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Observations of atmospheric reactive nitrogen species in Rocky Mountain National Park and across northern Colorado

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HIGHLIGHTS

- There are strong gradients in reactive nitrogen concentrations across Colorado.
- Reduced nitrogen concentrations are highest on the eastern plains of Colorado.
- Oxidized nitrogen concentrations are highest along the Front Range urban corridor.
- Upslope winds periodically transport emissions from source regions east of RMNP.
- Observations indicate there are large contributions of atmospheric nitrogen from sources east of the park.

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ABSTRACT

Increasing rates of nitrogen deposition are a concern in many protected ecosystems. Understanding the sources influencing these regions can be a challenge as there are often few observations available to understand the transport of key species. Several field campaigns were conducted in and around Rocky Mountain National Park (RMNP) from 2006 to 2009 to assess the impacts of various reactive nitrogen sources and regional meteorology on reactive nitrogen deposition. Measurements of ammonia, ammonium, nitric acid, and nitrate at ground-level sites across northern Colorado were used to examine spatial gradients in atmospheric reactive nitrogen concentrations, the influence of wind direction on reactive nitrogen transport in the regional atmosphere, and anthropogenic contributions to reactive nitrogen concentrations in RMNP. The highest concentrations of reduced nitrogen occurred on the eastern plains of Colorado while oxidized nitrogen concentrations were highest along the Front Range urban corridor. Both regions lie east of RMNP. Upslope (easterly) winds associated with mountain–valley wind patterns and larger, synoptic scale forcing, transport emissions from these sources westward up the eastern slope of the Rockies and into RMNP; the highest ammonium and nitrate concentrations in RMNP were clearly associated with this upslope transport pattern. Concentrations of key reactive nitrogen species east of the Continental Divide in RMNP were, on average, more than 50% higher than those observed at a background site located west of the park, further indicating large contributions from sources east of the park. These observations highlight the need to focus on controlling reactive nitrogen emissions east of the park as part of ongoing efforts to reduce reactive nitrogen deposition in RMNP.

1. Introduction

Nitrogen deposition is an important and growing ecological issue, especially in national parks and other ecosystems of the western United States. Analysis of wet nitrogen deposition patterns at 217 sites nationally showed 45 sites had an increasing trend in wet nitrogen deposition; more than half of these sites were in remote areas previously thought to be relatively pristine, including Rocky Mountain National Park (RMNP) in Colorado, Bryce Canyon National Park in Utah, and Sequoia National Park in California (Williams and Tonnessen, 2000). Changes to biological systems occur as a result of excess nitrogen deposition including changes in diatom speciation and abundance (Baron et al., 2000), changes in zooplankton (Williams and Tonnessen, 2000), and effects on trees

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(Craig and Friedland, 1991; Williams et al., 1996). Grasslands in Europe show decreased species richness with increased total inorganic nitrogen deposition and even in areas with low background nitrogen deposition amounts, where current nitrogen deposition is below the critical load, a reduction in species richness was observed (Stevens et al., 2010). A study of national parks in the northern Great Plains showed a strong positive relationship between nitrogen deposition and forest expansion suggesting that even low rates of nitrogen deposition may change plant communities, in this study the expansion of forest into temperate grasslands (Kochy and Wilson, 2001). Increased nitrogen deposition in National Parks is of particular importance since they are classified as class 1 areas and protected by the Clean Air Act of 1977, which mandates the preservation and protection of air quality in national parks. As excess reactive nitrogen deposition adversely impacts ecosystems in National Parks and elsewhere it is important to understand the types of species and sources that contribute to reactive nitrogen to identify control strategies capable of preventing further degradation and to improve air quality in these regions.

A critical load is the "quantitative estimate of ecosystem exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur, according to present knowledge" (Nilsson and Grennfelt, 1988). These thresholds can be used to define deposition above which natural resources can be negatively affected (Williams and Tonnessen, 2000). Measurements of nitrogen deposition and analysis of ecosystem changes have shown evidence of the reactive nitrogen critical load in RMNP being exceeded. For example, diatom assemblages in high alpine lakes in RMNP have changed and these changes are associated with wet deposited inorganic nitrogen ($NO_3^- + NH_4^+$) above 1.5 kg N ha^{-1} yr^{-1} (Baron, 2006). Natural background levels of reactive nitrogen deposition in the Rocky Mountain region are estimated to be 0.5 kg N ha^{-1} yr^{-1} while current estimates indicate that as much as 4.6 kg N ha^{-1} yr^{-1} of wet inorganic nitrogen is deposited in the Rocky Mountain region of Colorado and Wyoming (Burns, 2003). An analysis of nitrogen deposition data from 1995 to 2009 from the National Trends Network/National Atmospheric Deposition Program and Clean Air Status and Trends Network for the sites located in RMNP indicates current levels of nitrogen deposition are above the critical load. From 1995 to 2009 an average of 2.9 kg N ha^{-1} yr^{-1} was deposited including both the wet and dry deposition pathways and ranged from 2.1 to 4.3 kg N ha^{-1} yr^{-1}. Wet deposition is the larger deposition pathway contributing 60–83%, with an average of 70%, to total network-quantified nitrogen deposition. While dry deposition of reactive nitrogen species in particles and gases is smaller than wet deposition, it is important to remember that the material deposited in precipitation comes from the scavenging of gases and particles.

Measurements of reactive nitrogen deposition in RMNP during the 2006 Rocky Mountain Atmospheric Nitrogen and Sulfur (RoMANS) study demonstrated that in 5 weeks during March and April 0.45 kg N ha^{-1} of reactive nitrogen was deposited; during 5 weeks in the summer (July and August) the deposition flux almost doubled to 0.95 kg N ha^{-1} (Beem et al., 2010). These 2006 observations included traditionally measured reactive nitrogen deposition pathways (wet deposition of ammonium and nitrate) as well as wet deposition of organic nitrogen and calculated dry deposition of ammonia, nitric acid, ammonium, and nitrate. Increases in deposition of organic nitrogen and ammonia above background levels are unquantified since there are few measurements of these nitrogen deposition pathways in this region.

The largest deposition pathway during the RoMANS study period was wet deposition of ammonium followed by wet deposition of nitrate and dry deposition of ammonia. These three pathways accounted for 72% of quantified reactive nitrogen deposition in the spring and 78% in the summer study periods. Gebhart et al. (2011) used a back trajectory based model to better understand the sources of nitrogen in the region during the RoMANS study. They found that more than half of the ammonia measured in RMNP during this study was emitted from within the state of Colorado.

