Final report for Task # J2350075147 (August 2007 – December 2008)

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1. Overview of Project

The National Parks are immensely popular public resources. Protection of these national treasures requires understanding of various threats to park resources. Included are threats to visibility and to sensitive ecosystems. The research in this project relates directly to diagnosing and remedying air quality problems in our national parks. It provides the basis for informed decision-making about steps to protect park resources by improving and managing air quality.

The long-term goals of this project are to improve understanding of deposition of pollutant species to sensitive park ecosystems, to improve understanding of visibility degradation in national parks, to diagnose contributors to air quality problems in specific parks, and to generate fundamental new knowledge about specific pollutant species contributing to air quality problems in national parks. Attainment of these goals involves the design of new measurement approaches and the planning, execution, and analysis of field measurements of air quality at select national parks.

2. Major National Park Service Research Activities Completed by CSU

- ***Characterizing Pollutant Deposition at Rocky Mountain National Park***

Rocky Mountain National Park is experiencing a number of deleterious effects due to atmospheric nitrogen compounds. These effects include visibility degradation and changes in ecosystem function and surface water chemistry from atmospheric deposition of reactive nitrogen. The nitrogen compounds include both oxidized and reduced nitrogen. Prior to the 2006 Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) study, little was known about the concentrations of, or deposition of, gaseous ammonia in RMNP. One finding of the RoMANS study was that abundant gaseous ammonia in the local atmosphere contributes substantially to total reactive nitrogen deposition.

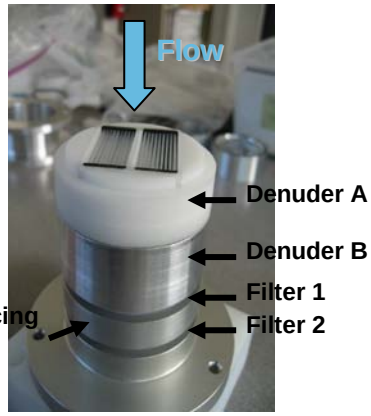
In order to facilitate more routine measurements of gaseous ammonia in routine measurement networks, this project was designed to develop a compact, robust sampling system capable of ammonia sampling at daily to weekly time intervals.

Following discussions with USEPA scientists with the Clean Air Status and Trends Network (CASTNet) and the Chemical Speciation Network (CSN), it was decided to pursue a modification of the existing Met One PM Speciation sampler (the SASS sampler) by adding an extractable denuder for collection of gaseous ammonia. In the effort to produce a compact, robust, extractable denuder for use with the SASS sampling system, two denuder prototypes have been designed, manufactured and tested. These denuder systems were designed and constructed in collaboration with project subcontractor Aerosol Dynamics, Inc. and with project collaborator Met One, Inc., the manufacturer of the SASS sampler.

Prototype I Denuder

Since the physical dimensions of the denuder are constrained by the size of the SASS sampling canister, Prototype I sought to combine maximized sampling efficiency and surface area with easy handling and extractability. SASS denuder Prototype I featured two removable 'denuder cartridges' that fit within a holder in the SASS canister. Each cartridge contained a number of parallel etched quartz slides that could be coated with various chemicals to collect ammonia or nitric acid gases; the interstitial spaces were calculated to yield efficient collection of these gases by diffusion to the slides. The cartridges could be removed from the denuder housing and fit into a 25mL test tube for extraction, washing, and coating.

Prototype I denuders fit into a test tube



SASS Sampling Setup with Prototype I denuders

Assembled SASS Canister

Regarding sampling performance, the most important features of a successful prototype are high collection efficiency for both ammonia and nitric acid and low blank values for those and other common species such as sodium, potassium, nitrite/nitrate, and sulfate. It is also necessary that the denuder have a sufficient load capacity to handle the CASTNet one-week

sampling period at expected ambient concentrations. To streamline testing, both prototypes were tested with cationic species: ammonia, sodium, potassium, magnesium, and calcium.

To test collection efficiency, two prototype denuders are run in series, where Denuder A is the first to contact the sample stream and Denuder B is the backup; the formula:

$$\text{Collection Efficiency} = 1 - (B/A)$$

can be used to calculate the collection efficiency of the prototype denuder. Since URG denuders had a 99.89 +/- 0.15% efficiency for ammonia and a large load capacity, a set of URG denuders was run parallel to the SASS system for comparison. During prototype testing, ammonia gas was generated by a Dynacalibrator permeation tube device and the sample flow was diluted and split between URG and SASS systems both running at 6.7 LPM for simultaneous periods. All denuders were coated with a 1% phosphorous acid solution and dried under nitrogen. Denuders A and B were extracted separately and analyzed via ion chromatography.

