Trends of monitored nitrogen species at monitoring sites in North America

Leiming Zhang¹, Irene Cheng¹, Xiaohong Yao²

¹ Air Quality Research Division, Environment and Climate Change Canada, Toronto
² Ocean University of China, Qingdao, China
Contents


Goals

First study:
- Analyze long-term geographical and temporal trends of \( \text{NO}_3^- \) and \( \text{NH}_4^+ \) in atmosphere and wet deposition in Canada
- Determine scavenging ratios of \( \text{NO}_3^- \) and \( \text{HNO}_3 \)
- Estimate the relative contributions of particulate and gaseous nitrogen species to total nitrate and ammonium wet deposition.

Second Study
- Explore long-term trends of \( \text{NH}_3 \) and related causes at monitoring sites in Canada and U.S.
- Assess the uncertainties between different trend analysis tools
Methodology

First study:
- Daily air and wet deposition samples for major inorganic ions and trace gases. Valid air concentrations from 1983-2010 at 16 sites and precipitation measurements from 1984-2011 at 30 sites
- Temporal trends analysis using regression and the Mann-Kendall analysis (Gilbert, 1987)
- Monthly scavenging ratios - a pollutant’s concentration in precipitation to that in air
- Relative contributions of gaseous and particulate species to nitrate and ammonium wet deposition using the scavenging ratio approach:
  \[
  [\text{pNO}_3^-]_{\text{prec}} = W_{\text{fPM}} [\text{pNO}_3^-]_{\text{air}} P_f + W_{\text{cPM}} [\text{pNO}_3^-]_{\text{air}} (1-P_f),
  \]
  \[
  [\text{HNO}_3^-]_{\text{prec}} = [\text{total NO}_3^-]_{\text{prec}} - [\text{pNO}_3^-]_{\text{prec}}
  \]

Second study:
- Ammonia trend analysis using two trend analysis tools: Mann-Kendall analysis (Gilbert, 1987) and the Ensemble Empirical Mode Decomposition (Wu et al., 2009)
Map of 30 CAPMoN sites

Quebec and eastern Canada (12 sites)

western/central Canada (10 sites)

southern Ontario (8 sites)
Results

Widespread decline in atmospheric NH$_4^+$ in Canada, no significant trend in NH$_4^+$ wet deposition
Results

- Widespread decline in annual $\text{NO}_3^-\text{wet deposition, but different trends in air concentration before and after 2001}$

- 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
Results

- Average scavenging ratio of HNO$_3$ was greater than pNO$_3$-
- Most W$_{pNO3}$ in literature are determined from total nitrate in precipitation and pNO$_3$- in air, which overestimates W$_{pNO3}$ (by a factor of 6 on average)
- When wet NH$_3$ scavenging is excluded, scavenging ratios of NH$_4^+$ can be overestimated by 4-48% (average: 22%).
Results

- Average contribution to nitrate wet deposition: $28 \pm 23\%$ from pNO$_3^-$ and $72 \pm 23\%$ from HNO$_3$
- Wet scavenging of pNO$_3^-$ was higher at the sites closest to industrial and urban areas and at coastal sites
- Average contribution to ammonium wet deposition: $70 \pm 19\%$ from pNH$_4^+$ and $30 \pm 19\%$ from NH$_3$
- Particulate contributions were greater during cold months and lower during summer.
Map of sites with NH₃ data

Six Canadian sites and eight U.S. sites (> 7-year data)
Results

Monthly average NH$_3$ and long-term trend extracted using Ensemble Empirical Mode Decomposition at the eight U.S. sites.
Results

Exponential correlations between atmospheric NH$_3$ and T at six Canadian sites
Results (second study)

- Moderate exponential correlations between atmospheric NH$_3$ and ambient T were found at nine sites - local biogenic emissions and/or NH$_3$/NH$_4^+$ partitioning were likely dominant factors at these sites.
- At the four Canadian sites, no decreasing trends in atmospheric NH$_3$ were found despite significant decreases in anthropogenic NH$_3$ emissions from main sectors in the last decade. The decreased NH$_3$ anthropogenic emission was compensated or overwhelmed by the increased biogenic emission and/or changes in NH$_3$/NH$_4^+$ partitioning. This was supported by pNH$_4^+$ data which exhibited a decreasing trend, likely caused by a combination of reduced SO$_2$ and NO$_x$ emission and increased temperature.
- The M-K analysis showed an increasing trend in atmospheric NH$_3$ at seven out of the eight U.S. sites, which was also supported by the EEMD-extracted results.
- NH$_3$ increased by 20-50% from 2008 to 2015 at the three rural/agriculture sites and by 100%-200% at the four remote sites.