A seasonal nitrogen deposition budget for Rocky Mountain National Park

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Abstract. Nitrogen deposition is a concern in many protected ecosystems around the world, yet few studies have quantified a complete reactive nitrogen deposition budget including all dry and wet, inorganic and organic compounds. Critical loads that identify the level at which nitrogen deposition negatively affects an ecosystem are often defined using incomplete reactive nitrogen budgets. Frequently only wet deposition of ammonium and nitrate are considered, despite the importance of other nitrogen deposition pathways. Recently, dry deposition pathways including particulate ammonium and nitrate and gas phase nitric acid have been added to nitrogen deposition budgets. However, other nitrogen deposition pathways, including dry deposition of ammonia and wet deposition of organic nitrogen, still are rarely included. In this study, a more complete seasonal nitrogen deposition budget was constructed based on observations during a year-long study period from November 2008 to November 2009 at a location on the east side of Rocky Mountain National Park (RMNP), Colorado, USA. Measurements included wet deposition of ammonium, nitrate, and organic nitrogen, $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 μm, nitrate, and ammonium) concentrations of ammonium, nitrate, and organic nitrogen, and atmospheric gas phase concentrations of ammonia, nitric acid, and NO_2. Dry deposition fluxes were determined from measured ambient concentrations and modeled deposition velocities. Total reactive nitrogen deposition by all included pathways was found to be 3.65 kg N·ha^{-1}yr^{-1}. Monthly deposition fluxes ranged from 0.06 to 0.54 kg N·ha^{-1}yr^{-1}, with peak deposition in the month of July and the least deposition in December. Wet deposition of ammonium and nitrate were the two largest deposition pathways, together contributing 1.97 kg N·ha^{-1}yr^{-1} or 54% of the total nitrogen deposition budget for this region. The next two largest deposition pathways were wet deposition of organic nitrogen and dry deposition of ammonia; combined they contributed 1.37 kg N·ha^{-1}yr^{-1} or 37% of the total nitrogen deposition budget. To better understand the nitrogen cycle and key interactions between the atmosphere and biosphere we need to include as many sources and types of nitrogen as possible and understand their variability throughout the year. Here we examine the components of the nitrogen deposition budget to better understand the factors that influence the different deposition pathways and their seasonal variations.

Key words: ammonia; atmospheric deposition; dry deposition; nitrogen; organic nitrogen; Rocky Mountains; wet deposition.

INTRODUCTION

Human activities have increased atmospheric concentrations of reactive nitrogen species and altered the nitrogen cycle. Changes have resulted from the production and use of fertilizer, fossil fuel combustion, increased production of nitrogen fixing crops, biomass burning, land clearing and conversions, and drainage of wetlands (Vitousek et al. 1997). As a result of increased nitrogen emissions, more atmospheric nitrogen is deposited in ecosystems, and the rate of nitrogen deposition has risen (Burns 2003, Galloway et al. 2008, Sutton et al. 2008). There have been many efforts around the world to measure and better understand current levels and impacts of nitrogen deposition, including studies in many European countries (Holland et al. 2005, Sutton et al. 2007, van der Swaluw et al. 2011, Kryza et al. 2012), China (Chen and Mulder 2007, Lui et al. 2011), and North America (Watmough and Dillon 2003, Burns 2004, Holland et al. 2005, Elser et al. 2009). In this work, we focus on understanding reactive nitrogen inputs to Rocky Mountain National Park

(RMNP). Protection of ecosystems is mandated by United States Federal Statutes including the Clean Air Act, the Wilderness Act, and the National Park Service Organic Act of 1969. Main goals of these acts include "prevention of significant deterioration" (42 USCS 7470) in National Parks, Forests, and Wilderness areas and an objective to "leave them unimpaired for future use and enjoyment" (16 USCS 1131). Understanding the processes and sources that lead to nitrogen deposition is important to keep protected areas from being severely and irreversibly impacted. This study focused on RMNP due to concerns about high levels of nitrogen deposition in the region but was also motivated by concerns that current estimates of nitrogen deposition in RMNP and elsewhere are missing important components.

Critical loads are ecosystem thresholds that have been established as a policy tool to protect areas from the negative effects of nitrogen deposition (Porter et al. 2005). They have been used extensively in Europe as a tool to aid in emission reduction targets (De Vries 1993, Hettelingh et al. 1995, Skeffington 1999, Matejko et al. 2009) and their use in U.S. policy has been increasing (Porter et al. 2005, Burns et al. 2008, Pardo et al. 2011). Critical loads can be calculated or empirically measured depending on available information and measurements and are based on the level at which negative changes occur (Williams and Tonnessen 2000, Baron 2006, Baron et al. 2011, Pardo et al. 2011, Nanus et al. 2012). Sediment cores have been used to examine ecological communities through time in RMNP lakes. There is evidence that diatom assemblages changed from ultra-oligotrophic to mesotrophic in four high-alpine lakes in RMNP (Wolfe et al. 2003). The change in diatoms took place between 1950 and 1964 when wet inorganic nitrogen deposition ($NH_4^+ + NO_3^-$) was approximately 1.5 kg $N \cdot ha^{-1} \cdot yr^{-1}$ (Baron 2006). Bowman et al. (2012) examined the ecological response of a dry alpine meadow community in RMNP by adding nitrogen to experimental plots and suggested a critical load of 3 kg $N \cdot ha^{-1} \cdot yr^{-1}$ based on the results. In the western United States, critical loads range from 1 to 3 kg $N \cdot ha^{-1} \cdot yr^{-1}$ while, in the northeastern United States, critical loads are higher, ranging from 3.5 to 6 kg $N \cdot ha^{-1} \cdot yr^{-1}$ (Baron et al. 2011). The spatial extent of nitrogen deposition in the West and levels at which effects occur remain poorly defined (Fenn et al. 2003). Efforts to define critical loads and wet deposition rates at high spatial resolutions indicate critical loads may be exceeded in approximately 21% of the Rocky Mountains and these areas are often at high elevations (Nanus et al. 2012).

Nitrogen is a limiting nutrient in many terrestrial systems (LeBauer and Treseder 2008) but when nitrogen is deposited beyond the ecosystem's capacity nitrogen saturation can occur. Nitrogen saturation happens when the nitrogen inputs from nitrogen mineralization and atmospheric deposition exceeds the ability of the ecosystem to process the nitrogen resulting in nitrate leaching (Johnson and Lindberg 1992). Leached nitrate has several effects including increased export of nutrient cations from the root zone and increased Al mobilization leading to reduced root activity and nutrient uptake (Johnson and Lindberg 1992, Vitousek et al. 1997). Leached nitrate will also travel to streams and bodies of water contributing to acidification (Aber et al. 1989, Vitousek et al. 1997, Fenn et al. 1998). Ecosystem response to nitrogen deposition is a function of the biome, strong interactions between the carbon and nitrogen cycles, and geography, including latitude, temperature, and precipitation (LeBauer and Treseder 2008). Many studies have linked changes in soils, lakes, and plants to increased nitrogen deposition (e.g., Rueth and Baron 2002, Bergstrom and Jansson 2006, Bowman et al. 2006). Resulting biological impacts from nitrogen saturation may include alteration of biota in a system, such as reduced species richness (Stevens et al. 2004) and increased biological production or eutrophication (Bergstrom and Jansson 2006). Growth of invasive species, alteration of fire cycles, and impacts on threatened and endangered species are also of concern in nitrogen saturated ecosystems (Fenn et al. 2003).

