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

Joshua Stratton[1], Thomas Borch[1, 2,*], Jay Ham[2], Jeffrey L. Collett, Jr.[3], and Jessica G. Davis[2]

[1]Department of Chemistry, [2]Department of Soil and Crop Sciences, [3]Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523-1170

[*]borch@colostate.edu; Ph. 970-491-6235

[*]Corresponding author contact: phone 970-491-6235; email borch@colostate.edu

Introduction

Colorado State University (CSU) is pleased to provide the second 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 Two (12 months; 2009):

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

Figure 1: Picture of laboratory chamber system. **A**. Ventilation system **B**. Steel Manifold **C.** 10 L/min flow meter **D**. Sample Chamber **E**. Reinforcing 2x4 **F**. Acid Traps

Preliminary field sampling has been conducted at a CAFO throughout a 2 month period, July to August and gas samples have been collected at RMNP, as well as, from controlled forest fires at the Fire Testing lab in Missoula, Montana. As previously stated, a laboratory apparatus has been completed with some modifications from the previous report (Figure 1). Saline (NaCl, KCl, etc.) solutions proved to be difficult to control due to precipitation, and a refrigerator bath was implemented for relative humidity control. Additionally, the chamber system has been expanded to house up to twelve samples (intact soil cores, duff material, synthetic fertilized soils, RMNP soils, etc.) to enhance complexity of studies, as well as, throughput. Also, a ventilation system was installed to help control odor. Studies on CAFO soils have already been conducted to characterize ammonia emission. CAFO emissions are important to clarify because they are often among the top of suspected ammonia sources. Our first objective was to characterize important sources of ammonia, then proceed into isotopic studies to understand mechanisms controlling ammonia emission. Our current CAFO soil studies include emission differences between intact soil cores and loose duff material (non-compacted feces), effect of soil additives (water and synthetic urine), and investigations into effects of best management practices, such as scraping. Water application and scraping are important to study, because they may be viable best management practices (BMP) for limiting ammonia volatilization. The addition of synthetic urine was studied

*Corresponding author contact: phone 970-491-6235; email borch@colostate.edu

to investigate how quickly urea-N is converted into ammonia and emitted from feedlots. This was achieved by adding a known amount of urea and measuring the increase in emitted ammonia after application. Studies in 2010 will include the addition of 15N isotopically labeled urea to provide more insight into mechanisms that control the fate of urea (e.g., hydrolysis, sorption, microbial biotransformation) in CAFO soils.

Our findings have shown that intact CAFO soil cores have higher emissions (44.7%) than duff material (non-compacted feces) from CAFOs (Figure 2). Some important soil chemical properties are given in Table 1.

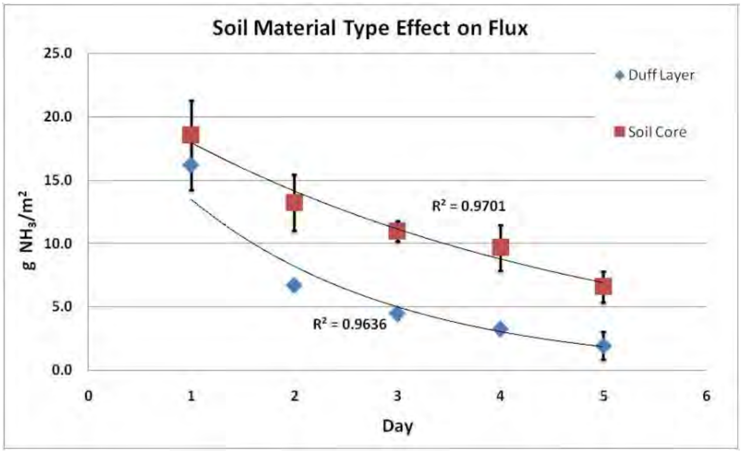

Figure 2: Ammonia flux in grams of ammonia (NH_3) per meter squared. Error bars represent on standard deviation (N=6)

Table 1: Chemical properties of Duff and Soil Cores

	Total N %	Organic-N %	Ammonium-N mg/kg
Duff	2.676	2.59	857.2
Soil Core	2.888	2.77	1134

Additionally, both follow pseudo-first order kinetics which supports other studies; however, it is uncertain as to what causes this type of decay. Future work is warranted. Both application of water and scraping can lower (8.3%, 40.4%, respectively) ammonia volatilization. Scraping consists of mounding all materials into the center of a pen as a mound. The scraped areas are the areas furthest from the

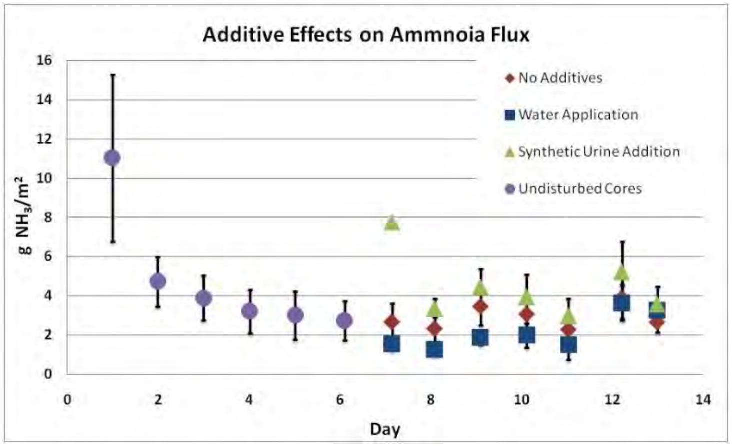

Figure 3: Ammonia flux in grams of ammonia (NH_3) per meter squared. The first six days were undisturbed with no additives (N=12). On day seven synthetic urine (green) and water (blue) were added to four cores respectively, while four cores with no additives (red). Error bars represent one standard deviation.