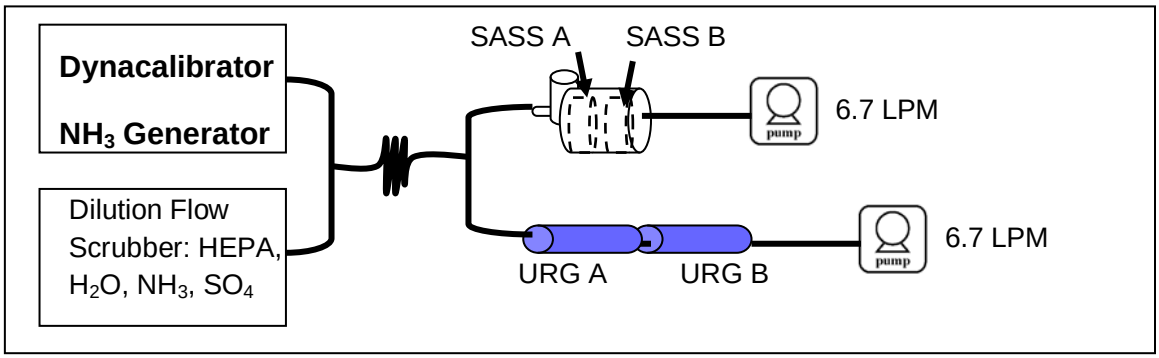


Figure 1: Schematic of the experimental setup for determining SASS denuder ammonia collection efficiency and load capacity.

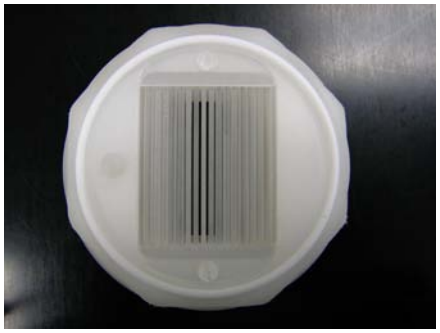
Prototype I ammonia collection efficiency measured 89.8 +/- 14.5 % and efficiency decreased in the presence of high loads, indicating that the Prototype I load capacity may be low. An analysis of expected Prototype I denuder performance under anticipated field sampling conditions indicated that the denuder efficiency was too low, the denuder capacity was insufficient, denuder handling was awkward and prone to operator contamination, too much water was required for extraction, and the Delrin used to manufacture the denuder portion holding the quartz slides was chemically degraded by the phosphorous acid coating solution. All of these were significant issues requiring correction. In order to remedy these issues, a 2nd generation denuder was designed and evaluated.

Prototype II Denuder:

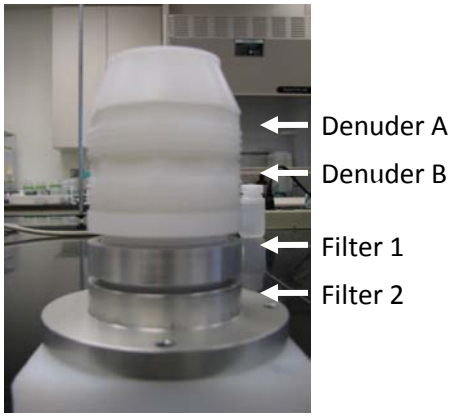
Experimental results from Prototype I brought a number of shortcomings to light which the design of Prototype II sought to rectify.

First, the quartz-slide denuders are now fixed into the holder. This eliminates a portion of the material surrounding the slides and allows room for more slides, increasing capacity. This fixed denuder is extracted and coated by capping both ends; this minimizes handling of extracted and coated surfaces, which can be a source of contamination, and reduces the volume of water required for denuder extraction. Lower extraction volumes improve the ammonia measurement detection limit by raising analyte concentrations in the extract solution.

Keck and Wittmaack (2006) worked on a somewhat similar denuder design in which microscope slide covers were used as the gas collection surface; the collection surface area of their design was very similar to that of the SASS prototype denuder. They found that increasing the phosphorous acid content of their coating solution from 1% to 5% increased the capacity of the denuder significantly and allowed them to achieve capacities suitable "for 1-week sampling at a semi-urban site" with "near unity" efficiency. Pursuant to their results, the Prototype II coating solution concentration was increased from 1% to 5% phosphorous acid, increasing total ammonia capacity. Lastly, the polypropylene materials used in Prototype II were selected for their chemical inertness and resistance to degradation by the coating solutions used.



SASS Denuder Prototype 2



Prototype 2 Sampling Setup

The SASS Denuder Prototype II ammonia collection efficiency was 94.08 +/- 5.07 % over eighteen test runs (Figure 2); most of the statistical variation comes from three anomalous runs. For comparison, the URG denuders had efficiencies of 99.89 +/-0.15 %. Prototype II had, in general, more calcium, magnesium, sodium, and potassium than was collected on the URG denuders operated in parallel, leading to suspicion of continued handling contamination or entrainment of room air during drying. Development of more rigorous use protocols and/or new drying apparatus may ameliorate these problems. Prototype II is resistant thus far to degradation by chemicals used in the coating process, despite the concentration increase. The higher coating solution is expected to yield a substantial increase in denuder capacity, rendering it suitable for

operation up to one week in environments sampled by the CASTNet program and for 24 hr sampling in more urban locations.