The state of Colorado has several distinct areas of reactive nitrogen emissions. The eastern plains of Colorado are home to large agricultural sources including confined animal feeding operations (CAFOs) while the Colorado Front Range is a densely populated urban corridor along a boundary between the mountains and plains. The Denver-Colorado Springs-Fort Collins, metropolitan areas are major sources of anthropogenic emissions including NO_x (Fig. 1a) and SO_2 (not shown). In Fig. 1b we see ammonia emissions are highest in northeastern Colorado and further east in Nebraska where there are large agricultural operations. The location of ammonia sources in Colorado, including livestock operations, can be found in the Rocky Mountain National Park Initiative – Nitrogen Deposition Reduction Contingency Plan (2010). In western Colorado emissions of ammonia are relatively low while emissions of NO_x are high and similar to emission levels along the Front Range. Based on the 2008 National Emissions Inventory for the state of Colorado agricultural emissions (fertilizer and livestock waste combined) contribute 93% to total ammonia emissions in the state. Vehicle emissions contribute 3% while fuel combustion of natural gas and wood and fires contribute the remaining 4%. However, ammonia emissions estimates remain highly uncertain and in

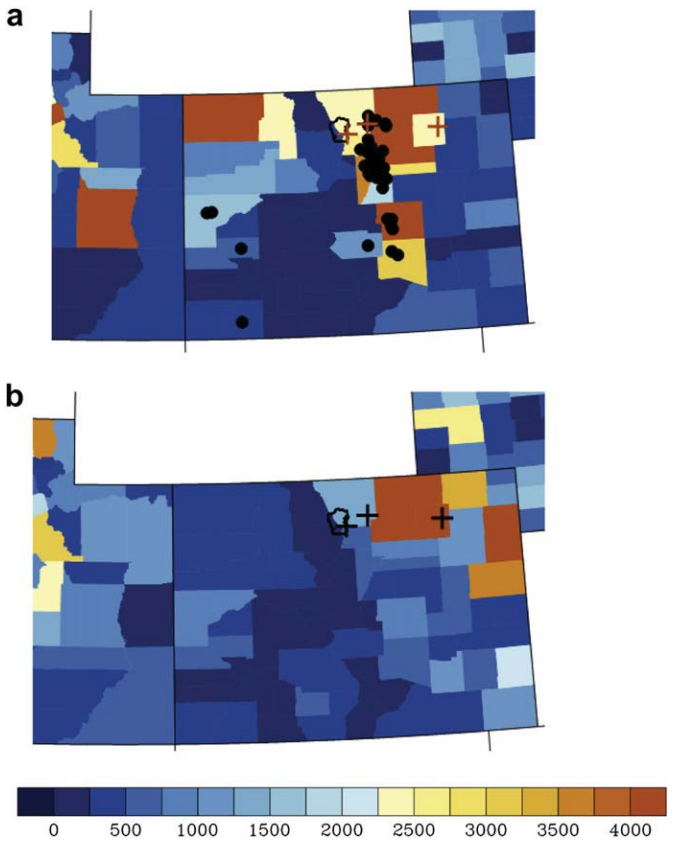

Fig. 1. Emissions (Mg N yr^{-1}) by county from 2008 in Colorado of a) NO_x and b) ammonia from National Emissions Inventory. Population centers larger than 15,000 are indicated by the black circles, Rocky Mountain National Park is outlined, and the yearlong sampling sites are indicated by the (+) signs.

urban areas vehicles can contribute significantly more to ammonia emissions (Kean et al., 2009).

In the Front Range point source emissions are one of the largest contributors to nitrogen emission, followed by highway mobile emissions and off-road (trains, construction, machinery) emissions (NEI, 2008; Baron et al., 2004; Williams and Tonnessen, 2000). Point sources include large electrical generating facilities and other industrial manufacturing and processing plants. Baron et al. (2004) examined emissions inventories and land use changes between 1985 and 1995 and found that counties just to the east of the mountains (Weld, Denver, and Adams) emitted greater than 8000 Mg of nitrogen in 1995, with the highest nitrogen emissions found in the South Platte Valley Basin. Emissions of nitrogen continue to increase in these counties; total nitrogen emissions in Weld county increased by 3400 Mg N from 2005 to 2008 and in 2008 were above 18,000 Mg N (NEI, 2005, 2008). However, county emissions vary by land use. For example, in Weld County, emissions are dominated by agriculture, not point or mobile sources (Baron et al., 2004; NEI, 2008). Sources in the mountains are more localized to small mountain communities. Understanding how concentrations of key nitrogen species change across the state as pollutants are transported is necessary to understanding which sources are important in RMNP, especially since RMNP straddles counties with both high (east side) and low (west side) emissions.

2. Methods

During the 2006 RoMANS campaign, a network of sampling sites was established across the state of Colorado (Table 1) to measure gas phase NH_3, HNO_3, and SO_2 as well as $PM_{2.5}$ NH_4^+, NO_3^-, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-}. Samples were collected across the sampling network from March 25th to April 28th, 2006 and from July 6th to August 10th, 2006. Two of the sampling sites were established within Rocky Mountain National Park on the east side of the Continental Divide: the main sampling site (MS, co-located with the RMNP Interagency Monitoring of Protected Visual Environments (IMPROVE) and EPA Clean Air Status and Trends Network (CASTNet) monitoring sites), and Beaver Meadows (BM, co-located with a RMNP National Atmospheric Deposition Program (NADP) wet deposition monitoring site). Three monitoring sites were established west of the Continental Divide. Timber Creek (TC) is located near the western boundary of RMNP, Gore Pass (GP) is located in the mountains approximately 53 km west of the park, and Dinosaur National Monument (DI) is located on the western border of Colorado with Utah. Four additional monitoring sites were established east of the park: Lyons (LY), Brush (BR), Grant, Nebraska (NE), and Springfield, CO (SP). Lyons is located immediately at the eastern edge of the Rocky Mountain foothills. Brush is located east of RMNP in a region of active agricultural and animal husbandry operations although such activities are limited in the immediate vicinity of the monitoring site. Grant is located in Nebraska, just across the eastern border of Colorado. All of the sites described thus far were selected to observe spatial gradients in reactive nitrogen species concentrations across northern Colorado. Springfield, located in the southeastern corner of Colorado, was selected to determine reactive nitrogen concentrations in the SE corner of the state in order to evaluate north–south concentration differences in eastern Colorado. All of the sites were operated during the RoMANS spring 2006 campaign. During the summer 2006 sampling campaign, the sites farthest away from RMNP (DI, NE, and SP) were not operated due to budget constraints. Daily 24 h samples were collected at each of these sites using URG Corporation (Chapel Hill, NC) annular denuder/filter-pack samplers from 8:00 a.m. to 8:00 a.m. MST with a nominal flow of 10 L min^{-1}. The sample was first drawn through a Teflon-coated cyclone ($D_{50} = 2.5$ μm) followed by a denuder (URG-2000-30X242-3CSS) coated with a sodium carbonate solution for collection of nitric acid and sulfur dioxide (Lee et al., 2008a) and then a denuder coated with phosphorous acid solution to collect ammonia. The air was then drawn through a nylon filter (PALL Nylasorb, 1 μm pore size) to collect particulate matter. Finally the flow traveled through a backup denuder coated with phosphorous acid to capture any ammonia volatilized from particulate ammonium on the nylon filter. Volatilized ammonium captured in the denuder as ammonia was added to the filter ammonium to obtain the total particulate ammonium concentration. We have shown previously (Yu et al., 2005) that any nitric acid volatilized from collected ammonium nitrate is quantitatively retained by the Nylasorb filter.

After the initial RoMANS field campaigns in 2006, a yearlong RoMANS II campaign was launched in November 2008 at the main sampling site in RMNP to determine the variability in reactive nitrogen species concentrations and deposition fluxes throughout the year. In addition to the 24-h URG annular denuder/filter-pack sampling in both 2006 and 2008, high time resolution $PM_{2.5}$ composition was measured at this main site using a Particle into Liquid Sampler (PILS) (Orsini et al., 2003; Weber et al., 2001, 2003; Lee et al., 2008b), for measurement of $PM_{2.5}$ major inorganic ion (NH_4^+, NO_3^-, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}) concentrations. The

Table 1
Site information including coordinates, elevation, abbreviation, and dates of operation for measurements presented here. The distance to the closest town is given along with the population from the town as of the 2010 US Census.