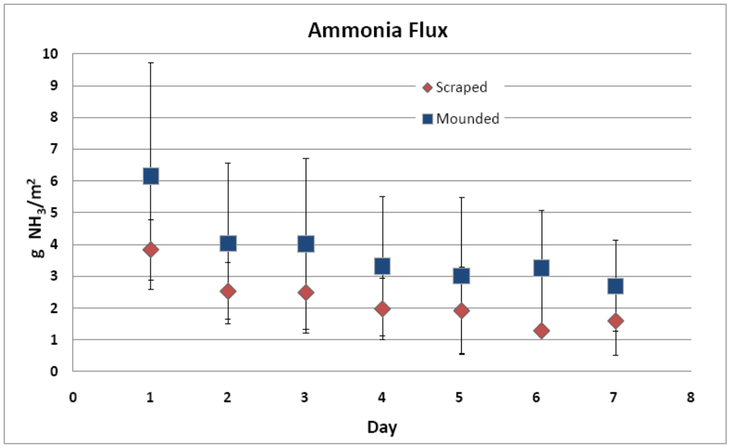

Figure 4: Ammonia flux in grams of ammonia (NH_3) per meter squared. Error bars represent on standard deviation. Scraped areas (N=3) and mounded samples (N=9) are three samples from the top and six from sloped sides.

center of the pen. These results show that both water application (Figure 3) and scraping (Figure 4) can be viable best management practices to help limit ammonia emissions. Lastly, investigations into how quickly synthetic urine is converted into emitted ammonia in CAFO soil cores found that 42.1% of the added urea-N in the synthetic urine was converted to NH_3 within seven days (Figure 3). This confirms that urine plays a large role in ammonia emission from CAFOs, and future investigations are important to better understand how to control N emissions from CAFOs.

Current State

To enhance our ability to sample sites simultaneously, three stationary samplers are being assembled for future ammonia studies. These samplers will be instrumental to finish field sampling for ammonia nitrogen isotopes at wastewater treatment plants, fertilized soils, automobile exhaust, etc.

Additionally, interest in RMNP soil emissions has grown, and evaluation of RMNP soil emissions is an area in need of exploration. Work by others has hypothesized that RMNP soils may be a significant source of NH_3 and contribute to the Total N budget within the park. Thus, preliminary testing to identify if the laboratory system can detect emitted ammonia from RMNP soils is being conducted. Both grassland and forest soils were collected and studied for a six day period. Ammonia emission was observed in the forest soils using the laboratory system (Figure 5). It is evident that there is a large variability between forest samples. Unfortunately, the grassland experiment has not been finished yet and is not reported on in the report.

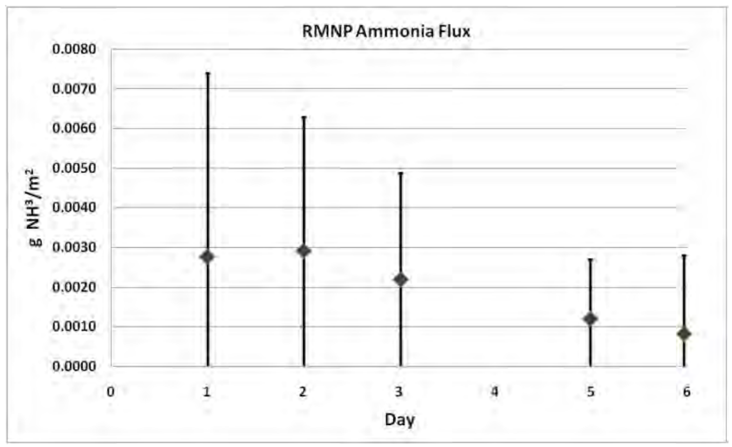

Figure 5: Grams of ammonia (NH_3) per meters squared emitted from soils collected at RMNP. Error bars represent one standard deviation based (N=6). *Day 4 is not shown due to contamination

Future Studies

Anticipated future work includes rate of urea hydrolysis within CAFO soils to better quantify its impact on ammonia emission. This study requires modifying the laboratory apparatus for temperature control for kinetic studies to obtain important chemical parameters like activation energy. Additionally, isotope labeling will grant more insight into NH_3 formation and release mechanisms in anticipated studies with CAFO soils, (synthetic) fertilized soils, and RMNP soils. This can be achieved by adding known amounts of isotope labeled urea-N or fertilizer-N to soil samples followed

*Corresponding author contact: phone 970-491-6235; email borch@colostate.edu

by a detailed analysis of the distribution (e.g., sorbed fraction vs. aqueous fraction) and transformation into e.g., ammonia or nitrate. These samples will be analyzed for isotope labeled nitrogen and a mass balance will be performed to better understand the fate of N in these complex systems. Once the additional samplers for field sampling are completed, sampling is anticipated at sites involving fertilized soils, waste water treatment plants, vehicle emissions, etc. In recent news, our research was reported in both ABC News and Business Week for its investigation into CAFO effects on RMNP nitrogen deposition.

Objectives for Next Year

1. Start or continue field sampling at CAFOs, RMNP, wastewater remediation sites, fertilized soils, and automobile exhaust and compile isotopic signatures from all sites
2. Move forward with mechanistic studies of what controls ammonia emission from important sources like CAFOs, fertilized soils, and possibly RMNP soils.

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*Corresponding author contact: phone 970-491-6235; email borch@colostate.edu