# Long-term trends in atmospheric reactive nitrogen across Canada: 1988–2007

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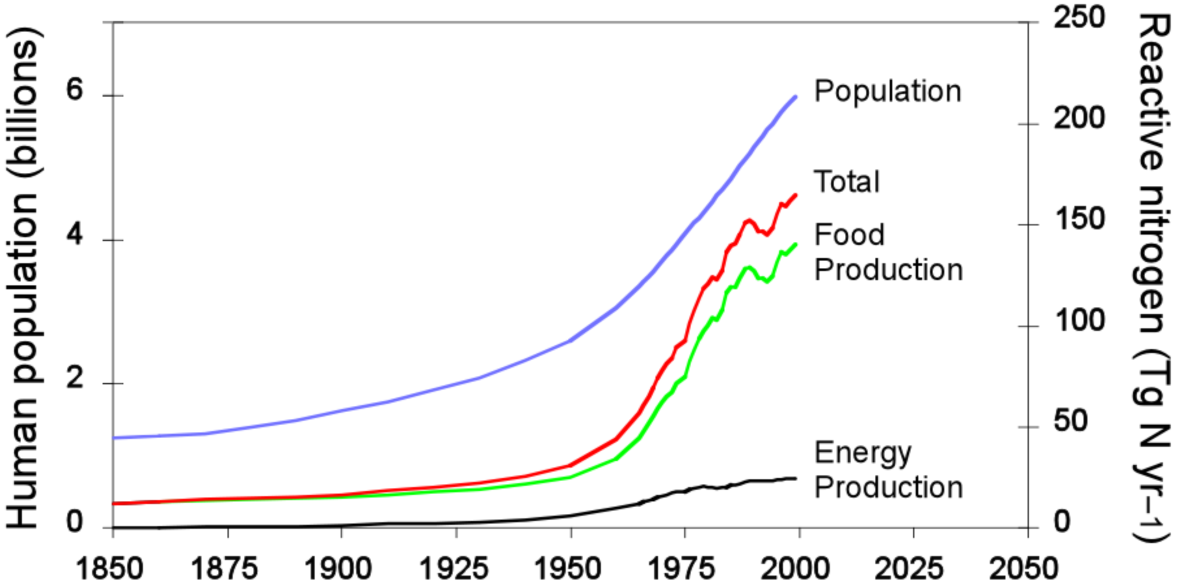
# Reactive Nitrogen issue

- 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)

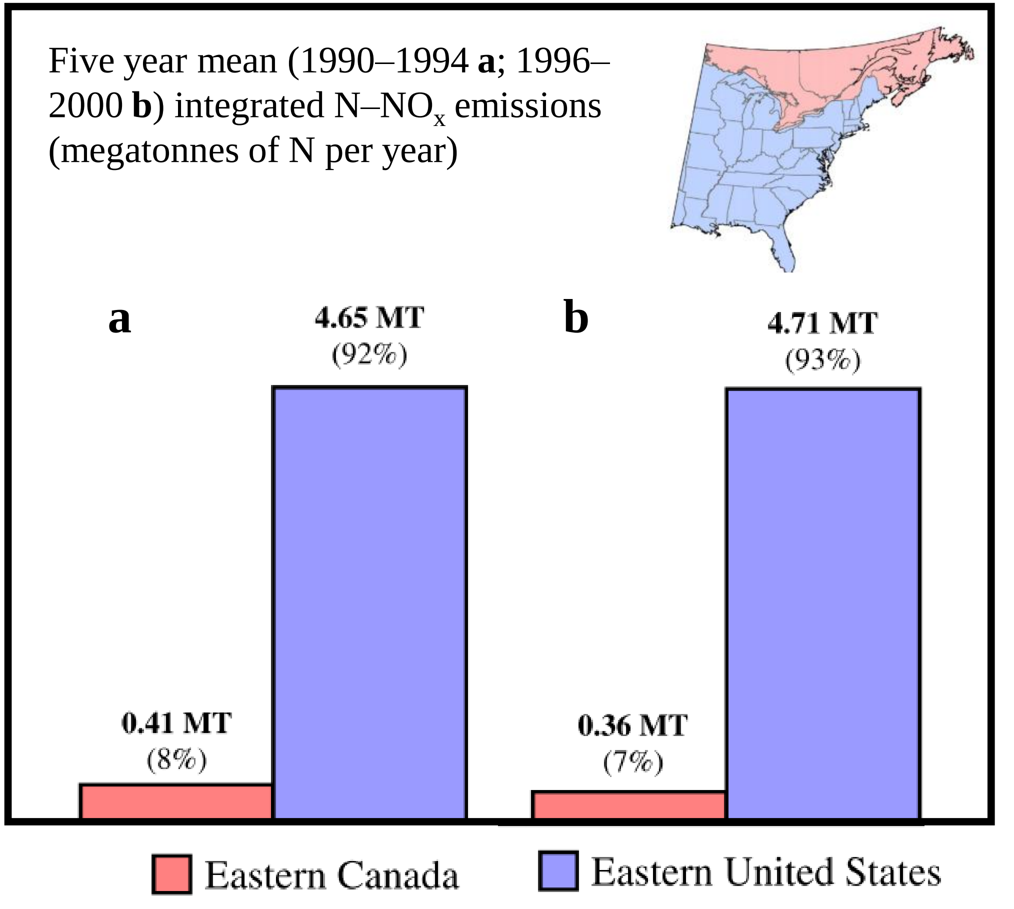
# Air Quality Agreements/Programs

- 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
  - $NO_x$ Budget Trading Program

# Eastern North America (1990s)

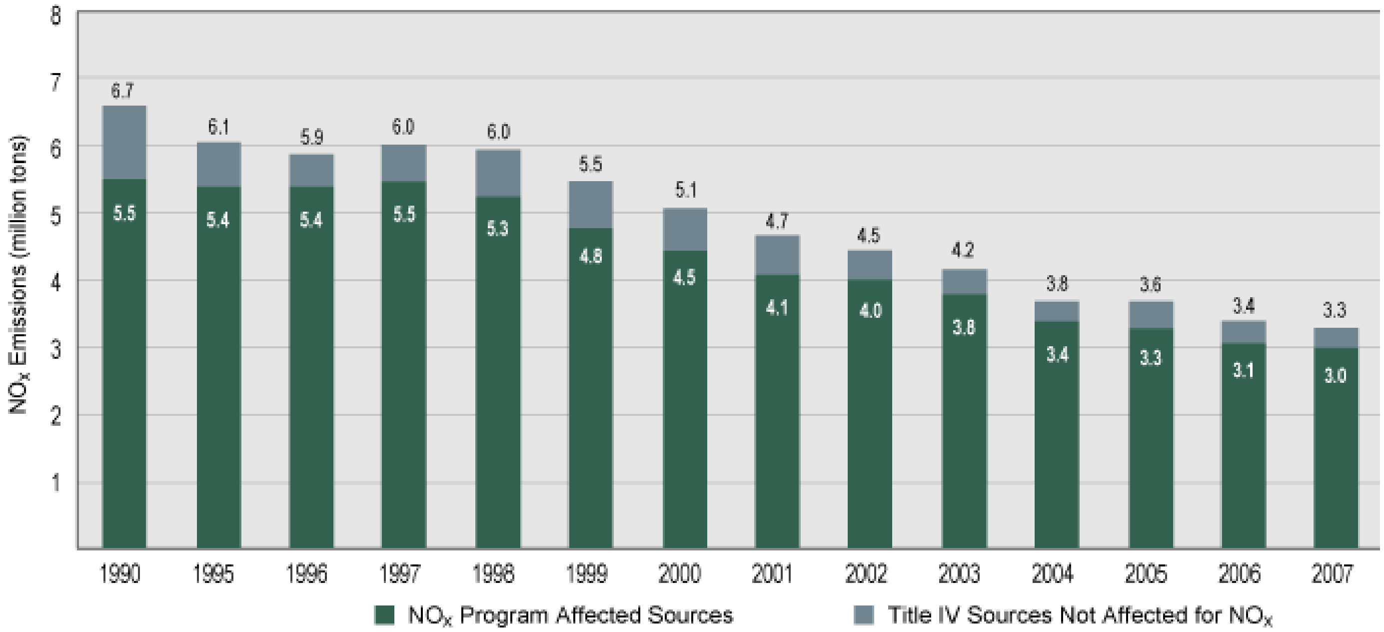
(Vet and Ro, 2008)

