International Plant Nutrition Institute (IPNI) - Summary - 2013

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

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Our project's goal is to assess the ability of isotopes as tracers to determine sources of ammonia contributing to nitrogen deposition in Rocky Mountain National Park (RMNP). The main project objectives are to:

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

Progress over the last funding period (12 months) includes progress on the radiello-based ammonia field campaign, analysis of wet deposition in RMNP, and RMNP soil emissions. In addition, preliminary studies on urea hydrolysis and experimental development towards investigating Henry's constant have begun. All wet deposition samples and RMNP soil emission studies have been analyzed for N-ammonia isotopes; additionally, a larger isotope dataset has been compiled for the radiello study. N-Ammonium isotopes in wet deposition samples exhibited sample variation over the study period with the exception of two weeks in mid May. Additionally, wet deposition samples were obtained from Loch Vale Watershed, a National Atmospheric Deposition Program site, and compared with N-ammonium isotopes to our RMNP site. The N-ammonium isotopes correlate well between the two sites during the study period. A larger dataset of N-ammonium isotopes from the radiello study showed that wastewater remediation exhibited a significantly more depleted (lower) value than dairy cattle, beef cattle, and cropland. Furthermore, dairy cattle and beef cattle were significantly different. However, cropland was not significantly different from both beef and dairy cattle. HYSPLIT is a commonly used dry (no precipitation) meteorological model to assess large scale (>20 km) air flow. We used this model to help understand the meteorology during our study period. 24 hour back trajectories were calculated for the entire study period. A relation can be seen between high deposition event and/or lower isotope values with flow coming from the east of RMNP. Discussion to explain this correlation is continuing but currently, we believe that air east of RMNP leads to high deposition of nitrogen in RMNP and the air mass's residence time affects the isotopic value.

Preliminary studies on urea hydrolysis on dairy cattle feedlot soils show that urea hydrolysis is fast. Half lives were shown to be as short as 28.5 min at 25 degrees Celsius. Urea hydrolysis activation energy (51.9KJ mol^{-1}) was calculated using kinetics from 5 – 25 degrees Celsius. The current work compared well with precious work done in urine/fecal mixtures (51.8 KJ mol^{-1}). Lastly, an experimental chamber has been designed to measure the Henry's constant for complex matrices. The system uses a knife valve to separate the gaseous phase from the aqueous. This eliminates small pH changes from carbon dioxide/carbonate buffers. as well as, creates two independent systems for sample collection and analysis. Additionally, porous Teflon tubing is being used to measure ammonia in the aqueous and allows for separation of ionized and unionized forms of ammonia. We believe this approach will allow for an empirical measurement of the Henry's constant in complex matrices, however work is ongoing.

We are thankful for the International Plant Nutrition Institute's support in this important work.
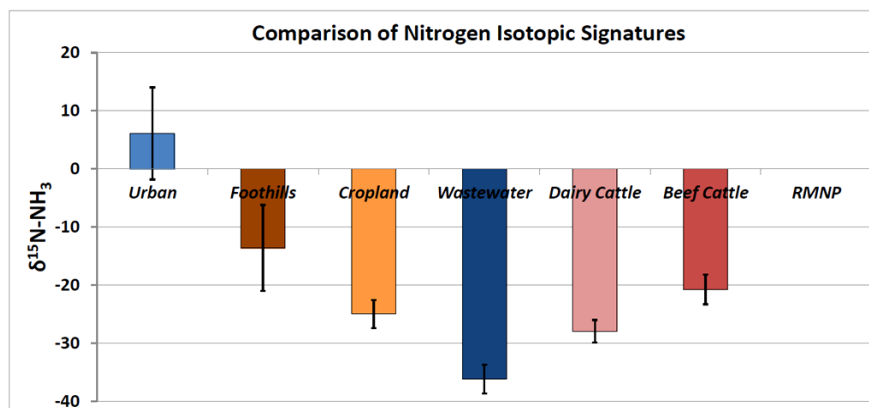

Figure 1. Comparison of ammonia nitrogen isotopes for sources in the Front Range. RMNP has not been measured due to low mass. Error bars represent one standard deviation (n=7, except for urban and foothills 2,3 respectively).