ID	Site name	Latitude	Longitude	Elevation (m)	Spring & summer 2006 (daily)	Yearlong 2008–2009	Distance to…
NE	Grant, NE	40.87	−101.731	317	March 25–April 28		3 km N of Grant, NE (pop. 1159)
SP	Springfield	37.37	−102.743	405	March 25–April 28		12 km SE Springfield, CO (1454)
BR	Brush	40.3138	−103.6022	333	March 25–April 28 July 6–Aug. 10	Dec. 11, 08–Dec. 10, 09 (weekly, 52 samples)	6.5 km NE Brush, CO (5292)
	Loveland	40.426	−105.107	1551		Dec. 11, 08–Dec. 10, 09 (weekly, 52 samples)	In Loveland (68,203) 74 km N of Denver, CO
LY	Lyons	40.2273	−105.2751	1684	March 25–April 28 July 6–Aug. 10		0.5 km NW Lyons, CO (2067)
MS	Main Site (RMNP)	40.2783	−105.5457	2784	March 25–April 28 July 6–Aug. 10	Nov. 11, 08–Nov. 11, 09 (daily, 366 samples)	10 km S of Estes Park, CO (5976)
BM	Beaver Meadows	40.3560	−105.5810	2509	March 25–April 28 July 6–Aug. 10		4 km SW of Estes Park, CO (5976)
TC	Timber Creek	40.3800	−105.8500	2767	March 25–April 28 July 6–Aug. 10		28 km W of Estes Park, CO (5976)
GP	Gore Pass	40.1172	−106.5317	2641	March 25–April 28 July 6–Aug. 10		13.5 km NW of Kremmling, CO (1414)
DI	Dinosaur	40.437	−109.3047	1463	March 25–April 28		7.5 km NE of Jensen, UT (412)

PILS was coupled to two ion chromatographs (PILS-IC) for real-time online analysis. Meteorological measurements were made at the main site during RoMANS I and II by a 10 m tower operated by the CASTNet program.

During the RoMANS II study two additional URG annular denuder/filter-pack sampling sites were operated and collected weekly samples beginning in December 2008: a suburban Front Range site located east of RMNP in Loveland, CO and the previously described site in Brush, CO. The URG sampler flow rate was lowered to 3 L min^{-1} at Brush during RoMANS II and a second ammonia denuder was added before the filter to ensure the capacity of the denuder was not exceeded as a result of high ammonia concentrations typical at the site. No evidence of breakthrough was observed as only a small amount of ammonia was observed in the second denuder compared to the first. The ammonia collected on each of the ammonia denuders before the filter was added together to obtain the atmospheric ammonia concentration.

Blanks were collected weekly at the RMNP site during all study periods but installing a denuder/filter-pack sampler in the field in the same manner as a sample except no air was drawn through the sampler. Blank values were low and a minimum level of detection (MDL) was calculated for each species. The MDL for the particulate species were 0.049 μg m^{-3} for NO_3^-, 0.089 μg m^{-3} for SO_4^{2-}, 0.018 μg m^{-3} for NH_4^+ and for the gas phase species were 0.011 μg m^{-3} for HNO_3, 0.091 μg m^{-3} for SO_2, and 0.13 μg m^{-3} for NH_3. A separate travel blank was collected for the Loveland and Brush sites during the 2009 study and all blanks were low (Day et al., 2012).

Filter extracts were analyzed for both cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) and anions (Cl^-, NO_3^-, NO_2^-, and SO_4^{2-}) by ion chromatography. Denuder extracts were analyzed either for ammonium (phosphorous acid-coated denuders) or for sulfate and nitrate (carbonate-coated denuders). Cations were separated on a Dionex CS12A column followed by a CSRS ULTRA II suppressor and a Dionex CD-20 conductivity detector. Anions were separated on a Dionex AS14A column followed by an ASRS ULTRA II suppressor and a Dionex CD-20 conductivity detector. Each ion chromatograph was calibrated daily using standards prepared from analytical grade salts. Periodic standard and replicate sample analyses were used to monitor calibration stability and analytical precision during batch analyses. In addition, Dionex NIST-traceable standards were analyzed during each run to independently check the accuracy of analysis.

3. Results

The network of measurement sites during RoMANS 2006 provides a unique opportunity to look at the distribution of reactive nitrogen species concentrations in an east–west gradient across northern Colorado. In Fig. 2 the seasonal average concentrations of ammonia, ammonium, nitric acid, nitrate, sulfur dioxide and sulfate are plotted for both the spring and summer 2006. Table 2 summarizes the average, minimum, and maximum concentrations of the nitrogen species measured at each site during each 2006 sampling campaign. The complete set of data can be found in the supplement. Average ammonia concentrations are higher, on a molar basis, than those of the other measured species in both the spring and the summer. Ammonia and ammonium exhibit similar trends: they are highest on the northeastern plains, and concentrations drop at higher elevation sites to the west as well as in SE Colorado. Concentrations of ammonium are higher in Grant, NE compared to Brush during the spring while ammonia concentrations are lower. While Fig. 2 depicts the average seasonal gradients, the patterns observed here for reduced nitrogen species concentrations are qualitatively similar on most individual days of the study. The average ratio of ammonia concentrations at Brush (east of RMNP) to Gore Pass (west of RMNP) is 43.1 in spring and 25.9 in summer. For ammonium concentrations, the equivalent site concentration ratios are 9.3 for spring and 2.4 for summer. The larger spatial gradients observed for ammonia are consistent with large sources of ammonia emissions in NE Colorado and the shorter atmospheric residence time of ammonia versus ammonium. Brush is located in a region where there are many confined animal feeding operations (CAFOs); however, the monitoring site location was selected so that it was not in the immediate vicinity (within several km) of such an operation. Results from Day et al. (submitted for publication) indicate concentrations of NH_3 at Brush fall in the middle concentration range of ammonia observations in the region. Ammonia concentrations are higher at all sites in the summer compared to spring, while ammonium concentrations at all but Gore Pass are similar in spring and summer. The average ammonium concentration at Gore Pass approximately doubles from spring to summer.

In contrast to ammonia and ammonium, nitric acid concentrations, on average, were highest at Lyons (Fig. 2), located in the urban Front Range corridor, and dropped off to both the east and the west. This is consistent with peak NO_x emissions centered in the Front Range urban corridor, and the loss of nitric acid due to deposition and reaction to form ammonium nitrate particles. Not surprisingly, average summertime nitric acid concentrations were higher than spring concentrations at all sites, consistent with greater photochemical activity and higher temperatures that cause more nitric acid to remain in the gas phase due to the instability of ammonium nitrate at higher temperature. A sharp gradient was also observed both in spring and summer for $PM_{2.5}$ nitrate concentrations, which were highest at Lyons and Brush and decreased moving westward into the mountains. The similarity in nitrate concentrations between Brush and Lyons reflects the importance of ammonium nitrate formation as the nitric acid derived from urban NO_x emissions mixes over the eastern plains with ammonia from agricultural emissions. Watson et al. (1998) observed a similar regional phenomenon a decade earlier in the Northern Front Range Air Quality Study. It is also interesting to note that, while reduced nitrogen species concentrations at the Gore Pass are similar to or lower than at the Timber Creek site on the western boundary of RMNP, the oxidized nitrogen species concentrations at Gore Pass tend to be a bit higher than at Timber Creek. This may reflect an increase in NO_x emission sources west of RMNP, including growing oil and gas recovery activities (COGCC Statistics Library, 2012).

