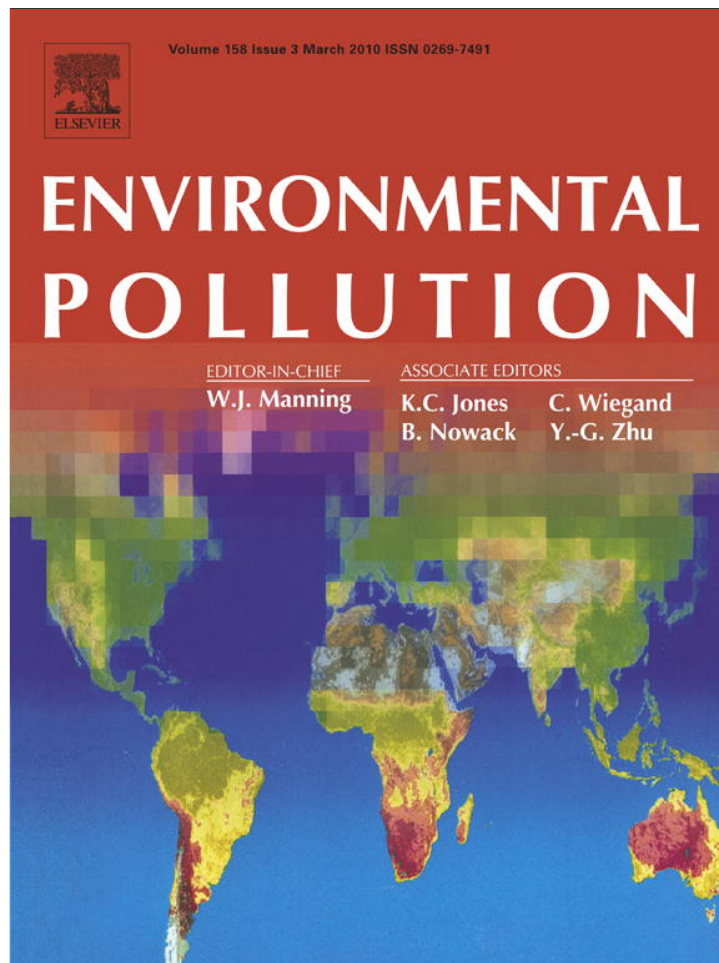


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## Deposition of reactive nitrogen during the Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) study

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The reactive nitrogen deposition budget for Rocky Mountain National Park.

### ARTICLE INFO

#### Article history:

Received 29 April 2009

Received in revised form

10 September 2009

Accepted 23 September 2009

#### Keywords:

Atmospheric nitrogen deposition

Organic nitrogen

Ammonia deposition

Rocky mountains

### ABSTRACT

Increases in reactive nitrogen deposition are a growing concern in the U.S. Rocky Mountain west. The Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) study was designed to improve understanding of the species and pathways that contribute to nitrogen deposition in Rocky Mountain National Park (RMNP). During two 5-week field campaigns in spring and summer of 2006, the largest contributor to reactive nitrogen deposition in RMNP was found to be wet deposition of ammonium (34% spring and summer), followed by wet deposition of nitrate (24% spring, 28% summer). The third and fourth most important reactive nitrogen deposition pathways were found to be wet deposition of organic nitrogen (17%, 12%) and dry deposition of ammonia (14%, 16%), neither of which is routinely measured by air quality/deposition networks operating in the region. Total reactive nitrogen deposition during the spring campaign was determined to be 0.45 kg ha<sup>-1</sup> and more than doubled to 0.95 kg ha<sup>-1</sup> during the summer campaign.

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### 1. Introduction

Human activity has substantially enhanced rates of nitrogen (N) fixation on land (Smil, 1990; Vitousek and Matson, 1993; Ayers et al., 1994; Galloway et al., 1995). Combustion of fossil fuels, production of nitrogen fertilizers, cultivation of nitrogen-fixing legumes, and other actions have been identified as major sources altering the global N cycle (Galloway et al., 1995). Wet and dry deposition of ammonia and atmospheric oxidation products of nitrogen oxides produced by combustion processes represent significant nitrogen inputs in many environments.

Wet and dry deposition of several inorganic nitrogen species are measured in the U.S. by the National Atmospheric Deposition Program (NADP) and the Clean Air Status and Trends Network (CASTNet). One area receiving increasing attention, due to the sensitive nature of its high elevation ecosystems, is the Rocky

Mountain west. Atmospheric N deposition to the Rocky Mountain region of Colorado and southern Wyoming measured during 1995–1999 ranged from 1 to 7 kg ha<sup>-1</sup> yr<sup>-1</sup> (Burns, 2003). Within Rocky Mountain National Park (RMNP), an area of particular interest, wet deposition of inorganic nitrogen (nitrate and ammonium) currently contributes approximately 3 kg ha<sup>-1</sup> yr<sup>-1</sup> to total nitrogen input. Dry deposition of nitric acid, particulate nitrate, and ammonium increase total measured nitrogen deposition to approximately 4 kg ha<sup>-1</sup> yr<sup>-1</sup>. These current nitrogen deposition flux values appear to represent approximately a 20-fold increase above pre-industrial values for the western U.S. (Galloway et al., 1982, 1995; Hedin et al., 1995). While the work presented here focuses on just a single region, nitrogen deposition is a widespread issue. Significant work has been conducted, for example, in Europe on the exchange of NH<sub>3</sub> between the atmosphere and ecosystem (e.g. Sutton et al., 1993; Wyers and Erisman, 1998) and on quantifying nitrogen fluxes (Balestrini et al., 2000; Sutton et al., 2007).

Increased deposition of nitrogen in RMNP has been demonstrated to contribute to a number of important ecosystem changes (see Blett and Morris, 2004, for a review). Among these are changes in the chemistry of old-growth Engelmann spruce forests (Rueth and Baron, 2002), shifts in population of lake diatoms (Baron et al., 2000),

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excess nitrogen leakage into lakes and streams at certain times of the year (Campbell et al., 2000), and alterations in biogeochemical cycling associated with increased microbial activity in high elevation soils and taluses (Campbell et al., 2000, 2002; Rueth and Baron, 2002). Several of these effects have been noted mainly on the east side of the Continental Divide that runs through RMNP. Nitrogen deposition levels have also been determined to be higher on the eastern slope of the park (Burns, 2003). With growing evidence of increases in nitrogen deposition and its impacts, a cooperative effort between the U.S. National Park Service, the U.S. Environmental Protection Agency, and the State of Colorado recently resulted in establishment of a nitrogen deposition reduction plan for RMNP.

Although much has been learned about nitrogen deposition in RMNP and its effects, several key issues need further 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 identification of important nitrogen sources and transport pathways.

Routine measurements of nitrogen deposition fluxes in RMNP include neither quantification of dry and wet inputs of organic nitrogen species nor dry deposition inputs of ammonia. Previous studies in western Colorado and in the Colorado Front Range suggest that approximately 20% of total N wet deposition was associated with organic nitrogen (Williams et al., 2001; Sickman et al., 2001). Although measurements of gas phase ammonia in the region are rare, the substantial contribution of ammonium to wet nitrogen deposition (ammonium and nitrate contributions are currently similar), suggests that dry deposition of ammonia is important.