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).

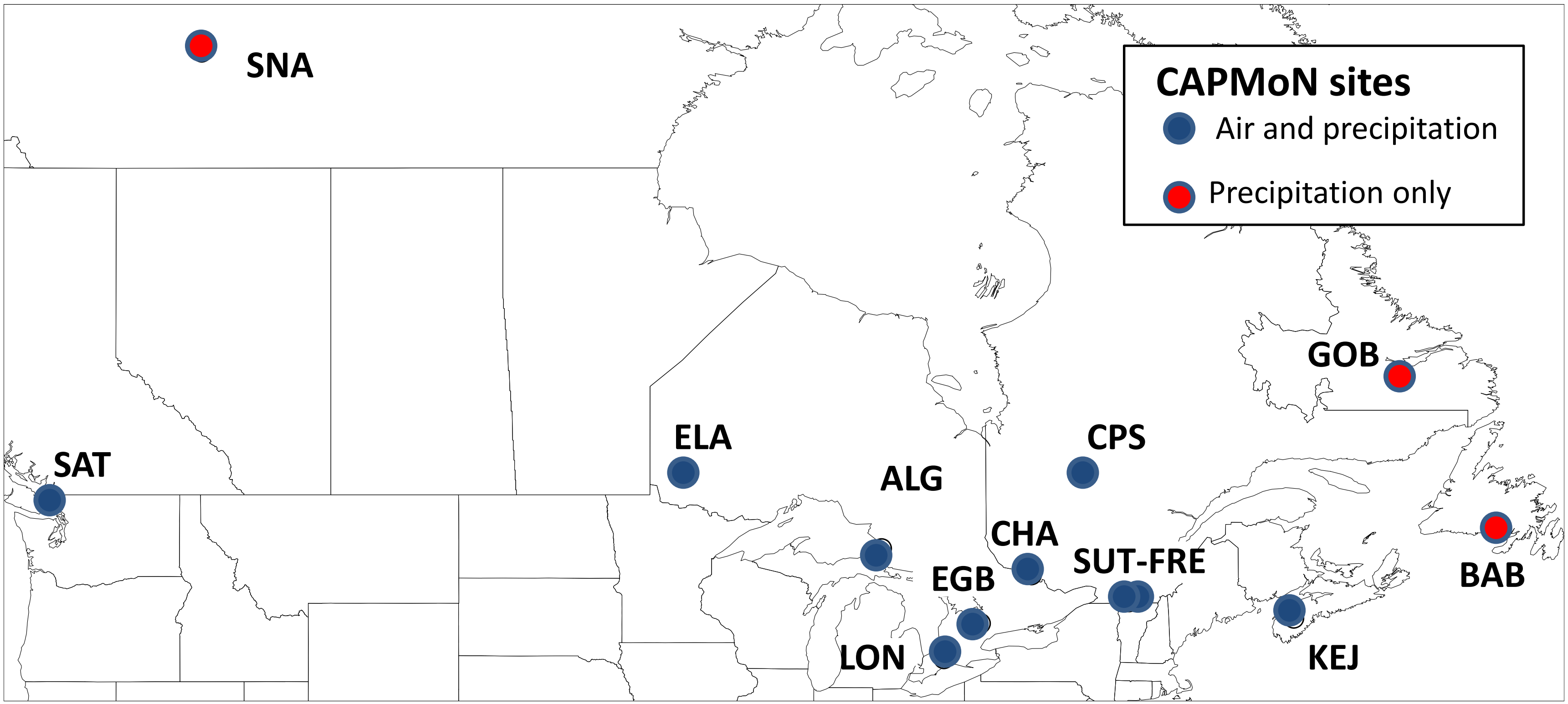



http://www.epa.gov/airmarkt/progress/ARP09_1.html#noxcompliance

# 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.

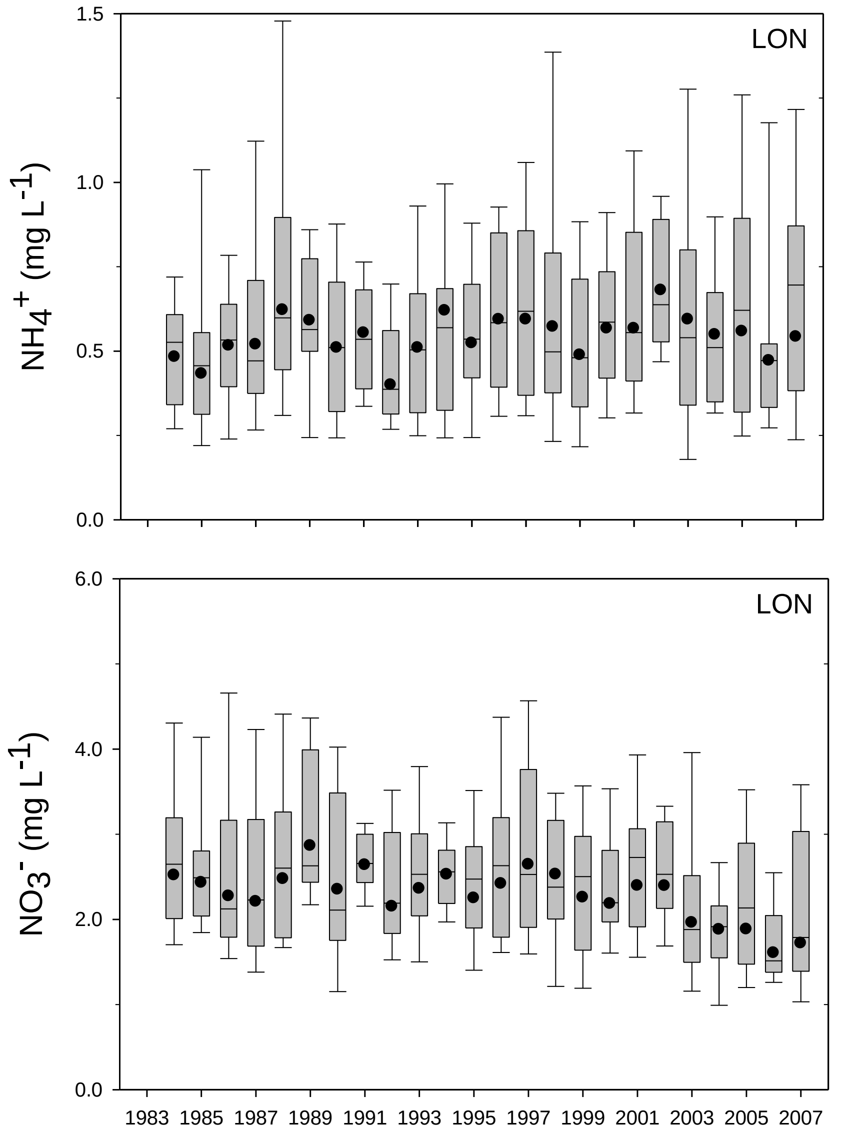
# CAPMoN Sites




**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.

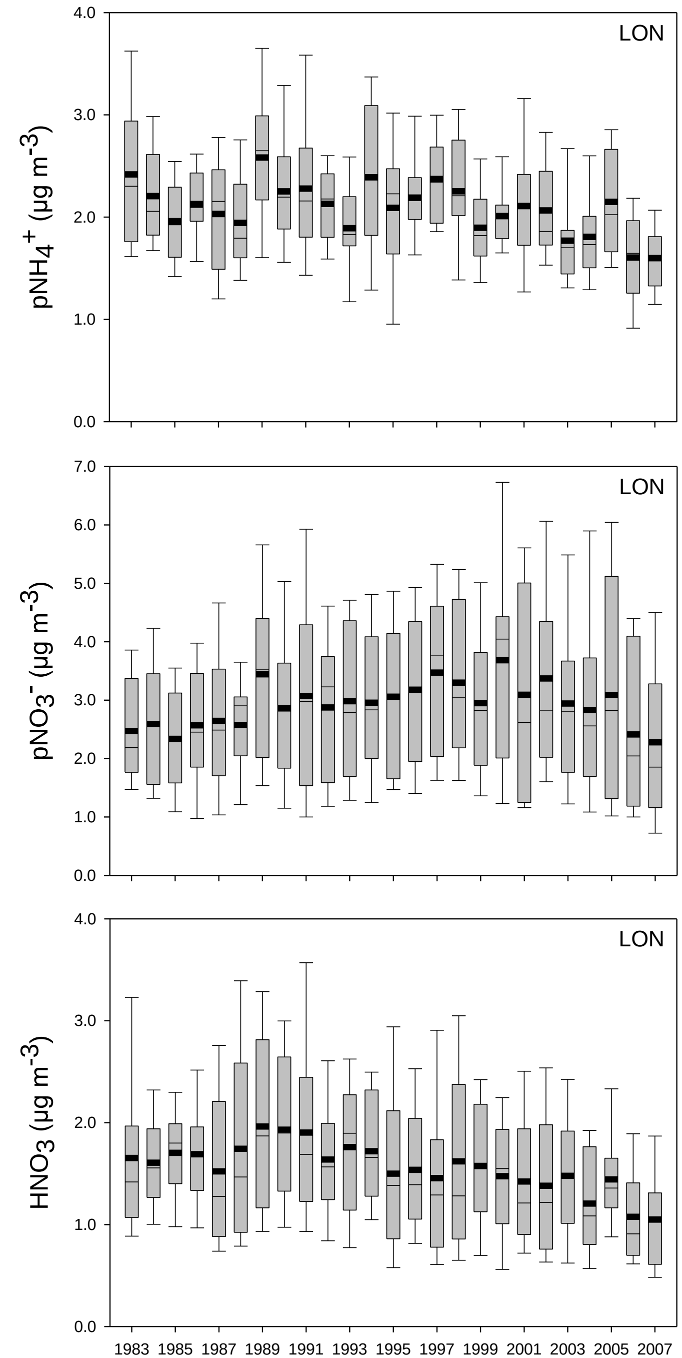
