, such as improving the performance of samplers in winter conditions (effects of low temperatures and snow sometimes lead to wetting of filters or cracking of sampler components), or increasing the number of field replicates. Considering that in optimal field conditions in California both samplers performed very well, such improvements seem to be possible and should be explored. The monitoring network provided reliable results for most of the AOSR area. However, there were also areas which from a perspective of the calculated prediction error did not perform satisfactorily. Therefore, improvements in spatial coverage of the monitoring network are needed. The reliability maps show that some areas, even in the middle of the monitoring network, are under-represented and require additional monitoring sites. However, selection of such sites will not be easy considering big differences in the reliability of the monitoring network for various pollutants and during different seasons.

Long-term exposure to elevated concentrations of N gases and the resulting increased N deposition can have serious ecological implications and should be better understood in the AOSR. At the recorded levels, the direct toxic effects of HNO$_3$ and NH$_3$ on vascular plants are not likely to occur (Bytnerowicz et al. 1998, 1999 b). However, elevated NH$_3$ levels may have potentially detrimental effects on lichen communities; recent results from Great Britain show that critical levels of NH$_3$ for lichens should be set at 1 µg m$^{-3}$ as an annual average (Cape et al. 2009). In addition, other negative effects related to the increased N deposition on forests and other ecosystems should be seriously considered (Laxton et al. 2010, this issue). Geostatistical surfaces of ambient concentrations of the two gases resulting from this study, their deposition velocity values obtained from literature (Zhang et al. 2003, 2009), and information on vegetation cover obtained from remote sensing (such as MODIS images) could be utilized for generation of the GIS-based maps of atmospheric N dry deposition. Such maps together with information on N wet deposition could be used for the evaluation of ecological risks from atmospheric N in the AOSR (Laxton et al. 2010, this issue). It seems that potential risks could be much higher from NH$_3$ considering its high ambient concentrations, proportionally more N contained in the NH$_3$ molecule, and similar deposition velocities of the two gases (Lovett 1994). The resulting increased N deposition caused by elevated ambient NH$_3$ and HNO$_3$ concentrations could include shifts in N and carbon allocation, increase ecosystem biomass production, and change of species composition (Fenn et al. 2003; Magnani et al. 2008). A better understanding of potential threats by elevated levels of N pollutants and N deposition is needed for a sound assessment of...
ecological risks in the AOSR and the surrounding area. Such information is essential for the ecologically-responsible continuation of the present industrial activities and planned future expansion of oil exploitation and processing in the AOSR.

5. CONCLUSIONS

Information on spatial and temporal distribution of N pollutants is essential for understanding their potential effects on ecosystems health and sustainability in the areas affected by the oil recovery and processing. Multi-year monitoring of HNO₃ and NH₃ showed that concentrations of these pollutants were elevated and highly variable in space and time. Ammonia concentrations were higher, contributing more N for atmospheric dry deposition and potentially posing a more serious threat to forests and other ecosystems of the AOSR than HNO₃.

For a better understanding of a spatial distribution of HNO₃ and NH₃ in the AOSR, further refinement of the monitoring network is needed. There is also a need for acquiring data on spatial and temporal concentrations of NOₓ, particulate NH₄ and NO₃ as well as organic N compounds in order to have a better understanding of atmospheric N deposition levels and effects. This also includes better characterization of the air pollution distribution and atmospheric deposition patterns on vertical gradients in forest canopies, in forest openings and along forest edges.

Development of empirical models of dry N deposition to forests and other ecosystems based on the results of air pollution monitoring and establishment of critical loads for nutrient N and acidity is recommended. Such models and GIS-based maps of N deposition, N critical levels and N critical loads are needed for understanding potential ecological risks from air pollution in the AOSR. One of the first steps towards that could be generation of maps showing exceedances of critical levels of NH₃ for lichens.

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