

Rocky Mountain Atmospheric Nitrogen and Sulfur Study (RoMANS)

Overview

March 2009

Background

Nitrogen (N) compounds are essential nutrients for life. In excess, however, N can be toxic, even life threatening, and in national parks excess wet and dry deposition of N can upset the delicate balances in natural ecosystems. In dry deposition, gases and particles are directly transported to the Earth's surface where they become incorporated into aquatic and terrestrial ecosystems. Wet deposition is the result of particles and gases being incorporated into atmospheric water droplets or ice crystals, through in-cloud and below-cloud scavenging processes. The wet deposition rate is dependent on the ambient concentrations, properties of the gases and particles, and properties of the precipitation. Total wet deposition amounts are dependent on precipitation frequency and rates, which are highly variable in space and time.

The current inorganic N deposition fluxes appear to represent approximately a 20-fold increase above pre-industrial values for the western United States. In the last 20 years concentrations of inorganic nitrate in wet deposition increased from 10% to 50% throughout the Rocky Mountains and surrounding areas. During this time period, the increase in ammonium wet deposition concentrations was even greater, increasing from 50% to 90%.

Human activity, including combustion of fossil fuels, application of N fertilizers, and animal husbandry has substantially altered the global N cycle. Most ambient inorganic oxidized N is a secondary product of nitrogen oxides (NO_x : the sum of NO and NO_2). In the United States and Colorado it is estimated that about a third of NO_x is from point sources such as coal-fired power plants, a third is from on-road mobile sources, and the remaining third consists of various source categories such as nonroad mobile, biogenic, and fertilizer applications. Most ambient inorganic reduced N is due to NH_3 emissions. While NH_3 emissions inventories are not as certain as NO_x inventories, it is estimated that two-thirds of NH_3 emissions in the United States is due to agricultural activities, primarily animal husbandry. This is estimated to be over 80% in Colorado. In Colorado, mobile sources are estimated to account for 11% while area sources account for another 3%.

Within Rocky Mountain National Park (RMNP) wet deposition of inorganic N (nitrate and ammonium) currently contributes approximately 2–3 kg/ha/yr to total N input, depending on elevation. Dry deposition of gaseous nitric acid (HNO_3) and particulate nitrate and ammonium (NH_4^+) increases total measured N deposition to approximately 3–4 kg/ha/yr. These are lower limits to the total N deposition, since important deposition inputs, including dry and wet deposition of organic N particles and gases and dry ammonia gas deposition, are not currently measured in routine networks.

The rate of deposition of inorganic N compounds in RMNP exceeds the "critical load" of inorganic wet deposition of 1.5 kg/ha/yr, which the park established as a management goal and Colorado and the U.S. Environmental Protection Agency Region 8 supported. A critical load is the quantitative estimate of an exposure to one or more pollutants, below which significant effects on specified sensitive elements of the environment are not expected to occur. Achieving this target will necessitate an approximately 50% reduction in wet N deposition from current

levels. The NPS, the State of Colorado and the U.S. Environmental Protection Agency have drafted a Nitrogen Deposition Reduction Plan to facilitate reaching this goal.

RoMANS Method and Objectives

The RoMANS study included two representative 5-week sampling periods in 2006. One was a spring campaign from March 25 through April 30 and the second a summer campaign from July 7 through August 11. For the purposes of the Nitrogen Deposition Reduction Plan, relevant objectives of the RoMANS study were to

- identify the overall mix of oxidized and reduced N in the air and precipitation on both the east and west sides of the Continental Divide,
- identify the relative contributions of N at Rocky Mountain National Park from emissions originating within the state of Colorado versus outside the state, as well as relative contributions of various in-state regions,
- identify the relative contributions of various source types including mobile, agricultural, other area sources, and large and small point sources.

A weight-of evidence approach, comparing and contrasting results from multiple analyses, was used to apportion the ambient and deposited N and S species to source regions within and outside of Colorado. This was done through a multistep process, starting from simple qualitative spatial data analysis to a final quantitative hybrid-receptor modeling technique. Each successive analysis built on the previous method, incorporating new data and/or more sophisticated statistical methods to refine the results.

