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 third 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 Three (12 months; 2010):

1. *Collect atmospheric samples from RMNP, forest fires, and confined animal feeding operations (CAFOs).*
2. *Completion of a laboratory apparatus to study ammonia emissions and isotopic signatures from various possible sources including CAFOs, RMNP soils, fertilized soils, etc.*

Research Summary

Progress over the last funding period (12 months) includes completion conditional samplers for field studies, field sampling, and ammonia studies from native soils from RMNP. To enhance our ability to sample sites with lower ammonia emissions and prevent possible source mixing, three conditional samplers have been constructed (Image 1). These samplers are capable of turning on/off based on the wind speed and direction. Preliminary field sampling has been conducted at a smaller ammonia sources such as wastewater reclamation plants. These have proven to be difficult; this conditional sampler modification was motivated due to difficulty in sampling low ammonia concentration in urbanized areas. This modification will prevent mixing from neighboring sources, such as waste water remediation and vehicular locations, to allow us to identify a single source's isotopic signature.

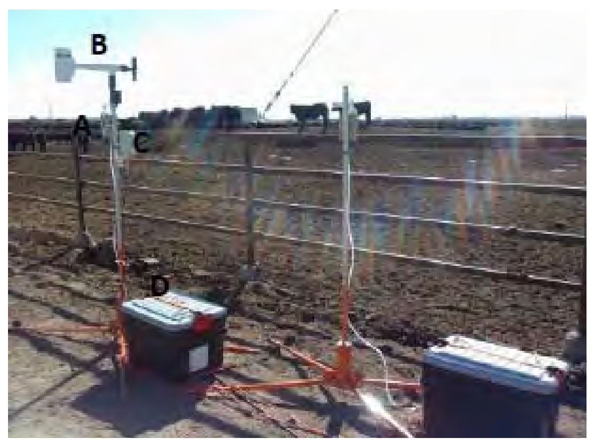

Image 1. Conditional samplers at a CAFO. **A** is the denuder used for sampling, **B** is an anemometer used to monitor wind direction and speed, **C** is used to monitor temperature and humidity, and **D** is an enclosure for the pump and electronics.

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Sampling Results

Samples have been collected from CAFOs, a waste water treatment facility, forest fires at the Fire Testing lab in Missoula, Montana, and at RMNP. Some of these samples have encountered difficultly due to low ammonia masses and other analytical approaches are being investigated. Currently, numerous gas samples have been collected from a cattle feed yard. Figure 1 shows the ammonium concentration from a cattle feed yard. Ammonia concentrations can vary greatly depending on environmental conditions, but we believe these samples are a good subset of samples for winter isotopic data. Sampling will continue into the summer or 2011.

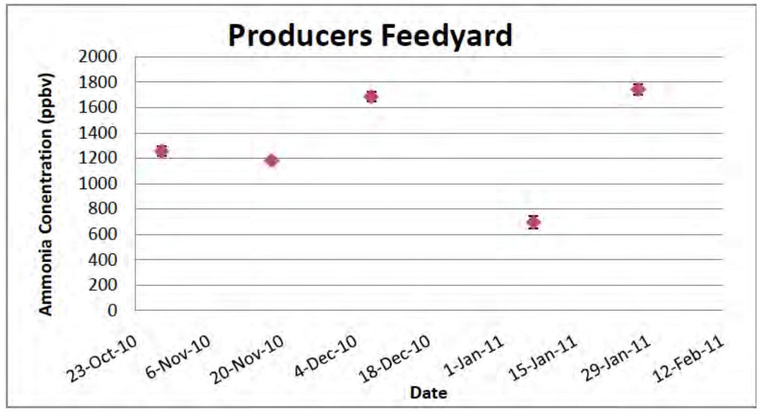

Figure 1. Ammonia concentrations over the winter season at a cattle feed yard near Greeley, CO. Error bars represent one standard deviation (n=2).

Current RMNP samples have proven difficult. All precipitation samples contain complex nitrogen pools, including ammonium, nitrate, and organic nitrogen, as well as, may have low masses. A diffusion method has been developed to separate the ammonium from other nitrogen pools. Although the ammonia masses are small, ammonium isotopic signatures from these samples are expected to be determined in the near future by compiling similar samples together.