# Precipitation chemistry

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



# Air chemistry

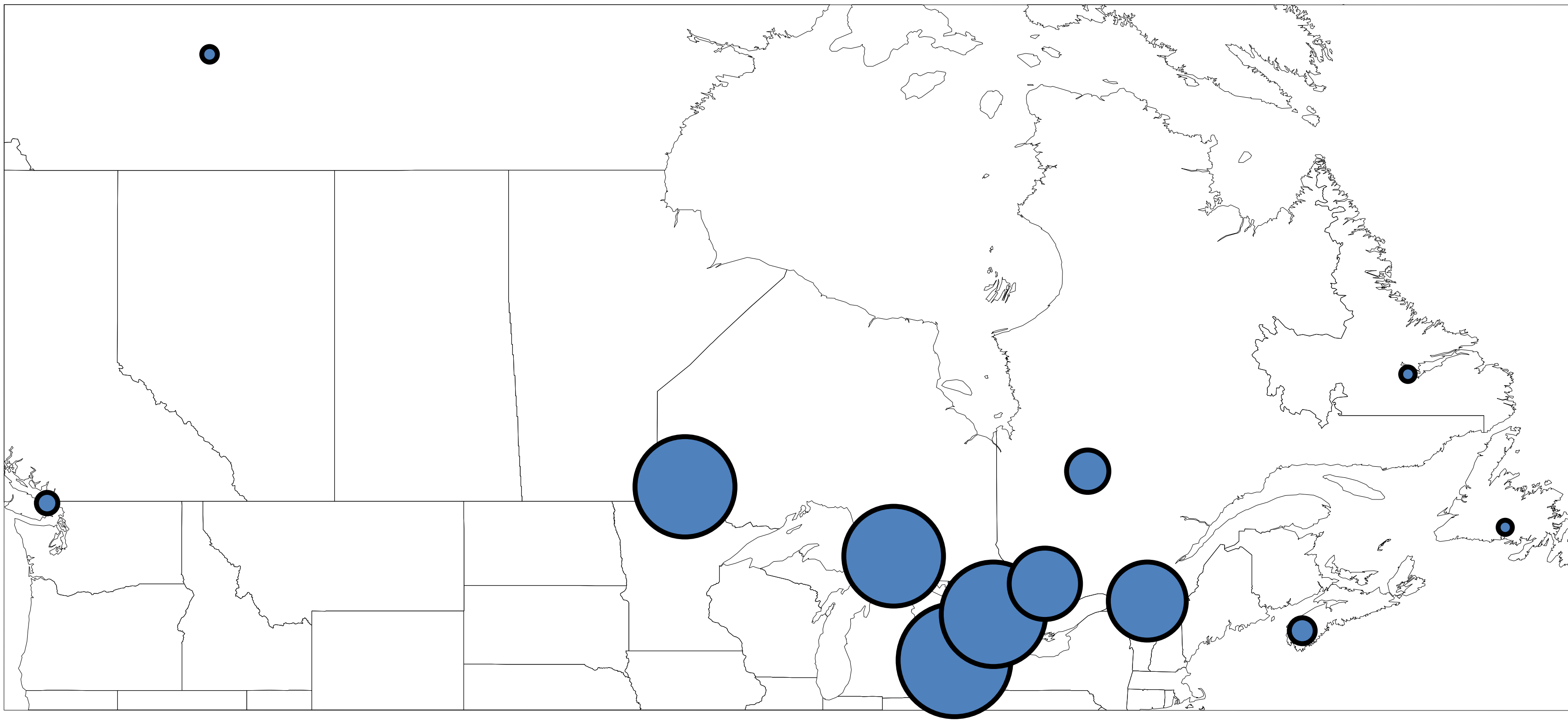
- Monthly and annual air chemistry summaries from the Canadian National Atmospheric Chemistry (NAtChem) database.
(www.on.ec.gc.ca/natchem)



