

# Trends of monitored nitrogen species at monitoring sites in North America

Leiming Zhang<sup>1</sup>, Irene Cheng<sup>1</sup>, Xiaohong Yao<sup>2</sup>

<sup>1</sup> Air Quality Research Division, Environment and Climate Change Canada, Toronto (leiming.zhang@canada.ca)

<sup>2</sup> Ocean University of China, Qingdao, China

## Abstract

Long-term (1983-2011) air concentrations and annual wet deposition of ammonium and nitrate at 30 Canadian sites were analyzed. Long-term median atmospheric  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ranged from 0.1-1.7 and 0.03-2.0  $\mu\text{g}/\text{m}^3$  among the sites, respectively. Median annual wet deposition varied from 0.2-5.8 and 0.8-23.3 kg/ha for  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , respectively. Long-term decline in atmospheric  $\text{NH}_4^+$  from 1994-2010 was observed, whereas atmospheric  $\text{NO}_3^-$  increased from 1991-2001 and then declined from 2001-2010. Annual wet deposition of  $\text{NO}_3^-$  decreased at most sites by 0.07-1.0 kg/ha/a. Average gaseous  $\text{HNO}_3$  and particulate  $\text{NO}_3^-$  wet scavenging contributions to nitrate wet deposition were  $72\pm 23\%$  and  $28\pm 23\%$ , respectively. Gaseous  $\text{NH}_3$  and particulate  $\text{NH}_4^+$  contributed  $30\pm 19\%$  and  $70\pm 19\%$  to wet  $\text{NH}_4^+$  deposition.

Interannual variabilities in atmospheric ammonia during the most recent seven to eleven years were investigated at fourteen sites across North America. The long-term average of  $\text{NH}_3$  ranged from 0.8 to 2.6 ppb among the four urban and two rural/agriculture sites in Canada. The annual average at these sites did not show any decreasing trend with largely decreasing anthropogenic  $\text{NH}_3$  emission. An increasing trend was actually identified from 2003 to 2014 at one urban site. In the U.S., average  $\text{NH}_3$  from 2008 to 2015 was 2.2-4.9 ppb at three rural/agriculture sites and was 0.3-0.5 ppb at four remote sites. A stable trend at one and increasing trends at three rural/agricultural sites were identified. Increasing trends at the four remote sites were also identified. Changes in  $\text{NH}_4^+/\text{NH}_3$  partitioning and/or air-surface exchange process as a result of the decreased sulfur emission and increased ambient temperature were believed to be the causes of  $\text{NH}_3$  at some of the sites.

## Key Words

Inorganic nitrogen, air concentration, natural emission, gas-particle partitioning, wet deposition.

## Introduction

The Canadian Air and Precipitation Monitoring Network (CAPMoN) measures gaseous  $\text{HNO}_3$  and particulate  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , among other water-soluble inorganic ions, in air and precipitation across Canada. CAPMoN data are used to study trends in atmospheric pollutants related to smog and acid rain. The precipitation scavenging of  $\text{HNO}_3$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  have direct impacts on acid rain by increasing the input of nitrate to soil and surface water. Nitrate in soil depletes essential plant nutrients, such as base cations, and increases inorganic aluminum which is toxic to biota. Acid rain has been detrimental to red spruce and sugar maple trees (Driscoll et al. 2001) and contributed to lake acidification in Canada and northeastern U.S., which has resulted in detrimental effects on zooplankton and fish (Driscoll et al. 2001; Clair et al. 2002). It is therefore important to continually study the wet deposition of nitrogen species and acid rain. This dataset has been studied for (1) analyzing long-term geographical and temporal trends in atmospheric and wet deposition of  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , (2) determining scavenging ratios of  $\text{NO}_3^-$  and  $\text{HNO}_3$ , and (3) estimating the relative contributions of particulate and gaseous nitrogen species to total nitrate and ammonium wet deposition.

National Air Pollution Surveillance (NAPS) in Canada and Ammonia Monitoring Network (AMoN) in the U.S. started monitoring  $\text{NH}_3$  in recent years considering its important roles in the formation of fine particles and related impacts on air quality, climate, and ecosystem.  $\text{NH}_3$  data during the most recent seven to eleven years at fourteen selected sites from NAPS and AMoN were analyzed for understanding its long-term trends and interannual variabilities.