The timing and intensity of deposition may also be important factors determining the impact of nitrogen deposition on high-elevation ecosystems. Snow builds up during cold winter months withholding much of the deposited nitrogen until the snow melts in the spring, while summer rainstorms deposit nitrogen directly to the surface. The initial stages of snowmelt can have from three to six times higher concentrations than the bulk concentrations of snow from the same snow pit (Williams et al. 2002). The release of acidic species from snowpack melt can produce episodic acidification of surface waters. Johnson and Lindberg (1992) examined effects of atmospheric deposition on forest ecosystems and nutrient cycling at 11 sites in North America, including both wet and dry deposition fluxes, but did not investigate sites in the Rocky Mountain region. Concern about nitrogen deposition in the Rocky Mountains stems from impacts observed in more recent ecological studies in the region and special concerns over protecting national parks in the region, including Rocky Mountain, Grand Teton, Yellowstone, and Glacier National Parks. The Rocky Mountains are more susceptible to excess nitrogen inputs than many other regions, due to the geology and climate of the region. A limited soil horizon with exposed bedrock and short growing seasons limit vegetation growth and diversity in the region (Fenn et al. 1998). The greatest changes in RMNP have been observed in alpine lakes on the eastern slope of the continental divide where upslope winds can transport nitrogen species from the urban corridor located east of the park to well above 3000 m (Wolfe et al. 2003). Between 1995 and 1999 in the Rocky Mountains of Colorado and southern Wyoming, levels of wet inorganic deposition east of the continental divide ranged from 0.7 to 4.6 kg $N \cdot ha^{-1} \cdot yr^{-1}$ indicating the high spatial
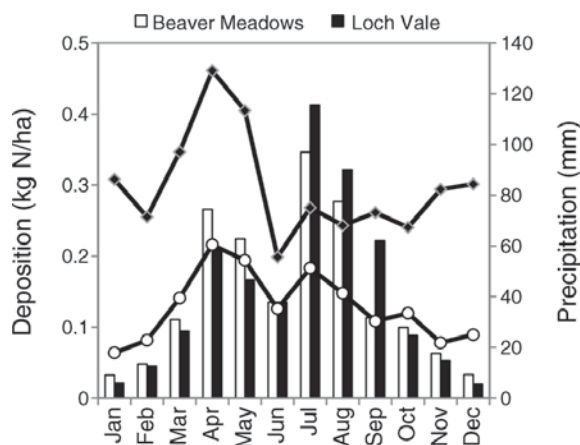
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Fig. 1. Monthly average deposition amounts (bars) from 2000–2011 at the Beaver Meadows (CO19; open bars, open circles) and Loch Vale (CO98; solid bars, solid diamonds) National Atmospheric Deposition Program (NADP) sites plotted with the average precipitation amount for each month (Beaver Meadows, open circles; Loch Vale, solid diamonds).

variability of nitrogen deposition and exceedance of the critical load at all but one site (Burns 2003).

There are other important nitrogen deposition pathways, beyond wet deposition of ammonium and nitrate, which are not accounted for by National Atmospheric Deposition Program/National Trends Network (NADP/NTN) measurements. The Clean Air Status and Trends Network (CASTNet) collects samples for air quality and dry deposition analysis. Measurements included in this network include gaseous nitric acid (HNO_3) and fine particle nitrate (NO_3^-) and ammonium (NH_4^+). Dry deposition is inferred from the product of measured airborne concentrations and modeled deposition velocities. The model used to determine deposition velocities for CASTNet is the National Oceanic and Atmospheric Administration multilayer inferential dry deposition velocity model (MLM; Meyers et al. 1998, Cooter and Schwede 2000). Inputs into this model include vegetation and surface characteristics such as distribution of major plant species and leaf area index (Clarke et al. 1997). Meteorological conditions are also measured at the site for inclusion in the model, including wind speed, wind direction, temperature, relative humidity, and surface wetness.

Sites from the NADP and CASTNet networks and the Interagency Monitoring of Protected Visual Environments (IMPROVE) network are located in RMNP. During most months, measured nitrogen wet deposition (ammonium and nitrate) rates are greater than estimated dry deposition (nitric acid and $PM_{2.5}$ [particulate matter with an aerodynamic diameter less than 2.5 μm] nitrate and ammonium) rates and, from March through August, wet deposition accounts for 65–80% of the monthly deposition. The spring/summer peak in wet deposition is driven by higher monthly mean precipitation amounts during this time of year (Baron and Denning 1993). Average monthly deposition from 2000

to 2011 in Fig. 1 shows the difference in precipitation at two NADP sites in RMNP but the more similar average deposition. Wet nitrogen deposition has two peak periods: April, when precipitation is high, and July, when concentrations and precipitation rates are large (Fig. 1). The inferred dry deposition rates are greatest during the summer months, peaking in June, when the particle and gaseous nitric acid concentrations measured by CASTNet are highest.

Not included in these national network measurements are dry deposition of ammonia and wet deposition of organic nitrogen, previously shown to be important to spring and summer nitrogen deposition in RMNP (Beem et al. 2010). We continue to recognize the importance of deposition pathways not included in national networks (e.g., Holland et al. 2005) but we still have a limited understanding of the spatial and seasonal variability of these deposition pathways. Here we examine a more complete annual reactive nitrogen deposition budget that includes dry deposition of NO_2 and ammonia and wet deposition of organic nitrogen, along with traditionally measured pathways including wet deposition of ammonium and nitrate and dry deposition of nitric acid, nitrate, and ammonium. We also provide a first look at dry deposition of $PM_{2.5}$ organic nitrogen. The importance of each of these pathways and the seasonal variability of nitrogen deposition in RMNP will be discussed. This in-depth look at the different deposition pathways can and should be extended to other areas improving the measurements and estimates of total reactive nitrogen deposition.