As one example data analysis technique, spatial concentration gradients are often the result of spatial variations in emissions, with increasing gradients pointing toward high emission regions that potentially contribute to the receptor ambient concentrations and deposition fluxes. Gradients in short-lived, primary species, such as NH_3 and HNO_3 , tend to be sharp compared to those for secondary, longer-lived species, such as particulate sulfate and nitrate.

Quantitative hybrid receptor models were used to develop fractional estimates of source contributions to nitrogen at the primary receptor or core site. NH_3 and NH_4 both originate primarily from NH_3 emissions and were combined into a reduced, inorganic N deposition (RIND) category. Similarly, particulate NO_3 and HNO_3 both originate from NO_x emissions and were combined into an oxidized, inorganic N deposition (OIND) category. Organic N does have a significant contribution to N deposition, but the information to apportion source contributions to organic N was not available and was not included in the analysis.

Results

Although the spring and summer relative ambient aerosol concentration and deposition rates were similar, they were due to very different meteorological processes. In the spring virtually all of the wet deposition was due to a single synoptic-scale event associated with sustained upslope transport. In the summer, elevated concentrations and deposition occurred almost daily, due to convective activity.

Overall Nitrogen Deposition Budget

The fractional contributions of the wet-deposited N species are similar in both seasons, with about 34% of the measured deposited N due to wet ammonium (NH_4), 24–28% due to wet nitrate (NO_3), and 12–17% due to wet organic N. 26% of measured N deposition occurred by

dry processes, with NH_3 accounting for approximately 15%. Figure 1 shows the combined spring and summer deposition budget.

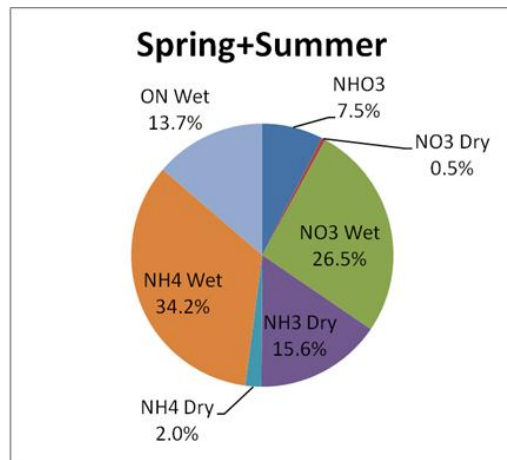


Figure 1: Relative contributions of individual N deposition pathways to total measured N deposition at the RoMANS core site during the spring and summer campaigns.

Together, wet deposition of organic N and dry deposition of gaseous ammonia composed ~30% of the total RoMANS N deposition budget, and neither of these two inputs is measured by the routine monitoring network. Furthermore, dry deposition of organic N was not measured in RoMANS.

Implications of Overall Mix of Oxidized and Reduced N Concentrations and Deposition on the East and West Sides of RMNP

In both the spring and summer campaigns, average concentrations for most species were highest in northeastern Colorado, with a sharply decreasing, east-to-west gradient, and the lowest measured concentrations occurred at Gore pass and Timber Creek, which are west of the Continental Divide. For instance, the ammonia concentrations in eastern Colorado (Brush) were 10–100 times greater than in

RMNP. The peak concentrations in northeastern Colorado indicate significant local sources of ammonia contributing to elevated levels of ammonia in RMNP. While oxidized N species concentrations also varied across the network, the differences were not as dramatic as seen for reduced N. Similar spatial patterns were also found in the average wet deposition concentration data.

Furthermore, it was found that N species concentrations generally increased in RMNP when the transport was from the east, and the concentrations remained relatively low when the transport was from the west during both the spring and summer.

Relative Contributions of N at RMNP from In-State versus Out-of-State Emissions and from Various In-State Regions

Quantitative hybrid receptor models were used to develop fractional estimates of source contributions to nitrogen at the primary receptor or core site. During the spring transport of N into RMNP is dominated by single, large deposition events associated with upslope flow from east of the Continental Divide. Referring to Figure 2, one sees that nearly 45% of total spring