# 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).

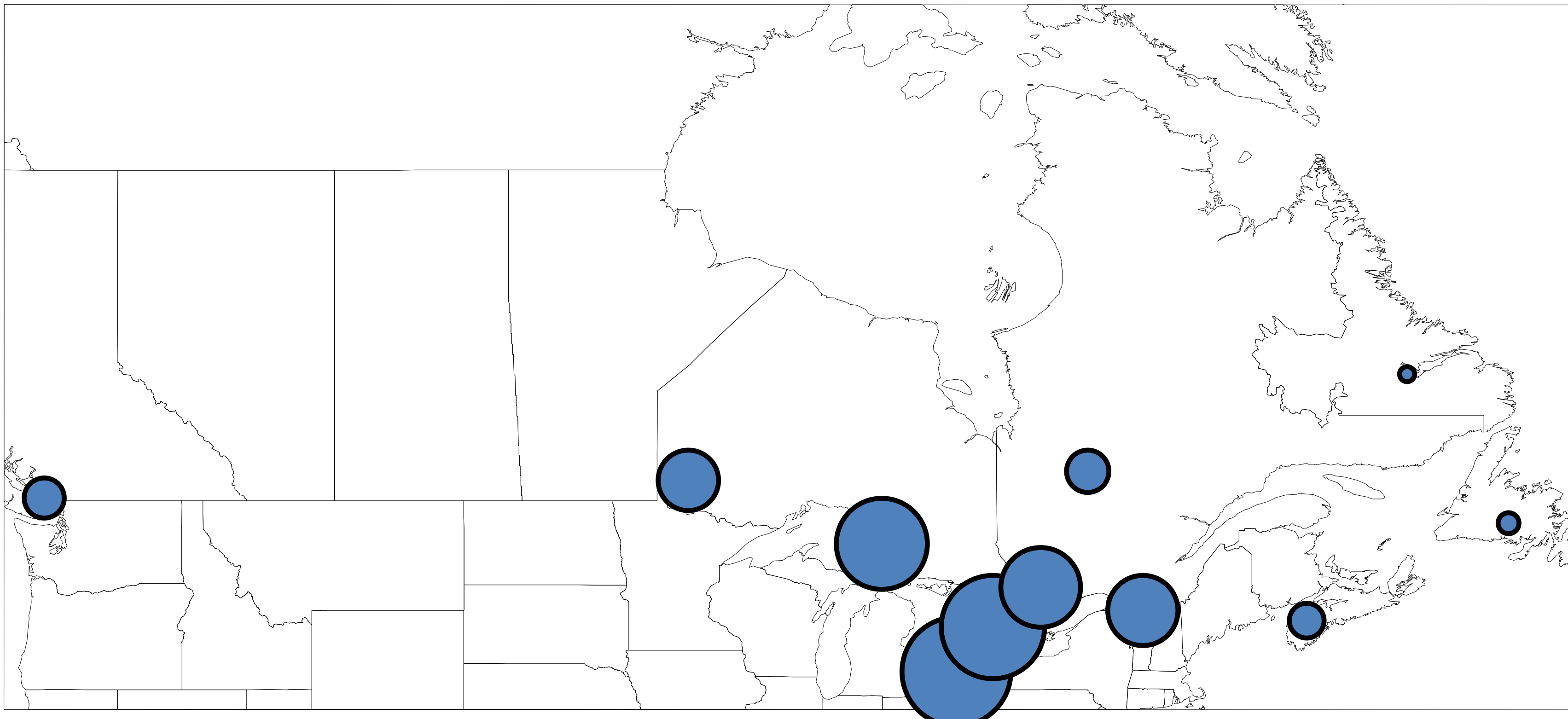
# Precipitation: $N\text{-}NH_4^+$



= 0.1 (mg $L^{-1}$) = 0.5 (mg $L^{-1}$)