METHODS

Measurements were made in Rocky Mountain National Park during several different time periods. These observations were made on the eastern side of RMNP (40.2783° N, 105.5457° W; 2784 m) at the same location used for air monitoring by the IMPROVE and CASTNet programs and previously used as the core study site during RoMANS (Beem et al. 2010). Results presented here will focus mainly on one full year of measurements (11 November 2008 through 11 November 2009). For comparison and analysis of year-to-year variability, observations made in 2006 (25 March–6 April and 6 July–10 August) and 2010 (23 April–21 September) will also be presented. Observations of gas, particle, and precipitation chemistry were made during all sampling periods. Denuders and filter packs were used to collect 24-h samples for determination of gaseous NH_3 and HNO_3, and $PM_{2.5}$ NH_4^+ and NO_3^- concentrations. All samples were refrigerated or frozen until they were returned to our laboratory at Colorado State University where the analyses were performed. The 24-h samples were collected using URG annular denuder/filter-pack samplers (URG Corporation, Chapel Hill, North Carolina, USA) from 08:00 to 08:00 MST with a nominal flow of 10 L/minute at ambient

conditions. Actual sample volume was monitored by a dry gas meter. Denuders were coated with a sodium carbonate solution for collection of nitric acid and sulfur dioxide or with phosphorous acid solution to collect ammonia. Filters were extracted and analyzed by ion chromatography for major anions (Cl^-, NO_3^-, NO_2^-, and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}). Denuder extracts were analyzed either for ammonium (phosphorous acid-coated denuders) or for sulfate and nitrate (carbonate-coated denuders). Further details on the sample collection and analysis techniques can be found in Benedict et al. (2013). Detection limits were 0.21, 0.11, 0.07, and 0.03 $\mu g/m^3$ for HNO_3, NH_3, NO_3^-, and NH_4^+, respectively. Daily precipitation samples were collected using an automated precipitation collector (Yankee Environmental Systems, Turners Falls, Massachusetts, USA). Sampling buckets were cleaned with deionized (DI) water, shaken to remove water, covered with clean Al foil, and allowed to dry. The bucket was weighed prior to installation in the field and upon returning to the lab to determine the total collected precipitation volume. pH was measured after returning to the lab using a pH meter and combination pH electrode calibrated with pH 7 and 4 buffers. The remaining sample was frozen until analysis. Blanks were taken periodically by pipetting 30 mL of DI water into the bucket.

Precipitation samples were analyzed by ion chromatography for anions (Cl^-, NO_2^-, NO_3^-, SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}). Cations were separated on a CS12A column followed by a CSRS ULTRA II suppressor and a Dionex CD-20 conductivity detector (all from Dionex Corporation, Sunnyvale, California, USA). Anions were separated on a Dionex AS14A column followed by an ASRS ULTRA II suppressor (Dionex) and a Dionex CD-20 conductivity detector. Total nitrogen in the samples was measured using a Shimadzu TOC V_{CSH} total organic carbon (TOC) analyzer (Shimadzu, Kyoto, Japan) with a total nitrogen module. The analyzer measures total sample nitrogen as NO after high temperature oxidation on a catalyst. Organic nitrogen in RMNP samples was determined as the difference between total nitrogen and inorganic nitrogen ($NH_4^+ + NO_3^-$; nitrite was below detection in all samples and not included in the calculation) measured by ion chromatography. Several methods have previously been used to quantify total water soluble nitrogen (TWSN) in aqueous samples, including UV photo-oxidation and persulfate wet chemical oxidation. Both of these methods are labor intensive and have variable oxidation efficiencies (Scudlark et al. 1998). In addition, detection of inorganic nitrogen compounds, NH_4^+, NO_3^-, and NO_2^-, must take place before and after oxidation to determine the amount of organic nitrogen. High temperature oxidation (720°C) on a catalyst, in which all nitrogen compounds are converted to NO and detected by chemiluminescence, only requires a single measurement

of the inorganic components. This technique has been used by several investigators (Keene et al. 2002, Kieber et al. 2005, Gioda et al. 2008, Lin et al. 2010, Rastogi et al. 2011) to determine TWSN and water soluble organic nitrogen (WSON) concentrations in precipitation and aerosol samples. Tests in our laboratory showed high efficiency oxidation of a wide range of model organic and inorganic nitrogen compounds. Wet deposition fluxes were determined from the concentration of the sample, volume of the sample, sample period length, and cross-section area of the collection bucket. Detection limits (based on study blanks) for NH_4^+ and NO_3^- were 42 and 18 μg N/L and for total nitrogen the detection limit was 90 μg N/L in the precipitation samples.

Weekly $PM_{2.5}$ samples were collected using a Thermo Fisher Scientific TSP (total suspended particulate) high-volume sampler (ThermoScientific, Pittsburgh, Pennsylvania, USA) with a $PM_{2.5}$ impactor plate for determination of water soluble $PM_{2.5}$ organic nitrogen (PON). Whatman Quartz Microfibre Filters (20.3 × 25.4 cm; GE Healthcare Life Sciences, Piscataway, New Jersey, USA) were pre-baked to remove background carbon and nitrogen. After sample collection, filters were wrapped in aluminum foil and frozen until analysis. A portion of the filter was ultrasonically extracted in deionized water. Filtered extracts were analyzed for total nitrogen, ammonium, nitrate, and nitrite in order to determine water soluble organic nitrogen as the difference between total nitrogen and the sum of the inorganic nitrogen species concentrations. These weekly filters were collected from April through November 2009 and during the 2010 study.

NO_2 was measured using a Teledyne Instruments Ultra-Sensitive $NO/NO_2/NO_x$ Analyzer Model 200E (Teledyne Analytical Instruments, Industry, California, USA). The instrument was modified to be similar to the ultra-low concentration Model 200EU by using a gold-plated reaction cell and a high-vacuum pump to lower the reaction cell pressure to aid in detection of the low concentrations encountered. The inlet line consisted of a 4-m 1/4" (0.625 cm) outer diameter Teflon line with an inlet at a height of approximately 3 m above ground level and included a 47-mm Nylasorb inline particulate filter (2 um pore size; Pall, Ann Arbor, Michigan, USA) in a Teflon filter holder to remove particulate matter and HNO_3. This chemiluminescence analyzer converts NO_2 to NO using a high-temperature molybdenum converter at 315°C. NO is then detected by reaction with O_3, which forms NO_2 in an excited state and emits radiation as it decays to ground state (Fontijn et al. 1970). The detected radiation is proportional to the NO concentration. Concentrations of NO_2 were calculated from the response of previously analyzed standards. Calibration relied on nightly zeroes, span concentrations of 20 ppb (corresponding to the upper end of the concentrations measured at the site), and gas phase titration using a Teledyne-API zero air generator (Teledyne-API model

TABLE 1. Source and range of deposition velocities (V_d) from the Multilayer Deposition Velocity Model (MLM) that were calculated over the course of the year-long study for the sampling site.

| | V_d (cm/s) | | |
Species	Minimum	Maximum	Source
$PM_{2.5}$	0.007	0.48	MLM
HNO_3	0.13	3.34	MLM
NH_3	0.09	2.34	$0.7 \times V_d(HNO_3)$†
NO_2	0.064	0.12	$0.667 \times V_d(O_3)$†

† V_d from MLM.

701) and dilution calibrator (Teledyne-API model 700E).

The gas calibration standard was a NIST-traceable NO source gas mixture (NO, SO_2, and CO mixed with a balance of oxygen-free nitrogen, Scott-Marrin Specialty Gases, Riverside, California, USA) Periodically, other test gas concentrations down to approximately 4 ppb were generated to ensure linear response. The conversion is not specific to NO_2 (Demerjian 2000, Parrish and Fehsenfeld 2000, Dunlea et al. 2007) and other NO_y compounds that pass through the Nylasorb filter and sample inlet line may be detected simultaneously, so measured concentrations should be treated as an upper bound on actual NO_x concentrations.