While prevailing winds in RMNP are usually from the west, transport patterns in the region can be complex. Transport of air masses from the east can occur, for example, in conjunction with mountain-valley circulations (Ahrens, 2002), especially in summer. Larger scale pressure gradients also periodically produce upslope transport from the east that can result in significant precipitation along the eastern slope of RMNP. Periods of transport from the east are of particular interest because of large  $\text{NO}_x$  and  $\text{NH}_3$  emissions from population centers and agricultural regions east of RMNP. It is difficult to use the routine CASTNet and NADP measurements to identify key regions and source types contributing most to increasing levels of N deposition, because wet and dry deposition fluxes are determined at a weekly time resolution while changes in transport patterns typically occur on shorter timescales. The Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) study was initiated to improve our understanding of oxidized sulfur as well as oxidized and reduced nitrogen in the context of 1) their sources, 2) their forms in the atmosphere and transformation during transport, and 3) their deposition rates. The RoMANS study includes both field measurement and modeling efforts. We report here on key findings from two field campaigns conducted in 2006. Included are an overview of wet deposition fluxes across the RoMANS measurement network, an analysis of how changes in transport are associated with high N and S deposition fluxes in one precipitation episode that dominated the spring deposition budget, and a discussion of the relative importance of various wet and dry N deposition pathways in the important spring and summer deposition seasons.

## 2. Experimental methods

The RoMANS study included two field campaigns focused in RMNP but also extending across the western and eastern boundaries of the state of Colorado. Spring and summer campaigns were scheduled to capture periods, as indicated by past records, of important nitrogen deposition. The spring campaign was conducted from March 25th to April 28th 2006. The summer campaign was conducted from July 6th to August 10th 2006. Fig. 1 shows locations of key measurement sites used during

the field studies. The most sophisticated and highest time resolution measurements were made at the study Core Site in RMNP. The Core Site is located approximately 11 km SSE from Estes Park (pop. 6268), approximately 37 km W of the Front Range urban corridor, and approximately 70 km W of the nearest large agricultural operations. Sites at Lyons and at Gore Pass, referred to as secondary sites, were somewhat more sophisticated in terms of measurement capabilities than the remaining "satellite" sites in the network, some of which measured only precipitation and some of which also measured aerosol and trace gas composition. Table 1 provides a complete listing of site names, locations, and operating periods. Some differences in network configuration were implemented between the spring and summer campaigns as a result of the possibility of high altitude access in summer and project budget constraints.

At the Core Study site, event-based wet deposition samples were collected using manually-deployed high density polyethylene (HDPE) buckets (23.0 cm in diameter). Sub-event samples (typically ~1 h time resolution) were also collected here using a large PE funnel (diameter of 52.7 cm). 24 h precipitation samples were collected at the Core Site using an automated, wet-only precipitation collector (Yankee Environmental Systems Model TPC-3000, bucket diameter = 25.3 cm). Similar precipitation measurements were made at the Lyons site, although the TPC-3000 sampler used at Lyons in spring was moved to Gore Pass in summer. Precipitation samples were collected (typically at daily intervals ~8 a.m. to 8 a.m. local MST) at other RoMANS study sites using open HDPE buckets.

Collected precipitation samples were weighed and an aliquot was taken within 2 h of collection for measurement of pH. Measurements were made using a pH meter and combination pH electrode calibrated with pH 4 and 7 buffer solutions. An additional aliquot was prepared and refrigerated for later analysis of inorganic ions in our laboratory at Colorado State University (CSU). Sample aliquots were also prepared shortly after collection from samples collected at the Core Site, Gore Pass, and Lyons for organic nitrogen (ON) analysis. These aliquots were stored frozen in 15 mL amber PE bottles, to prevent biological or photo-degradation of N species.

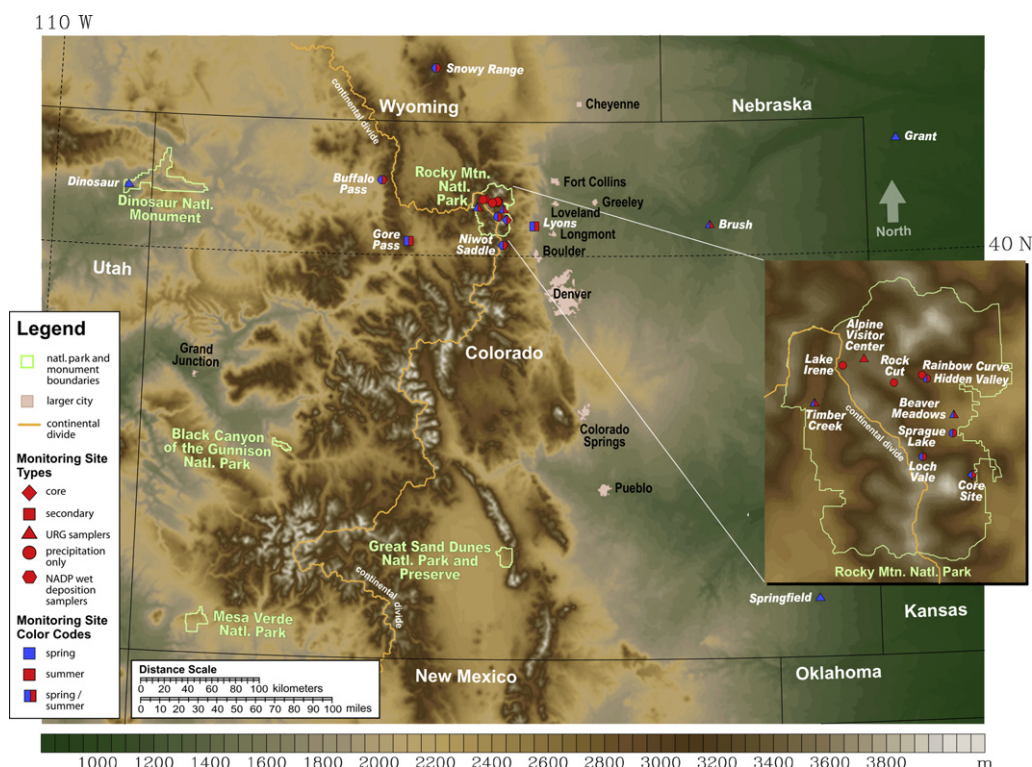
All sites shown in Fig. 1, except those indicated as measuring only precipitation, measured 24 h integrated ammonia, nitric acid, and sulfur dioxide gas concentrations and the ionic composition of particulate matter less than 2.5  $\mu\text{m}$  aerodynamic diameter ( $\text{PM}_{2.5}$ ) using URG annular denuder/filter-pack samplers. Air was drawn through a Teflon-coated cyclone ( $D_{50} = 2.5 \mu\text{m}$ ) and through two coated annular denuders in series, followed by a filter pack and a backup denuder, to collect the gaseous and particulate species of interest. The first denuder was coated with sodium carbonate for collection of nitric acid and sulfur dioxide (Lee et al., 2008a). The second denuder was coated with phosphorous acid to collect ambient ammonia. The remaining air stream was then filtered through a nylon filter (PALL Nylasorb, 1  $\mu\text{m}$  pore size) to collect particulate matter. A backup denuder coated with phosphorous acid was used to capture any volatilized particulate ammonium. We have demonstrated previously (Yu et al., 2005) that volatilized nitrate is retained by the nylon filter. 24 h samples were collected from 8:00a.m. to 8:00a.m. MST with a nominal flow rate of 10 L  $\text{min}^{-1}$ . Flow was controlled by a mass flow controller and the actual sample volume was independently measured using a dry gas meter with appropriate correction for measured system pressure drop.