Concentrations of ammonia, ammonium, nitric acid, nitrate, and sulfur dioxide measured at Springfield in SE Colorado were lower than those observed at Brush and Grant, NE to the north. Springfield is located significantly further south than any of the other sampling sites and the different concentrations measured there in spring 2006 reflect different regional emissions. Moving from Gore Pass west to Dinosaur, concentrations of NH_3, HNO_3, NO_3^-, and SO_2 increase. This trend in concentrations is consistent with higher NO_x emissions in western Colorado, southwest Wyoming, and eastern Utah and increased ammonia emissions from agricultural operations in regions close to Dinosaur.

Both nitrate and sulfate concentrations are low at all sites. The spring average maximum concentration of nitrate was 0.01 μmol m^{-3} (0.85 μg m^{-3}) and the summer average maximum concentration was 0.006 μmol m^{-3} (0.37 μg m^{-3}). The spring and summer average maximum concentration of sulfate was 0.01 μmol m^{-3} (0.99 μg m^{-3}).

While the focus of discussion here is on reactive nitrogen species, it is interesting to note that fairly strong east–west gradients were observed in sulfur dioxide concentrations during both spring and summer (highest concentrations in the east), while

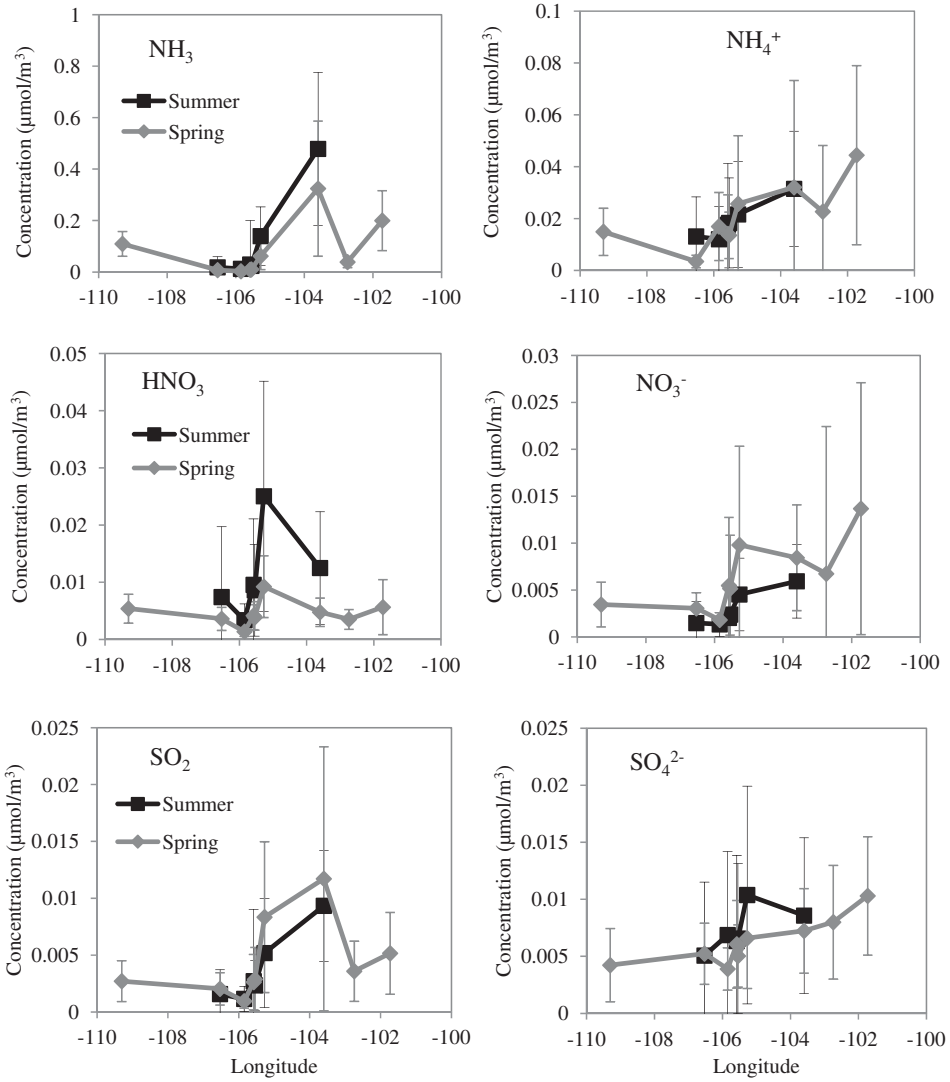

Fig. 2. Seasonal average concentrations of ammonia, ammonium, nitric acid, nitrate, sulfur dioxide and sulfate are plotted for spring and summer of 2006. Error bars represent the standard deviation of daily concentrations measured during each season. From west to east, the included sites are Dinosaur, Gore Pass, Timber Creek, Beaver Meadows, Main Site, Lyons, Brush, Springfield, and Grant, NE.

Table 2
Summary of 24-h atmospheric reactive nitrogen concentrations (μmol m^{-3}) measured during the 2006 sampling campaigns.

		n	HNO_3			NH_3			NH_4^+			NO_3^-		
			Min	Average	Max	Min	Average	Max	Min	Average	Max	Min	Average	Max
NE	Spring	34	0.001	0.006	0.028	0.044	0.2	0.536	0.006	0.044	0.173	0.002	0.014	0.057
	Summer	0												
BR	Spring	34	0.001	0.005	0.012	0.055	0.324	1.203	0.005	0.032	0.211	0.001	0.008	0.028
	Summer	31	0.005	0.013	0.025	0.16	0.479	1.233	0.011	0.031	0.074	0.002	0.006	0.019
SP	Spring	35	0.001	0.004	0.007	0.012	0.039	0.091	0.001	0.023	0.154	0.001	0.007	0.094
	Summer	0												
LY	Spring	35	0.003	0.009	0.021	0.006	0.062	0.198	0.001	0.026	0.138	0.001	0.01	0.038
	Summer	34	0.001	0.025	0.077	0.01	0.14	0.314	0.003	0.022	0.056	0	0.005	0.021
MS	Spring	36	0.001	0.004	0.011	0.003	0.01	0.036	0.003	0.014	0.036	0	0.005	0.024
	Summer	36	0.002	0.009	0.023	0.01	0.024	0.093	0.008	0.018	0.042	0.001	0.002	0.008
GP	Spring	35	0.001	0.004	0.008	0	0.008	0.014	0.001	0.003	0.009	0.001	0.003	0.007
	Summer	36	0.002	0.007	0.014	0	0.018	0.029	0.004	0.013	0.023	0.001	0.001	0.003
TC	Spring	34	0	0.001	0.003	0.002	0.003	0.009	0.003	0.017	0.062	0.001	0.002	0.003
	Summer	36	0.001	0.003	0.013	0.003	0.013	0.029	0.001	0.012	0.028	0	0.001	0.006
DI	Spring	35	0.002	0.005	0.011	0.031	0.11	0.21	0.001	0.015	0.036	0.001	0.003	0.013
	Summer	0												
BM	Spring	35	0.001	0.004	0.013	0.001	0.009	0.05	0.002	0.014	0.079	0.001	0.005	0.032
	Summer	37	0.002	0.01	0.022	0.01	0.029	0.097	0.007	0.018	0.054	0.001	0.002	0.007

spatial gradients in $PM_{2.5}$ sulfate concentrations are fairly small. The lack of strong sulfate spatial gradients suggests a fairly uniform concentration of sulfate is typical in the region. The regional nature of particulate sulfate has been noted at locations throughout the United States (Hand et al., 2012). The oxidation of SO_2 to form SO_4^{2-} takes several days in the absence of cloud processing so that even when there are gradients in SO_2 concentrations gradients in sulfate concentrations tend to be smaller.

