Identification of Sources Contributing to Ammonia Deposition in Rocky Mountain National Park by Isotope Ratio Mass Spectrometry

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Introduction

Colorado State University (CSU) is pleased to provide the fourth annual report for the project entitled "Identification of Sources Contributing to Ammonia Deposition in Rocky Mountain National Park (RMNP) by Isotope Ratio Mass Spectrometry". The summer of 2008 marked the startup of the project. Our project's goal is to:

1. Determine $\delta^{15}N$ values for NH_3 sources that have the potential for contributing nitrogen to RMNP
2. Assess the potential of using $\delta^{15}N$ measurements for quantification of ammonia sources.

Major Objectives for Year Four (12 months; 2011):

1. *Complete a field campaign at various sources in the Front Range of Colorado to assess efficacy of nitrogen isotopes to distinguish gaseous ammonia from known sources.*
2. *Collection of weekly wet deposition in RMNP and bimonthly measurements of ammonia emission from RMNP native forest and grassland soils.*

Research Summary

Progress over the last funding period (12 months) includes completion of a Radiello field campaign, collection of wet deposition in RMNP, and a RMNP soil emission study. The goal was to perform these 3 aspects simultaneously to access the efficacy of nitrogen isotopes for quantification of ammonia sources. With this approach, it is possible to accounts for both modes of deposition, dry and wet deposition, into RMNP, as well as, some local influences on ammonia, mainly from soils. These studies were conducted from May 2011 until October of 2011. The Radiello is a passive ammonia sampler adapted by the National Atmospheric Deposition Program (NADP) to monitor gaseous ammonia (AMoN sites). Radiellos are extremely useful in their applicability to environmental systems because they can be used in both high and low concentration environments, as well as, for long durations. Weekly wet deposition was collected in RMNP since it is the primary mode of nitrogen deposition in RMNP. The RMNP soil study was designed to estimate the magnitude of soil emissions over time. Grassland and forest soil cores were taken every two weeks and studied in the laboratory chamber apparatus for five days.

Image 1. Complete Radiello setup with the blue diffusive resistant body, plastic sample container, and phosphorous acid-impregnated polyethylene adsorbing cartridge.

Approach

Radiello Field Study

Radiello sites were chosen based on the following criteria: 1) all sites must be near a weather station to access local environmental conditions, and 2) must represent a known/suspected source of ammonia or represent a possible transport pathway. Samples have been collected from confined animal feeding operations (CAFOs), cropland, a waste water treatment facility, near a busy interstate (urban), at a rural location (foothills), and at RMNP (Image 2). Samplers were deployed for two week and monthly integrations.

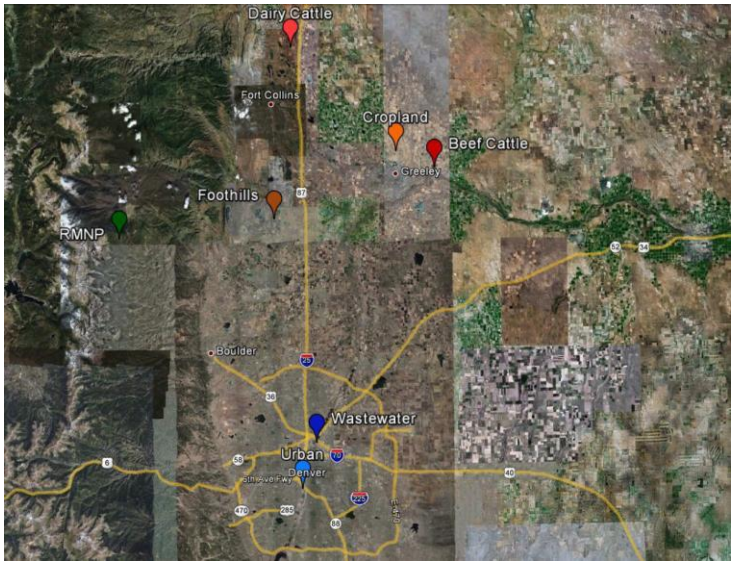

Image 2. Map of Radiello locations. Sites are color coordinated with red representing animal production, orange representing cropland/rural communities, blue represents urbanized sources and green represents native.

