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A hybrid modeling approach for estimating reactive nitrogen deposition in Rocky Mountain National Park

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HIGHLIGHTS

- Total nitrogen deposition at Rocky Mountain National Park (RMNP) is modeled.
- Only a few percent of nitrogen deposition originates from eastern United States.
- 40% of total deposition at RMNP is from sources within that state of Colorado.
- 27% of nitrogen disposition is from the Front Range.
- Reduced nitrogen, other than the WON, makes up 66% of the deposition budget.

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ABSTRACT

Changes in ecosystem function at Rocky Mountain National Park (RMNP) are occurring because of nitrogen deposition associated with emissions of nitrogen from sources in Colorado as well as other areas of the North American continent and beyond. Nitrogen species are in both reduced and oxidized forms. A year-long monitoring program was initiated to better understand their origins as well as the complex chemistry occurring during transport from source to receptor. Specifically, the goals of the study were to characterize the atmospheric concentrations of nitrogen species in gaseous, particulate, and aqueous phases in RMNP and to identify the emission sources of these various species. The apportionment strategy was designed to focus on differentiating between sources within and outside the state of Colorado and then further differentiate between sources along the Front Range of Colorado and the rest of Colorado. It was also desirous to identify the relative contributions to atmospheric nitrogen species from mobile sources, agricultural activities, and large and small point sources within the state of Colorado. The Particle Source Apportionment Technology (PSAT) module available in the chemical transport model, the Comprehensive Air quality Model with extensions (CAMx), is used to develop first-principle estimates of the contributions from different areas of North America. The CAMx_PSAT results are combined with measured species concentrations in a receptor modeling approach to develop final estimates of source apportionment of the various species' concentrations and deposition.

1. Introduction

Increased deposition of nitrogen in Rocky Mountain National Park (RMNP) has been demonstrated to contribute to a number of important ecosystem changes (Fenn et al., 1998; Baron et al., 2000; Campbell et al., 2000; Rueth and Baron, 2002; Wolfe et al., 2003; Blett and Morris, 2004). The rate of deposition of nitrogen compounds in RMNP has crossed a crucial threshold called the "critical load" (Baron, 2006). This means that the changes occurring to park ecosystems may soon reach a point where they are difficult or

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impossible to reverse. Ecosystem change has been noted to occur more on the eastern slope, where nitrogen deposition levels are greater, than on the western slope of RMNP (Burns, 2003). Interestingly, it has been pointed out by Hand et al. (2011) and Lehmann et al. (2005) that, at RMNP, atmospheric particle concentrations of nitrate and nitrate wet deposition have increased by about 10–20% over the past ten years, while ammonium wet deposition has increased by about 50%. Current nitrogen deposition flux values appear to represent approximately a twenty-fold increase above pre-industrial values for the western United States (Galloway et al., 1982, 1995; Hedin et al., 1995).

Several key issues need attention to develop an effective strategy for protecting park resources from adverse impacts of elevated nitrogen deposition. These include determining the importance of previously unquantified nitrogen inputs within the park and of nitrogen sources and transport pathways. The Rocky Mountain Atmospheric Nitrogen and Sulfur (RoMANS) study was initiated to better understand the origins and physical/chemical and optical characteristics of nitrogen species as well as the complex chemistry occurring during transport from source to receptor. Assessing changes in ambient concentrations of aerosol and trace gas species and wet deposition as a function of changing ammonia and nitrogen oxide emissions is dependent on a number of chemical and physical mechanisms as well as meteorological conditions and transport characteristics.

Nitrogen oxides (NOx) and ammonia (NH_3) emissions, precursors to the formation of nitric acid and ammonium nitrate, arise from different source areas that are often not found in the same geographic region. As a species such as ammonium nitrate is transported over large distances, it volatilizes and reforms a number of times, maintaining thermodynamic equilibrium with ammonia and nitric acid that deposit from the atmosphere at greater rate than ammonium nitrate. If there is sufficient nitric acid along the transport pathway, a change in ammonia emissions at a more-distant ammonia source may or may not have much effect on measured ammonia concentrations at the receptor. This, of course, is also true for nitrate concentrations at a receptor site as they relate to more-distant NOx sources. Conversely, if nitric acid from a more-distant source is deposited before it can react with mid-distant ammonia sources, ammonia/ammonium transport may be inhibited. Also, ammonia can increase particle mass by reacting with acidic sulfate aerosols and organic acids, and nitric acid can add to particle mass by reacting with alkaline soil dust or sea salt aerosol. The condensation of ammonia onto particles is dependent on the acidity of the particles and ambient relative humidity. These reactions do not necessarily take place at or near the source of ammonia but over the transport pathways from source to receptor (Seinfeld and Pandis, 1998). Regardless of the chemical form and phase of the nitrogen, it will ultimately be deposited onto terrestrial or aquatic surfaces, but where these species are deposited depends on the chemical form and phase of the nitrogen.