Dry deposition was not directly measured during this study. Instead dry deposition was calculated based on the atmospheric concentration of the species of interest and deposition velocities determined from co-located CASTNet observations. Deposition velocities are modeled with the NOAA Multilayer Deposition Velocity Model (MLM) described by Meyers et al. (1998). The model separates the vegetative canopy into 20 layers and only requires input of meteorological data after the inclusion of site survey data. Each CASTNet site is surveyed for input information including type and quantity of vegetation, which includes an estimation of leaf area index (LAI). Deposition velocities (V_d) were calculated by CASTNet using the MLM for nitric acid and fine particles ($PM_{2.5}$ ammonium, nitrate, and organic nitrogen).

The deposition velocities for ammonia and NO_2 are not modeled in the MLM. Multiple studies have indicated a compensation point for NO_2 (Hanson and Lindberg 1991, Thoene et al. 1991, Sparks et al. 2001, Teklemariam and Sparks 2006) and have observed bidirectional exchange of NH_3 (Sutton et al. 1995, Wyers and Erisman 1998, Sutton et al. 1999). NO_2 bidirectional exchange is related to stomatal conductance (Saxe 1986, Hanson and Lindberg 1991, Hargreaves et al. 1992, Weber and Rennenberg 1996, Sparks et al. 2001, Gut et al. 2002, Teklemariam and Sparks 2006, Eller and Sparks 2006, Sparks 2009) while NH_3 exchange applies to both the leaf surface and stomata (Wyers and Erisman 1998). Since modeling the flux and exchange of these species was beyond the scope of the

project we scaled NH_3 and NO_2 deposition velocities to the deposition velocities calculated for other species in the MLM to estimate NO_2 and NH_3 dry deposition contributions to the overall reactive nitrogen deposition budget. Following the approach previously used by Beem et al. (2010), the deposition velocity for ammonia was estimated as 70% of the MLM nitric acid deposition velocity. In a similar approach as for ammonia, the O_3 deposition velocity at the site was scaled by two-thirds to estimate the dry deposition velocity of NO_2, as this relationship was observed by Wesely and Eastman (1982) from eddy covariance measurements. Estimated deposition velocities of NO_2 ranged from 0.064 to 0.12 cm/s, similar to measured and calculated NO_2 deposition velocities from other studies (Hanson and Lindberg 1991, Joss and Graber 1996, Zapletal 1998, Stutz et al. 2002). Low NO_2 concentrations observed in RMNP suggest we are generally below the compensation points, so that NO_2 deposition estimates likely represent an upper bound. Nitric oxide (NO) deposition velocities are small compared to NO_2 (Hanson and Lindberg 1991) and at this site NO_x is primarily composed of NO_2 (88% on average). Consequently, we did not determine a dry deposition flux for NO. The range of deposition velocities computed for this study and their source are presented in Table 1.

RESULTS AND DISCUSSION

Yearly deposition budget

Wet deposition occurs when species are removed from the atmosphere by clouds and precipitation and dry deposition occurs when gas and particle phase species are transferred directly to the earth's surface without precipitation. Occult deposition, which includes scavenging and deposition by fog or cloud droplets, without precipitation, is not considered in this study due to a low frequency of fog and cloud interception events at the study site. At higher elevation sites in RMNP, occult deposition may be an important factor and should be investigated. Collett and co-workers (Collett et al. 1991a), for example, showed a strong increase in cloud interception and occult deposition at higher elevations in the Sierra Nevada.

There are many factors that influence the rate of wet and dry deposition pathways. Cloud and precipitation microphysical properties and in-cloud and below cloud scavenging efficiencies, along with gas solubility and particle sizes, exert an important influence on wet deposition. Dry deposition is governed by a number of factors, including boundary layer conditions, surface properties, and the properties of the depositing gases and particles.

Dry deposition of nitrogen species is also strongly influenced by atmospheric concentrations. In Fig. 2, the monthly average RMNP concentrations of gaseous ammonia, nitric acid, and nitrogen dioxide and $PM_{2.5}$ ammonium and nitrate are presented for the year-long study period. Both nitric acid and ammonia had similar
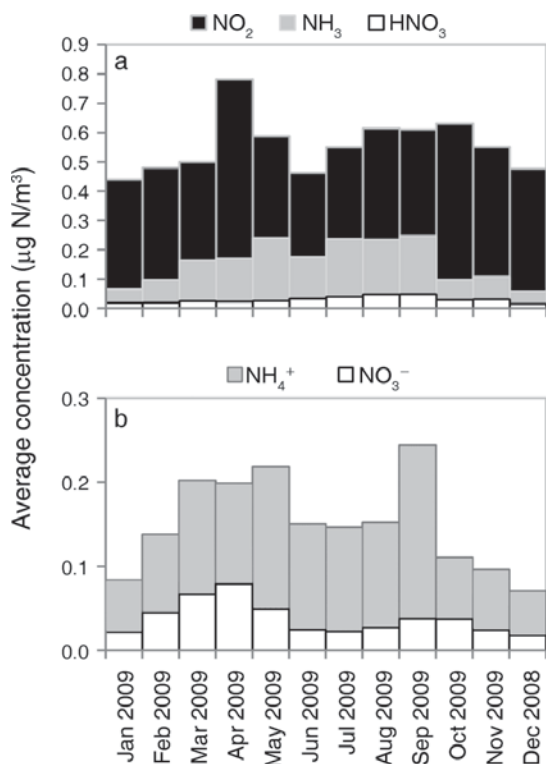
Fig. 2. Average monthly atmospheric concentrations for (a) gaseous NH$_3$, HNO$_3$, and NO$_2$ and (b) particulate matter with an aerodynamic diameter less than 2.5 μm (PM$_{2.5}$) NH$_4^+$ and NO$_3^-$. Concentrations are displayed as the mass of N in a given species per volume of air, to facilitate comparisons between concentrations of different species. The 2008 December observations are plotted at the right of the figure to visually conform to a typical annual calendar arrangement.

monthly trends with concentrations highest in the late summer and lowest in the winter (Fig. 2a). Monthly average ammonia concentrations were highest during May and from July through September at approximately 0.24 μg N/m^3. Nitric acid concentrations peaked during August and September at approximately 0.05 μg N/m^3. Monthly average nitric acid concentrations were always lower than ammonia (Fig. 2a) in RMNP and PM$_{2.5}$ nitrate concentrations were always lower than ammonium (Fig. 2b). Concentrations of NH$_3$, NH$_4^+$, HNO$_3$, and NO$_3^-$ were low from October through January. Monthly average concentrations of NO$_2$ were higher than NH$_3$ and HNO$_3$ concentrations during the entire year, peaking in April and October.

Annual reactive nitrogen deposition, from 11 November 2008 through 10 November 2009, was determined to be 3.65 kg N/ha. This deposition budget includes wet deposition of nitrate, ammonium, and organic nitrogen and dry deposition of ammonia, nitric acid, nitrogen dioxide, and PM$_{2.5}$ ammonium, nitrate, and organic nitrogen. One potentially important missing component is dry deposition of gas phase organic nitrogen. The critical load for RMNP was established based on the sum of wet deposition of nitrate and

ammonium and does not consider wet deposition of organic nitrogen or any dry deposition pathways. In the current study, wet deposition of ammonium plus nitrate totaled 1.97 kg N/ha for the year, well in excess of the established critical load for the region of 1.5 kg N·ha^{-1}yr^{-1} (Baron 2006). These results indicate deposition in Rocky Mountain National Park is at the level where nitrogen deposition will negatively impact ecosystems in the region. Other regional studies have found similar and in some cases higher (Williams et al. 1996, Burns 2003) deposition totals, likely a function of the complex transport and topography in the region as well as interannual variability in precipitation and atmospheric reactive nitrogen concentrations.