RMNP Wet Deposition

Wet deposition was measured weekly with an N-CON NTN Atmospheric Deposition Sampler. The sampler only collects during precipitation events and closes at all other times. Sampling containers are weighed before deployment and measured after collection. pH, cations, anions, and organic nitrogen were measured on all samples and frozen for later isotopic analysis. Wet deposition is determined by using the volume of precipitation collected, the concentration or mass of analytes, and the area of the collection containers.

RMNP Soil Studies

RMNP intact soil cores were collected from both grassland (n=6) and forest (n=6) soils every two weeks. Intact samples were collected along a fifty meter transect early in the morning within four inch stainless steel rings. Samples were placed in a cooler and brought into the laboratory chamber apparatus and studied for five days. Volatilized ammonia is collected in an acid trap and is swapped out every two days. All acid extracts are measured for ammonia on an Ion Chromatograph and frozen for later isotopic analysis.

Isotopic Measurement

All ammonia samples are aqueous and may contain other forms of nitrogen, such as, nitrate and organic nitrogen. To ensure accurate measurements of only ammonium-N, the aqueous samples are diffused onto acid impregnated filters. All samples are made brackish, then a filter pack is added and the samples are adjusted to a pH of 9.4. Ammonium is converted to ammonia and volatilizes onto the filter.

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Current State

Radiello Field Study

Radiellos were placed at seven sites including animal husbandry, urbanized sources, cropland, foothills, and RMNP. The average ammonia concentrations in Figure 1 fall into two groups—CAFOs and all other sources. CAFOs had the highest average ammonia concentrations, ranging from 4x to 100x higher than other sources. Beef cattle varied over the sampling period and is believed to be due to changes in head of cattle. Interestingly, the wastewater treatment plant was 3rd highest among sampling sites, and appeared to show some variability with temperature. Preliminary isotopic values have been measured for some of the Radiello samples (Figure 2). Nitrogen from dairy cattle is the most depleted or lowest in delta value, while urban sources had the highest values. CAFOs, wastewater and cropland had similar isotopic values as expected since the mechanism for ammonia loss is similar. The foothills site was chosen due to its location. It is surrounded by the city center of Denver, the agricultural northeastern part of Colorado and RMNP. Thus, the foothills value could represent a mixture of urban and agricultural sources; however, further research is needed to verify this idea. Unfortunately, RMNP has not been determined due to low masses; however, other methods are being investigated to accommodate these samples. Overall, it appears isotopes may be able to distinguish urban versus agricultural sources.

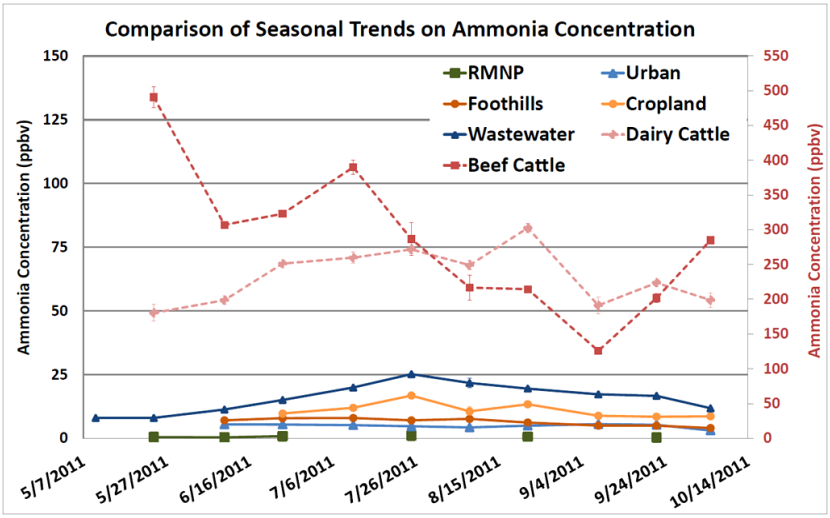

Figure 1. Time series of average ammonia concentration over the study period. Points represent 2 week periods, except for RMNP– monthly integrations. Dairy and beef cattle are plotted on secondary axis. Error bars represent standard error (n=2).