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

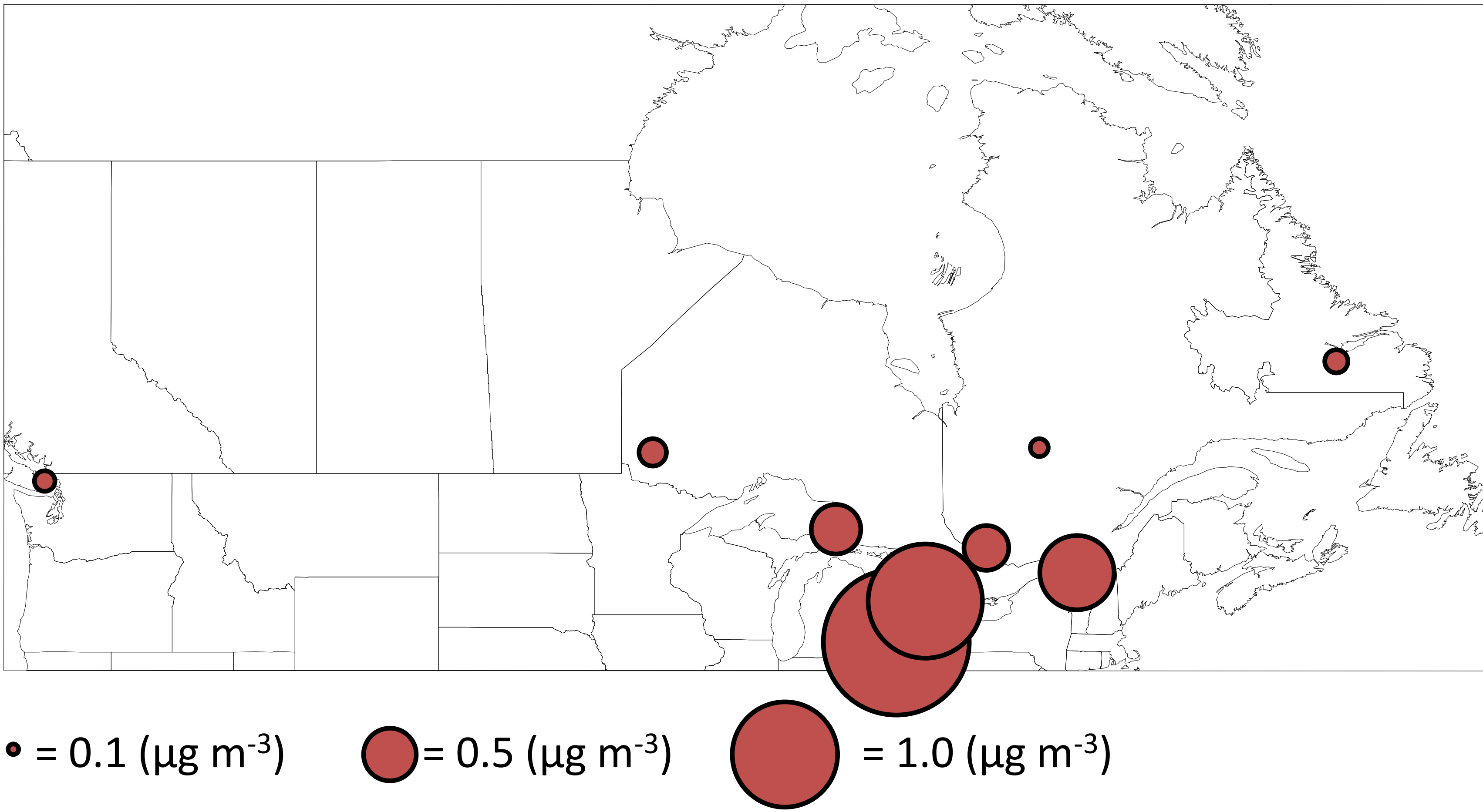
# Precipitation: $N\text{-}NO_3^-$



= 0.1 (mg $L^{-1}$) = 0.5 (mg $L^{-1}$)

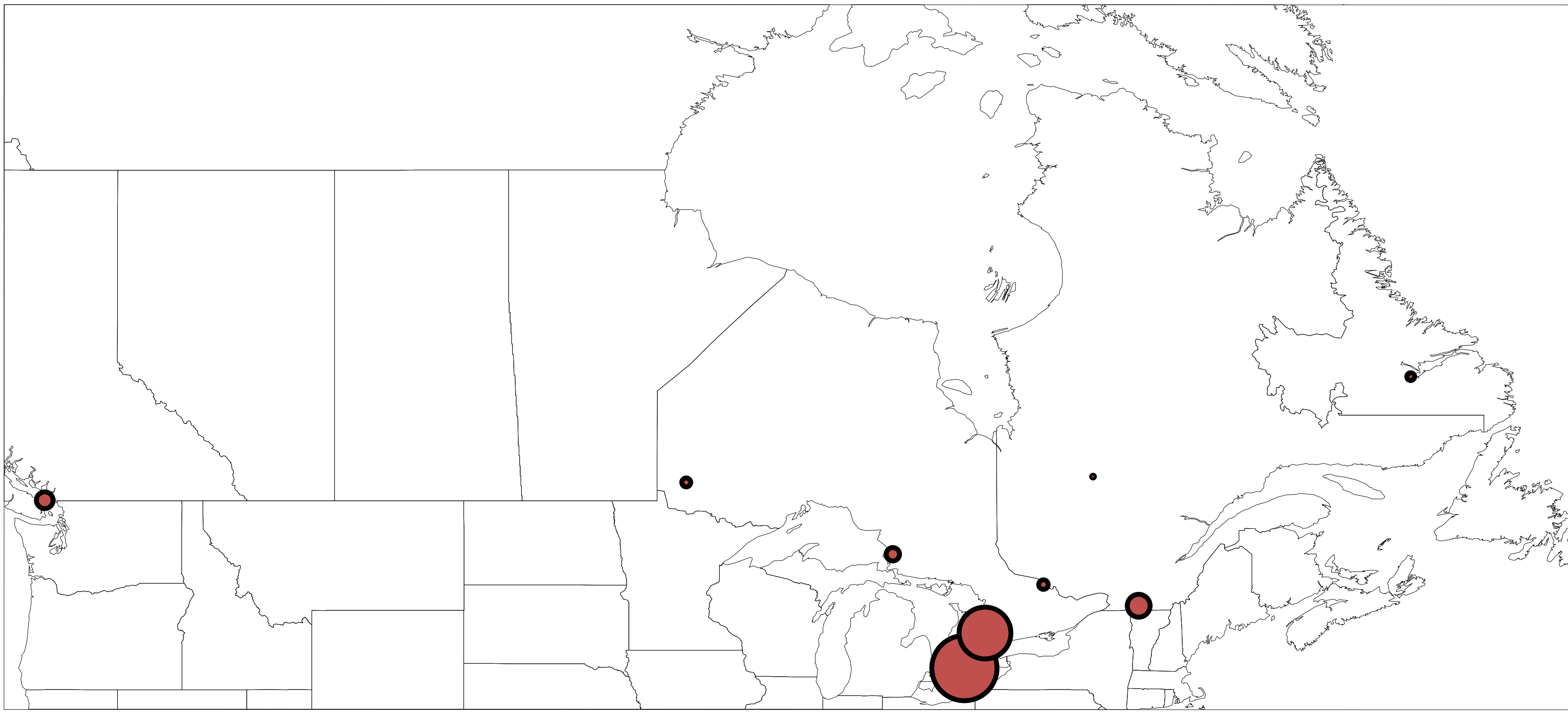
2005 – 2007 site average concentration (mg $L^{-1}$)

# Air: N-p$NH_4^+$




2005 – 2007 site average concentration (µg m$^{-3}$)