## Methods

### *Air and precipitation analyses*

Daily air samples were collected on filters and daily wet deposition was collected using a wet-only sampler. The samples were analyzed for major inorganic ions and trace gases in the air samples. Valid air concentrations from 1983-2010 at 16 sites and precipitation measurements from 1984-2011 at 30 sites were

analyzed. The monitoring sites are located across Canada, but predominantly in southeastern Canada. Geographical patterns and temporal trends in air concentrations and annual wet deposition were examined. Statistical analyses of temporal trends were performed using regression analysis and the Mann-Kendall and Seasonal Kendall Tests (Gilbert 1987).

#### *Scavenging ratio*

Monthly scavenging ratios, defined as a ratio of a pollutant's concentration in precipitation to that in air ( $W = C_{\text{prec}}/C_{\text{air}}$ ), were first determined for particulate-phase ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ). Scavenging ratio of coarse PM ( $W_{\text{cPM}}$ ) was determined by averaging  $W_{\text{Ca}}$ ,  $W_{\text{Mg}}$ , and  $W_{\text{Na}}$  since these base cations are predominantly in coarse PM.  $W_{\text{K}}$  was used as a surrogate for the scavenging ratio of fine PM ( $W_{\text{fPM}}$ ) for inland sites, whereas  $W_{\text{K}}/2$  was assumed for coastal sites to exclude the wet deposition of  $\text{K}^+$  in the coarse fraction.

#### *Relative contributions of gaseous and particulate species to nitrate and ammonium wet deposition*

Wet deposition of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  can be attributed to the precipitation scavenging of atmospheric  $\text{NO}_3^-$  and gaseous  $\text{HNO}_3$  and atmospheric  $\text{NH}_4^+$  and gaseous  $\text{NH}_3$ , respectively. However, most wet deposition networks including CAPMoN routinely measure total  $\text{NO}_3^-$  and  $\text{NH}_4^+$  wet deposition. To determine their relative contributions, particulate wet scavenging is first calculated from  $W_{\text{cPM}}$ ,  $W_{\text{fPM}}$ , particulate air concentration, and fine and coarse PM mass fractions. The difference between the total wet scavenging and particulate wet scavenging is assumed to be the wet scavenging contribution from gases. The wet scavenging of atmospheric  $\text{NO}_3^-$  ( $\text{pNO}_3^-$ ) was estimated as follows:

$[\text{pNO}_3^-]_{\text{prec}} = W_{\text{fPM}} [\text{pNO}_3^-]_{\text{air}} P_f + W_{\text{cPM}} [\text{pNO}_3^-]_{\text{air}} (1-P_f)$ , where  $P_f$  is the fine mass fraction of  $\text{NO}_3^-$ , which is temperature-dependent (assuming a  $P_f$  of 0.84 during winter and  $P_f$  of 0.29 for all other months). The contribution of  $\text{HNO}_3$  to nitrate wet deposition was calculated as follows:

$[\text{HNO}_3]_{\text{prec}} = [\text{total NO}_3^-]_{\text{prec}} - [\text{pNO}_3^-]_{\text{prec}}$ , where  $[\text{total NO}_3^-]_{\text{prec}}$  is the monthly volume-weighted  $\text{NO}_3^-$  precipitation concentration and  $[\text{pNO}_3^-]_{\text{prec}}$  is the wet scavenging of  $\text{pNO}_3^-$  previously determined. The relative contributions of particulate and gaseous species to  $\text{NO}_3^-$  wet deposition were calculated as follows:

$\% \text{pNO}_3^- = ([\text{pNO}_3^-]_{\text{prec}}/[\text{total NO}_3^-]_{\text{prec}}) * 100\%$  and  $\% \text{HNO}_3 = ([\text{HNO}_3]_{\text{prec}}/[\text{total NO}_3^-]_{\text{prec}}) * 100\%$ . These equations were used to estimate the wet scavenging contributions of atmospheric  $\text{NH}_4^+$  and gaseous  $\text{NH}_3$ .

#### *Ammonia trend analyses*

Two trend analysis tools, i.e., the Mann-Kendall (M-K) analysis (Gilbert, 1987) and the Ensemble Empirical Mode Decomposition (EEMD, Wu et al., 2009), were used to resolve the time series of atmospheric  $\text{NH}_3$  in mixing ratio at these sites.