Higher time resolution (15 min)  $\text{PM}_{2.5}$  composition measurements were also made at the study Core Site using a Particle into Liquid Sampler (PILS) (Orsini et al., 2003; Weber et al., 2001, 2003; Lee et al., 2008b). The PILS grows aerosol particles to a size easily collected by inertial impaction by mixing a denuded aerosol stream with supersaturated steam. The collected particles are washed off of the impactor into a flowing liquid stream. The liquid stream, containing an internal LiBr (lithium bromide) standard to determine dilution by condensed water vapor, is split into two streams which are injected every 15 min to two ion chromatographs (Dionex, ICS-1500) for measurement of major inorganic ion ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) concentrations.

Meteorological measurements were made on-site by a 10 m tower operated by the CASTNet program. High time resolution measurements of aerosol physical and optical properties (Levin et al., 2009) and key trace gases ( $\text{NO}_x$ ,  $\text{O}_3$ ,  $\text{NH}_3$ , and CO) were also made at the Core Site but will not be discussed here.

Major inorganic anions and cations were analyzed in precipitation samples and in denuder and filter extracts by ion chromatography using two Dionex DX-500 systems. Samples were analyzed for both cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) and anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ ) by ion chromatography. Cations were separated with a methanesulfonic acid eluent on a Dionex CS12A column followed by a CSRS ULTRA II suppressor and a Dionex CD-20 conductivity detector. Anions were separated with a carbonate/bicarbonate eluent on a Dionex AS14A column followed by an ASRS ULTRA II suppressor and a Dionex CD-20 conductivity detector.

Samples were thawed completely immediately before ON analysis. Analysis of ON was performed according to the methods described by Cornell and Jickells (1999), with the exception that the RoMANS samples were processed un-filtered. The nitrogen species analyzed during inorganic ion analysis ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ) provided the sum of inorganic nitrogen before ON analysis. ON samples were acidified to a pH of approximately 3 using concentrated  $\text{H}_2\text{SO}_4$  (5% (v/v)). Using a carousel photolysis chamber samples were exposed to UV radiation for 24 h. Samples were reanalyzed by ion chromatography after sample photo-oxidation. The ON concentration was determined as the difference between the sum of inorganic N before and after photo-oxidation.



**Fig. 1.** Map showing key measurement locations during the 2006 RoMANS study. The inset shows site locations in Rocky Mountain National Park in greater detail. Sites denoted by triangles, squares and diamonds generally featured at least daily trace gas and PM<sub>2.5</sub> composition measurements plus wet deposition measurements. The RoMANS Core Site featured several additional and higher time resolution measurements. Sites shown as circles featured only precipitation collection. A separate color shading scheme is used to indicate whether each site operated in spring, in summer, or during both seasons.

Major species were generally undetectable in precipitation collector blanks. Based on analytical precision at low concentration levels we estimate minimum detection levels (MDLs) for precipitation concentrations of 0.10 mg L<sup>-1</sup> for NH<sub>4</sub><sup>+</sup>, 0.14 mg L<sup>-1</sup> for NO<sub>3</sub><sup>-</sup>, 0.11 mg L<sup>-1</sup> for SO<sub>4</sub><sup>2-</sup>, and 0.12 mg N L<sup>-1</sup> for ON. For gas and particle sampling with the URG denuder/filter pack, detection limits were determined from numerous field blanks collected in an earlier study by our group (Yu et al., 2006) using the same sampling approach. The MDLs for HNO<sub>3</sub>, NH<sub>3</sub>, NO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, SO<sub>2</sub>, and SO<sub>4</sub><sup>2-</sup> are 0.058, 0.083, 0.068, 0.030, 0.037 and 0.046 μg m<sup>-3</sup>, respectively.

### 3. Results and discussion

#### 3.1. Wet deposition

Approximately 500 precipitation samples were collected and analyzed from the RoMANS campaigns. Table 2a and 2b list the

precipitation volume-weighted average concentrations of key species measured in precipitation collected at different RoMANS network sites during the spring and summer campaigns, respectively. Not surprisingly, the most abundant species in the spring and summer RoMANS precipitation samples were generally nitrate, sulfate, and ammonium. The volume-weighted average pH at the various sites in spring ranged from approximately 5.29–7.11. The following average pH values are all volume-weighted averages. The lowest average pH, 5.29, was observed at Gore Pass west of RMNP. Most of the park sites had slightly higher average pH values than the Core Site average pH of 5.54. Average pH values ranging from 6.27 to 7.11 were observed at the sites on the eastern plains (Brush, Grant, and Springfield). Average pH values decrease somewhat in summer. The average pH at Lyons, for example,

**Table 1**  
Locations of monitoring sites for the spring and summer campaigns of RoMANS.

Site name	Site type	Latitude	Longitude	Elevation (m)	Precipitation	Gas and particle	Spring	Summer
Core Site	Core Site	40.2783°	-105.5457°	2784	X	X	X	X
Gore Pass	Secondary	40.1172°	-106.5317°	2641	X	X	X	X
Lyons	Secondary	40.2273°	-105.2751°	1684	X	X	X	X
Alpine VC	Satellite	40.4420°	-105.7540°	3599	X	X		X
Beaver Meadows	Satellite	40.3560°	-105.5810°	2509	X	X	X	X
Brush	Satellite	40.3138°	-103.6022°	333	X (spring only)	X	X	X
Dinosaur	Satellite	40.4372°	-109.3047°	1463	X	X	X	
Lake Irene	Satellite	40.3413°	-105.8190°	3260	X	X		X
Loch Vale	Satellite	40.2878°	-105.6628°	3170	X	X	X	X
Grant, Nebraska	Satellite	40.8696°	-101.7307°	317	X	X	X	
Rainbow Curve	Satellite	40.3998°	-105.6630°	3271	X	X		X
Rock Cut	Satellite	40.3920°	-105.7200°	3664	X	X		X
Springfield	Satellite	37.3690°	-102.7430°	405	X	X	X	
Sprague Lake	Satellite	40.3217°	-105.6071°	2656	X	X	X	X
Timber Creek	Satellite	40.3800°	-105.8500°	2767	X	X	X	X

**Table 2a**

Precipitation-weighted average concentrations and concentration ranges for each site operated during the spring campaign of RoMANS. Included in the table are the number of samples per site (n).

	NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )			NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )			SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )			ON (mg N/L <sup>-1</sup> )		
	Average (n)	Min	Max	Average (n)	Min	Max	Average (n)	Min	Max	Average (n)	Min	Max
Core Site	0.65 (11)	0.000	1.19	1.58 (11)	0.000	2.17	1.07 (11)	0.34	2.83	0.23 (6)	0.11	0.94
Gore Pass	0.14 (12)	0.000	1.73	0.79 (12)	0.453	3.50	0.59 (12)	0.22	4.07	0.0057 (5)	0.00	1.18
Lyons	1.25 (4)	0.213	2.39	2.85 (4)	0.902	5.44	1.78 (4)	0.22	4.65	0.024 (3)	0.00	1.28
Beaver Meadows	0.90 (6)	0.011	4.15	2.28 (6)	0.751	11.07	1.55 (6)	0.36	14.99	no data		
Brush	2.47 (1)	2.469	2.47	5.51 (1)	5.512	5.51	2.91 (1)	2.91	2.91	no data		
Dinosaur	0.18 (8)	0.000	5.51	1.40 (8)	0.474	11.13	1.23 (8)	0.62	16.93	no data		
Loch Vale	0.26 (4)	0.211	0.27	1.38 (4)	1.178	2.02	0.95 (4)	0.60	4.49	no data		
Grant (NE)	1.79 (5)	0.619	7.28	1.95 (5)	0.000	2.19	1.18 (5)	0.48	20.09	no data		
Springfield	1.06 (3)	0.000	1.65	1.51 (3)	0.000	4.82	1.16 (3)	0.00	3.99	no data		
Sprague Lake	0.28 (13)	0.000	0.83	1.33 (13)	0.648	3.48	1.04 (13)	0.45	4.36	no data		
Timber Creek	0.35 (14)	0.109	1.91	1.07 (14)	0.223	4.80	0.92 (14)	0.00	4.95	no data		

decreased from 5.82 in spring to 5.07 in summer. Likewise, the average pH at the RoMANS Core Site decreased from a spring value of 5.54–4.69. Most sites in RMNP exhibited average summer pH values similar to the Core Site.