Wet deposition is the largest contributor to RMNP reactive nitrogen deposition as seen in Fig. 3. Wet deposition of ammonium contributes the most to total deposition (35% of the total budget) followed by wet deposition of nitrate (19%). Dry deposition of ammonia and wet deposition of organic nitrogen are the third and fourth largest contributors to reactive nitrogen deposition, contributing 18% and 17% of the total budget, respectively. Neither of these two deposition pathways is routinely monitored. Dry deposition of nitric acid contributes 6% of the budget. Much smaller contributions are made by dry deposition of ammonium (3%) and dry deposition of gaseous nitrogen dioxide, water soluble PON, and nitrate (each less than 1%).

The contribution of ammonia dry deposition may be even larger than estimated here since the deposition velocity relationship used to estimate ammonia deposition velocities is likely a conservative estimate. Several studies have found the deposition velocity of ammonia to be similar to or greater than the deposition velocity for nitric acid (Harrison and Allen 1991, Andersen and Hovmand 1995, Neirynck et al. 2007) while the ammonia deposition velocity assumed here, also based on a literature review, was 70% of the nitric acid deposition velocity. On the other hand, reemission of deposited NH$_3$ would reduce the effective deposition of
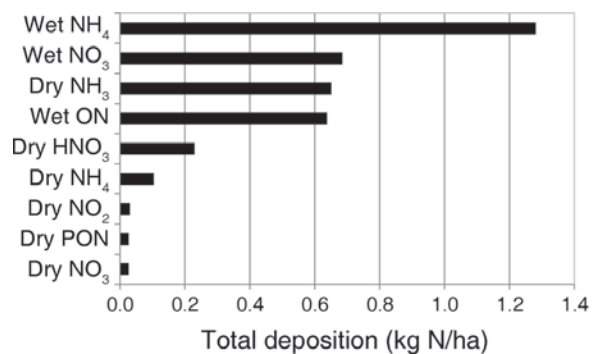

Fig. 3. Total deposition by pathway for a year of measurements beginning November 2008. Measurements of PM$_{2.5}$ organic nitrogen (PON) began in April 2009 and continued through November 2009. The plotted PON deposition amount represents only contributions from this eight-month period.

TABLE 2. Influence of NH₃ deposition velocity scaling factor on ammonia and total nitrogen deposition.

NH₃ scaling factor†	NH₃ dry deposition (kg N/ha)	Total deposition (kg N/ha)	NH₃ contribution (% of total)
0	0	3.02	0
0.5	0.39	3.41	11
0.7	0.54	3.56	15
1.0	0.77	3.79	20
2.0	1.54	4.57	34

Note: A scaling factor of 0.7 was used as the base case.
† Assumed ratio of the deposition velocities of ammonia to nitric acid.

NH₃ (Walker et al. 2006). By scaling the deposition velocity of ammonia to nitric acid, meteorological and surface characteristics of the site are included, which is an improvement from selecting one NH₃ deposition value for all days. Since modeling the bidirectional exchange of NH₃ was beyond the scope of this project we examine the influence of the NH₃ deposition velocity scaling factor on the deposition total and the importance of the NH₃ dry deposition pathway. The deposition velocity of HNO₃ was scaled by a range of values that have been observed in literature (Table 2); across a range of scaling factors from 0.5 to 2.0, the contribution of NH₃ dry deposition to total nitrogen deposition varies from 11% to 34%.

Particle dry deposition contributions for all species are small because of slow removal of fine particles to the surface (Seinfeld and Pandis 2006). The $PM_{2.5}$ water soluble organic nitrogen (PON) dry deposition estimate represents a lower bound on this pathway; PON concentrations were measured for only eight months of the year, from April to November. Concentrations of fine particle species tend to be low, however, during winter at the site (see Fig. 2). Additionally, the measured PON concentrations reflect only the water soluble fraction of fine particle organic nitrogen. Water insoluble forms of organic nitrogen would likely not be captured by the total nitrogen measurement of the filtered aqueous aerosol extracts.

Coarse nitrogen-containing particles are not included in the nitrogen deposition budget, which included only $PM_{2.5}$ aerosol. Several studies have observed organic nitrogen in the coarse particle mode (Nakamura et al. 2006, Calderon et al. 2007) and primary biological aerosols, including proteins, spores, and algae, can be a significant source of atmospheric aerosol (Jaenicke 2005) and atmospheric nitrogen that we did not include in our measurements. Inorganic nitrogen can also be present in coarse particles and is often associated with sea salt and dust in nonurban areas (Lee et al. 2008). Coarse sea salt is unlikely to be important at RMNP due to its limited atmospheric residence time and distance from the coast; however, nitrate in reacted dust particles may be important. The Thermo Fisher Scientific TSP aerosol sampler used in this study does have a first-stage filter that collects particles larger than $PM_{2.5}$. Analyses of these filters indicate total nitrogen concentrations of coarse aerosol particles were approximately a factor of 10 lower on average than total nitrogen concentrations of $PM_{2.5}$. The low concentrations of coarse particle nitrogen, however, are offset by higher deposition velocities for larger particles. Future studies should measure the concentrations and size distribution of coarse particle nitrogen to permit an estimate of its contribution to regional deposition budgets.

Measurements of gas phase organic nitrogen (ON) were not included in this study. A lack of knowledge about the species present, or their concentrations, makes estimating the amount of dry gas phase ON deposition flux difficult. In addition, very little is known about the deposition velocities of gaseous ON species. Some work has been done to investigate the deposition of several ON species (e.g., Farmer et al. 2006) but we presently lack sufficient information to quantify this component of nitrogen deposition for RMNP.

Examining the relative inputs of reactive nitrogen (excluding PON) by month (Fig. 4), we see that monthly deposition amounts varied from 0.06 to 0.54 kg N/ha. Wet deposition was greater than 50% of total nitrogen deposition in every month except December. Wet deposition of NH_4^+ was almost always the single largest contributor; however, in March wet deposition of organic nitrogen exceeded wet deposition of ammonium. Wet deposition of NO_3^- varied between 8% and 28% of the monthly total. Dry deposition of nitrate and ammonium were always small and ammonia deposition always exceeded nitric acid dry deposition. In the sections below we investigate the deposition pathways individually to better understand the factors that control deposition at this site.

Components of deposition

Wet deposition.—NADP records indicate April and July are the most important months for wet inorganic nitrogen deposition at the RMNP Loch Vale and Beaver Meadows sites (Fig. 1). This is fairly consistent with the results of our three field campaigns. In Fig. 5, wet nitrogen deposition totals are plotted for our three RMNP field campaigns (2006, 2008–2009, 2010) along with the precipitation total for each month of measurements. Wet nitrogen deposition is higher from April to July. Interestingly, wet nitrogen deposition fluxes in all three study years are fairly similar, despite more than a factor of three variability in precipitation amount. Wet deposition is expected to show some correlation with precipitation amount and often higher deposition totals are observed when there was more precipitation (e.g., April). However, January illustrates that this isn't always the case; total precipitation amount in January was rather high while the deposition for the month was low.