## **Results**

#### *Geographical and temporal trends in air concentrations*

Air concentrations ranged from 0.018-5.8  $\mu\text{g}/\text{m}^3$  for  $\text{NH}_4^+$ , 0.009-8.7  $\mu\text{g}/\text{m}^3$  for  $\text{NO}_3^-$ , and 0.014-5.0  $\mu\text{g}/\text{m}^3$  for  $\text{HNO}_3$ . These ions have similar geographical patterns. The highest median concentrations were found at agricultural sites in southeastern Canada, which are closest to industrial and urban areas.  $\text{NH}_4^+$  concentrations have been decreasing at 12/16 sites at a rate of -4 to -58  $\text{ng}/\text{m}^3/\text{a}$  (Figure 1a). This trend corresponds to declines in regional ammonia emissions since 2002. Increasing and decreasing trends in  $\text{NO}_3^-$  were observed from 1991-2001 and 2001-2010, respectively, and coincided with  $\text{NO}_x$  emissions trends in Canada.  $\text{NO}_x$  emissions in Canada increased annually from 1991-1997 and decreased from 1997-2010. In the U.S.,  $\text{NO}_x$  emissions were constant from 1991-1994 and decreased after 1994.

#### *Geographical and temporal trends in wet deposition*

Annual wet deposition of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ranged from 0.1-6.4 and 0.4-26.5 kg/ha, respectively. The highest annual wet deposition rates for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were found in southeastern Canada closest to industrial and urban areas. Lowest annual wet deposition was observed at higher latitude sites and in western/central Canada. Significant trends in the annual wet deposition of  $\text{NH}_4^+$  were observed at only 3/16 Canadian sites, unlike widespread declines in the U.S. (Lehmann et al. 2007). Declining trends in  $\text{NO}_3^-$  wet deposition was observed at 10/16 sites at magnitudes ranging from -0.07 to -1.0 kg/ha/a (Figure 1b). The largest decrease in  $\text{NO}_3^-$  wet deposition was found in southeastern Canada.

#### *Scavenging ratios (W)*

Monthly W ranged from 135-4272 for  $\text{pNO}_3^-$  and 7-16658 for  $\text{HNO}_3$  (mass basis). The average scavenging ratio of  $\text{HNO}_3$  was greater than  $\text{pNO}_3^-$  suggesting more efficient wet scavenging of  $\text{HNO}_3$ . Most  $W_{\text{pNO}_3^-}$  in literature are determined from total nitrate in precipitation and  $\text{pNO}_3^-$  in air, which overestimates  $W_{\text{pNO}_3^-}$ . Scavenging ratios of  $\text{pNO}_3^-$  based on total nitrate in precipitation are a factor of 1.4-18 higher depending on the site (average: factor of 6). Monthly  $W_{\text{pNH}_4^+}$  ranged from 63-4356. When wet  $\text{NH}_3$  scavenging is excluded, scavenging ratios of  $\text{NH}_4^+$  can be overestimated by 4-48% (average: 22%).

#### Relative contributions of particulates and gases to nitrate and ammonium wet deposition

Average wet scavenging contributions to nitrate wet deposition were  $28 \pm 23\%$  for  $\text{pNO}_3^-$  and  $72 \pm 23\%$  for  $\text{HNO}_3$ .  $\%\text{HNO}_3$  dominated  $\%\text{pNO}_3^-$  at most of the sites; however the wet scavenging of  $\text{pNO}_3^-$  was higher at the sites closest to industrial and urban areas and at coastal sites (Figure 2a). Average relative contributions of  $\text{pNH}_4^+$  and  $\text{NH}_3$  to total ammonium wet deposition were  $70 \pm 19\%$  and  $30 \pm 19\%$ , respectively, with no distinct geographical patterns (Figure 2b). Particulate contributions to nitrate and ammonium wet scavenging were greater during cold months and lower during summer. This is consistent with the greater particle scavenging efficiency of snow compared to rain for an equivalent amount of precipitation (Zhang et al. 2015). Wet scavenging of  $\text{HNO}_3$  can be a factor of 4 higher than that of  $\text{pNO}_3^-$  during warm months and also significant during cold months because of a large Henry's law constant, high absorption and retention of  $\text{HNO}_3$  on ice crystals, and greater below-cloud snow scavenging of  $\text{HNO}_3$  compared to rain (Chang 1984). Particle wet scavenging exceeded gas scavenging contributions to ammonium wet deposition in most months by a factor of 2.6.