Fig. 2 depicts the total measured precipitation and wet deposition amounts of nitrate, ammonium, and sulfate across the RoMANS network for the spring and summer campaigns.

The spring data reveal the typical tendency for higher elevation sites to receive more precipitation. It is important to note that the precipitation amounts (reported in mm) were not measured with a meteorological precipitation gauge, instead the precipitation amounts were calculated values from the HDPE buckets. Measured precipitation at sites in RMNP ranged from 19 mm at Beaver Meadows to almost 37 mm at Sprague Lake. Moving east of RMNP, spring precipitation dropped off sharply, with sampled amounts ranging between 7 and 13 mm at sites on the eastern plains. Higher precipitation amounts were collected at western RoMANS network sites, with 19 mm at Dinosaur and 29 mm at Gore Pass. Substantial differences were also observed in wet deposited nitrogen and sulfur across the network during spring, reflecting the combined influence of spatial gradients in precipitation amount and precipitation solute concentrations. While wet deposited ammonium was highest at Grant, the second and third highest amounts of deposited ammonium were measured at Beaver Meadows and at the RoMANS Core Site. Deposited amounts of ammonium at the high altitude Loch Vale site were less than measured at the other RMNP sites consistent with its more remote location. Spring nitrate and sulfate wet deposition were also highest at Grant followed closely by several sites in RMNP, including Beaver Meadows, Sprague Lake, and the Core Site.

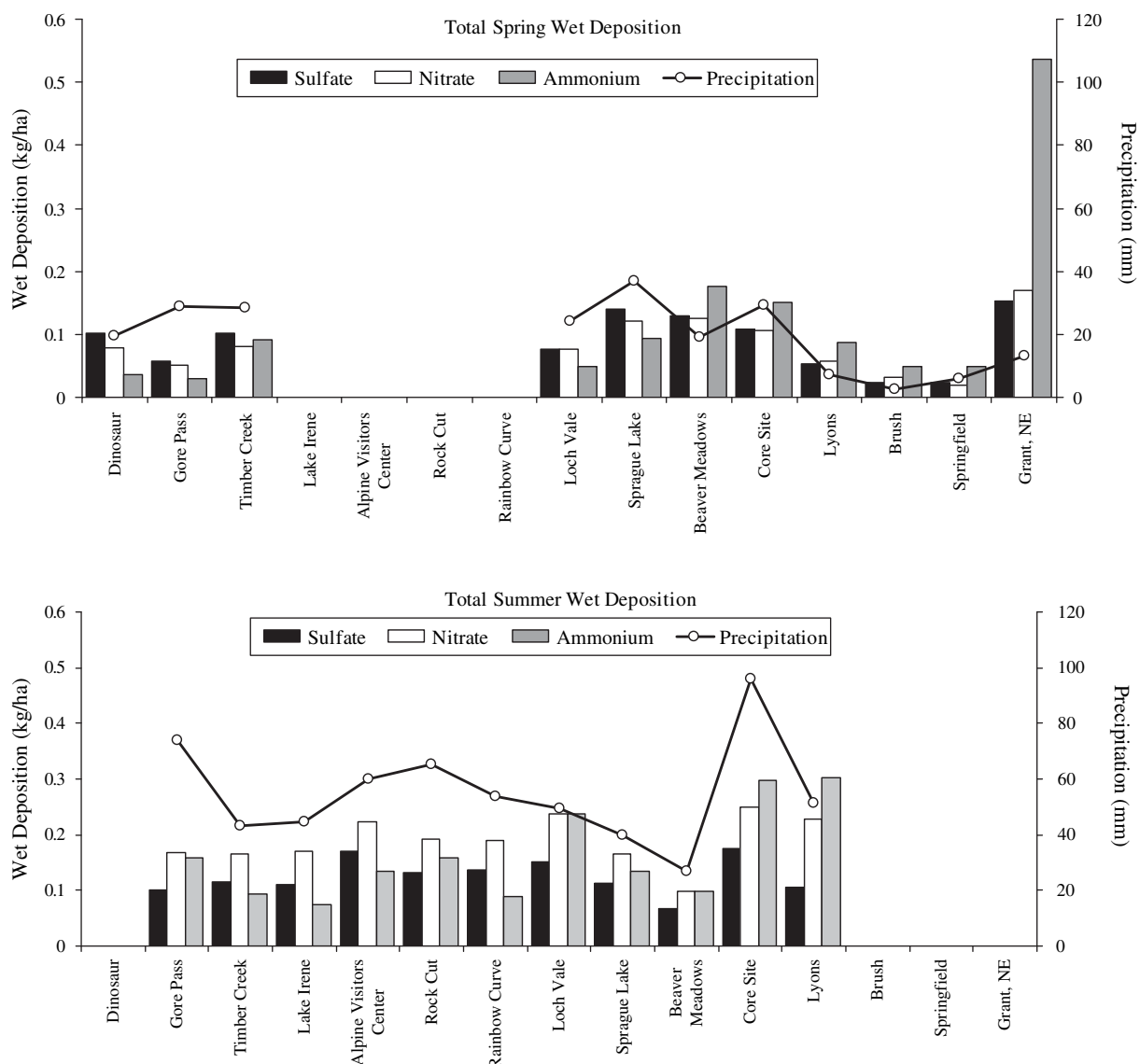
Summer observations show some different patterns than observed in spring. First, both amounts of precipitation and solute deposition fluxes observed in summer were generally much higher than measured in spring. Greater variability was also observed between sites in RMNP. For example, 96 mm of precipitation were sampled at the Core Site while only 27 mm were sampled at Beaver Meadows. Such a large difference in precipitation for two locations so close together (the Core Site is approximately 10 km SSE of Beaver Meadows) illustrates the strongly localized nature of summer convective precipitation events in this region. Other RMNP study sites had precipitation amounts between these two extremes, as did the Lyons and Gore Pass sites. The highest amounts of ammonium nitrogen wet deposited during the summer campaign were at the Core Site and at Lyons, each receiving approximately 0.30 kg of ammonium N per hectare. The highest amounts of wet deposition nitrate were observed at the Core Site (0.25 kg NO<sub>3</sub>-N ha<sup>-1</sup>), Loch Vale (0.24 kg NO<sub>3</sub>-N ha<sup>-1</sup>), Lyons (0.23 kg NO<sub>3</sub>-N ha<sup>-1</sup>), and Alpine (0.22 kg NO<sub>3</sub>-N ha<sup>-1</sup>). Sulfate wet deposition shows only modest changes across the entire summer monitoring network, with all sites measuring between 0.067 and 0.18 kg S ha<sup>-1</sup>.

Moving from the western RoMANS network sites toward the east, one sees a shift in the relative summer contributions of nitrogen from nitrate and ammonium. For sites near or to the west of the continental divide, nitrate contributes as much or more nitrogen to measured wet deposition than ammonium does. Inputs of nitrogen from ammonium and nitrate are nearly identical during summer at Loch Vale and at Beaver Meadows. Sprague Lake shows slightly more nitrate than ammonium contributions. At the RoMANS Core Site and at Lyons, however, ammonium N inputs exceed those from nitrate. A similar trend was observed during

**Table 2b**

Precipitation-weighted average concentrations and concentration ranges for each site operated during the summer campaign of RoMANS. Included in the table are the number of samples per site (n).

	NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )			NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )			SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )			ON (mg N/L <sup>-1</sup> )		
	Average (n)	Min	Max	Average (n)	Min	Max	Average (n)	Min	Max	Average (n)	Min	Max
Core Site	0.41 (20)	0.04	5.44	1.15 (20)	0.38	10.39	0.55 (20)	0.07	7.51	0.115 (13)	0.07	3.04
Gore Pass	0.30 (15)	0.00	7.62	1.16 (15)	0.26	13.82	0.53 (15)	0.03	7.02	0.270 (7)	0.00	5.17
Lyons	0.76 (6)	0.35	10.53	1.97 (6)	1.00	21.95	0.61 (6)	0.41	4.14	0.014 (6)	0.08	1.92
Beaver Meadows	0.26 (10)	0.00	18.45	0.87 (10)	0.00	8.82	0.41 (10)	0.26	28.53	no data		
Alpine VC	0.26 (11)	0.00	1.33	1.51 (11)	0.67	6.24	0.77 (11)	0.28	3.86	no data		
Lake Irene	0.17 (14)	0.00	2.60	1.35 (14)	0.29	11.07	0.60 (14)	0.10	3.97	no data		
Loch Vale	0.41 (16)	0.00	36.16	1.41 (16)	0.00	39.99	0.61 (16)	0.04	37.53	no data		
Rainbow Curve	0.11 (15)	0.00	12.56	0.82 (15)	0.25	16.64	0.39 (15)	0.07	18.50	no data		
Rock Cut	0.30 (13)	0.02	2.49	1.25 (13)	0.27	12.34	0.57 (13)	0.09	5.21	no data		
Sprague Lake	0.24 (13)	0.00	2.83	1.01 (13)	0.25	12.00	0.46 (13)	0.06	6.96	no data		
Timber Creek	0.24 (15)	0.00	1.34	1.50 (15)	0.20	5.77	0.70 (15)	0.10	2.44	no data		



**Fig. 2.** Total precipitation and wet deposition of sulfate, nitrate, and ammonium measured in the RoMANS sampling network during the spring (top panel) and summer (lower panel) campaigns. Sites are arranged from west (on the left) to east (on the right). Sites at Lake Irene, Alpine Visitors Center, Rock Cut, and Rainbow Curve were not included in the spring RoMANS network due to inaccessibility. The outlying sites at Dinosaur, Brush, Springfield, and Grant, Nebraska were not included in the summer RoMANS network.

spring as well, with nitrate N deposition exceeding ammonium N deposition at the westernmost sites (Dinosaur and Gore Pass) and a transition to ammonium dominance at sites on the eastern plains. RMNP sites make up part of this transition, with many exhibiting similar nitrate and ammonium inputs but with ammonium becoming more important at the easternmost Core Site and Beaver Meadows site.

The RoMANS Core Site precipitation observations are presented as daily deposition fluxes in Fig. 3. Substantial wet deposition inputs of sulfur and all three nitrogen forms (nitrate, ammonium, and ON) were observed. Particularly noticeable are differences between the spring and summer periods. By far, the highest Core Site daily deposition fluxes during spring are shown for April 23 and 24. These two samples actually come from a single snow event that began late on April 23rd and continued until early on April 25th. This single period of precipitation contributed the vast majority of the total spring Core Site wet deposition fluxes of sulfate (79%), nitrate (80%), ammonium (84%), and organic nitrogen (91%). During summer, by contrast, overall wet deposition of nitrogen and

sulfur species is more evenly spread across numerous precipitation events. The April 23–25 event also dominated spring wet deposition budgets at other RoMANS RMNP measurement sites. The high deposition fluxes are the result of both the large precipitation amount associated with this event combined with reasonably high average precipitation solute concentrations. The time evolution of precipitation solute concentrations and cumulative solute deposition during this important spring wet deposition event at the Core Site is depicted in Fig. 4. The highest concentrations are observed at the start of the event, followed by a steep decline over the first 4 h of snowfall. As precipitation intensity picks up around midnight, the solute concentrations remain low. Interestingly, the highest initial concentrations of nitrogen species during this event are seen for ammonium followed by ON.

The amount of solute deposited by wet deposition depends on the amount of precipitation that falls, the availability of gas and particle phase species to be scavenged by the precipitation, and the efficiency of both in-cloud and below-cloud scavenging processes. Changes in precipitation solute concentrations can be strongly

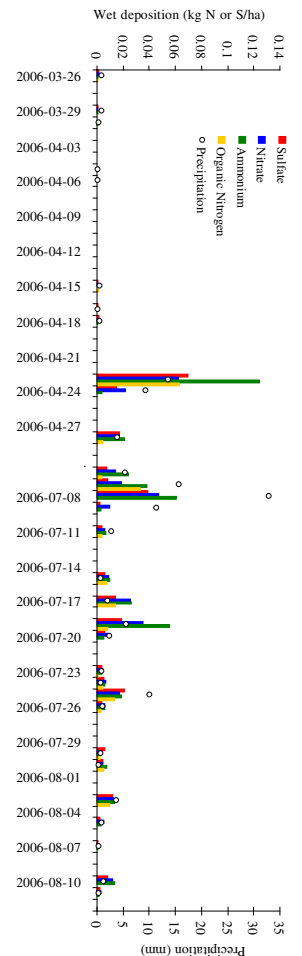


Fig. 3. Timeline of daily wet deposition fluxes of major nitrogen and sulfur species at the ROMANS Core Site.

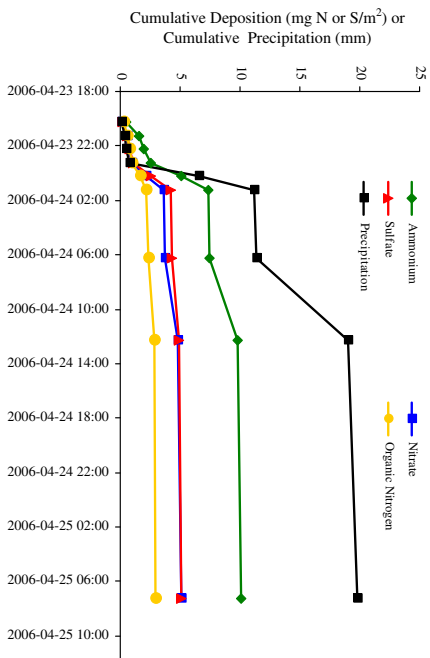
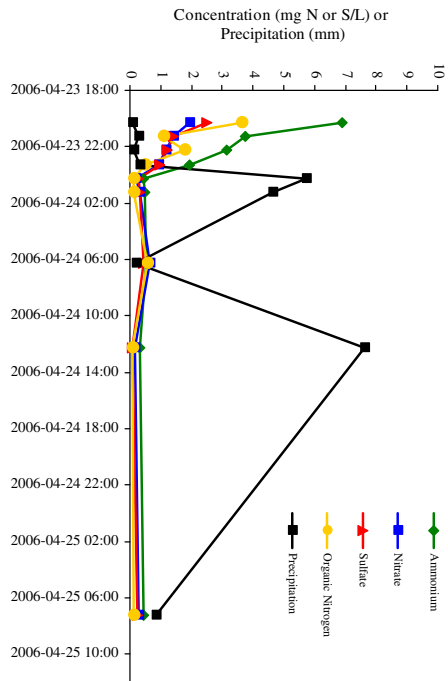


Fig. 4. Time evolution of precipitation solute concentrations and cumulative deposition at the ROMANS Core Site during the period 2006-04-23 to 2006-04-25 (local MST).

influenced by a variety of physical processes, including changes in the composition of the air mass producing the precipitation and changes in precipitation microphysics (Collett et al., 1991). In locations, like RMNP, that are removed from major emission sources, deposition flux magnitudes can depend strongly on the interplay between pollutant transport and precipitation formation. Given the dominance of the April 23–25 precipitation event for nitrogen and sulfur deposition, it is instructive to look in further detail at these issues.