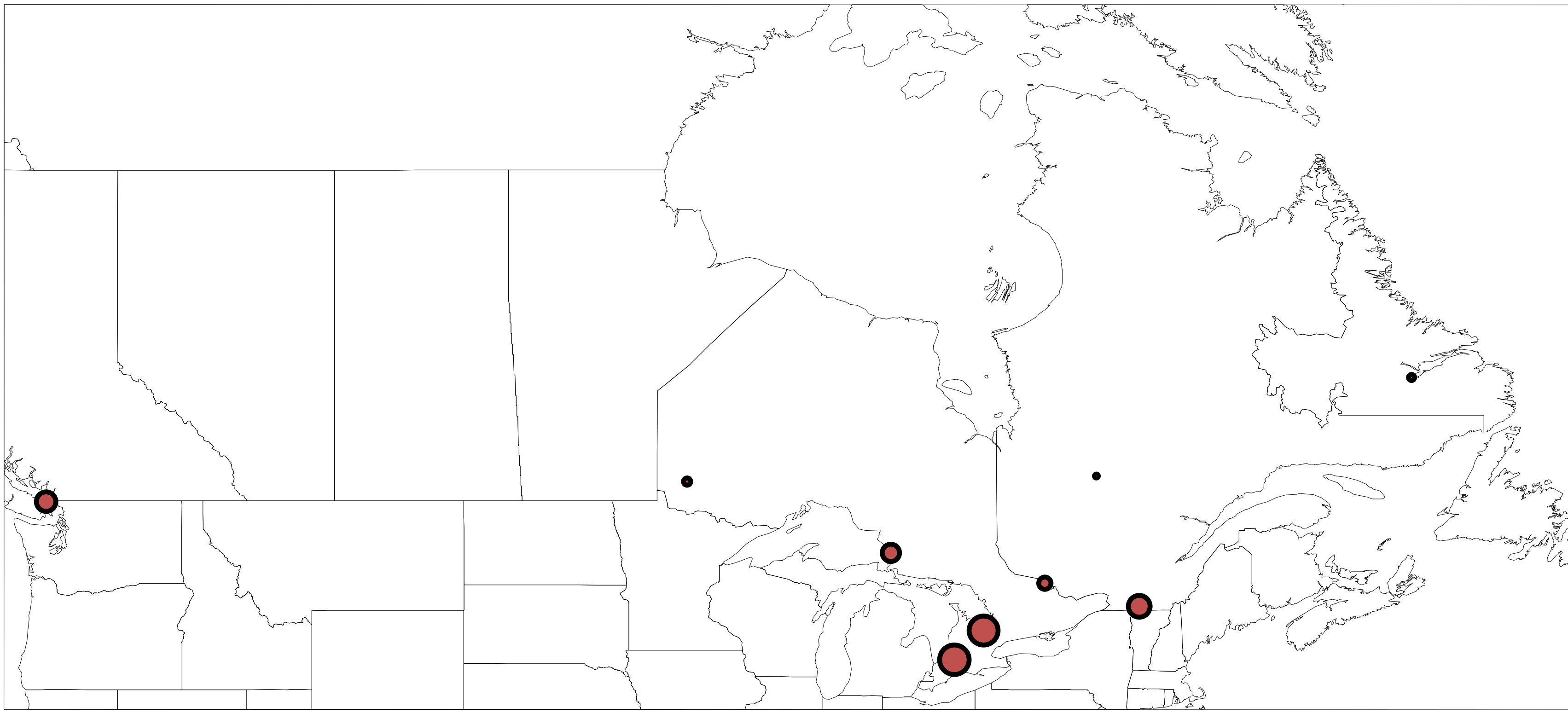
# Air: N-p$NO_3^-$



• = 0.1 (µg m$^{-3}$)  ● = 0.5 (µg m$^{-3}$)  ● = 1.0 (µg m$^{-3}$)

2005 – 2007 site average concentration (µg m$^{-3}$)

# Air: N-$HNO_3$

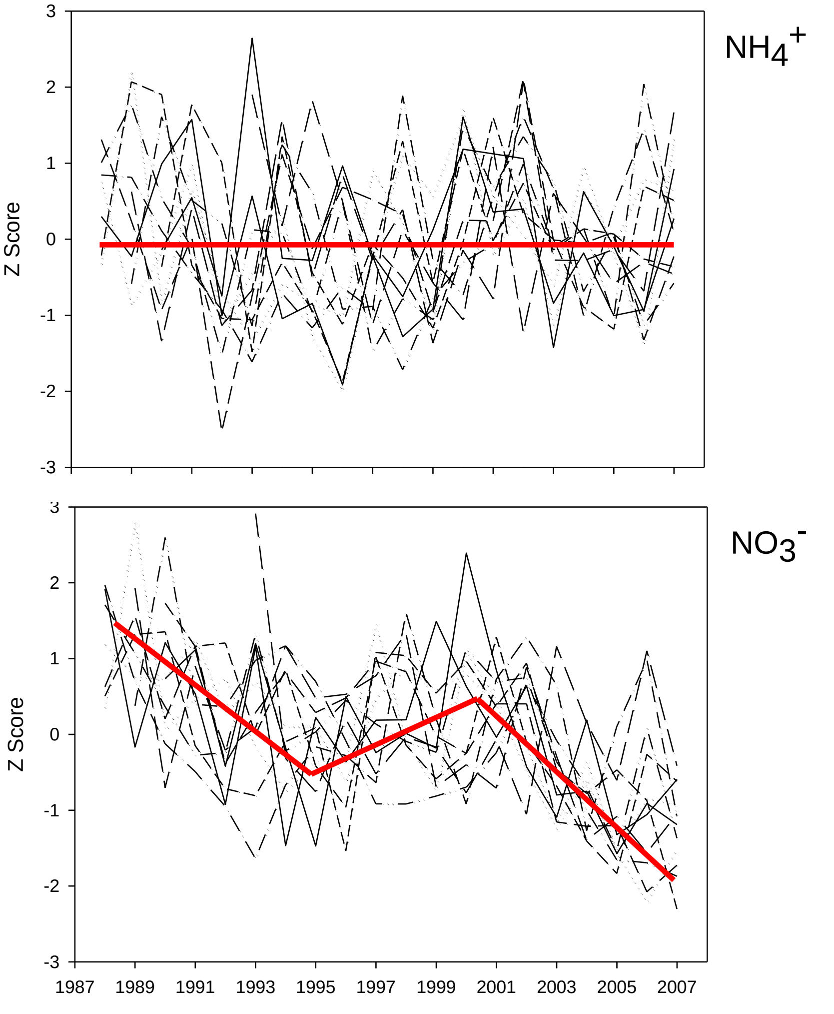


• = 0.1 (µg $m^{-3}$) ● = 0.5 (µg $m^{-3}$) ⬤ = 1.0 (µg $m^{-3}$)

2005 – 2007 site average concentration (µg $m^{-3}$)