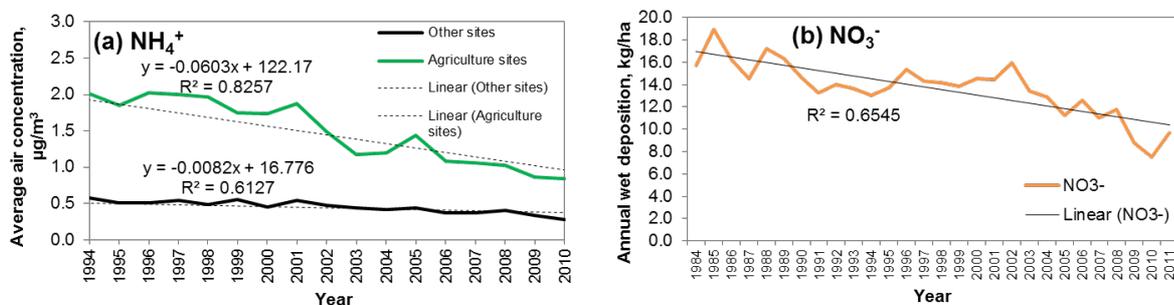


Figure 1. (a) Widespread decline in atmospheric  $\text{NH}_4^+$  and (b) widespread decline in annual  $\text{NO}_3^-$  wet deposition in Canada.

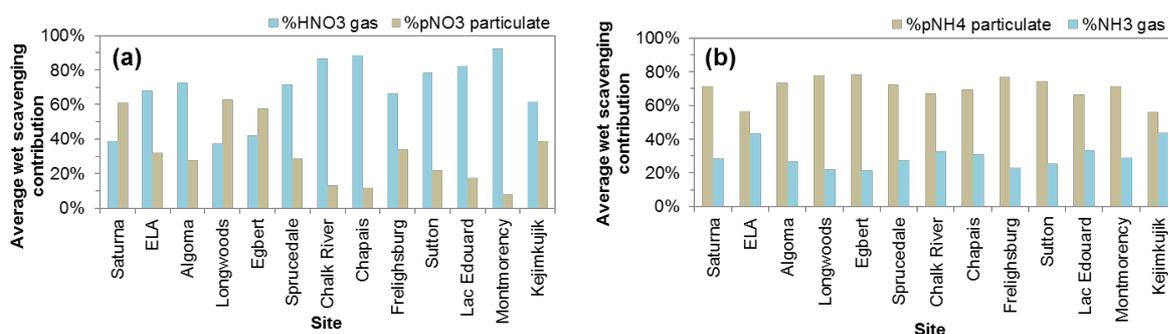
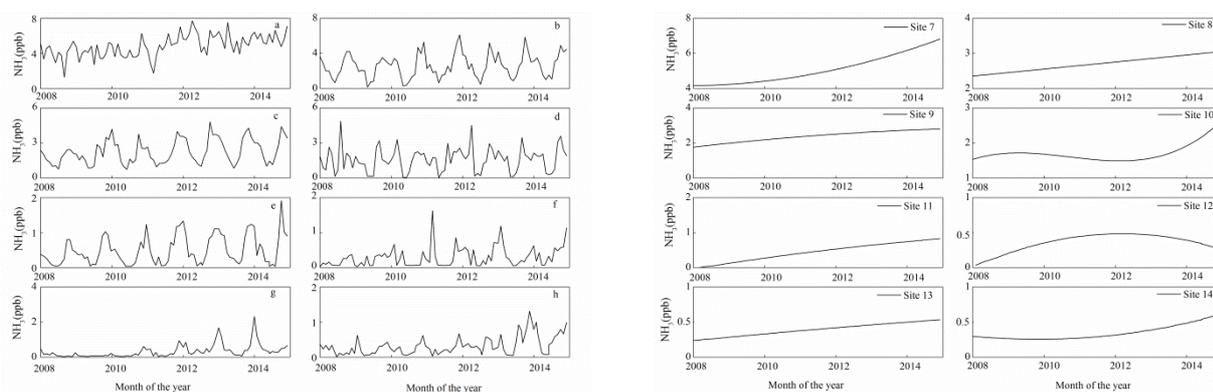


Figure 2. Average wet scavenging contributions of (a)  $\text{HNO}_3$  and  $\text{pNO}_3^-$  to nitrate wet deposition and (b)  $\text{pNH}_4^+$  and  $\text{NH}_3$  to ammonium wet deposition at CAPMoN sites.

