Final report for Task # H2370094000/P11AT70958

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GrandTRENDS: the Grand Teton Reactive Nitrogen Deposition Study

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1. Overview of Project

The National Parks are immensely popular public resources. Protection of these national treasures requires understanding of various threats to park resources. Included are threats to visibility and to sensitive ecosystems. The research in this project relates directly to diagnosing and remedying air quality problems in our national parks. It provides the basis for informed decision-making about steps to protect park resources by improving and managing air quality.

The long-term goals of this project are to improve understanding of deposition of pollutant species to sensitive park ecosystems, to diagnose contributors to air quality problems in specific parks, and to generate fundamental new knowledge about specific pollutant species contributing to air quality and visibility problems in national parks. Attainment of these goals involves the planning, execution, and analysis of field measurements of air quality at select national parks and in surrounding regions.

The major goals of this task included continued efforts to characterize transport and deposition of reactive nitrogen species in Grand Teton NP, ongoing analysis and publication of findings from nitrogen deposition studies in Rocky Mountain NP, and implementation of a pilot-scale IMPROVE sub-network for routine monitoring of atmospheric concentrations of ammonia plus $PM_{2.5}$ ammonium (NHx) in the Rocky Mountain region.

2. Major National Park Service Research Activities Completed by CSU

Reactive nitrogen species concentrations and deposition in Rocky Mountain National Park

Recent research in Rocky Mountain National Park (RMNP) and Grand Teton National Park (GTNP) provides important new insights into the importance of various regional nitrogen deposition pathways and the sources of the deposited nitrogen. Extensive recent measurements in both parks, developed and led by Colorado State University (CSU), have documented the relative importance of various dry and wet reactive nitrogen deposition pathways.

During the 2006 Rocky Mountain Atmospheric Nitrogen and Sulfur (RoMANS) study, wet deposition of organic nitrogen and dry deposition of gaseous ammonia were found to be major contributors to reactive nitrogen deposition fluxes in the park. Prior to RoMANS, routine monitoring of gaseous ammonia and wet deposition of organic nitrogen were uncommon, especially in remote areas of the western U.S. CSU RMNP measurements from 2008-10 have confirmed the importance of these deposition pathways in subsequent years and extended information about the deposition budget across the full annual cycle. Figure 1 illustrates the seasonal contributions of multiple pathways to reactive nitrogen deposition in RMNP (Benedict et al., 2013a).

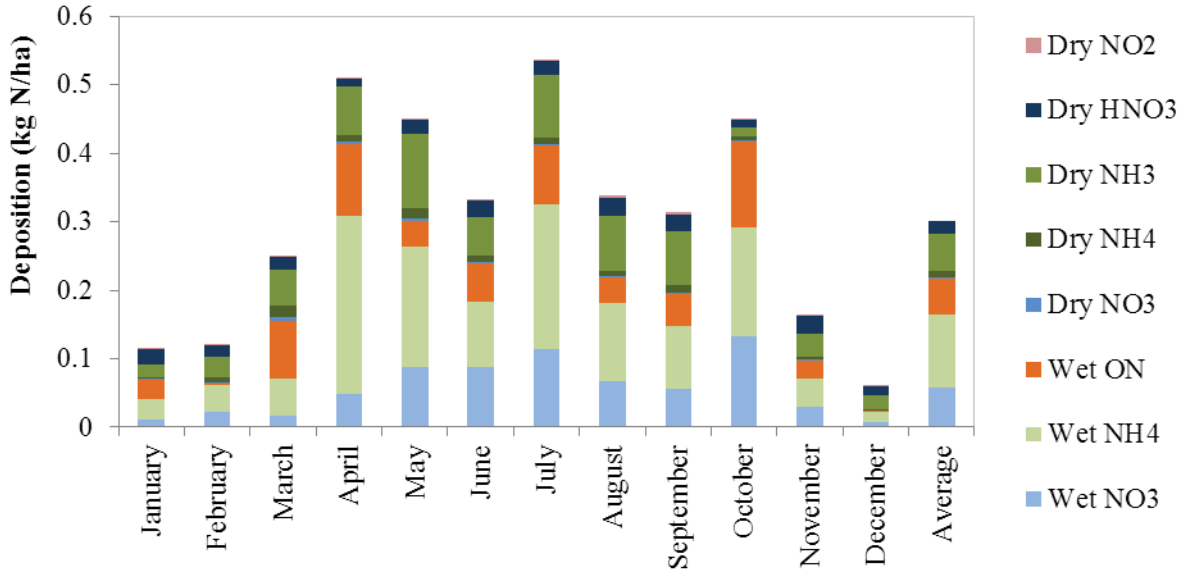

Figure 1. Total contributions to total nitrogen deposition for each pathway by month. The monthly average is also included. The blue shades indicate oxidized $N^{(V)}$ species while the green shades indicate the reduced $N^{(-III)}$ species. Organic nitrogen is shown in orange and NO_2 is in pink. Dry deposition of particulate organic nitrogen is not included in this figure because it was only available for 8 of the 12 study months.