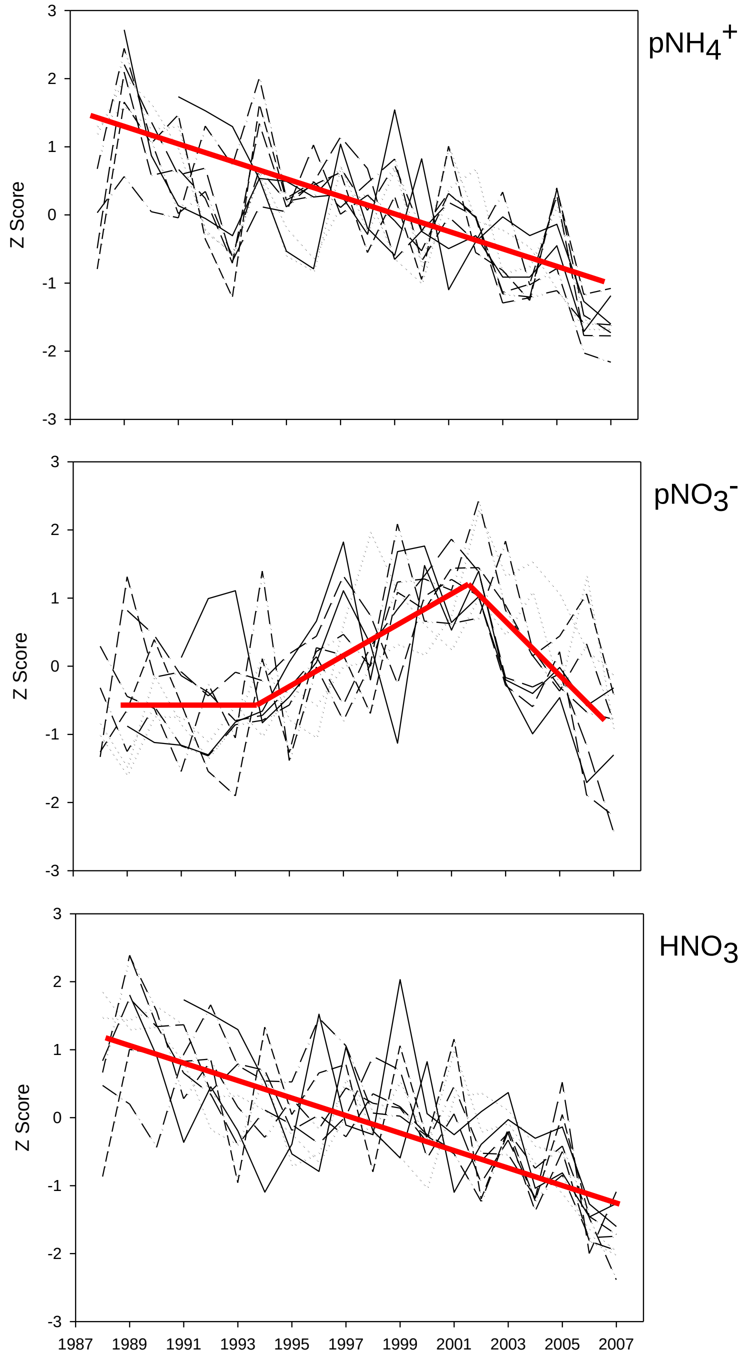
# Temporal trend – precipitation

- Annual average concentrations
  - Similar pattern across all CAPMoN stations
- $NH_4^+$
  - No significant trend, slope of zero
- $NO_3^-$
  - Significant decrease at 9 stations

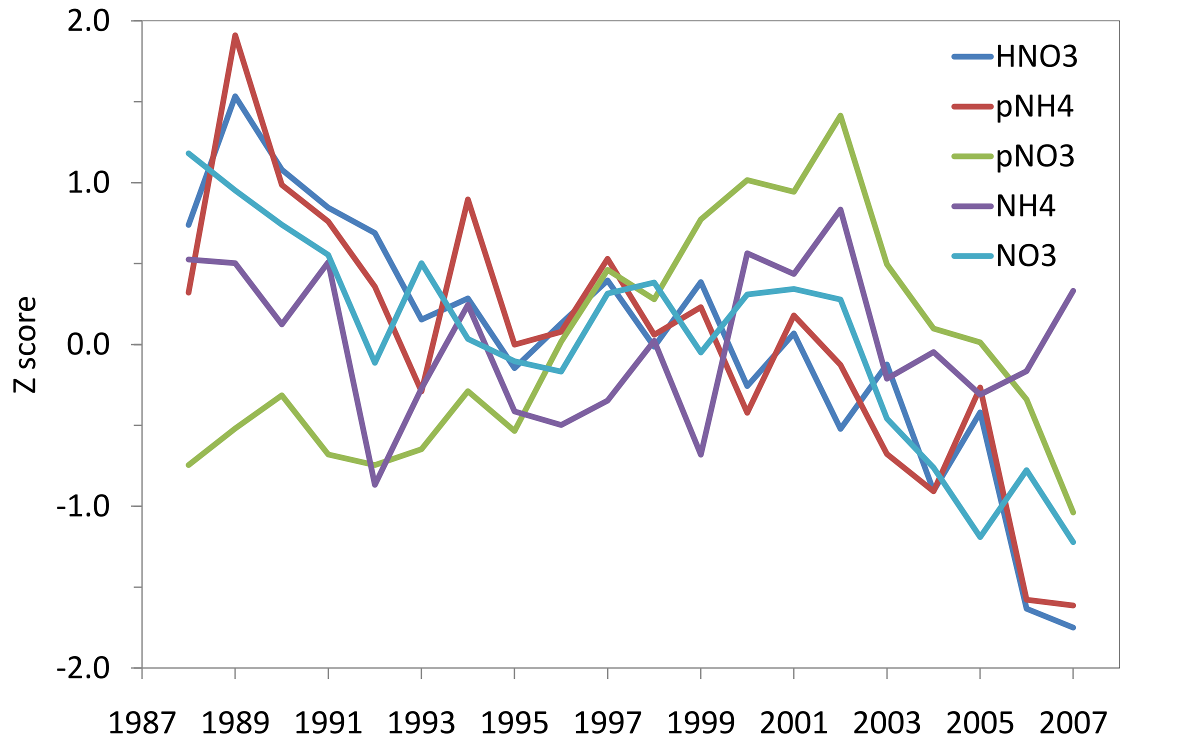


# Temporal trend – air

- Annual average concentrations
  - Similar pattern across all CAPMoN stations
- $pNH_4^+$ and $HNO_3$
  - Significant decrease at all stations
- $pNO_3^-$
  - Significant increase at four stations
  - Not monotonic trend, significant decrease observed around 2001