Fig. 5 presents a timeline of PM<sub>2.5</sub> composition measured with the PILS system at the RoMANS Core Site during the spring campaign. The concentration units used in the figure (nanoequivalents/m<sup>3</sup>) permit a direct comparison of the relative amounts of nitrate, sulfate, and ammonium in the sampled aerosol. Some periods feature very low concentrations. The period April 9–19, for example, features low concentrations of ammonium and sulfate with even lower amounts of nitrate. Other periods feature rapid transitions between low and high concentrations. Periods in both early and late April follow this pattern. Some concentration spikes (e.g., on the afternoon of April 23) contain a mixture of ammonium, nitrate, and sulfate, while others are comprised mainly of ammonium nitrate (e.g., April 20–21) or ammonium sulfate (e.g., April 28–30).

Fig. 6 provides a closer look at the PM<sub>2.5</sub> composition variability during the last part of April. In addition to the PM<sub>2.5</sub> major ion concentration timelines, the figure contains a record of the local wind direction measured from the 10 m CASTNet meteorological tower at the RoMANS Core Site. One sees here an interesting pattern: PM<sub>2.5</sub> concentration spikes tend to be associated with periods of sustained southeasterly or “upslope” flow. A few hours after upslope flow develops on April 20, for example, a sharp increase is observed in the amount of ammonium nitrate at the Core Site. Ammonium nitrate concentrations start to decrease after the wind returns to northwesterly. A change to upslope flow on April 23 is also accompanied by an increase in the amounts of ammonium, nitrate, and sulfate. Despite sustained upslope flow overnight and through the entire day of April 24, however, PM<sub>2.5</sub> major ion concentrations are observed to drop off starting late on the 23rd and remain very low throughout April 24th. The dramatic decrease in concentrations is associated with the development of heavy precipitation associated with this upslope snowstorm. The arrow in Fig. 6 denotes the approximate time period of heavy precipitation. As precipitation diminishes early on the 25th, PM<sub>2.5</sub> major ion concentrations return to previously high levels but drop substantially later that day when the winds return to a more westerly pattern.

Increases in both particle and gas phase reactive nitrogen species were commonly observed in both spring and summer

during periods when transport brought air from the east into RMNP. This observation is not surprising given the large emissions of both oxidized and reduced nitrogen found in population centers (including the Front Range urban corridor) and agricultural regions east of the Rockies. Observations of key particle and gas phase reactive nitrogen species, made using the URG denuder/filter-pack system, reveal a strong gradient in concentrations of reduced and oxidized nitrogen from RMNP toward the east. Fig. 7 illustrates the average east-west gradient in total inorganic nitrogen (gaseous nitric acid and ammonia plus PM<sub>2.5</sub> nitrate and ammonium) observed across the RoMANS measurement network during the spring and summer field campaigns. Transport from the east, therefore, can move material down this gradient and bring high pollutant concentrations into RMNP. Because air moved from east to west is forced to rise as it is pushed up against the east slope of the Rockies, this transport pattern can also be associated with heavy precipitation. The fact that flow from the east can transport pollutants into RMNP, while resulting in heavy precipitation that can efficiently scavenge and deposit those pollutants, means that episodes of this type can be important, even dominant, contributors to seasonal deposition budgets despite their limited duration. The April 23–25 event is a good example of this.

### 3.2. Dry deposition

Past data records from the NADP and CASTNet programs indicate that nitrogen deposition in RMNP is dominated by wet deposition processes. With the more complete set of species measurements (including wet ON and gaseous NH<sub>3</sub>) made during RoMANS, it is worthwhile revisiting this issue to assess the most important pathways, both dry and wet, contributing to N deposition in RMNP. Wet deposition fluxes have already been discussed in some detail above. Here we focus on estimating dry deposition fluxes for the RoMANS measurement periods and then construct a combined wet plus dry deposition budget.

Concentrations of gaseous nitric acid, sulfur dioxide, and ammonia, and PM<sub>2.5</sub> ammonium, sulfate, and nitrate were measured at the RoMANS Core Site during both the spring and summer field campaigns. These measurements were made at 24 h time resolution using the URG annular denuder/filter-pack sampling approach described earlier. Dry deposition velocities ( $V_d$ ) were calculated by CASTNet for sulfur dioxide, nitric acid, and fine particles. Since  $V_d$  is site specific and the Core Site is the only RoMANS site co-located with a CASTNet site, it is the only site where dry deposition fluxes will be calculated.

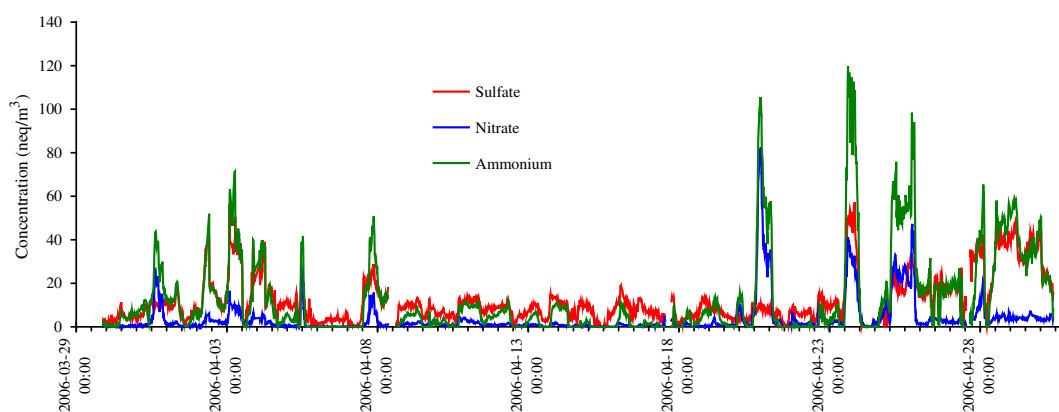
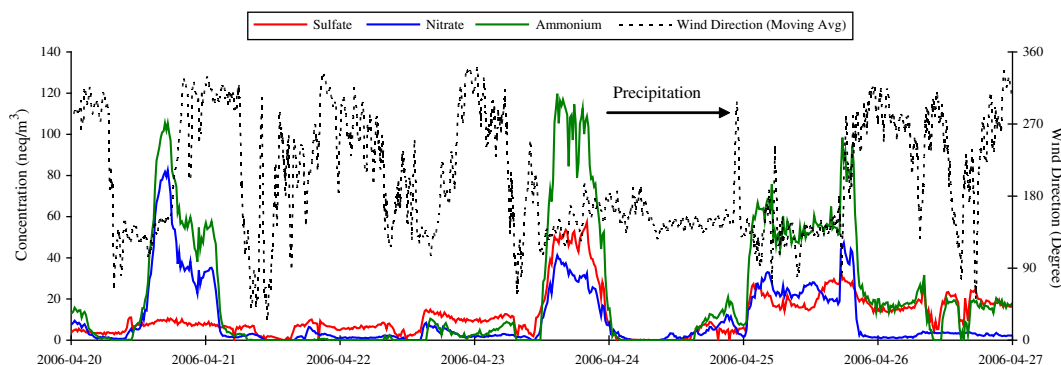


Fig. 5. Fifteen minute time resolved PM<sub>2.5</sub> major ion concentration timelines measured at the Core Site during the RoMANS spring campaign. Concentrations are expressed in nanoequivalents m<sup>-3</sup>.





