The Presence of Reactive Nitrogen in Fine and Coarse Aerosol

Christina McCluskey[1], Katie Beem[2], Jeff Collett[2]

[1]Coastal Carolina University, Conway, South Carolina, [2]Colorado State University, Fort Collins, Colorado

1.Introduction

Nitrogen deposition is a vital aspect of the nitrogen cycle, which is necessary for an ecosystem to function. Perturbation of the nitrogen cycle can lead to a series of problems, including acidification of soils and nitrogen in vegetation (Vitousek et al., 1997). Fossil fuel combustion, use of fertilizers, and other human activities are contributing to an the amount of species (Blett et al., 2004). Better understanding of the causes, impacts, and possible restoration requires more research and investigation. Although inorganic nitrogen deposition is becoming better understood (Wittig et al., 2004; Beem et al., 2009; Mehlmann et al., 1995; Pakkanen et al., 1995), little is known about organic nitrogen deposition. This study measures inorganic and organic nitrogen in samples from the Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) study. The impact of the Station Fire on fine and coarse aerosol was also considered as part of this effort. The Station fire covered over 160,000 acres and started on August 26, 2009 in Burbank, California.

2. Methodology

Rocky Mountain National Park Lab Site Information (right)

Samples taken for this study were obtained at the Core Site marked with a diamond. Temperature was also measured at this location.

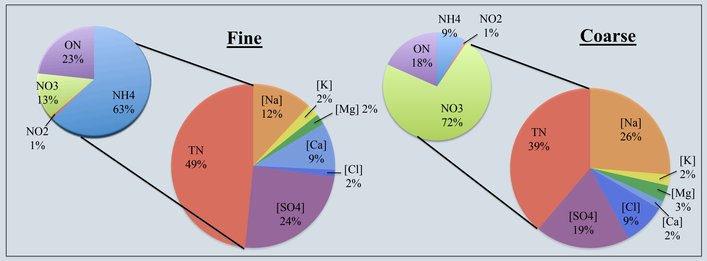
High – Vol Filter Samples

- Samples were taken during the RoMANS spring and summer campaign
- Fine (< 2.5 µm) and coarse (< 10 µm) filter samples were collected using a Thermo Fisher Scientific Hi-vol sampler with a $PM_{2.5}$ and PM_{10} impactor plate. (see left).
-Collection start date: April 6, 2009
-Collection end data: November 13,2009

Analysis

- Extracted using sonication and a hot water bath.
- Samples were filtered.
- Fine and coarse filters were analyzed for inorganic ions (Na^+, NH_4^+, K^+, Mg^{+2}, Ca^{+2}, Cl^-, NO_3^-, and SO_4^{-2}) using ion chromatography (IC).
- Total nitrogen (TN) was determined using a total organic carbon/total nitrogen analyzer.
- Calibration curves were used to quantify concentrations based on instrument responses.
- Organic nitrogen was not directly measured, but was determined by calculating the difference between TN and total inorganic nitrogen.

3. Characteristics of Fine and Coarse Aerosol



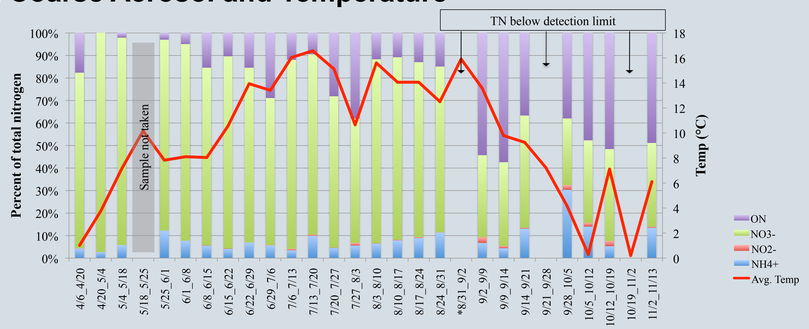
The average percent contributions of non-nitrogen species to TN in fine and coarse aerosol are shown. The concentration units of the nitrogen species and non-nitrogen species are µg N/m^3 and µmol/L respectively.