While the spring and summer seasonal average trends provided important information about the differences between concentrations in the plains, Front Range, and mountains, investigating full annual cycles of these species' concentrations is important for identifying potential transport patterns and/or sources that might change seasonally. The 2008/09 RoMANS II sampling campaign at the RMNP main site, Loveland, and Brush provides insight into the annual cycle of species concentrations in the park and locations to the east where strong gradients were observed in 2006. In Fig. 3 the daily concentrations measured at RMNP and the weekly concentrations measured at Brush and Loveland are plotted by species. As in the spring and summer 2006 observations, a sharp concentration gradient is observed for most species moving from the eastern plains and urban Front Range corridor into the mountains, with concentrations typically much lower at RMNP for most species and time periods.

Ammonia concentrations at Brush are highest in the winter and summer and concentrations are generally highest at Brush among all three sites throughout the year. At Loveland the change in ammonia concentrations throughout the year is not as dramatic as at Brush but the highest concentrations also occur during the summer. At RMNP ammonia concentrations are always much lower than at the other two sites but there are increases in concentration beginning in the spring. Ammonium concentrations tend to be fairly similar at Brush and Loveland, as observed in the spring and summer 2006 Brush-Lyons comparison (Lyons is 16 km northwest of Loveland). RMNP ammonium concentrations are still generally lowest of the three sites, especially in the fall and winter, but gradients during warmer times of the year are suppressed. While NH_4^+ concentrations at Brush and Loveland tend to rise in winter and fall, decrease in summer, a somewhat different pattern was observed at RMNP. Here, ammonium concentrations are low in late

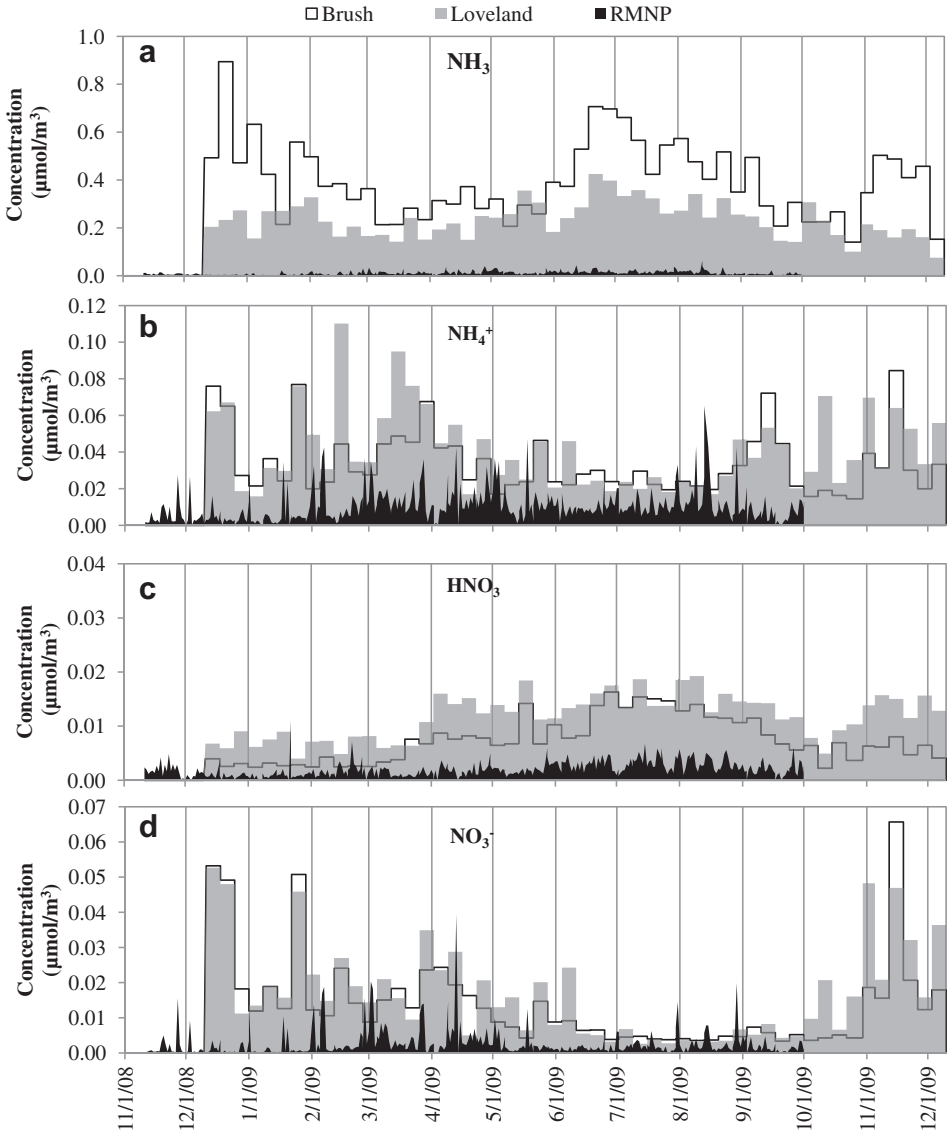

Fig. 3. Seasonal cycles of NH_3 (a), NH_4^+ (b), HNO_3 (c), and NO_3^- (d) at the Brush, Loveland, and RMNP sampling sites.

fall and early winter, then increase moving through winter into spring and summer. It appears that both changes in transport and in gas-particle partitioning contribute to the observed annual cycles of ammonium concentrations and the observed spatial gradients. The low concentrations of both ammonia and ammonium at RMNP in winter suggest that this high elevation region is typically fairly isolated from lower elevation emission sources, especially large sources east of the park, at this time of year. As temperatures warm up in the region moving into spring and summer and greater vertical mixing and enhanced mountain–valley circulation patterns are strengthened, transport of pollutants into the park is increased. The cooler temperatures at high elevation in RMNP, however, continue to favor particle phase formation of ammonium nitrate even at generally warmer times of the year, while higher temperatures at Brush and Loveland are associated with a shift from particle phase ammonium and nitrate to gas phase ammonia and nitric acid. Further analysis of gas-particle partitioning will be discussed below.