#### Ammonia trend

Only the EEMD-extracted long-term trend at the eight U.S. sites are shown here as an example (Figure 3). The long-term trend showed an increase in atmospheric  $\text{NH}_3$  from 4.2 ppb in August 2008 to 6.8 ppb in July 2015 at Site 7, from 2.4 ppb in August of 2008 to 3.0 ppb in July of 2015 at Site 8, from 1.8 ppb in August of 2008 to 2.8 ppb in July of 2015 at Site 9, a complex varying pattern during the period from August 2008 to July 2015 at Site 10, and an increasing trend (by 0.3-0.5 ppb, or 100-200% in percentages) at Sites 11-14. The percentage increases (100-200%) in  $\text{NH}_3$  mixing ratio from 2008 to 2015 at the remote sites were substantially larger than those at the rural/agriculture sites (20-50%).



**Figure 3. Monthly average NH<sub>3</sub> (left) and long-term trend extracted using EEMD (right) at the eight U.S. sites.**

## Conclusion

Widespread declines in atmospheric NH<sub>4</sub><sup>+</sup> (1994-2010) and annual wet deposition of NO<sub>3</sub><sup>-</sup> (1984-2011) were observed in Canada. Atmospheric NO<sub>3</sub><sup>-</sup> increased from 1991-2001 and then decreased from 2001-2010, consistent with NO<sub>x</sub> emissions trends in Canada and in the U.S. Wet scavenging of HNO<sub>3</sub> dominated particulate NO<sub>3</sub><sup>-</sup> contributions to nitrate wet deposition at most locations. Ammonium wet deposition was dominated by particulate NH<sub>4</sub><sup>+</sup> wet scavenging. Higher particulate wet scavenging during cold months provides further evidence of the efficient scavenging of particles by snow. Knowledge of the relative scavenging contributions of gases and particles may improve the wet deposition modeling of nitrate and ammonium.

Moderate exponential correlations between atmospheric NH<sub>3</sub> and ambient T were found at nine sites, implying that local biogenic emissions and/or NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> partitioning were likely dominant factors causing the long-term trends in atmospheric NH<sub>3</sub> at these sites. At the four Canadian sites, no decreasing trends in atmospheric NH<sub>3</sub> were found despite significant decreases in anthropogenic NH<sub>3</sub> emissions from main sectors in the last decade. The decreased NH<sub>3</sub> anthropogenic emission was compensated or overwhelmed by the increased biogenic emission and/or changes in NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> partitioning. This was supported by pNH<sub>4</sub><sup>+</sup> data which exhibited a decreasing trend, likely caused by a combination of reduced SO<sub>2</sub> and NO<sub>x</sub> emission and increased temperature. The M-K analysis showed an increasing trend in atmospheric NH<sub>3</sub> at seven out of the eight U.S. sites, which was also supported by the EEMD-extracted results. NH<sub>3</sub> increased by 20-50% from 2008 to 2015 at the three rural/agriculture sites and by 100%-200% at the four remote sites.

## References

- Chang TY (1984). Rain and snow scavenging of HNO<sub>3</sub> vapor in the atmosphere. *Atmospheric Environment* 18(1), 191-197.
- Clair TA, Ehrman JM, Ouellet AJ, Brun G, Lockerbie D and Ro C-U (2002). Changes in freshwater acidification trends in Canada's Atlantic provinces: 1983-1997. *Water Air and Soil Pollution* 135(1-4), 335-354.
- Driscoll CT, Lawrence GB, Bulger AJ, Butler TJ, Cronan CS, Eagar C, Lambert K, Likens GE, Stoddard JL and Weathers KC (2001). Acidic Deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and Management Strategies. *Bioscience* 51(3), 180-198.
- Gilbert RO (1987). *Statistical Methods for Environmental Pollution Monitoring*. Van Nostrand Reinhold Company Inc., New York.
- Lehmann CM, Bowersox VC, Larson RS and Larson SM (2007). Monitoring long-term trends in sulfate and ammonium in US precipitation: Results from the National Atmospheric Deposition Program/National Trends Network. *Water Air and Soil Pollution* 7, 59-66.
- Wu, Z. and Huang, N. E. (2009). Ensemble empirical mode decomposition: a noise-assisted data analysis method. *Advances in adaptive data analysis* 1, 1-41.
- Zhang L, Cheng I, Muir D and Charland J-P (2015). Scavenging ratios of polycyclic aromatic compounds in rain and snow at the Athabasca oil sands region. *Atmospheric Chemistry and Physics* 15, 1421-1434.