Atmospheric reactive nitrogen species concentrations and deposition fluxes tend to be low during winter, when RMNP is fairly isolated from large emissions sources at lower elevations. Both concentrations and deposition fluxes increase during spring, summer, and fall, as the atmospheric boundary layer deepens and upslope flow from east of the Rockies transports emissions from large sources east of the park into RMNP (Benedict et al., 2013b). Figure 2 illustrates spatial gradients in key reactive nitrogen airborne species concentrations observed during the spring and summer 2006 RoMANS campaigns while Figure 3 illustrates a year-long set of observations of these spatial gradients from RMNP east to the Front Range urban corridor (Loveland) and into NE Colorado (Brush).

While spring upslope precipitation events were previously identified as important vectors for the transport and deposition of agricultural and urban emissions from eastern Colorado, the 2008-09 measurements also revealed the importance of similar events in autumn (Benedict et al., 2013b). Based on the local wind direction measured at RMNP, upslope flow from the east occurred less than 20% of the time (based on hourly winds) and during upslope winds (40-160°), precipitation fell less than 15% of the time. However, more than 50% of the yearly nitrogen wet deposition occurred during easterly upslope winds, indicating a strong nitrogen deposition contribution from source areas east of RMNP (Benedict et al., 2013a). These observations support the expectation that wet deposition fluxes depend on meteorological conditions that yield high nitrogen species concentrations in RMNP and also produce precipitation. The efficiency with which pollutants are scavenged and deposited by precipitation can also be influenced by cloud microphysical processes such as the extent of ice crystal riming, an issue not investigated in this study.