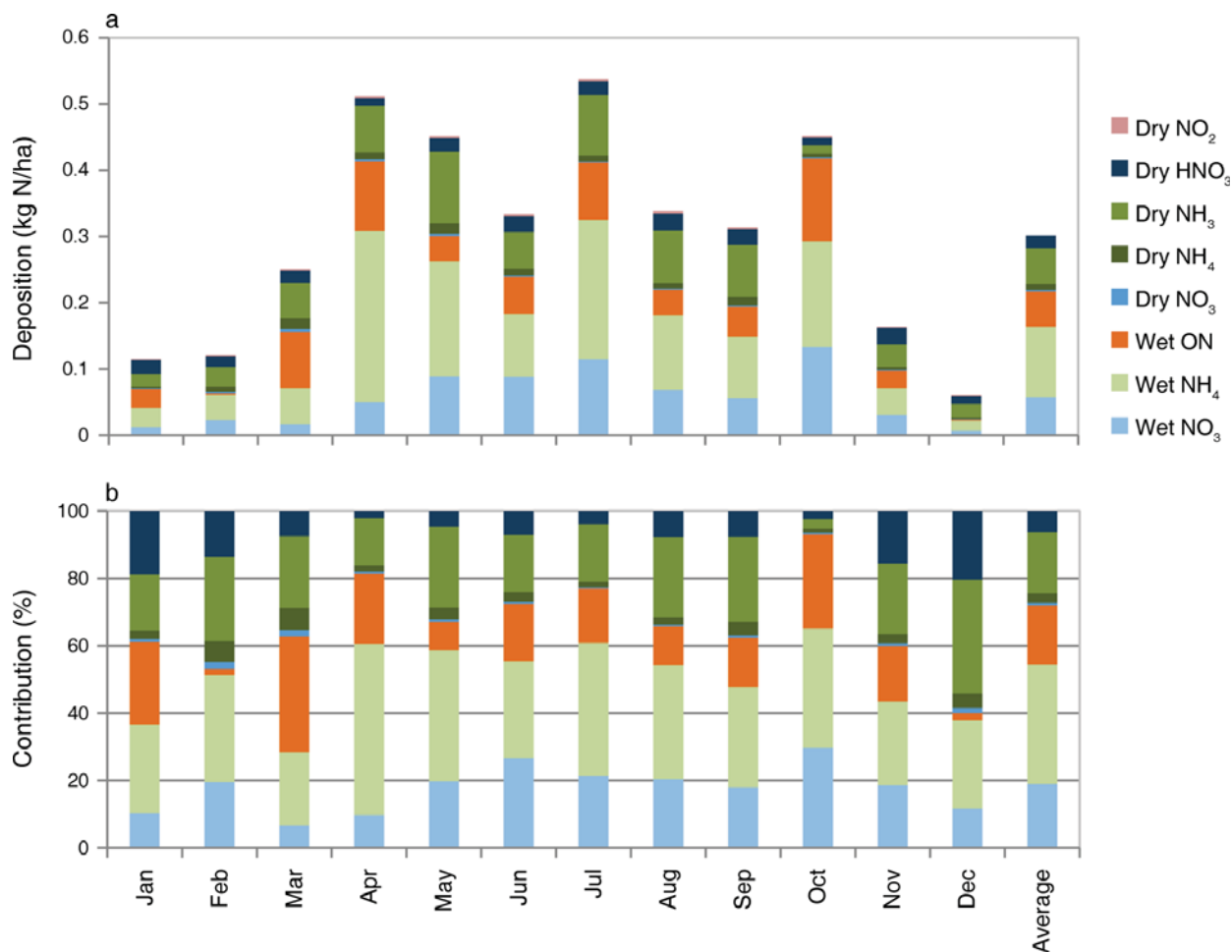In addition to precipitation amount, wet deposition fluxes can also be strongly influenced by the airborne

FIG. 4. (a) Total and (b) relative contributions to total nitrogen deposition for each pathway by month. The monthly average is also included. The blue shades indicate $N^{(V)}$ species while the green shades indicate the $N^{(-III)}$ species. Organic nitrogen is shown in orange, and NO_2 is in pink. Dry deposition of PON is not included because it was only available for 8 of the 12 study months.
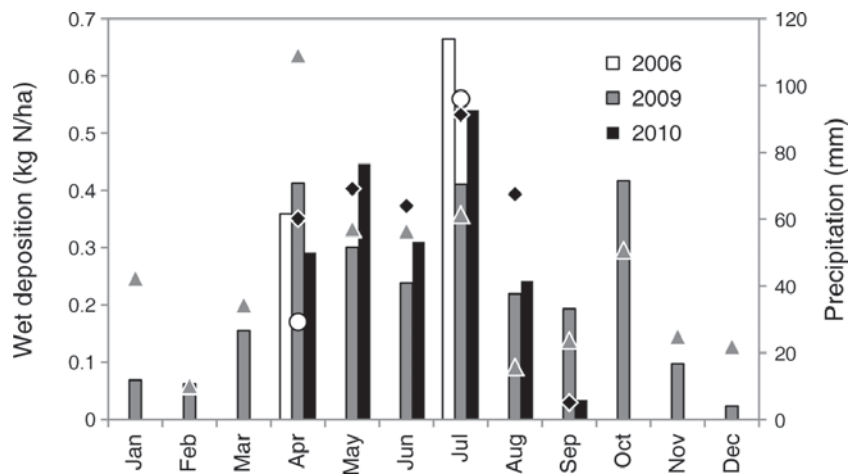

FIG. 5. Comparison of monthly wet deposition totals (bars) for each study period and the amount of precipitation for each month (symbols).
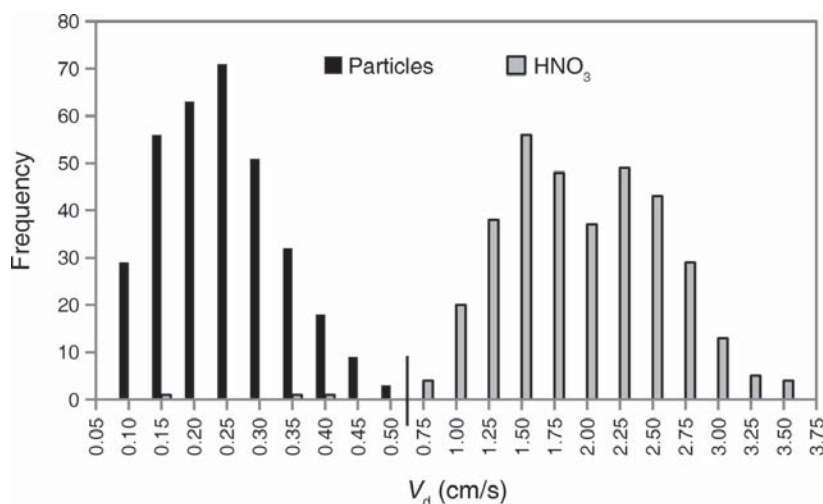
FIG. 6. Distribution of daily dry deposition velocities (V_d) from the Multilayer Deposition Velocity Model (MLM) for particles (black) and nitric acid (gray). Note that divisions in the x-axis scale are different in the right and left halves

