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Reactive Nitrogen issue

- Globally reactive nitrogen (Nr) production has drastically increased.
- Awareness of environmental impacts.
- National and international negotiations and agreements to control emissions.

Timeline of global Nr creation by human activity

Galloway et al. (2003)
Air Quality Agreements/Programs

- Canada–United States Air Quality Agreement (AQA)
  - Control transboundary air pollution between the two countries.
- Environment Canada
  - Clean Air Regulatory Agenda (CARA)
- United States Environmental Protection Agency (EPA)
  - Acid Rain Program
  - NO\textsubscript{x} Budget Trading Program
Emissions in the eastern United States (EUS) contribute to wet deposition in eastern Canada (EC), implying that future emission reductions in the EUS will reduce wet deposition in EC.
Emission reductions

- NO$_x$ emission reductions observed from the Acid Rain Program and NO$_x$ Budget Trading Program (Monks et al., 2009, USEPA Clean Air Markets, Emission and Compliance Data).

http://www.epa.gov/airmarkt/progress/ARP09_1.html#noxcompliance
Study objective

Evaluate the long-term trends in atmospheric chemistry of Nr species at Canadian Air and Precipitation Monitoring Network (CAPMoN) stations across Canada from 1988–2007 in response to changes in emissions primarily driven by emission reduction programs.
Precipitation: Ammonium (NH$_4^+$), Nitrate (NO$_3^-$)
Air: particulate Ammonium (pNH$_4^+$), particulate Nitrate (pNO$_3^-$), gaseous Nitric acid (HNO$_3$)
Study Period: 1988-2007, longest record time in which a large number of CAPMoN stations had data set.
Precipitation chemistry

- Daily precipitation data from CAPMoN database. (www.on.ec.gc.ca/capmon)
- Converted to volume-weighted average monthly and annual concentrations.
Air chemistry

- Monthly and annual air chemistry summaries from the Canadian National Atmospheric Chemistry (NAtChem) database. (www.on.ec.gc.ca/natchem)
Methods – trend detection

• Non-parametric Mann-Kendall test
  • Determine monotonic trends in annual chemistry.
  • Trend significance assumed at 0.05 confidence level.
  • Widely used (Aherne et al., 2010; Fagerli and Aas, 2008; Hole et al., 2009; Lehmann et al., 2005) allows for a comparable metric.
  • Non-parametric Sen’s method to determine trend slope.

• Evaluation of trend synchronicity across all stations
  • Long-term air and precipitation concentrations were visually assessed following z-score transformation (i.e., mean of 0 and standard deviation of 1).
Precipitation: N-NH$_4^+$

2005 – 2007 site average concentration (mg L$^{-1}$)

= 0.1 (mg L$^{-1}$)    = 0.5 (mg L$^{-1}$)
Precipitation: N-NO$_3^-$

2005 – 2007 site average concentration (mg L$^{-1}$)
Air: N-pNH$_4^+$

- $= 0.1 \, (\mu g \, m^{-3})$
- $= 0.5 \, (\mu g \, m^{-3})$
- $= 1.0 \, (\mu g \, m^{-3})$

2005 – 2007 site average concentration (µg m$^{-3}$)
Air: N-pNO$_3^-$

$\bullet = 0.1 \, (\mu g \, m^{-3}) \quad \bullet = 0.5 \, (\mu g \, m^{-3}) \quad \bigcirc = 1.0 \, (\mu g \, m^{-3})$

2005 – 2007 site average concentration (\mu g \, m^{-3})
Air: $\text{N-HNO}_3$

- $0.1 \text{ (µg m}^{-3}\text{)}$
- $0.5 \text{ (µg m}^{-3}\text{)}$
- $1.0 \text{ (µg m}^{-3}\text{)}$

2005 – 2007 site average concentration ($\mu g \text{ m}^{-3}$)
Temporal trend – precipitation

- Annual average concentrations
  Similar pattern across all CAPMoN stations
- NH$_4^+$
  No significant trend, slope of zero
- NO$_3^-$
  Significant decrease at 9 stations
Temporal trend – air