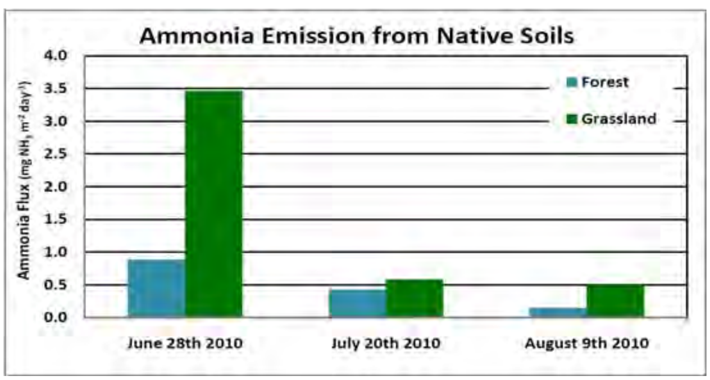

Figure 2. Comparison of the average ammonia flux observed over 7 days from forest and grassland soils. The sampling dates are shown on the x-axis.

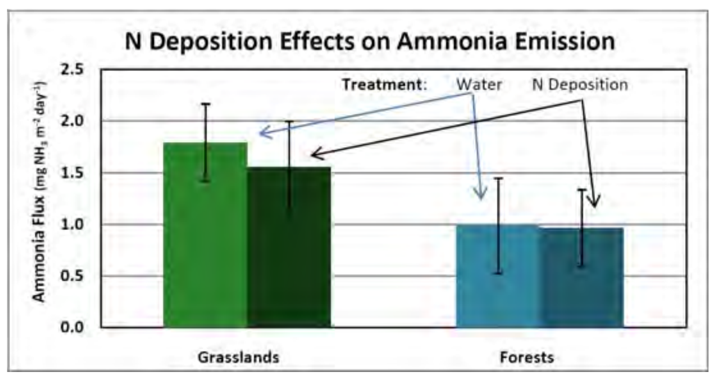

Figure 3. Comparison of average ammonia flux from forests and grassland soils treated with water (low nitrogen) or high nitrogen. Error bars represent one standard deviation (n=3)

With the increasing uncertainty in nitrogen adversely affecting RMNP, interests in RMNP soil emissions and evaluation of RMNP local emissions have increased. Our objectives were to determine the magnitude of ammonia flux from native soils and to determine the fate of ammonium deposited in the park via precipitation. During the fall of 2010, forest and grassland soil cores were collected

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three times to determine ammonia flux over the fall period, and replicate soil cores were collected to determine the fate of ammonium deposited via precipitation events. To determine the fate of the ammonium deposited on the soil cores, the ammonium was labeled with ^{15}N.

Our findings from the RMNP native soils studies have shown that ammonia flux can vary greatly with sampling period (Figure 2). Additionally, grassland soils have higher ammonia emissions than forest soils. Preliminary analysis of volatilized ammonia shows that nitrogen deposited in RMNP via precipitation is retained within the soil (Figure 3). These isotopic signature of the volatized ammonia will be use to validate this conclusion.

Current State

Currently, construction of a controlled temperature system has been completed. Our objectives include low temperature urea hydrolysis kinetics and elevated temperatures for isotope transformations. Various configurations have been tested to verify both the magnitude and variation of temperatures that the systems can produce. However, the general design can be seen in Image 2. The temperature system contains a separate heating and cooling system and numerous fans to ensure superior mixing to prevent temperature gradients within the system. The power supply and controller have been fastened to the top of the system to allow for portability and ease of use (Image 2).

Preliminary testing of the temperature range and possible gradients have been conducted. Research goals are to study urea hydrolysis as low as 10°C and diffuse samples at 40°C. Four temperature probes were placed evenly apart in the system along with water filled flasks to emulate future studies. Results are shown in figure 4. The dynamic range needed has been achieved and the temperature gradients are small. One drawback is the lag time to achieve the desired temperature.