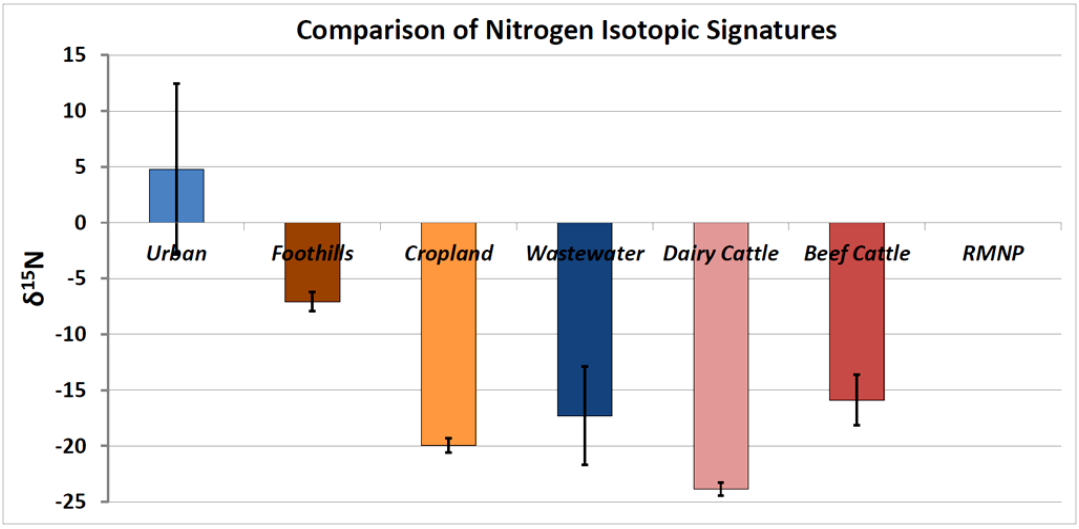

Figure 2. Comparison of ammonia nitrogen isotopes for sources in the Front Range. RMNP has not been measured due to low mass. Error bars represent standard error (n=2, 3, or 4).

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RMNP Wet Deposition

The amount of total nitrogen deposited during the spring and summer periods were 1.57 and 1.72 kg N ha^{-1}, respectively. This is similar to previous values measured at this site. Ammonia contributed 45% and 38% to total N during the spring and summer period, respectively. Nitrate contribution to deposition was relatively constant with 30% and 32% during the spring and summer, respectively. Organic nitrogen contributed a significant portion to nitrogen deposition increasing from 21% in the spring to 30% in the summer. Interestingly, previous studies have shown that fewer events occur in the spring than the summer and can contribute higher magnitudes. However, this study found that the number of events that occurred in the spring is similar to the number of events in the summer, and the summer contained the single largest deposition event.

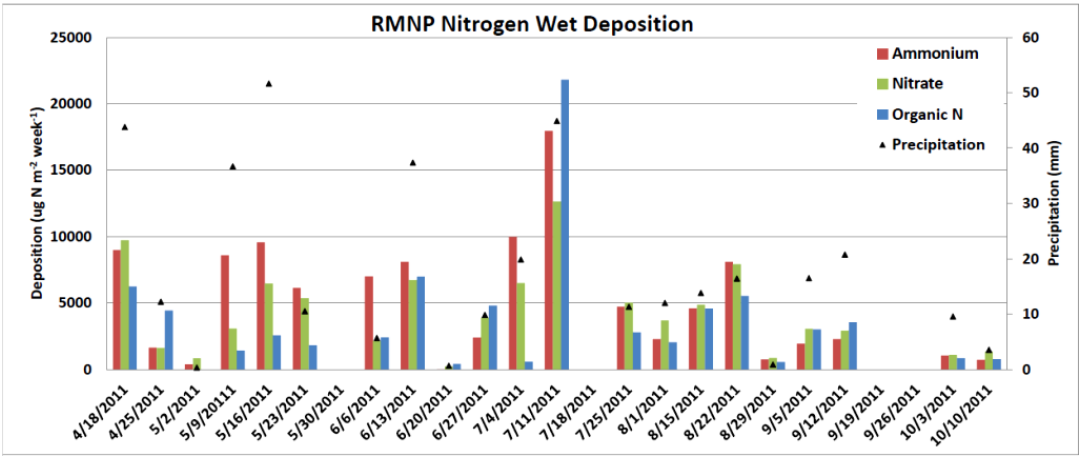

Figure 3. Comparison of nitrogen wet deposition measured in RMNP during the field study of 2011. Precipitation is shown on the secondary access. Ammonium (red) and nitrate (green) appear to be similar throughout most of the deposition events. Organic nitrogen varied strongly over the study period.