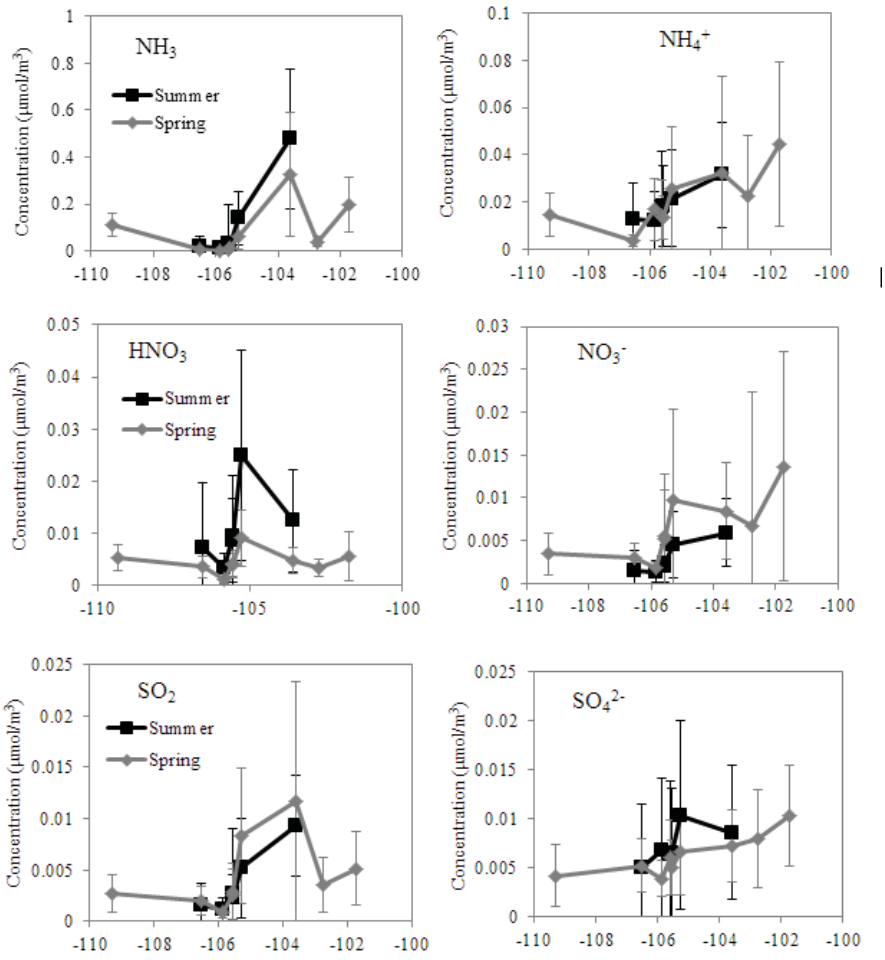

Figure 2. Seasonal average concentrations of ammonia, ammonium, nitric acid, nitrate, sulfur dioxide and sulfate are plotted for spring and summer of 2006. Error bars represent the standard deviation of daily concentrations measured during each season. From west to east, the included sites are Gore Pass,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