These issues are potentially even more striking when trying to assess the transport of the more-volatile organic molecules, especially as they relate to smoke emissions. Semivolatile organic carbon (SVOC) emissions are released during the combustion process, volatilize as they disperse, and reconstitute into various secondary particles as they are transported and react over long distances (hundreds of kilometers). Furthermore, the measurement of species such as ammonia may be biased in relation to interpreting it as being representative of ammonia being transported from some source to the receptor or measurement site. The reaction of ammonia with nitric acid to form the reaction product, ammonium nitrate, is temperature and humidity dependent and can go from predominantly gases to particles with diurnal shifts in temperature and relative humidity. Molecules such as ammonium nitrate as well as some organics can deposit during cooler evening hours and re-volatilize during daytime hours. To some degree, diurnal cycling also occurs during plant respiration processes. Therefore, measured concentrations of species such as ammonia may not be solely the result of transport from distant sources but rather from re-emission of ammonia that was transported and deposited to the receptor site at another an earlier time.

Ultimately, it is desirous not only to know the relative contributions of sources and source areas to measured species concentrations at the receptor site but to also be able to answer the key regulatory question of how those concentrations change as emissions are incremented up or down ($\Delta C_i/\Delta E_j$). C_i is the concentration of species i, and E_j is some related emission species that contributes to C_i. Developing an understanding of $\Delta C_i/\Delta E_j$ is beyond the scope of this study.

To better understand these issues, a one-year study was initiated in November 2008 to characterize the atmospheric concentrations and deposition of measurable nitrogen species in gaseous, particulate, and aqueous phases (precipitation). The monitoring program consisted of intensive, high-time-resolution measurements of particles, gas, wet deposition, and meteorology at a core site in RMNP (Benedict et al., 2013a; Malm et al., 2013). Other objectives of the program were to identify the relative contributions to atmospheric nitrogen species in RMNP from within and outside of the state of Colorado; from emission sources along the Colorado Front Range versus other areas within Colorado; and from mobile sources, agricultural activities, and large and small point sources within the state of Colorado. This paper will focus on apportioning measured concentrations of nitrogen-containing aerosols at RMNP to sources of gaseous and particulate nitrogen-containing compounds using first-principle, deterministic modeling in combination with hybrid receptor modeling techniques.

2. Receptor attribution studies

The complex topography in this region, where mean observed wind directions can vary substantially within a few kilometers, presents a challenge for meteorological and source attribution models. The prevailing wind direction is generally westerly, but easterly upslope winds occur, due both to diurnal mountain–valley circulations and some synoptic weather patterns (Doesken et al., 2003). The most densely populated region of Colorado is the Front Range urban corridor (FRUC), located east of the park, running north–south through the center of the state along the transition between foothills and plains. Most agricultural activities are also east of the mountains, primarily in northeastern Colorado, including some in the FRUC, so understanding the easterly upslope flow is important. Additionally, the diurnal patterns of several factors that are influential for source attribution are all highly correlated. These include easterly winds, mixing heights, temperatures, ammonia emissions, and airborne concentrations of nitrogen compounds. All peak during midday, on average, making it difficult to separate their relative influences.

A variety of techniques to estimate contributions of sources to nitrogen have been employed. These include analyses of spatial and temporal patterns in observed airborne concentrations, snow pack, deposition, and meteorology (Lewis et al., 1984; Baron and Denning, 1993; Heuer et al., 2000; Losleben et al., 2000; Malm et al., 2009; Beem et al., 2010; Day et al., 2012; Benedict et al., 2013a), air mass back trajectory analyses (Sievering et al., 1996; Ingersoll et al., 2001; Malm et al., 2009; Gebhart et al., 2011, 2014), mesoscale chemical transport models (CTMs) (Neff, 1997; Malm et al., 2009; Rodriguez et al., 2011; Thompson et al., 2015) and hybrid techniques (Malm et al., 2009, 2013).

Several themes emerge from this work. Patterns in measured