Nitric acid concentrations (Fig. 3c) show a strong seasonal pattern; concentrations at both Brush and Loveland are highest from mid-March through September. Winter and spring are the times when nitrate concentrations are highest at Brush and Loveland, similar to the seasonal pattern observed for ammonium described above. Distinct sample to sample variability in nitrate concentrations is also observed. Nitrate concentrations are similar at Brush and Loveland throughout much of the year. A decrease in nitrate concentrations at RMNP doesn't occur until June and even then there are several instances when daily average RMNP concentrations approach weekly average concentrations at Brush and Loveland. Overall, during summer 2009 the spatial gradient in nitrate concentrations between the plains and mountains decreases as previously observed in 2006.

To understand changes in concentrations on shorter time scales, semi-continuous $PM_{2.5}$ speciation observations made at RMNP using a PILS-IC were examined. As noted previously for the 2006 RoMANS campaign (Beem et al., 2010), during the spring easterly upslope winds periodically transport aerosol and aerosol precursors from the Front Range and eastern plains up to RMNP. Mountain–valley wind circulations are common in mountainous regions due to differential heating of the surface at different elevations (Ahrens, 2002). In Fig. 4 ammonium, nitrate, and sulfate concentrations are plotted along with wind direction for the spring and fall 2009 time periods. Precipitation events are also identified. Almost every day during late May between 10 a.m. and 2 p.m. the wind changed to blow from the east or southeast (easterly upslope flow channeled by local topography) followed by an increase in ammonium concentrations (Fig. 4a). For example, there is a shift in wind direction from north/northwest to east/southeast beginning around 10:00 a.m. on 5/26, which is immediately followed by a rapid increase in concentration. The concentration stays high while winds are from the southeast; once winds shift to the north again later in the day concentrations begin to decrease. Most of the days in this timeline had precipitation associated with the development of upslope flow which can contribute to precipitation initiation.

In the fall 2009 timeline (Fig. 4b), one does not see the same regular, diurnal pattern of upslope/downslope winds observed in spring. During this 20 day period, however, several upslope events were recorded and were associated with significant precipitation events. In addition, notice the different scales in Fig. 4a and b, the concentrations were more than 2 times higher in fall compared to spring. While the spring upslope wind events illustrated in Fig. 4a lasted several hours during mid day, the fall upslope events lasted much longer and were associated with larger, synoptic scale events. The larger scale forcing driving the fall upslope events also resulted in substantially higher $PM_{2.5}$ reactive nitrogen concentrations reaching RMNP, with several periods reaching the 1–4 μg m^{-3} range. Note the rapid drop in $PM_{2.5}$ species concentrations observed in the 2nd (Oct. 9–10) and last (Oct. 21) upslope events. This drop-off occurs following the onset of precipitation and despite sustained upslope winds, indicating the effective scavenging and removal of large amounts of fine particulate matter by wet deposition. These events are similar to the large spring 2006 RMNP upslope deposition event described by Beem et al. (2010)

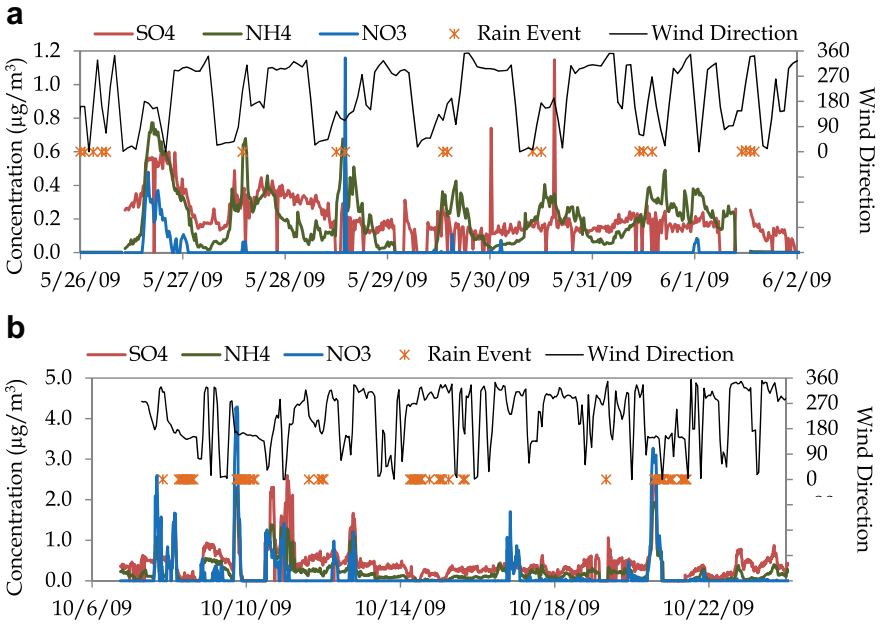

Fig. 4. $PM_{2.5}$ composition as measured by PILS-IC plotted with wind direction showing an a) spring trend and b) a typical fall trend. Wind direction (black), ammonium (green), sulfate (red), and nitrate (blue) are plotted. When the wind speed was less than 0.5 m s^{-1} the wind was considered calm and wind directions associated with those periods were removed from the analysis. Precipitation events (>0.1 mm h^{-1}) are also indicated on the timeline. Each plotted symbol represents a time period when precipitation was collected.

and illustrate that this important pattern (down-gradient transport of pollutants from eastern Colorado up into RMNP followed by precipitation scavenging and wet deposition) can also be important in autumn.

4. Discussion

4.1. Gradients and partitioning

Large changes in atmospheric concentrations of reactive nitrogen species occur across the state of Colorado. These differences are largely the result of different regional emissions and transport. In northeastern Colorado there are extensive agricultural activities, including large confined animal feeding operations. These agricultural operations are large ammonia sources (Bouwman et al., 1997; National Research Council, 2003; Steinfeld et al., 2006) and our observations during both 2006 and 2009 observed the highest ammonia concentrations at Brush in NE Colorado. The peak at Brush appears to reflect mainly NE Colorado ammonia emissions. Even though higher ammonia emission regions exist further east (e.g., Nebraska and Iowa), the spring 2006 observations at Grant, Nebraska (Fig. 2) show a ground-level concentration decrease from Brush to Grant, suggesting that transport from farther east is not likely a primary determinant of NE Colorado ammonia concentrations. This point is reinforced by observations discussed by Day et al. (2012) who used a network of passive ammonia samplers to examine spatial gradients in ammonia concentrations in NE Colorado. They observed substantial variability in ammonia concentrations, with higher concentrations at sites closer to Colorado animal feeding operations. Ammonia concentrations at Brush were in the middle of the observed concentration range. Large ammonia concentration gradients from the eastern plains westward into the mountains are not limited to just spring and summer; they occur year-round. Nitrate concentrations at Loveland and Lyons were often similar to Brush while nitric acid concentrations were usually higher at these two suburban Front Range corridor sites, consistent with higher NO_x emissions in this region.

East–west spatial ground-level concentration gradients from Brush through RMNP to Gore Pass are stronger in the summer for both ammonia (NH_3) and nitric acid (HNO_3), probably reflecting both higher concentrations in the source regions and a change in the thermodynamic partitioning of the NH_3–HNO_3–NH_4NO_3 gas-particle system. The lack of measurements in Dinosaur during summer 2006 prevents an analysis of seasonal changes in the concentration gradient further west of Gore Pass. Changes in partitioning have implications for the atmospheric lifetime and travel distance of each species, affecting the locations and amounts of nitrogen deposition. Much lower deposition rates for accumulation mode ammonium nitrate particles, versus gaseous nitric acid and ammonia, result in longer lifetimes and a greater chance that they will be transported to areas of interest, such as RMNP, that are spatially separated from large emission sources. On the other hand, dry deposition fluxes of reactive nitrogen will be greater in cases where local partitioning favors gaseous ammonia and nitric acid over fine particle ammonium nitrate.