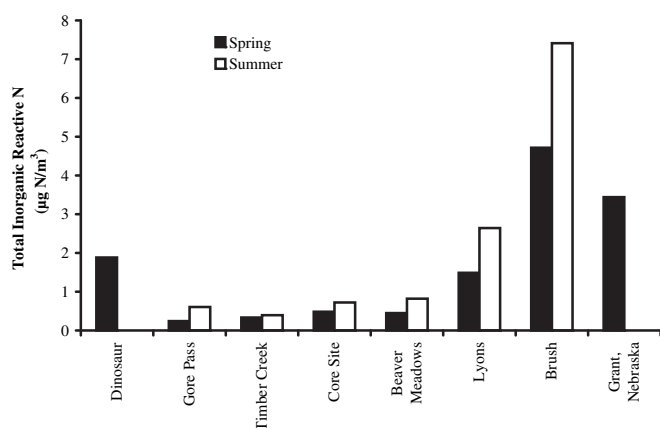
**Fig. 6.** Fifteen minute time resolved  $PM_{2.5}$  major ion concentrations and local 10 m wind direction timelines measured at the RoMANS Core Site during late April 2006. Flow from the SE corresponds to upslope flow at the site. The arrow indicates a period of heavy precipitation during an upslope snowstorm April 23–25.

Deposition velocities for nitric acid, sulfur dioxide, and fine particles ( $PM_{2.5}$  nitrate, sulfate and ammonium are all assumed to have equal deposition velocities) were calculated by CASTNet using the NOAA Multilayer Deposition Velocity Model (MLM) described by Meyers et al. (1998). The model separates the vegetative canopy into 20 layers. Site survey data (including type and quantity of vegetation and leaf area index) are provided to the model and dry deposition velocities are calculated utilizing observed meteorological parameters. Meyers et al. (1998) found that average MLM deposition velocities showed good agreement with little average bias relative to measured values. Finkelstein et al. (2000) found similar results but observed that the model generally underpredicts higher values of both  $O_3$  and  $SO_2$  deposition velocities during the day and at night; seasonal and diurnal cycles are reproduced quite well but the times and magnitudes of the average daily peaks are missed. Both of these studies focused on  $O_3$  and  $SO_2$ , since  $HNO_3$  observations were only available during the daytime. Meyers et al. (1998) observed that for  $HNO_3$  the model biases the deposition velocity low but the ranges of predicted and observed values are similar.

The lack of  $NH_3(g)$  measurements in the CASTNet network means that CASTNet does not calculate dry deposition velocities for  $NH_3$ . Since the goals of the RoMANS project include determining total reactive N deposition in the park, it is important that dry deposition of ammonia be considered. One complication in

estimating dry deposition velocities for ammonia is the bidirectional nature of its exchange with the environment. Ammonia exchange has been shown to be a result of interaction between physical, chemical, and biological processes (Wyers and Erisman, 1998). In some environments ammonia has been found to be both emitted and deposited depending on atmospheric conditions, concentrations, and the time of day (Langford and Fehsenfeld, 1992; Pryor et al., 2001; Wyers and Erisman, 1998). Flux evaluation in a forest generally shows deposition, in contrast to agricultural croplands where emissions are observed (Sutton et al., 1994). The net canopy compensation point, the air concentration below which  $NH_3$  is emitted and above which it is deposited, has been suggested to be near or below  $1 \mu g/m^3$  for a coniferous forest (Duyzer et al., 1994; Langford and Fehsenfeld, 1992). In semi-natural (not fertilized) and forest ecosystems the compensation point is frequently negligible but exceptions have been observed in very dry conditions ( $RH < 60\%$ ) and when an area is subject to large  $NH_3$  concentrations. While  $NH_3$  dry deposition is likely concentration dependent as well as dependent on other factors, we do not have sufficient information to represent the net flux of  $NH_3$  using a bidirectional model.

In order to estimate a reasonable ammonia deposition velocity for the RoMANS Core Site we examined results from previous studies, searching for a relationship between the deposition velocities of nitric acid and ammonia or an appropriate fixed value to use. While a consensus value for the  $NH_3$  dry deposition, not surprisingly, is difficult to find, there is a weight of evidence to suggest that the deposition velocity of ammonia is at least half and perhaps as much as that of nitric acid. This makes sense, intuitively, as we expect both ammonia and nitric acid to experience little or no surface resistance. A conservative estimate that agrees well with the findings of Neiryneck et al. (2007) and Nemitz et al. (2004) is  $V_d(NH_3) = 0.7V_d(HNO_3)$ . This relationship was used to estimate ammonia dry deposition velocities during RoMANS based on MLM modeled nitric acid deposition velocities. While this is certainly an oversimplification, we believe it suffices to illustrate, for the first time in RMNP, the relative importance of ammonia dry deposition to the total reactive N deposition budget. Further, we note that an analysis of daily concentration variability and MLM deposition velocities across all species reveals that daily changes in deposition fluxes are driven more strongly by changes in concentration (which were well measured in RoMANS) than by changes in deposition velocity (Beem, 2008).



**Fig. 7.** Average total reactive inorganic N (gaseous ammonia and nitric acid plus  $PM_{2.5}$  nitrate and ammonium) concentrations measured at selected sites during the RoMANS spring and summer field campaigns. The sites are arranged from west (left side of diagram) to east. Timber Creek is on the west side of the continental divide near the western boundary of RMNP. The Core Site and Beaver Meadows are both located east of the continental divide near the Park's eastern boundary.

### 3.3. Combined deposition

In the spring campaign a total of  $0.45 \text{ kg ha}^{-1}$  of reactive nitrogen was determined to be deposited by dry and wet deposition

pathways at the RoMANS Core Site, along with  $0.13 \text{ kg ha}^{-1}$  of sulfur. In the summer campaign, reactive nitrogen deposition more than doubled to  $0.95 \text{ kg ha}^{-1}$  while sulfur deposition increased by approximately 50% to  $0.20 \text{ kg ha}^{-1}$ . These are total amounts deposited per unit area over the spring (36 day) and summer (37 day) campaigns.

Wet deposition is the major process by which nitrogen is deposited in RMNP during both spring and summer. In the spring,  $\text{NH}_4^+$  wet deposition alone exceeds all the dry processes combined with 34% of deposited N followed by wet  $\text{NO}_3^-$  deposition with 24% and wet ON deposition with 17%. Only 26% of reactive N deposition occurred by dry processes: 14% from  $\text{NH}_3$ , 7.5% from  $\text{HNO}_3$ , 3.2% from  $\text{NH}_4^+(\text{p})$ , and 1.1% from  $\text{NO}_3^-(\text{p})$ . Despite the large increase in nitrogen deposition from spring to summer, the relative inputs of various nitrogen pathways and species are rather similar. In the summer, wet deposition of ammonium again represents the largest nitrogen input (34%), followed by wet deposition of nitrate (28%), dry deposition of gaseous ammonia (16%), wet deposition of ON (12%), and dry deposition of gaseous nitric acid (7.5%). The dry deposition inputs of fine particle ammonium (1.4%) and nitrate (0.20%) are even less important contributors than during spring.