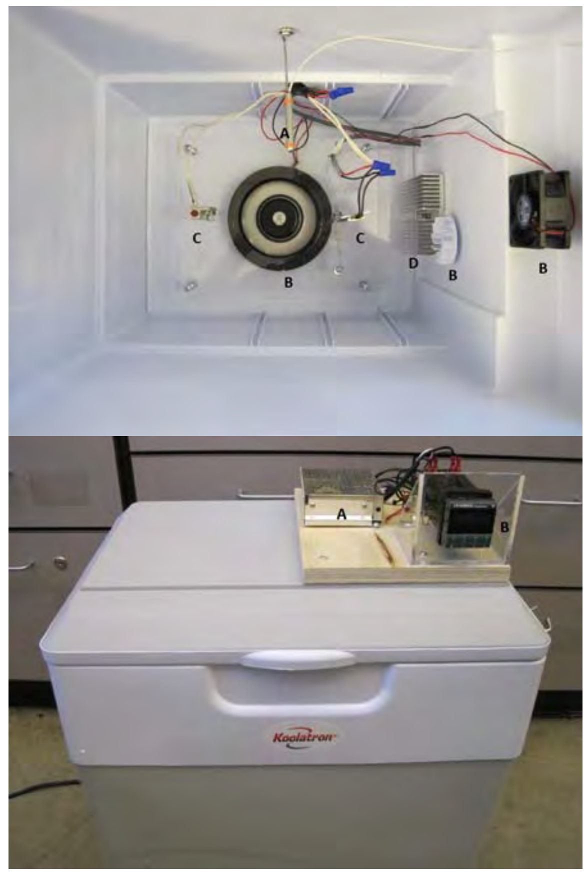

Image 2. (Top) Inner configuration of temperature controlled system. This includes **A** temperature sensor, **B** three fans, **C** two resistive heaters, and **D** Peltier cooler. (Bottom) User interface setup with **A** power supply and **B** temperature controller.

Future Studies

Research interests in the future include urea hydrolysis, continued RMNP ammonia emission studies, and a study to investigate anthropogenic influence on spring and summer deposition in RMNP. The urea hydrolysis study is expected to generate accurate kinetic constants for emission modeling from CAFOs by studying urea hydrolysis in sampled CAFO materials and at environmental conditions relevant to Colorado. The use of isotopic measurements of Front Range source, wet deposition monitoring in RMNP, and native soil emissions should reveal a better understanding between Front Range sources and ammonia deposition in RMNP.

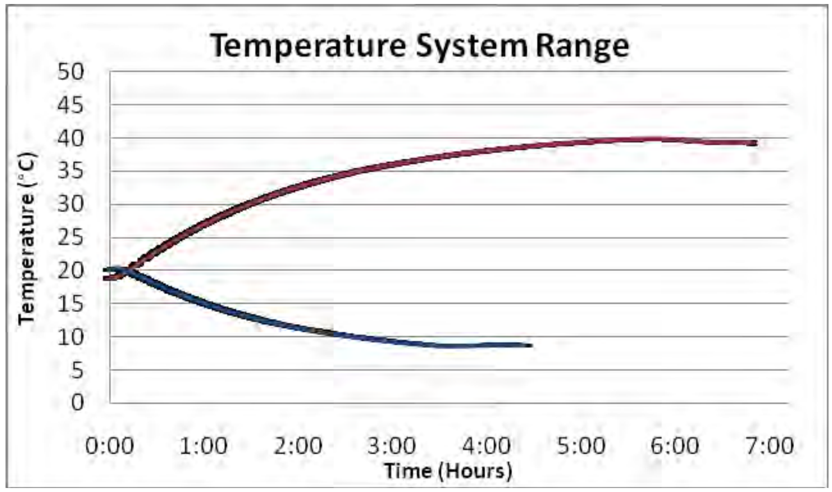

Figure 4. Heating and cooling trends from the temperature controlled systems. The red and blue lines represent the heating and cooling mode, respectively. Error bars represent one standard deviation among the four temperature sensors.

Objectives for Next Year

1. Continue field sampling at CAFOs, RMNP, wastewater remediation sites, and urban sources; and understand variability of isotopic signatures from all sites
2. Move forward with urea hydrolysis studies to accurately assess ammonia emission from important sources like CAFOs
3. Continue monitoring within park emissions, like native soils, and add wet deposition monitoring to better assess the impact of Front Range sources on RMNP

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