RMNP Soil Studies

Ammonia lost by RMNP native soils can be seen in Figure 4. A whisker box plot was chosen to show the range of ammonia flux. The average ammonia flux from grassland and forest soils was 1.09 and 0.519 mg NH_3 m^{-2} day^{-1}, respectively. These measurements are considered upper bounds, since they are held at room temperature and do not undergo diurnal variations in temperature. The ammonia flux from grasslands is higher than forests, which has also been observed in the past. Grasslands do exhibit a larger range of ammonia emission with a few samples (shown in red outliers) exhibiting extremely high ammonia losses. Furthermore, the forest did exhibit some outlier values, but their ranges are much more constrained. Large ammonia fluxes have been observed in the past, and it is believed that some of the grassland soils retain large amounts of water and can be waterlogged for extended durations depending on precipitation volume. This can lead to large amount of aqueous ammonium which can volatilize when the water evaporates.

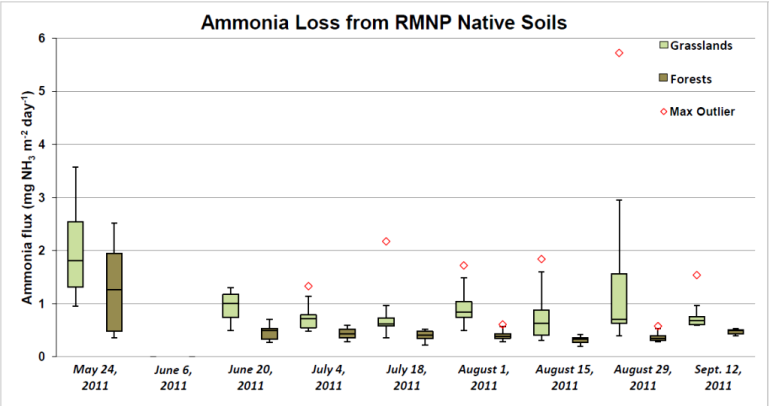

Figure 4. Whisker box plot comparison of ammonia flux from grassland (green) and forest (brown) soil during the 2011 study. The box represents the 25th, 50th and 75th percentile with outliers shown as red diamonds. A mistake was made during the June 6th study and the results are not shown.

Future Studies

Future work includes completion of isotope analysis from the radiello, wet deposition, and the RMNP soil studies. Wet deposition and RMNP soil extracts are being measured on site at CSU; due to low collected masses, a small set of radiellos are being sent to a commercial lab. In addition, integration of a back trajectory model, HYSPLIT, into the radiello study is anticipated to add evidence to the isotopic data by possibly excluding certain sources based on air mass locations. A short study is expected to be performed on crops soils, with focus on isotopic values of recently fertilized systems. Furthermore, a study of urea hydrolysis dependence on temperature is expected to start soon, with an emphasis on low temperature (5-15 ^{o}C) dependence.

Objectives for Final Report

1. Finish isotopic analysis from field study of 2011, and integration of HYSPLIT into a weight of evidence approach to ammonia deposition in RNNP.
2. Move forward with urea hydrolysis studies to accurately assess ammonia emission from important sources like CAFOs.
3. Assess the potential for large isotopic shifts in recently fertilized soils.

Acknowledgement

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Publications/Presentations:

Joshua J Stratton, Jay M Ham, Christina Williams, Damaris Roosendaal, Thomas Borch. **2011**. Assessing the Ability of Nitrogen Isotopes to Distinguish Ammonia Sources Affecting Rocky Mountain National Park. AGU Fall Meeting. Dec. 8th, 2011. San Francisco, CA

Galles, K.; Ham, J.; Westover, E.; Stratton, J.; Wagner, J.; Engle, T.; Bryant, T.C. Influence of Reduced Nitrogen Diets on Ammonia Emissions from Cattle Feedlot Pens. *Atmosphere* **2011**, *2*, 655-670.

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