concentrations of reactive nitrogen species available to be scavenged. In Benedict et al. (2013), the importance of easterly upslope winds transporting pollutants to RMNP was illustrated. The strong vertical lifting associated with these upslope events also lead frequently to precipitation formation. Based on the local wind direction measured at RMNP, upslope flow from the east occurred less than 20% of the time (based on hourly winds) and during upslope winds (40–160°), precipitation fell less than 15% of the time. However, more than 50% of the yearly nitrogen wet deposition occurred during easterly upslope winds, indicating a strong nitrogen deposition contribution from source areas east of RMNP. These observations support the expectation that wet deposition fluxes depend on meteorological conditions that yield high nitrogen species concentrations in RMNP and also produce precipitation. The efficiency with which pollutants are scavenged and deposited by precipitation can also be strongly influenced by cloud microphysical processes such as the extent of ice crystal riming (e.g., Collett et al. 1991b), an issue not investigated in the current study.

Overall, wet deposition of ammonium and nitrate from this study (1.97 kg N·ha^{-1}·yr^{-1}) is slightly lower than the 11-year average (2000–2011) for both Beaver Meadows (2.0 kg N·ha^{-1}·yr^{-1}) and Loch Vale (3.0 kg N·ha^{-1}·yr^{-1}). In 2009, wet nitrogen deposition at Beaver Meadows was 1.3 kg N·ha^{-1}·yr^{-1} and at Loch Vale it was 2.5 kg N·ha^{-1}·yr^{-1}. The difference in deposition may reflect spatial and elevational differences in precipitation and potentially an east to west gradient in deposition. In 2009 RMNP October deposition was similar to April deposition, which contrasts with the 2000–2011 average monthly NADP deposition pattern shown in Fig. 1. Wet nitrogen deposition in October is on average much lower than in April. The total precipitation during October 2009 was similar to the 11 year average suggesting that the observed deposition enhancement may have resulted

from greater pollutant transport into the park or greater coupling between periods of pollutant transport and precipitation. In general, lower precipitation amounts and lower gas and particle phase nitrogen species concentrations in the fall and winter tend to keep wet deposition low during those months.

Dry deposition and deposition velocities.—Dry deposition was determined using measured airborne concentrations and deposition velocities determined from the collocated CASTNet monitoring station. Deposition velocities vary with the chemical species and the surface to which deposition is occurring. Summer features higher concentrations of the species of interest (Fig. 2) and deposition is also higher. Gas phase deposition of NH_3 is the largest contributor to dry deposition (Fig. 4). Deposition of NH_3 varies more month to month than HNO_3 due to larger changes in atmospheric concentrations. Of the measurements that took place over the whole year, dry deposition of NO_3^- is the smallest dry deposition pathway considered here. While the atmospheric concentrations of both NO_3^- and NH_4^+ were low compared to NO_2, NO_2 deposition for the year was similar to NO_3^- and NH_4^+, reflecting its low deposition velocity. The atmospheric concentration is often the dominant term in seasonal changes in nitrogen deposition flux at this site for both gases and particles suggesting that in areas where deposition velocity hasn't been explicitly measured or calculated, an estimate of the deposition velocity may be adequate to determine an approximate deposition flux or at least its seasonal variability. This is due to the larger range and magnitude of measured concentrations compared to the deposition velocities calculated by CASTNet.

The distribution of modeled RMNP deposition velocities for nitric acid and fine particles are illustrated in Fig. 6. Here we see both the spread in deposition velocities across the year for a given species and the much larger values computed for nitric acid than for fine

particles. The phase, gas or particle, of the species is an important factor influencing the deposition total; HNO_3 deposition velocities are typically approximately ten times higher than fine particle deposition velocities. This is an important factor when considering seasonal differences in deposition. Even if concentrations of $N^{(-III)}$ ($NH_3 + NH_4^+$) or $N^{(V)}$ ($HNO_3 + NO_3^-$) do not vary much across seasons, changes in gas-particle partitioning can have a large impact on dry deposition fluxes. For example, higher temperatures and lower relative humidities both favor dissociation of particulate ammonium nitrate to release gaseous nitric acid and ammonia. To examine the impact of partitioning on deposition fluxes we consider a bounding scenario where all $N^{(-III)}$ and $N^{(V)}$ are in the gas phase, as this would yield the maximum amount of nitrogen deposited. Although this situation is not typical, it illustrates a limiting bound of the problem. Partitioning all $N^{(-III)}$ to the gas phase (i.e., all ammonium is present as ammonia) would increase $N^{(-III)}$ dry deposition by 59% or 0.5 kg N/ha. If all $N^{(V)}$ is in the gas phase (i.e., all nitrate is present as nitric acid) $N^{(V)}$ dry deposition would increase by approximately 55% or 0.2 kg N/ha. These numbers aren't insignificant; under this scenario, gas phase dry deposition of $N^{(-III)}$ would be 1.23 kg N/ha for the year and become the second largest nitrogen deposition pathway.

Another important consideration is how species lifetimes differ between particles and gases. Particles have longer atmospheric lifetimes (due to their lower deposition velocities) and are more likely to get transported to RMNP, while ammonia and nitric acid gases will deposit to surfaces faster limiting their atmospheric lifetimes and transport distances. Large emissions of ammonia on the eastern plains of Colorado and large emissions of NO_x (which reacts to form HNO_3) in the Front Range urban corridor create an ideal situation for formation of particulate ammonium nitrate, which has a longer lifetime than the gas phase precursors and is more likely to survive long enough in the atmosphere to be transported to RMNP. If only urban emissions existed, NO_x would still form nitric acid but much of this fast-depositing gaseous product would be removed from the atmosphere before it could be transported all the way to RMNP. Likewise, if only agricultural sources existed, much of the emitted ammonia would be rapidly removed by dry deposition and the amount surviving transport to RMNP would be decreased. To illustrate this we consider a very simple case to compare the transport distance required for the concentrations of NH_3, NH_4^+, HNO_3, and NO_3^- to fall to $1/e$ of their original value using average concentrations and deposition velocities for each species in an atmosphere with a mixed layer depth of 500 m and a wind speed of 1 m/s, a typical wind speed observed during upslope flow at the study site. Under this scenario, NH_3 would travel approximately 32 km for its concentration to fall to $1/e$ of its original value.

Similarly, HNO_3 would travel approximately 23 km and both NO_3^- and NH_4^+ would travel approximately 126 km. The Front Range is approximately 37 km east of RMNP suggesting the particle forms of these nitrogen species are more likely to make it to RMNP than the gas phase. The combination of NO_x and ammonia emission sources east of RMNP, along with the periodic occurrence of upslope easterly winds that carry these reacting emissions west into the park and simultaneously produce substantial precipitation, all combine to produce elevated reactive nitrogen deposition fluxes in the park.