In Fig. 5 we examine the change in gas-particle partitioning across the sites during the 2006 RoMANS spring and summer studies. Ratios of ammonium to the sum of ammonium and ammonia and of nitrate to the sum of nitrate and nitric acid are considered. As expected during summer when temperatures are warmer, there is at all sites a greater fraction of oxidized nitrogen ($N^{(V)} = HNO_3 + NO_3^-$) in the gas phase compared with spring. A similar pattern is observed between spring and summer for reduced nitrogen ($N^{(-III)} = NH_3 + NH_4^+$) at most sites. Due to a large excess of ammonia, the $N^{(-III)}$ partitioning doesn't change much between seasons at Brush. Additionally, the higher elevation sites generally have a larger fraction of $N^{(-III)}$ in the particle phase, consistent with cooler temperatures at higher elevations year round. Higher $N^{(-III)}$ and $N^{(V)}$ concentrations in RMNP during summer (Fig. 3) along with the shift in partitioning toward gas phase species possessing higher deposition velocities (Fig. 5), both favor higher amounts of RMNP nitrogen dry deposition in the warmer months. We should note that change in the partitioning of ammonium-nitrate is not the only factor in driving the trend in Fig. 5. The gas-particle partitioning of $N^{(-III)}$ is also influenced by the inclusion of ammonium in sulfate salts. There may also be shifts in the relative importance of the sources and type of nitrogen compounds. Emissions of ammonia increase during the warmer months because of increased volatilization from surfaces. In addition, nitrate has been shown to be an important component of coarse mode particles at some rural locations (Lee et al., 2008a) and there may be a seasonal shift in $N^{(V)}$ gas-particle partitioning associated with the aerosol in the region that is not captured by only examining nitric acid and $PM_{2.5}$ nitrate.

4.2. Effect of upslope events on deposition

Upslope events have previously been shown to be important contributors to spring deposition in RMNP (Beem et al., 2010). The movement of polluted air from the east up against the mountains, accompanied by heavy precipitation can produce large wet deposition pollutant fluxes. As mentioned above, the inclusion of fall monitoring in 2009 revealed that important upslope deposition events occur in the autumn as well (Fig. 4b). To better explore the relationship between high $PM_{2.5}$ species concentrations and wind

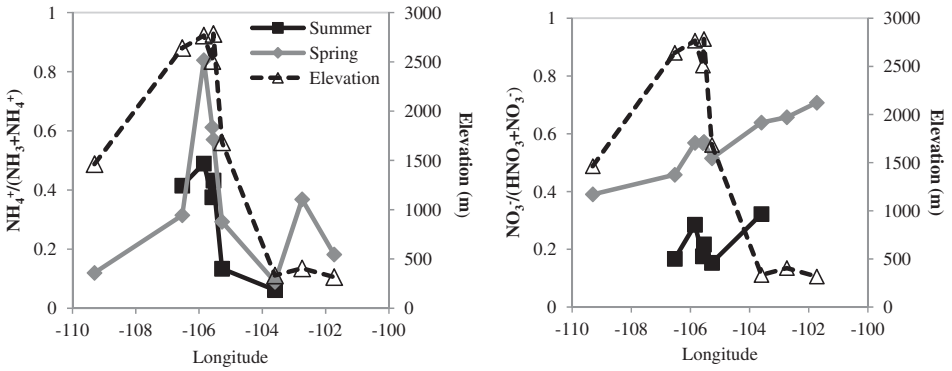

Fig. 5. Partioning across sites during the spring (gray) and summer (black) 2006 studies for both ammonium/ammonia ($N^{(-III)}$) system and nitrate/nitric acid ($N^{(V)}$) system. For reference, elevation is also plotted using the righthand axis.

direction, a conditional probability function (CPF) was calculated based on the number of 90th percentile concentrations in a 5° wind sector compared to the total number of samples in the same 5° wind sector (Kim et al., 2003; Xie and Berkowitz, 2006; Lee et al., 2008b). The hourly wind distribution was also plotted according to the fraction of time that wind was blowing from a given 5° sector (Fig. 6a). Winds at the sampling site blow most often from the northwest. There is a sharp decrease in wind frequency outside of the 270–360° range with a secondary maximum centered at 150°. Winds from approximately 150° correspond to upslope flow