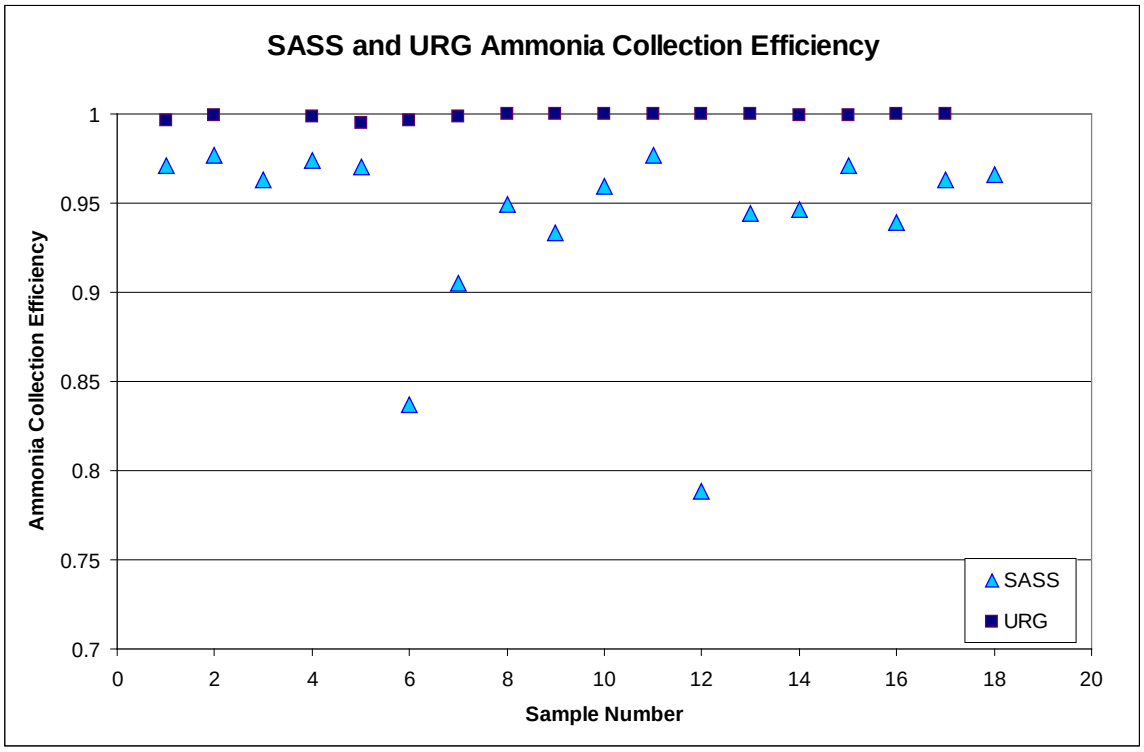


Figure 2: Ammonia collection efficiency for URG and SASS denuder prototype II sets run in parallel.

Ongoing collaboration is planned with USEPA and NPS to refine denuder coating and extraction procedures to minimize possible contamination and to conduct a field evaluation of denuder prototype II performance.

Chief accomplishments from our efforts are outlined below:

- Denuder –based sampling approach and incorporation into existing Met One SASS sampler decided upon in consultation with EPA scientists
- Prototype I denuder designed and constructed
- Prototype I denuder evaluated for efficiency, capacity, and operator handling
- Prototype II denuder designed to overcome shortcomings identified in the 1st generation design
- Prototype II denuder constructed in collaboration with Aerosol Dynamics and Met One, Inc.
- Prototype II efficiency testing and materials compatibility testing completed.

Project Deliverables

Deliverables for this project include this final report and the design of an extractable denuder for ammonia sampling for the CASTNet program. Two prototype denuders have been designed and tested. Each is compatible with current EPA sampling methods using the Met One SASS sampler. Prototype II denuder design drawings are available at Met One, Inc. the SASS sampler manufacturer.

Project publications and presentations

Misha Schurman (1), Jeffrey L. Collett, Jr. (1), Susanne V. Hering (2), Derek E. Day (3), William C. Malm (3), and Brian Lee (4), "Developing and Testing Prototype Compact Denuders for Ambient Air Sampling Applications", presented at the American Association for Aerosol Research Annual Confernce, Orlando, Florida, October 2008.

Authors (Affiliations):

1: Department of Atmospheric Science, Colorado State University, Fort Collins, CO; 2: Aerosol Dynamics Inc., Berkeley, CA; 3: Cooperative Institute for Research in the Atmosphere (CIRA)/National Park Service, Colorado State University, Fort Collins, CO; 4: USEPA, Washington, DC