Final report for Task # J2350075182 (September 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 planning, execution, and analysis of field measurements of air quality at select national parks.

2. Major National Park Service Research Activities Completed by CSU

• Airborne Nitrogen Concentrations and Deposition at Rocky Mountain National Park

Rocky Mountain National Park is experiencing a number of deleterious effects due to atmospheric nitrogen and sulfur 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. Emissions of both nitrogen and sulfur compounds will need to be reduced to alleviate these deleterious effects. A large field campaign was conducted in spring/summer 2006 to further our understanding of what will be needed in the longer term to address effects at the park, and to reduce uncertainties for future planning efforts.

During this project we completed analysis of aerosol, trace gas, and precipitation data collected during the 2006 Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) study. This

included both time-integrated samples and real-time monitoring data such as particle size distributions, trace gas concentrations, and fine particle composition. Findings from the RoMANS study were presented both to stakeholder groups, including USEPA and the Colorado Department of Public Health and Environment, and at scientific conferences, including meetings of the American Geophysical Union and the National Atmospheric Deposition Program. Work was initiated on the preparation of multiple manuscripts for publication in peer-reviewed journals. Chief accomplishments from our efforts are outlined below:

- Revised, final RoMANS field data set (aerosol, trace gas and precipitation composition; particle size distributions) submitted to NPS.
- Preparation of extensive RoMANS project final report in conjunction with NPS researchers. Report is currently undergoing peer review.
- Development and validation of a simpler, combustion method for total N analysis
- Development and testing of methods for organic N speciation at trace levels. Application of these methods to RoMANS and related wet deposition samples.
- Intercomparison of precipitation organic nitrogen measurement methods with the NADP Central Analytical Laboratory
- Preparation for year-long nitrogen and sulfur measurement campaign in Rocky Mountain National Park. Campaign begun Nov. 2008.
- Construction of final nitrogen and sulfur deposition budgets for the RoMANS core site. Identification of most important pathways for reactive nitrogen deposition, including two not routinely measured: wet deposition of organic nitrogen and dry deposition of gaseous ammonia.
- Evaluation of the importance of high time resolution meteorological measurements for accurately determining dry deposition fluxes at the Rocky Mountain NP CASTNet site.
- Development and testing of a new multi-channel gas measurement system for monitoring real-time speciation of gas phase reactive nitrogen including NO_x, NH₃, NO_y, and HNO₃.
- Presentations of RoMANS findings at the 2007 (Invited) and 2008 Fall Meetings of the American Geophysical Union
- Spring 2008 invited presentation of RoMANS organic nitrogen findings at the annual meeting of the European Geosciences Union
- Spring 2008 invited presentation of RoMANS findings to the American Chemical Society Northwest Section.
- Presentation of key RoMANS findings to representatives of the USEPA, NPS, and the State of Colorado.
- Preparation of journal manuscript (Levin et al., 2009) highlighting particle size distributions measured during RoMANS. Accepted for publication in *Atmospheric Environment*.
- Preparation of draft journal manuscript (Beem et al., in prep.) highlighting wet and dry deposition fluxes during the RomANS study

• Analysis and publication of findings from previous NPS air quality monitoring projects

During this project CSU researchers continued to analyze and publish data from prior NPSsponsored field campaigns. The primary focus was on publication of findings from the Nitrate Study campaigns conducted during the 2003-04 period and from the 2002 Yosemite Air Quality Study. Two journal manuscripts describing the importance of coarse particle nitrate and examining temporal variability in PM2.5 speciation at several rural IMPROVE sites were published in *Atmospheric Environment* (Lee et al., 2008a,b).

• Maintenance and operation of the NPS Mobile Air Sampling Laboratory

During this project CSU researchers continued to maintain, improve, and operate the NPS Mobile Air Sampling Laboratory (MASL). The MASL was deployed during this time period in support of smoke characterization studies conducted in spring 2008 at near Missoula, Montana and in support of airborne nitrogen monitoring and deposition efforts in RMNP (Fall 2008). The MASL was also deployed for a few days to Colorado Springs in early 2008 for an educational activity at Colorado College where students learned about air quality measurements.