-Organic Nitrogen (ON) contributes 18-23% to the TN in both fine and coarse aerosol, similar to the findings of previous studies (Mace *et al*., 2003; Zhang *et al*., 2002).

-The largest contributor to the TN in fine aerosol is from ammonium (NH_4^+). Measurements show a large amount of sulfate, indicating ammonium sulfate [$(NH_4)_2SO_4$] is likely present. This was also found in a study of the smoky mountains (Stevens *et al*., 1980).

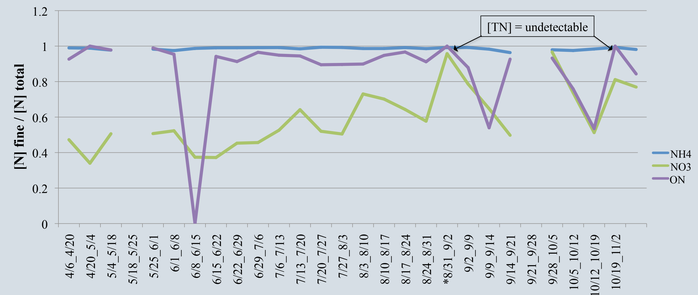
-The largest contributor to the TN in coarse aerosol is from nitrate, (NO_3^-) (72%). The high amount of sodium (26%) suggests sodium nitrate ($NaNO_3$) to be of importance in coarse aerosol.

4. Coarse Aerosol and Temperature



As temperature decreases through the summer, the amount of NO_3^- decreases and ON increases. An increase in ON production may be due to increase in biological activity or a decrease in the formation of coarse particle nitrate. Also, dust particle abundance is typically highest during the spring from dust outbreaks, which is a sink for gaseous nitric acid.

5. Nitrogen Relationships

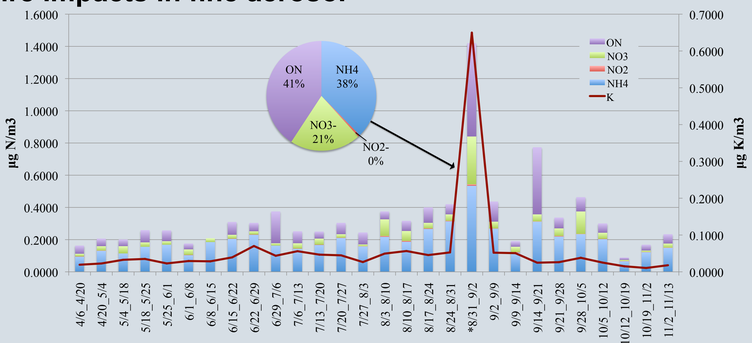


-The ratio of NH_4^+ in fine aerosol to total aerosol NH_4^+ is close to 1, showing most of NH_4^+ exists in fine aerosol. This relationship is constant with time and temperature.

-The ratio of ON in fine aerosol to total aerosol shows the majority of ON to come from fine aerosols. However, the further into the summer, when temperatures are decreasing, the amount of ON in coarse aerosol in comparison to total aerosol increases.

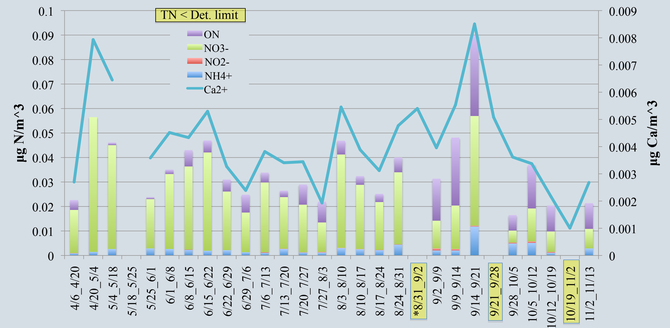
-Throughout the study, the NO_3^- fine aerosol fraction increases with time. This may indicate a change in gas-particle partitioning of fine particle ammonium nitrate. It also suggests changes in the abundance of reaction sinks, such as ammonium or alkaline coarse particles.