Estimates of uncertainty in the various reactive nitrogen deposition pathway fluxes were computed based on available information from the RoMANS study and prior investigations. Wet deposition measurement precision was estimated from co-located precipitation collection. Sub-event and automated precipitation sampler comparisons at the RoMANS core site indicated wet deposition flux measurement precisions (relative standard deviation (RSD)) of 26% for  $\text{NO}_3^-$ , 22% for  $\text{NH}_4^+$ , and 33% for ON. These estimates include uncertainties associated with analytical measurements, sampler location, and the dependence of precipitation collection efficiency on sampler geometry. The RSD for co-located precipitation amount between the two sampler types was approximately 20%. A separate comparison of the automated sampler with 24 h open bucket samples showed better agreement for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  but greater scatter in measured  $\text{NH}_4^+$  wet deposition fluxes, perhaps reflecting a tendency for greater changes in  $\text{NH}_4^+$  content in uncovered samples. For dry deposition, uncertainties were estimated using errors for MLM-computed deposition velocities from Sickles and Shadwick (2002) and concentration precision estimates from an earlier measurement precision study in our group using the same URG sampling approach (Lee et al., 2008b). Propagated RSDs for dry deposition fluxes are 8.7% for  $\text{NO}_3^-$ , 8.2% for  $\text{NH}_4^+$ , and 11% for  $\text{HNO}_3$ . The uncertainty in  $\text{NH}_3$  dry deposition fluxes was estimated to be approximately twice the  $\text{HNO}_3$  dry deposition flux uncertainty, based on the range of  $\text{NH}_3/\text{HNO}_3$  deposition velocity ratios reported in the literature for similar environments.

Neither wet deposition of organic nitrogen nor dry deposition of ammonia is quantified in routine monitoring networks such as NADP or CASTNet. Addition of these measurements during RoMANS clearly demonstrates the importance of both pathways to total N inputs in RMNP. Fig. 8 shows nitrogen deposition inputs (and corresponding uncertainties) by the various pathways, arranged from the largest contributors on the left to the smallest contributors on the right. Organic nitrogen wet deposition and ammonia dry deposition constitute the third and fourth most important nitrogen deposition pathways in spring. In summer the order of these two inputs is reversed. In both seasons, these two pathways are exceeded in importance only by wet deposition of ammonium and nitrate. They are considerably more important than dry deposition inputs of nitric acid and fine particle nitrate and ammonium, all of which are measured in RMNP by CASTNet.

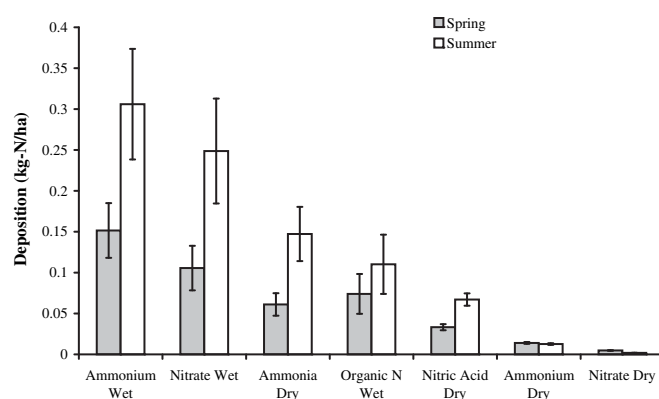


Fig. 8. Nitrogen deposition totals by various species and pathways in order of contribution to total reactive N deposition at the RoMANS Core Site. Error bars represent one standard deviation.

#### 4. Summary and conclusions

Current levels of reactive N deposition in RMNP are estimated to be approximately 20 times natural background levels. Routine deposition network measurements indicate substantial increase in deposition of reduced and oxidized nitrogen over recent decades. Ecological impacts associated with current N deposition levels have prompted state and federal authorities to set a critical load for N deposition in RMNP and to draft a nitrogen reduction plan. The RoMANS study was designed to improve understanding of the total RMNP reactive N deposition budget, elucidate the most important reactive N deposition pathways, and identify the regions and sources contributing most to RMNP N deposition.

Measurements of precipitation composition and amount, key  $\text{PM}_{2.5}$  nitrogen and sulfur species concentrations, and key nitrogen and sulfur trace gas concentrations allow construction of deposition flux budgets for RMNP during spring and summer. Wet deposition contributed much more than dry deposition to reactive nitrogen deposition fluxes in RMNP. During both the spring and summer RoMANS campaigns wet deposition contributed approximately three-fourths of the total nitrogen deposition measured at the study Core Site. Total measured N deposition in RMNP was substantially higher in the summer RoMANS campaign than in the spring campaign. Both wet and dry deposition fluxes increased.

Wet deposition in the spring 2006 RoMANS period was dominated by a single, upslope snowstorm; the combination of pollutant transport from the east and heavy precipitation associated with lifting of air up the east slope of the Rockies created ideal conditions for large wet deposition fluxes of reduced and oxidized nitrogen. The relative contribution of ammonium in particular to wet reactive N deposition was generally observed to increase moving from western Colorado east across the continental divide, reflecting higher concentrations of airborne reduced nitrogen observed in the eastern part of the state. The importance of springtime upslope snowstorms for reactive N deposition in RMNP east of the continental divide suggests that emissions reductions east of RMNP will be necessary to significantly reduce reactive N deposition during this season, despite the fact that transport on most days predominantly brings air masses from the west. Wet deposition in summer was divided more evenly across several precipitation events and no single transport pattern was observed to be associated with high deposition periods.

Wet deposition of ammonium and nitrate were the two largest reactive N deposition pathways during both the spring and summer measurement periods. Wet deposition of organic nitrogen and dry deposition of gaseous ammonia were the 3rd and 4th largest deposition pathways. Together wet deposition of

organic nitrogen and dry deposition of gaseous ammonia comprise approximately 30% of the total RoMANS reactive nitrogen deposition budget. Wet deposition of organic nitrogen and dry deposition of gaseous ammonia are not currently determined in U.S. monitoring networks operating in the Rocky Mountain region. The absence of measurements of these important inputs, and their changes over time, from long-term observation records makes assessing a suitable critical load for nitrogen in RMNP and progress relative to that level problematic. Lack of knowledge regarding dry deposition inputs of organic nitrogen, which were not measured even during the RoMANS study, further compounds this problem.

The work presented here, along with other high time resolution measurements of select species at the RoMANS Core Site, has set the stage for separate RoMANS modeling efforts which will provide greater insight into particular source types and regions that contribute most significantly to RMNP reactive N deposition. A year-long series of measurements at the RoMANS Core Site, begun in 2008, also promises to improve our understanding of the full annual cycle of reactive N deposition within the Park and the seasonality of contributions by the individual dry and wet reactive N deposition pathways. Interest also appears to be growing in establishing routine measurements of organic nitrogen wet deposition and gaseous ammonia concentrations across the country. These should both be important priorities as the U.S. looks to better assess the impacts of reduced and oxidized N emissions on its diverse ecosystems.

## Acknowledgments

This work was funded by the National Park Service with additional support from the Colorado Department of Public Health and Environment. We are grateful to the organizations and individuals that provided access to the various sampling sites, particularly for the cooperation of Rocky Mountain National Park. We are also grateful to Air Resource Specialists for assistance in the preparation and conduct of the study. We would also like to thank UC Davis for use of the mobile lab. GRM was supported by a US Department of Energy Global Change Education Program (GCEP) Graduate Research Environmental Fellowship. The assumptions, findings, conclusions, judgments, and views presented herein are those of the authors and should not be interpreted as necessarily representing the National Park Service.

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