Project Deliverables

Deliverables for this project include peer-reviewed journal articles and submission of this final report. In addition, quarterly progress reports were delivered throughout this project to NPS personnel. A list of journal articles is provided below. Copies of those published (Lee et al., 2008a,b) and in press (Levin et al. (2009) are being provided to the CESU along with this report. A summary of CSU RoMANS field project findings has already been provided to NPS officials as part of an extensive RoMANS project final report.

Journal publications

Beem, K., Raja, S., Schwandner, F., Taylor, C., Lee, T., Sullivan, A., McMeeking, G., Day, D., Hand, J., Kreidenweis, S., Chichtel, B., Malm, W., and Collett, Jr., J. (2009) Deposition of reactive nitrogen during the Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) Study, in preparation for submission.

Lee, T., Yu, X.-Y., Kreidenweis, S. M., Malm, W. C., and Collett, Jr., J. L. (2008a) Semi-continuous measurement of PM2.5 ionic composition at several rural locations in the United States. *Atmos. Environ.*, 42:6655-6669; doi:10.1016/j.atmosenv.2008.04.023.

Lee, T., Yu, X.-Y., Ayres, B., Kreidenweis, S. M., Malm, W. C., and Collett, Jr., J. L. (2008b) Observations of fine and coarse particle nitrate at several rural locations in the United States. *Atmos. Environ.*, 42:2720-2732; doi:10.1016/j.atmosenv.2007.05.016.

Levin, E.J.T., Kreidenweis, S.M., McMeeking, G.R., Carrico, C.M., and J.L. Collett, Jr. (2009) Aerosol physical, chemical and optical properties during the Rocky Mountain Airborne Nitrogen and Sulfur study. *Atmos. Environ.*, in press.

Malm, W. C., McMeeking, G. R., Kreidenweis, S. M., Levin, E., Carrico, C. M., Day, D. E., Collett, Jr., J. L., Lee, T., Sullivan, A. P., and Raja, S. (2009) Using high time resolution aerosol and number size distribution measurements to estimate atmospheric extinction, *J. Air Waste Manage. Assn.*, in review.

Project presentations and reports

Beem, K., Collett, J., Raja, S., Schwandner, F., Carrico, C., Taylor, C., Lee, T., Sullivan, A., Day, D., McMeeking, G., Mack, L., Kreidenweis, S., Hand, J., Schichtel, B., and Malm, W., A spatial analysis of precipitation chemistry coupled with aerosol and gas concentrations during the Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) Study, presented at AGU Conference, San Francisco, CA, December 15-19, 2008.

Collett, J.L., S. Raja, C. Taylor, C.M. Carrico, F. Schwandner, K. Beem, T. Lee, A. Sullivan, D. Day, G. McMeeking, S. Kreidenweis, J. Hand, B. Schichtel, W. Malm, Nitrogen transport and deposition during the Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) study, Eos Trans. AGU, 88(52), Fall Meet. Suppl., B24A-02, 2007. (INVITED)

Collett, J., S. Raja, C. Taylor, C. Carrico, F. Schwandner, K. Beem, T. Lee, A. Sullivan, D. Day, G. McMeeking, S. Kreidenweis, J. Hand, B. Schichtel, and W. Malm. Nitrogen emission, transport, and deposition in Colorado. Presented to the CDPHE Agricultural Air Quality Committee, Fort Collins, Colorado, Feb. 22, 2008. (INVITED)

Collett, J., Mazzoleni, L., Herckes, P., Schwandner, F., Beem, K., Raja, S., Liu, Y., Sun, Y., and Zhang, Q., Organic nitrogen in clouds and precipitation, Presented at EGU 2008, Vienna, Austria, April 14-18, 2008 (INVITED)