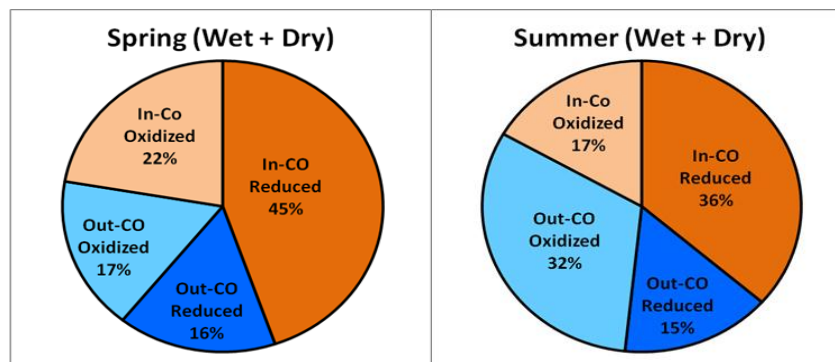


Figure 2: Wet plus dry deposition budgets for in- vs. out-of-Colorado sources for oxidized and reduced nitrogen.

deposition came from reduced nitrogen that had its origins from within the state of Colorado, primarily northeastern Colorado. About 22% of total spring deposition was linked to Colorado sources, primarily the Denver metro area. Therefore the split between N originating from within and

without the state of Colorado is about 2/3 to 1/3, respectively.

During the summer, the split between sources of in- versus out-of-state nitrogen was not much different than spring, at about 53:47. Of the total summer deposition, in-state, reduced nitrogen was 36%, while in-state, oxidized nitrogen was 17%. However, while during the spring most of the reduced nitrogen was from northeastern Colorado, during the summer natural respiration processes and western Colorado were the largest sources. During the summer, sources of oxidized nitrogen were quite varied, with population areas, oil and gas development, and power plants to the southwest making significant contributions.

Overall Relative Contributions of Source Types of N in RMNP

The average source apportionment budget for total inorganic N deposition, wet plus dry and spring plus summer, between in state versus out of state, was predicted to be about 55:45. The source area deposition budget for total deposition is shown in Figure 3. The total inorganic N deposition is spread nearly evenly between transport from Denver, western and northeastern Colorado, local sources, and the southwest, which includes California plus southern Nevada and the Four Corners region. Although the RoMANS study period was only 10 weeks in 2006, analyses of airmass transport patterns and air quality data indicate that there should be broad similarities in the RoMANS N deposition source attribution results compared to those for a typical year.

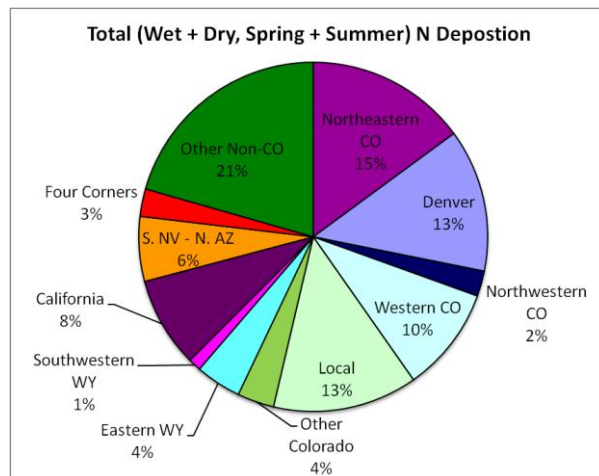


Figure 3: The contributions of source regions to the total inorganic N deposition from both dry and wet processes, measured at RMNP during the spring and summer RoMANS campaigns.

Synopsis

The source attribution results indicate that roughly half of the N deposition in RMNP originates from sources east of RMNP and half from sources west of RMNP; however, the mechanisms causing the deposition from east and west sources are quite different. In general, emissions of N compounds west of RMNP are low or distant from the park, but airmass transport to RMNP is persistently from the west. This leads to a diverse set of westerly sources that continually contributes low levels of N to RMNP's ecosystems. The high frequency of low rates of N deposition results in a high contributions of N over the study period.

To the east of RMNP are a number of high N emission regions, including the nearby Front Range and the agriculturally intensive northeastern Colorado. The upslope, easterly airmass transport is relatively infrequent; however, when it does occur, RMNP often experiences its highest ambient N concentrations. In addition, upslope transport is more frequently associated with precipitation at higher rates compared to westerly transport, causing high N deposition rates in RMNP. The less frequent but high rate of N deposition associated with sources east of RMNP leads to the high N contributions from these sources during the study period.