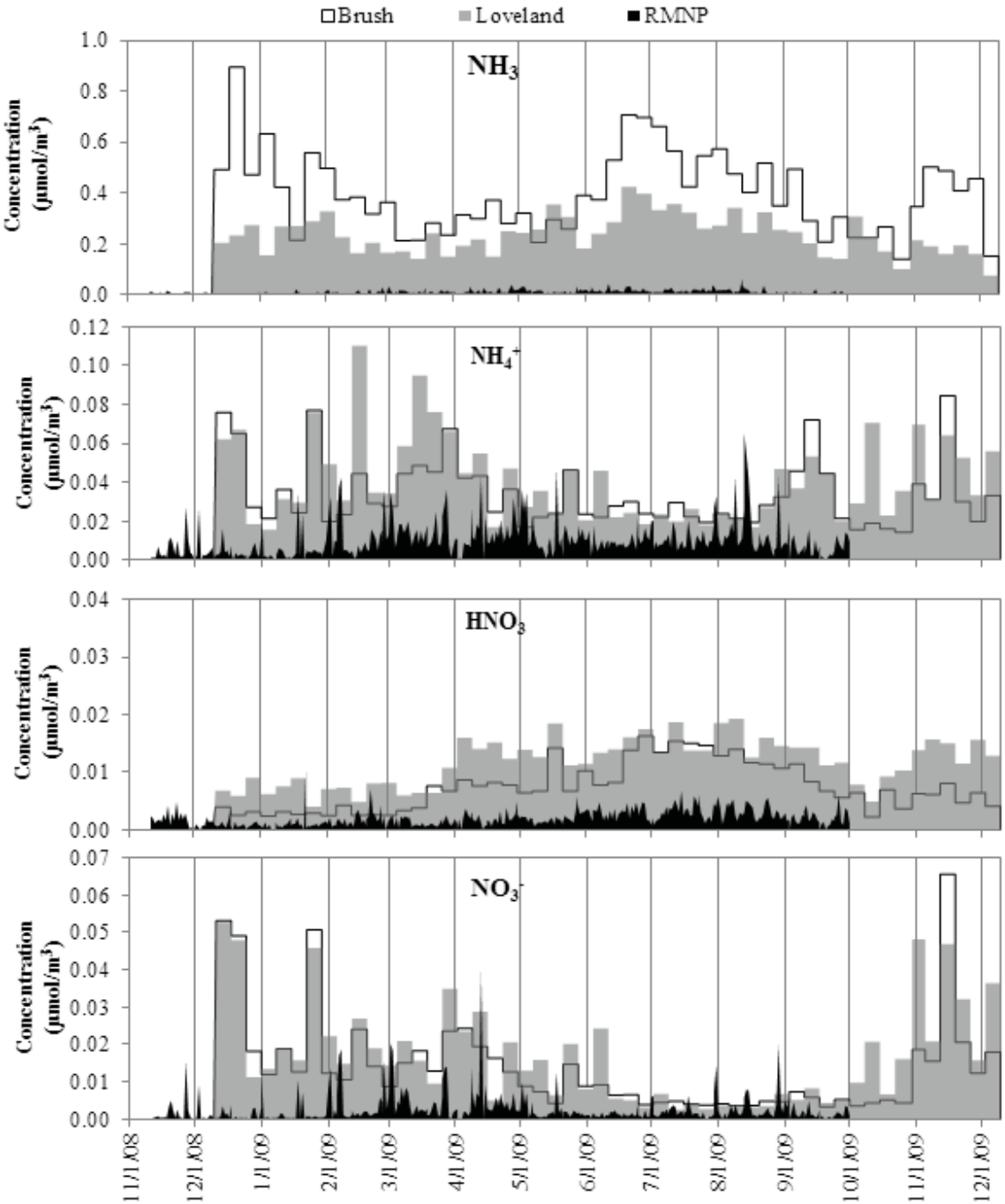

Figure 3. Seasonal cycles of gaseous NH_3, $PM_{2.5}$ NH_4^+, gaseous HNO_3, and $PM_{2.5}$ NO_3^- concentrations at the Brush, Loveland, and RMNP sampling sites.

On an annual basis, the largest measured contributor to reactive nitrogen deposition in RMNP is wet deposition of ammonium, followed by wet deposition of nitrate, dry deposition of ammonia, and wet deposition of organic nitrogen (see Fig. 4) (Benedict et al., 2013a). Smaller contributions are made by dry deposition of gaseous nitric acid and dry position of $PM_{2.5}$ ammonium, organic nitrogen, and nitrate. The total annual deposition by these pathways was approximately 3.65 kg N/ha. Dry deposition of gas phase organic nitrogen remains an unquantified, but potentially large, contributor to the RMNP reactive nitrogen deposition budget.

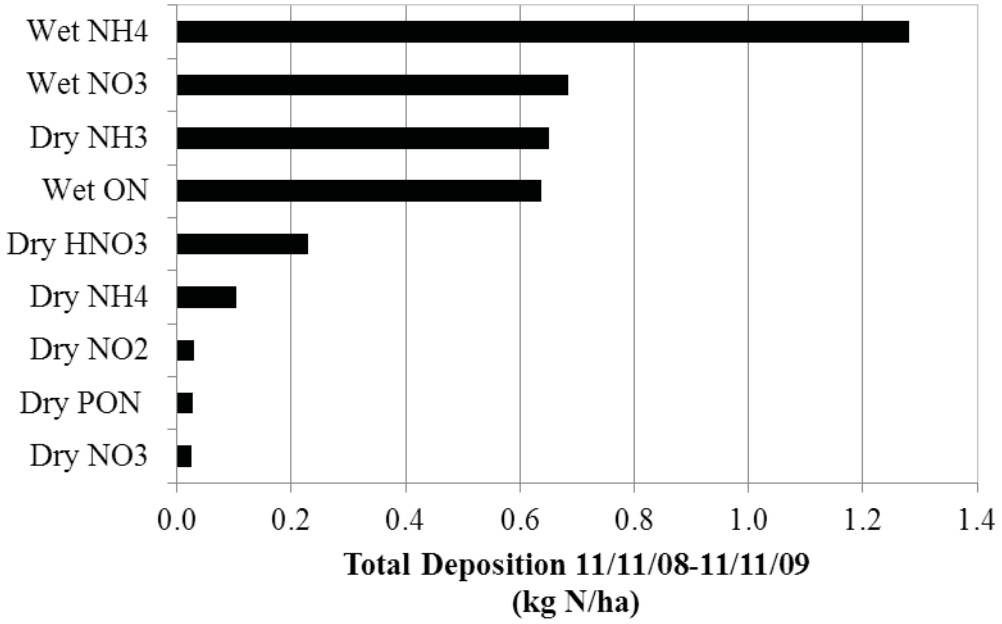

Figure 4. Total deposition by pathway for a year of measurements beginning November 2008. Measurements of $PM_{2.5}$ organic nitrogen (PON) began in April 2009 and continued through November 2009. The plotted PON deposition amount represents only contributions from this 8-month period.

The current critical load for nitrogen deposition in RMNP is based on wet deposition of ammonium and nitrate. Our analysis clearly indicates that these two pathways make the largest contributions to RMNP reactive nitrogen deposition but only contributed 54% of total nitrogen deposition. Wet deposition of organic nitrogen and dry deposition of ammonia, which have historically not been routinely monitored, together contribute 37% of the total nitrogen deposition budget for RMNP (Benedict et al., 2013a). Both of these deposition pathways are larger contributors to the total nitrogen deposition budget than the dry deposition pathways that are typically quantified by CASTNet: dry deposition of nitric acid and fine particle nitrate and ammonium. An important question from these results is: what does the critical load mean if it was established using only wet deposition of ammonium and nitrate when significant deposition of other nitrogen species was also occurring? Prediction and understanding of the nitrogen

biogeochemistry in RMNP is not complete without including wet and dry deposition of organic nitrogen and dry deposition of ammonia. Including these pathways is particularly important if a modeled mass balance approach to determine critical loads is to be utilized where inputs and output of nitrogen are examined over time since nitrogen retention will also be underestimated.