# Correlations



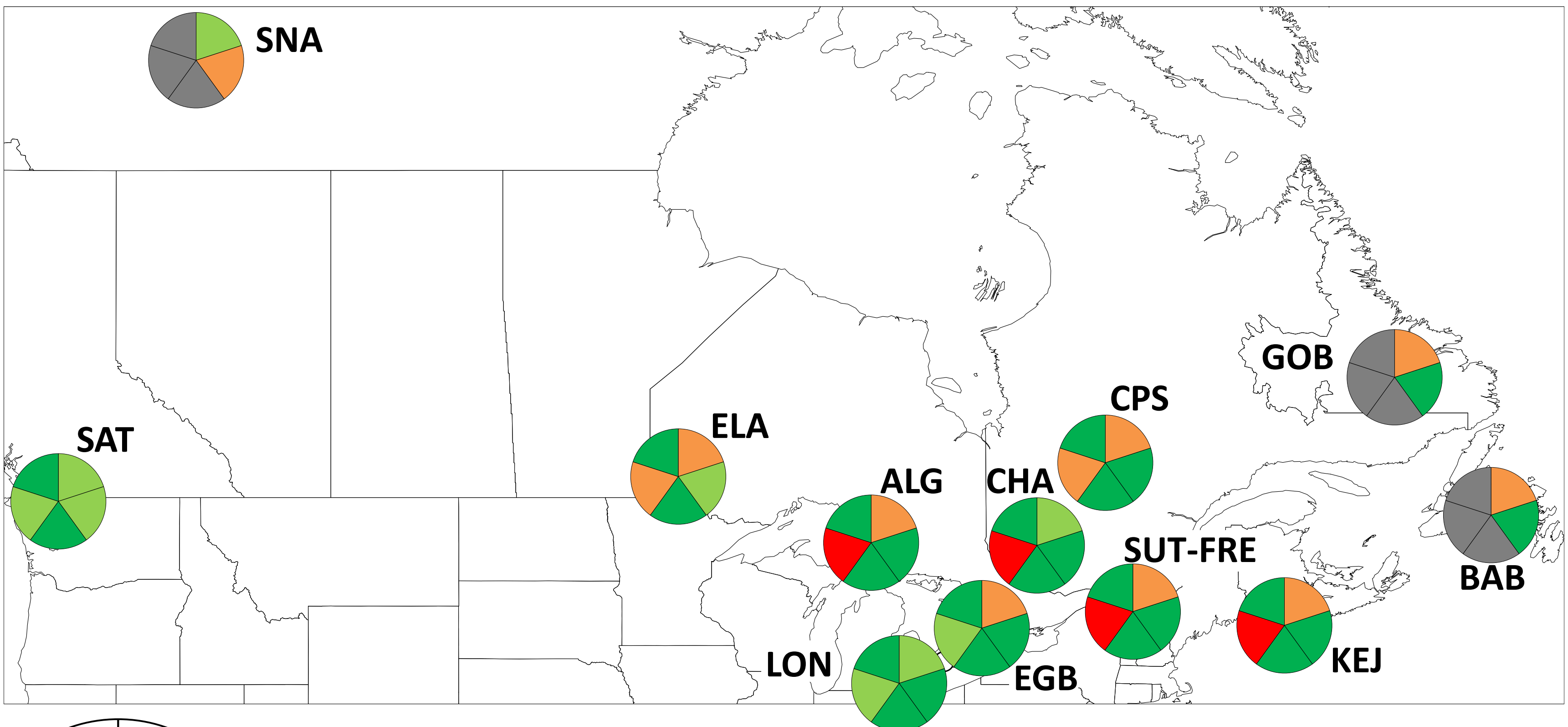

Correlation of Nr and S species to emissions of $NO_x$ and $SO_2$ (1995-2007) from Acid Rain Program 2009 Progress Reports, US Clean Air Markets

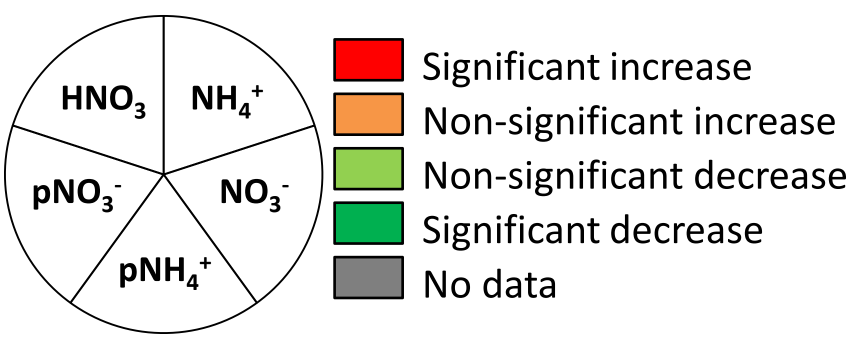
| | Total $NO_x$ | Total $SO_2$ |
|---|---|---|
| Total $NO_x$ | 1 | |
| Total $SO_2$ | 0.921 | 1 |
| $HNO_3$ | 0.850 | 0.877 |
| $pNH_4^+$ | 0.860 | 0.853 |
| $pNO_3^-$ | 0.117 | 0.027 |
| $NH_4^+$ | -0.239 | -0.273 |
| $NO_3^-$ | 0.813 | 0.734 |
| $SO_2$ | 0.841 | 0.934 |
| $pSO_4^{2-}$ | 0.880 | 0.849 |
| $nssSO_4^{2-}$ | 0.838 | 0.917 |

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

| | $HNO_3$ | $pNH_4^+$ | $pNO_3^-$ | $NH_4^+$ | $NO_3^-$ | $SO_2$ | $pSO_4^{2-}$ | $nssSO_4^{2-}$ |
|---|---|---|---|---|---|---|---|---|
| $HNO_3$ | 1 | | | | | | | |
| $pNH_4^+$ | 0.937 | 1 | | | | | | |
| $pNO_3^-$ | -0.104 | -0.055 | 1 | | | | | |
| $NH_4^+$ | 0.010 | 0.130 | 0.166 | 1 | | | | |
| $NO_3^-$ | 0.791 | 0.738 | 0.034 | 0.387 | 1 | | | |
| $SO_2$ | 0.898 | 0.812 | -0.401 | 0.117 | 0.779 | 1 | | |
| $pSO_4^{2-}$ | 0.848 | 0.873 | -0.200 | -0.044 | 0.589 | 0.742 | 1 | |
| $nssSO_4^{2-}$ | 0.852 | 0.777 | -0.378 | 0.197 | 0.825 | 0.941 | 0.694 | 1 |

# Conclusion




| | |
|---|---|
| $NH_4^+$ | no significant increase or decrease |
| $NO_3^-$ | significant decrease at 10 sites |
| $pNH_4^+$ | significant decrease at all sites |
| $pNO_3^-$ | significant increase at 4 |
| $HNO_3$ | 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


Acid Rain Program 2009 Progress Reports, US Clean Air Markets. Last updated on August-25-10, Accessed Oct. 14, 2010. http://www.epa.gov/airmarkt/progress/ARP09_1.html#noxcompliance

Aherne, J., Mongeon, A., Watmough, S.A., 2010. Temporal and spatial trends in precipitation chemistry in the Georgia Basin, British Columbia. Journal of Limnology 69.

Chan, E., Vet, R., 2010. Baseline levels and trends of ground level ozone in Canada and the United States. Atmospheric Chemistry and Physics 10, 8629–8647.

Fagerli H., Aas, W., 2008. Trends of nitrogen in air and precipitation: Model results and observations at EMEP sites in Europe, 1980–2003. Environmental Pollution 154, 448-461.

Galloway, J.N., Cowling, E.B., 2002. Reactive Nitrogen and The World: 200 Years of Change. Ambio 31, 2, 64-71.

Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., Cosby, B.J., 2003. The Nitrogen Cascade. BioScience 53, 341-356.

Hole, L.R., Christensen, J.H., Ruoho-Airola, T., Tørseth, K., Ginzburg, V., Glowacki, P., 2009. Past and future trends in concentrations of sulphur and nitrogen compounds in the Arctic. Atmospheric Environment 43, 928-939.

Lehmann, C.M.B., Bowersox, V.C, Larson, S.M., 2005. Spatial and temporal trends of precipitation chemistry in the United States, 1985-2002. Environmental Pollution 135, 347-361.

Monks, P.S., et al., 2009. Atmospheric composition change – global and regional air quality. Atmospheric Environment 43, 5268-5350.

Vet, R., Ro, C., 2008. Contribution of Canada-United States transboundary transport to wet deposition of sulphur and nitrogen oxides-A mass balance approach. Atmospheric Environment 42, 2518-2529.