6. Fire Impacts in fine aerosol



The timeline of fine aerosol concentration is shown. The data shows the increase in reactive nitrogen during the time of the Station fire (*8/31_9/2). The fire not only increased the amount of total nitrogen, but also changed the percentage breakdown of the nitrogen species (pie chart). The concentration of potassium serves as another indicator of forest fire.

7. Fire Impacts on Coarse Aerosol



-Impacts from the Station fire were not noticeable in the coarse aerosol. The filter extraction from the fire sample had total nitrogen levels, which were undetectable (< 0.226 mg N/L).

-An increase in calcium correlates with increase in total nitrogen in coarse aerosol. This suggests coarse nitrate may relate to dust.

- Note: No sample was taken from 5/18-5/25

8. Key Findings

-Organic nitrogen contributes to 18-23% in both fine and coarse aerosol.

-Ammonium is significant in fine aerosol reactive nitrogen in the form of ammonium sulfate.

-The main contributor to coarse aerosol reactive nitrogen is nitrate and seems to appear in the form of sodium nitrate.

-Coarse aerosol measurements suggest average temperature impacts the amount of organic nitrogen and nitrate concentrations.

-The ratio of fine aerosol to total nitrogen concentrations show fine aerosol contains most of the ammonium found in aerosol.

-The ratio of organic nitrogen and nitrate different with time and temperature, suggesting changes in the abundance of reaction sinks.

-Total nitrogen abundance increased during the smoke periods from the Station fire.

-Smoke is enriched with ON relative to aerosol typical found in RMNP.

9. Acknowledgements

This work has been supported by the National Science Foundation Science and Technology Center for Multi-Scale Modeling of Atmospheric Processes, managed by Colorado State University under cooperative agreement No. ATM-0425247. The samples analyzed during this study were collected with the support of the National Park Service.

10. References

Beem, K.B., Raja, S., Schwandner, F.M., Taylor, C., Lee, T., Sullivan, A.P., Carrico, C.M., McMeeking, G.R., Day, D., Levin, E., Hand, J., Kreideweis, S.M., Schichtel, B., Malm, W.C., Collett, J.L., 2009. Deposition of reactive nitrogen during the Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) Study. Environmental Pollution 158, 862-287.

Blett, T., Morris, K., 2004. Nitrogen Deposition: Issues and Effects in Rocky Mountain Nation Park Technical Background Document.

Lammel, G., Cape, J.N., 1996. Nitrous Acid and Nitrite in the Atmosphere. Chemical Society Reviews 25, 361-369.

Mace, K.A., Duce, R.A., Tintal, N.W., 2003. Organic Nitrogen in rain and aerosol at Cape Grim, Tasmania, Australia. Journal of Geophysical Research 108, 4338.

Mehlmann, A., Warneck, P., 1995. Atmospheric Gaseous HNO3, Particulate Nitrate, and Aerosol Size Distribution of Major Ionic Species at a rural site in Western Germany. Atmospheric Environment 29, 2359-2373.

Pakkanen, T.A., 1996. Study of Formation of Coarse Particle Nitrate Aerosol. Atmospheric Environment 30, 2475-2482

Stevens, R.K., Dzubay, T.G., Shaw, R.W., McClenny, W.A., Lewis, C.W., Wilson, W.E., 1980. Characterization of the Aerosol in the Great Smoky Mountains. Environ. Sci. Technol. 14, 1491-1498.

Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman, D.G., 1997. Human Alteration of the Global Nitrogen Cycle: Sources and Consequences. Ecological Application 7, 737-750.

Wittig, A.E., Takahama, S., Khlystov, A.Y., Pandis, S.N., Hering, S., Kirby, B., Davidson, C., 2004. Semi-continuous PM2.5 inorganic composition measurements during the Pittsburgh Air Quality Study. Atmospheric Environment 38, 3201-3213.

Zhang, Q., Anastasio, C., Jimenez-Cruz, M., 2002. Water-soluble organic nitrogen in atmospheric fine particles (PM2.5) from northern California. Journal of Geophysical research 107.