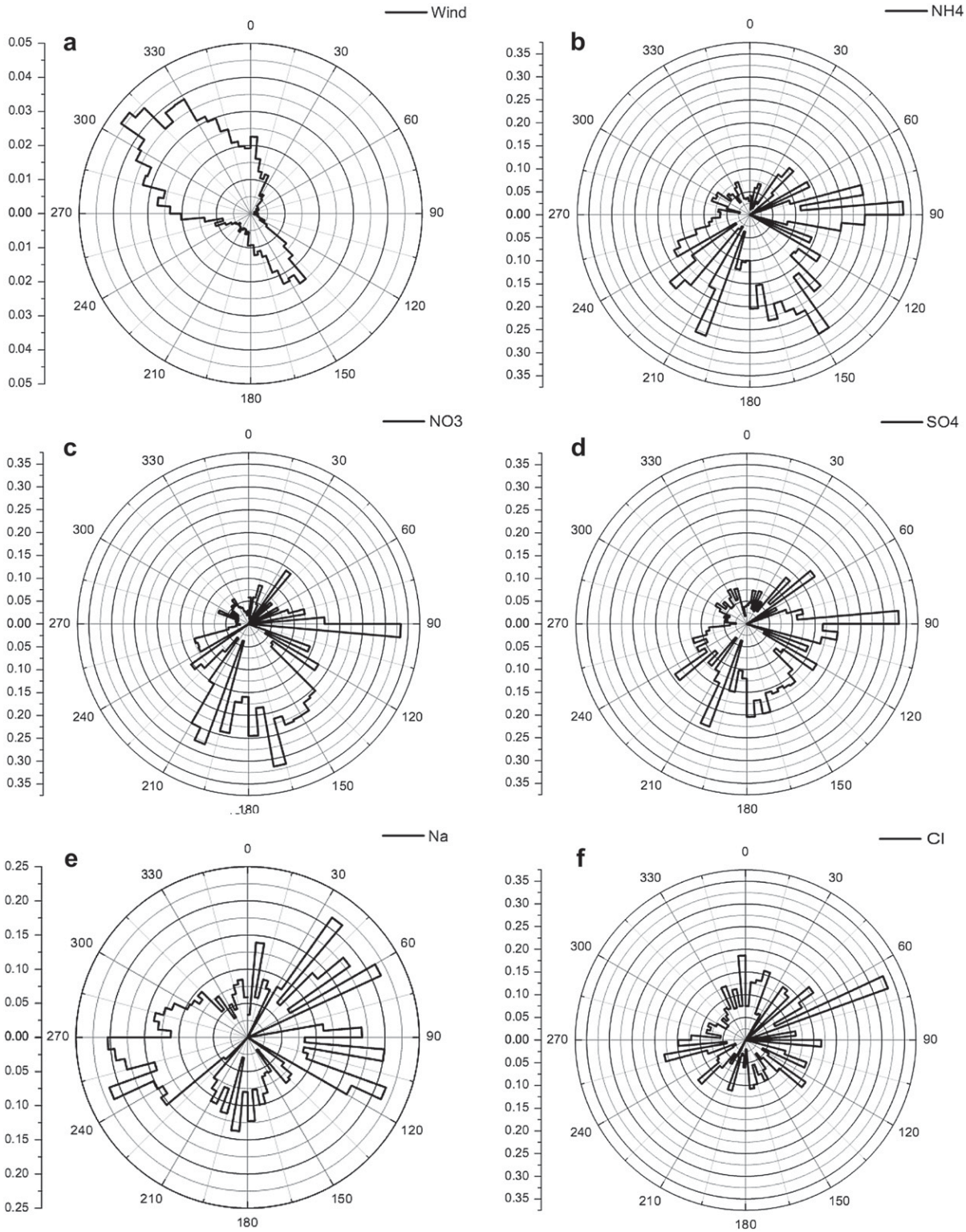

Fig. 6. a) Hourly wind data were plotted according to the fraction of time wind was from a given 5° sector. b–f) Conditional probability functions for NH_4^+, NO_3^-, SO_4^{2-}, Na^+, and Cl^- calculated based on the number of 90th percentile concentrations in a 5° wind sector, compared to the total number of samples in the same 5° wind sector. The radial scale is the fraction of time winds from a 5° wind sector were associated with the highest 10% of concentrations.

channeled by local topography. Conditional probability function plots are shown for several key species in Fig. 6b–f.

The highest concentrations of ammonium typically occur when winds are from the east or SE, corresponding to upslope transport from the region east of RMNP. Nitrate shows a similar pattern. Fig. 4 also indicates that precipitation often occurs during upslope events in 2009 (e.g., on 5/28, 5/29, 10/20) but not always (5/27) and upslope flow is not a necessary condition for precipitation (10/14–10/15).

Returning to the CPF plots (Fig. 6), higher concentrations of sulfate are not as strongly skewed to the southeast; there is a broader sector across which the highest concentrations originate reflecting the more uniform spatial pattern of sulfate concentrations discussed earlier. In comparison, sodium indicates a very different transport pattern, with highest concentrations when local winds are from the west. We might expect this pattern since the Great Salt Lake and Pacific ocean to the west could be important sources of the sodium ion we are measuring (Pratt et al., 2010). While chloride might be expected to be associated with the same source, it can be displaced to the gas phase as the aerosol is processed during transport, and it readily reacts with stronger acids such as nitric or sulfuric acid (e.g., Robbins et al., 1959; Keene et al., 1990; McInnes et al., 1994). Lee et al. (2008a,b) demonstrated that reaction of nitric acid or its precursors with both sea salt and soil dust commonly lead to formation of coarse mode nitrate particles in the U.S. The conditional probability function for chloride (Fig. 6f), in fact shows no obvious directional signal. A detailed evaluation of sources contributing to atmospheric nitrogen in the region can be found in Gebhart et al. (2011) where back trajectories are used for source apportionment related to the 2006 dataset.

4.3. Excess nitrogen

The high nitrogen concentrations to the east of RMNP and periodic transport from the east produce higher concentrations of nitrogen species in the park than occur under transport from the west, reflecting contributions of emissions from eastern Colorado and possibly beyond. The 2006 RoMANS study included two sites west of the Continental Divide, Timber Creek (TC) and Gore Pass (GP), where the impact of these eastern Colorado emissions is less. Using the average of the concentrations measured at these two western slope sites, "excess" nitrogen at sites in RMNP can be calculated to provide another perspective on the impacts of human activities east of the park. Because spatial/altitudinal gradients in temperature and relative humidity strongly affect gas-particle partitioning, we consider here excess concentrations of $N^{(V)}$, the molar sum of NO_3^- and HNO_3, and $N^{(-III)}$, the molar sum of NH_4^+ and NH_3. At the RMNP Main Site in spring 2006, $N^{(V)}$ concentrations were 83% (4 nmol m^{-3}) greater than at the two west slope sites while $N^{(-III)}$ concentrations were 61% (8 nmol m^{-3}) greater. During summer, $N^{(V)}$ was 61% (4 nmol m^{-3}) greater at the RMNP main site east of the Continental Divide than at the western slope sites while $N^{(-III)}$ was 51% (14 nmol m^{-3}) greater. These increases, all exceeding 50%, are another measure of the substantial impact of anthropogenic activities east of the park on RMNP air quality and ecosystems, despite the fact that winds in the region most commonly blow from the west.

5. Conclusions

Atmospheric observations of ground-level reactive nitrogen species concentrations reveal strong gradients across northern Colorado. Concentrations of both oxidized and reduced nitrogen are by far highest east of the park. Observations in RMNP and from the surrounding area indicate the highest concentrations of atmospheric reactive nitrogen originate from east of the park. High concentrations of both ammonia/ammonium and nitric acid/nitrate east of the Continental Divide in RMNP are associated with periods of upslope transport which move emissions from east of the park westward and up the east slope of the Rockies into the park itself. The northeastern plains of Colorado are an important source of ammonia emissions while the Front Range urban corridor is an important source of nitrogen oxides emissions which react in the atmosphere to form nitric acid. Atmospheric reaction of ammonia and nitric acid results in the formation of fine particle ammonium nitrate. Because the atmospheric lifetime of ammonium nitrate is much longer than the lifetimes of gaseous ammonia or nitric acid, the interaction of urban and agricultural reactive nitrogen emissions that occurs in NE Colorado may be an important factor contributing to the production of material that survives long enough to be effectively transported into RMNP.

While atmospheric transport into RMNP typically brings air from the west, periods of upslope transport from the east occur often enough that they are important contributors to reactive nitrogen deposition within the park, especially east of the Continental Divide. Clear association between defined periods of upslope transport from the east and elevated ground-level reactive nitrogen species concentrations in the park indicates the importance of this transport pathway. Upslope transport can occur as part of diurnally occurring mountain–valley wind circulations or in conjunction with larger scale, synoptically forced events. Because the lifting of air up the eastern slope of the Rockies also helps give rise to precipitation, these upslope events are particularly effective at delivering emissions from the east into the park at the same time that precipitation can scavenge and deposit that material into park ecosystems. While previous work during the RoMANS 2006 study indicated the importance of such upslope major deposition events in spring, evidence presented here also indicates the importance of this mechanism in the fall.

The importance of contributions from sources east of RMNP to reactive nitrogen species concentrations in the park is also illustrated by a simple comparison of concentration differences between the east and west sides of the Continental Divide. Concentrations east of the divide exceeded concentrations west of the divide by more than 50% for both $N^{(V)}$ and $N^{(-III)}$ in spring and summer, providing another indicator of the large impact anthropogenic emissions east of the park have on RMNP air quality. Understanding transport patterns and origins of key reactive nitrogen species is a first step to identifying important source types and regions currently contributing to reactive nitrogen deposition in RMNP and its impact on protected ecosystems.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2012.08.066.

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