Organic nitrogen

This study provided the first opportunity to examine how RMNP organic nitrogen deposition varies throughout the year. Previous studies have measured organic nitrogen in precipitation but often for shorter time periods. Previous measurements in southern Quebec, Canada, found that organic nitrogen was 38% of total wet nitrogen deposited (Dillon et al. 1991). In the Colorado Front Range 16% of wet nitrogen deposition was organic (Williams et al. 2001) and higher contributions have been estimated in some coastal areas (e.g., 59% in Gainesville, Florida, USA [Hendry and Brezonik 1980]). In Tampa Bay, Florida, organic nitrogen comprised 8.9% of total nitrogen in rainwater (Calderon et al. 2007). Previous measurements in RMNP during spring and summer of 2006 found organic nitrogen to contribute 23% and 20%, respectively, to wet nitrogen deposition and 17% and 12%, respectively to total quantified nitrogen deposition (Beem et al. 2010).

In the yearlong 2008–2009 RMNP data set, wet deposition of organic nitrogen constituted 18% of total quantified reactive nitrogen deposition and 25% of wet nitrogen deposition. The highest relative contributions to wet deposition were observed in January (40%) and March (55%) and the lowest in February (3%), December (6%), and May (13%). Relative contributions for the remaining months vary between 17% and 30%. The relative contributions depend not just on changing organic nitrogen sources but on changes in ammonium and nitrate as well. We might expect higher concentrations of organic nitrogen during the spring and summer when biological activity is high as others have observed (Jordon et al. 1995, Kieber et al. 2005) but if anthropogenic sources contribute significantly to observed atmospheric organic nitrogen concentrations and/or atmospheric concentrations of inorganic nitrogen are higher because of increased emissions, the relative change could be small. Biomass burning is another potential source of organic nitrogen compounds (Lobert et al. 1990, Mace et al. 2003). There is a seasonal cycle to biomass burning and the source is intermittent so a clear signal may be difficult to distinguish in the precipitation samples. Absolute values of organic nitrogen deposition are high throughout the spring and summer and low in the winter, which may at least

partly reflect seasonal precipitation rates as the pattern is similar to total wet deposition (Fig. 5).

More information is needed to better understand the sources of organic nitrogen, its composition and mechanisms that control the atmospheric concentration. The biological availability of the organic nitrogen compounds and effects on an ecosystem are poorly understood. Determining the anthropogenic and natural contributions to atmospheric organic nitrogen will improve our understanding of the impact of organic nitrogen on sensitive ecosystems and whether total wet organic nitrogen fluxes are likely to have changed substantially with increased human activity in the Rocky Mountain region.

Conclusions

This study provided the most comprehensive examination to date of reactive nitrogen deposition in RMNP. Total monthly deposition nitrogen ranged from 0.06 to 0.54 kg N/ha. Overall, wet nitrogen deposition exceeded dry nitrogen deposition almost every month. Wet nitrogen deposition fluxes were highest April through July when upslope transport events that move air westward from source regions east of RMNP bring both higher concentrations of atmospheric species and more precipitation to the park. Greater isolation of the high elevation terrain of RMNP from lower elevation source regions in winter yields lower RMNP airborne pollutant concentrations in winter. Precipitation is also lower in the winter. The combination of these two factors results in lower nitrogen deposition during winter months.

The current critical load for nitrogen deposition in RMNP is based on wet deposition of ammonium and nitrate. Our analysis clearly indicates that these two pathways make the largest contributions to RMNP reactive nitrogen deposition but only contributed approximately 50% to total nitrogen deposition. Wet deposition of organic nitrogen and dry deposition of ammonia, which have historically not been routinely monitored, together contribute 1.37 kg N·ha^{-1}·yr^{-1} or 37% of the total nitrogen deposition budget for RMNP. Both of these deposition pathways are larger contributors to the total nitrogen deposition budget than the dry deposition pathways that are typically quantified by CASTNet: dry deposition of nitric acid and fine particle nitrate and ammonium. An important question from these results is: what does the critical load mean if it was established using only wet deposition of ammonium and nitrate when significant deposition of other nitrogen species was also occurring? Prediction and understanding of the nitrogen biogeochemistry in RMNP is not complete without including wet and dry deposition of organic nitrogen and dry deposition of ammonia. Including these pathways is particularly important if a modeled mass balance approach to determine critical loads is to be utilized where inputs and output of

nitrogen are examined over time since nitrogen retention will also be underestimated (Cornell 2011).

There are limited spatial and temporal records of wet organic nitrogen deposition and atmospheric NH$_3$ concentrations to assess how these values have changed over time or how they factor into the changes observed in ecological communities. Adding these species to routine national network measurements and to field studies will allow us to determine the importance of these deposition pathways in other regions. Efforts are currently underway to expand measurements of wet organic nitrogen deposition within the NADP program while the addition of the Ammonia Monitoring Network (AMON) will help to close the gap in regard to concentrations of NH$_3$. Both of these efforts are important contributions to improved characterization of U.S. reactive nitrogen deposition budgets.

Uncertainties in the deposition budget presented here mainly arise from dry deposition velocities. This is an area where more research is needed to continue to understand the bi-directional exchange of NO$_2$ and NH$_3$ and to find ways to improve field measurements for widespread use. Further work to quantify the types of organic nitrogen that contribute most to deposition is also needed to understand potential sources and the relative contributions of anthropogenic and natural sources. The types of organic nitrogen species present may reveal information about the sources and bioavailability of organic nitrogen. It would also be informative to examine spatial trends in the types of species and their concentrations and to investigate if these factors change across elevation gradients and between urban and remote regions.

We combined analysis of atmospheric transport with deposition measurements to understand the regional factors that shape the RMNP nitrogen deposition budget, including the sources of different types of nitrogen compounds and the meteorology associated with locally complex mountainous terrain. While major sources of both oxidized and reduced nitrogen are located east of RMNP, a direction that is typically downwind, periodic changes in flow that move air from east of RMNP up against the east slope of the Rockies transport emissions from these large urban and agricultural sources into the park while also frequently producing heavy precipitation. Understanding these patterns can help in devising more effective deposition mitigation strategies to protect RMNP. In other regions where excess nitrogen deposition is a concern, the complex interplay between source and receptor location and the regional meteorology that affects both transport and precipitation should also be considered.

This study illustrates the benefits of a comprehensive analysis of atmospheric transport and deposition pathways for understanding the sources and seasonal variability of nitrogen deposition. While one site cannot fully capture the spatial variability of nitrogen deposition across a watershed we can use it to identify the

types and time resolution of the measurements that are most important for a watershed-scale study. For instance, wet deposition of ammonium, wet deposition of nitrate, dry deposition of NH_3, and wet deposition of organic nitrogen are important to include in monitoring in RMNP but in other areas, the relative importance of the nitrogen deposition pathways may change and different deposition pathways may need to be prioritized. If we are to fully appreciate the sources and mechanisms that contribute to excess nitrogen deposition in RMNP or other regions, it is clear that a comprehensive monitoring approach is required.

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