- Annual average concentrations
  - Similar pattern across all CAPMoN stations

- $p\text{NH}_4^+$ and $\text{HNO}_3$
  - Significant decrease at all stations

- $p\text{NO}_3^-$
  - Significant increase at four stations
  - Not monotonic trend, significant decrease observed around 2001
Correlations

Correlation of Nr and S species to emissions of NOx and SO2 (1995-2007) from Acid Rain Program 2009 Progress Reports, US Clean Air Markets

<table>
<thead>
<tr>
<th></th>
<th>Total NOx</th>
<th>Total SO2</th>
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<tbody>
<tr>
<td>Total NOx</td>
<td>1</td>
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<tr>
<td>Total SO2</td>
<td>0.921</td>
<td>1</td>
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<tr>
<td>HNO3</td>
<td>0.850</td>
<td>0.877</td>
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<tr>
<td>pNH4+</td>
<td>0.860</td>
<td>0.853</td>
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<tr>
<td>pNO3−</td>
<td>0.117</td>
<td>0.027</td>
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<td>NH4+</td>
<td>-0.239</td>
<td>-0.273</td>
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<tr>
<td>NO3−</td>
<td>0.813</td>
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<tr>
<td>SO2</td>
<td>0.841</td>
<td>0.934</td>
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<tr>
<td>pSO4²−</td>
<td>0.880</td>
<td>0.849</td>
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<tr>
<td>nssSO4²−</td>
<td>0.838</td>
<td>0.917</td>
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</table>

Correlation of Nr and S species average annual concentrations from all Canadian Air and Precipitation Monitoring Network stations from 1988 – 2007.

<table>
<thead>
<tr>
<th></th>
<th>HNO3</th>
<th>pNH4+</th>
<th>pNO3−</th>
<th>NH4+</th>
<th>NO3−</th>
<th>SO2</th>
<th>pSO4²−</th>
<th>nssSO4²−</th>
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<td>HNO3</td>
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<tr>
<td>pNH4+</td>
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<tr>
<td>NH4+</td>
<td>0.010</td>
<td>0.130</td>
<td>0.166</td>
<td>1</td>
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<tr>
<td>NO3−</td>
<td>0.791</td>
<td>0.738</td>
<td>0.034</td>
<td>0.387</td>
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<tr>
<td>SO2</td>
<td>0.898</td>
<td>0.812</td>
<td>-0.401</td>
<td>0.117</td>
<td>0.779</td>
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<td>pSO4²−</td>
<td>0.848</td>
<td>0.873</td>
<td>-0.200</td>
<td>-0.044</td>
<td>0.589</td>
<td>0.742</td>
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<tr>
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<td>-0.378</td>
<td>0.197</td>
<td>0.825</td>
<td>0.941</td>
<td>0.694</td>
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</tbody>
</table>
Conclusion

NH₄⁺ + NO₃⁻ pNH₄⁺ + pNO₃⁻ HNO₃

Significant increase
Non-significant increase
Non-significant decrease
Significant decrease
No data

NH₄⁺ no significant increase or decrease
NO₃⁻ significant decrease at 10 sites
pNH₄⁺ significant decrease at all sites
pNO₃⁻ significant increase at 4
HNO₃ significant decrease at all sites
Conclusion

• Long-term decreasing trend in NO$_3^-$, pNH$_4^+$ and HNO$_3$ (1988–2007).
• Post 2000, decreasing trend observed for pNO$_3^-$ as well.
• Wet NH$_4^+$ unaffected by emission reductions showing no trend.
• Strong correlation between air emissions (NO$_x$ and SO$_2$) and observed Nr species concentrations (except wet NH$_4^+$).
• Shows value of data from monitoring networks for use in assessing the success of emission reductions.

Acknowledgments

The Canadian Air and Precipitation Monitoring Network (CAPMoN) data were obtained from the National Atmospheric Chemistry (NAtChem) Database and Analysis Facility of Environment Canada (www.msc-smc.ec.gc.ca/natchem). The authors gratefully acknowledge the CAPMoN for their data and the NAtChem Database and Analysis Facility for access to the standardized data files and metadata.
References