Collett, J., Jr., Raja, S., Beem, K., Schwandner, F., Lee, T., Sullivan, A., Taylor, C., Carrico, C., McMeeking, G., Kreidenweis, S., Day, D., Hand, J., and Malm, W., Transport and deposition of airborne nitrogen in Rocky Mountain National Park, Presented to the Air and Waste Management Assn., Lakewood, CO. May 22, 2008 (INVITED)

Collett, Jr., J.L., Beem, K., Raja, S., Schwandner, F., Carrico, C., Lee, T., Taylor, C., Sullivan, A., McMeeking, G., Levin, E., Kreidenweis, S., Day, D., Hand, J., Schichtel, B., and Malm, W., Observations of airborne pollutants and deposition during the 2006 Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) study, Invited presentation at the Regional Meeting of ACS held in Park City, Utah, June 15-18 2008 (INVITED)

Collett, J., Raja, S., Schwandner, F., Lee, T., Sullivan, A., Taylor, C., Carrico, C., Day, D., McMeeking, G., Beem, K., Hand, J., Kreidenweis, S., and Malm, W., Spatial and temporal variability in trace gas and aerosol nitrogen species during the Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) study, presented at the AWMA Moab conference, April 28 -May 2, 2008

Collett, J., Beem, K., Raja, S., Talyor, C., Carrico, C., Schwandner, F., Lee, T., Sullivan, A., Day, D., McMeeking, G., Mack, L., Kreidenweis, S., Hand, J., Schichtel, B., and Malm, W., Nitrogen deposition budgets for Rocky Mountain National Park, presented at AGU Conference, San Francisco, CA, December 15-19, 2008.

Collett, Jr., J.L., Raja, S., Beem, K., Schwandner, F., Lee, T., Sullivan, A., Taylor, C., Carrico, C., McMeeking, G., Kreidenweis, S., Day, D., Hand, J., and Malm, W., Transport and deposition of airborne nitrogen in Rocky Mountain National Park, Invited presentation at Sonoma Technology, Inc., December 18, 2008.

Day, D., Beem, K., Schurman, M., Collett, J., and Malm, W., Ammonia and nitrate measurements from various network sampling systems, presented at the AWMA Moab conference, April 28 -May 2, 2008

Gebhart, K., Malm, W., Schichtel, B., Barna, M., Rodriguez, M., Hand, J., Collett, J., Carrico, C., Lee, T., and Sullivan, A., Preliminary back trajectory-based source assessment for airborne particulate matter and deposited ions at Rocky Mountain National Park, CO, presented at the AWMA Moab conference, April 28 -May 2, 2008

Hand, J., Collett, J., Taylor, C., Raja, S., Carrico, C., Lee, T., Schwandner, F., Day, D., Sullivan, A., McMeeking, G., Beem, K., and Kreidenweis, S, Spatial patterns in wet deposition during the 2006 Rocky Mountain atmospheric nitrogen and sulfur study, presented at the AWMA Moab conference, April 28 - May 2, 2008

Levin, E., Gavin McMeeking, Christian Carrico, Jeffrey Collett, Jr., Sonia Kreidenweis, William Malm, Aerosol Number and Volume Concentrations During the Rocky Mountain Nitrate and Sulfate Study (ROMANS), American Association for Aerosol Research Conference, Sept. 2007.

Malm, W., Barna, M., Schichtel, B., Gebhart, K., Collett, J., Jr., and Carrico, C., Source apportionment of sulfur and nitrogen species at Rocky Mountain National Park using modeled conservative tracer releases and tracers of opportunity, presented at the AWMA Moab conference, April 28 -May 2, 2008

Malm, W., McMeeking, G., Kreidenweis, S., Levin, E., Carrico, C., Day, D., and Collett, J., Jr., Using high time resolution aerosol and number size distribution measurements to estimate atmospheric extinction, presented at the AWMA Moab conference, April 28 -May 2, 2008

Schwandner, F.M., Beem, K.B., Raja, S., Desyaterik, Y., Kreidenweis, S., Malm, W., and Collett, J.L., Jr., Organic nitrogen (ON) in wet deposition in Rocky Mountain National Park, presented at NADP Annual Meeting, Madison Wisconsin, October 14-16, 2008.