Reactive nitrogen species concentrations and deposition in Grand Teton National Park

During 2011 CSU and NPS shifted measurement efforts to Grand Teton NP to conduct the Grand Teton Reactive Nitrogen Deposition Study (GrandTReNDS). Grand Teton NP was of particular interest because of its sensitive alpine ecosystems, its proximity to large ammonia emissions from the Snake River Valley and emissions of nitrogen oxides from oil and gas activity in Wyoming and beyond, and the absence of previous air quality and deposition measurements in the park.

Twelve measurement sites were installed as part of the GrandTReNDS study. Table 1 summarizes the site locations and types of measurements made at each site. The most extensive set of measurements was made at the Grand Targhee ski resort, where the NPS Mobile Air Sampling Laboratory was deployed. Specific real-time measurements included a PILS-IC system for $PM_{2.5}$ inorganic ion composition, several gas monitors for measurements of NO_x, NO_y, and NH_3, an aerosol mass spectrometer for measurement of PM_1 concentrations of inorganic and organic aerosol composition, aerosol size distributions, and a variety of meteorological parameters. These were complemented by 12 and 24 hr measurements of $PM_{2.5}$ aerosol composition and concentrations of key trace gases (HNO_3, NH_3, and SO_2) using a URG annular denuder/filter-pack system, 24-48 hr concentrations of organic (OC) and elemental carbon (EC) and organic nitrogen (ON) concentrations and smoke marker species concentrations using Hi-Vol filter sampling, daily wet deposition measurements (inorganic ion and ON concentrations), and passive sampler measurements of gaseous ammonia.

Table 1. Site information for the 2011 Grand Tetons Reactive Nitrogen Deposition Study.

		Latitude	Longitude	Elevation (m)	Start of Sampling	Passive Site	24 Hr Gas and Particle	Precipitation
Driggs	(DR)	43.7404	-111.8703	1947	4/6/2011	X	X	X
Upper Grand Targhee	(GT)	43.7782	-110.9438	2722	4/28/2011	X	X^+	X
Lower Grand Targhee	(TB)	43.7891	-110.9558	2454	4/21/2011		X	
NOAA Climate	(NC)	43.6614	-110.7120	1978	5/15/2011	X	X	X

Station						
Flagg Ranch	(FR)	44.0827	-110.6828	2086	7/5/2011	X
Holly Lake	(HL)	43.7890	-110.7939	2826	7/24/2011	X
Moran Junction	(MJ)	43.8276	-110.5156	2062	7/5/2011	X
Rendezvous Peak	(RP)	43.5969	-110.8703	3176	7/21/2011	X
South Badger	(SB)	43.8504	-110.9543	2166	7/21/2011	X
Surprise Lake	(SL)	43.7291	-110.7768	2922	7/24/2011	X
Death Canyon	(DC)	43.6566	-110.7818	2088	7/21/2011	X
Tetons Science School	(TS)	43.6709	-110.5996	2131	7/21/2011	X

[+]Precipitation and 24 hour gas and particle sampling began 7/24/2011.

Longer term data records were collected at a site near Driggs, ID and from the NOAA Climate Monitoring site on the east side of GTNP, each equipped with 24 hr URG denuder/filter-pack sampling, wet deposition samplers, passive gas samplers, and meteorological stations. The lower elevations of these sites permitted much earlier access for measurement equipment. Several additional sites were equipped with passive sampling devices for measurement of gaseous ammonia and nitric acid concentrations. A subset of these sites was equipped with automated wet deposition samplers.

Analysis of findings from the GrandTReNDS study are ongoing; initial findings are presented here. Measurements at the core Grand Targhee measurement site (GT) indicate that this region is typical in some respects of remote continental locations, with a study average particle number concentration of 1400 cm^{-3}. NO_x concentrations were also quite low, generally <1 ppb. Characterization of non-refractory submicron particulate matter via high resolution aerosol mass spectrometry also reveals low aerosol concentrations dominated by organics (Figure 5; organic avg = 1.6 $\mu g/m^3$). Inorganic species (Average: SO_4 = 0.3$\mu g/m^3$; NH_4 = 0.2$\mu g/m^3$; NO_3 = 0.08$\mu g/m^3$) are generally in constant proportion to each other and organics throughout the study, with some sulfate enhancement August 20-29. A peak in all concentrations is apparent August 15, when the site was impacted by biomass burning. The composition of the organic fraction is generally consistent with an aged aerosol. A pronounced $C_xH_yN^+$ fragment series (such as $C_4H_5N^+$ at *m/z* 67, Δ=-2) is indicative of the presence of amines. Work is ongoing to confirm this finding and determine possible sources for this reduced organic nitrogen aerosol type.

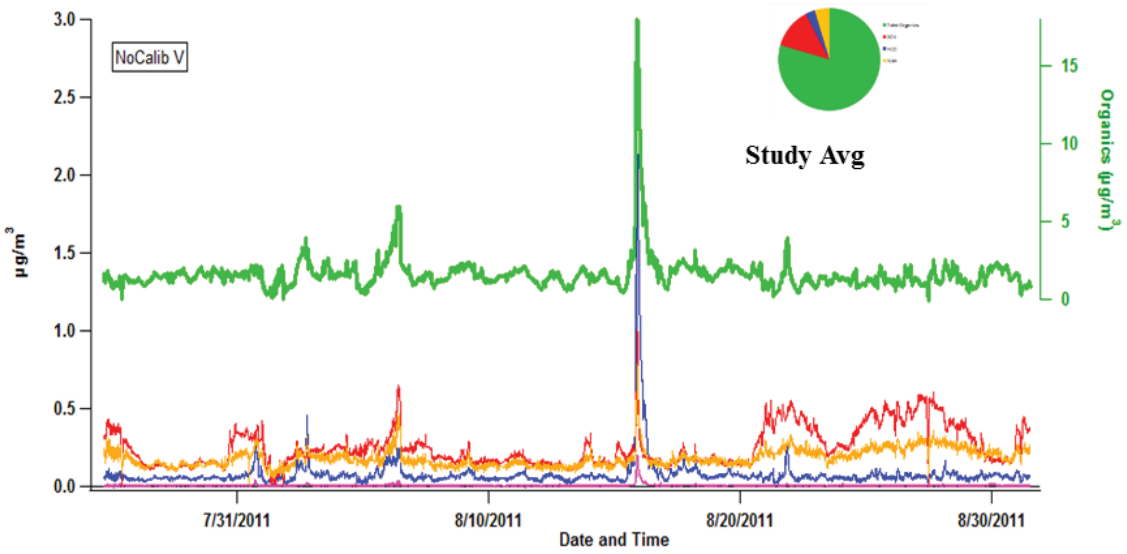

Figure 5. Time series of particulate organic (green), sulfate (red), nitrate (blue), and ammonium (yellow) concentrations during the intensive study period at the GrandTReNDS core study site.

Ammonia was determined to be the most abundant atmospheric nitrogen species in the region. Ammonia concentrations are plotted in Figure 6 for each of the sites where daily URG denuder/filter-pack measurements were made. Also included in Figure 6 are weekly average concentrations from the NADP Ammonia Monitoring Network (AMoN) site located at Craters of the Moon (ID03), approximately 200 km west of Driggs. The westernmost site of Driggs, ID had the highest average ammonia concentrations, exceeded at times by Craters of the Moon, while measurements at the NOAA Climate Center were generally the lowest, indicating that the main sources impacting the region came from the west. Concentrations were slightly higher in the spring than in the summer at Driggs, and in September concentrations were decreasing at all sites.

Measurements from the passive ammonia samplers also indicate a west-to-east concentration gradient (see Figure 7). These samplers were deployed at 11 sites throughout the area, providing higher spatial resolution than the more traditional measurement techniques. These measurements show a decrease in concentrations to the east, consistent with the location of large ammonia source regions west of the mountain range. Ongoing measurements of gaseous ammonia using passive samplers at Driggs (CSU) and at Craters of the Moon (NADP AMon) (see Figure 8) indicate that concentrations observed during the 2011 GrandTReNDS study may have been lower than observed in other years. This may have resulted from the above average local precipitation that occurred during 2011. These measurements are ongoing, so we will gain more insight into this issue moving forward, but it should be kept in mind that that the higher than typical precipitation may have shifted deposition away from dry pathways and toward wet pathways during GrandTReNDS.

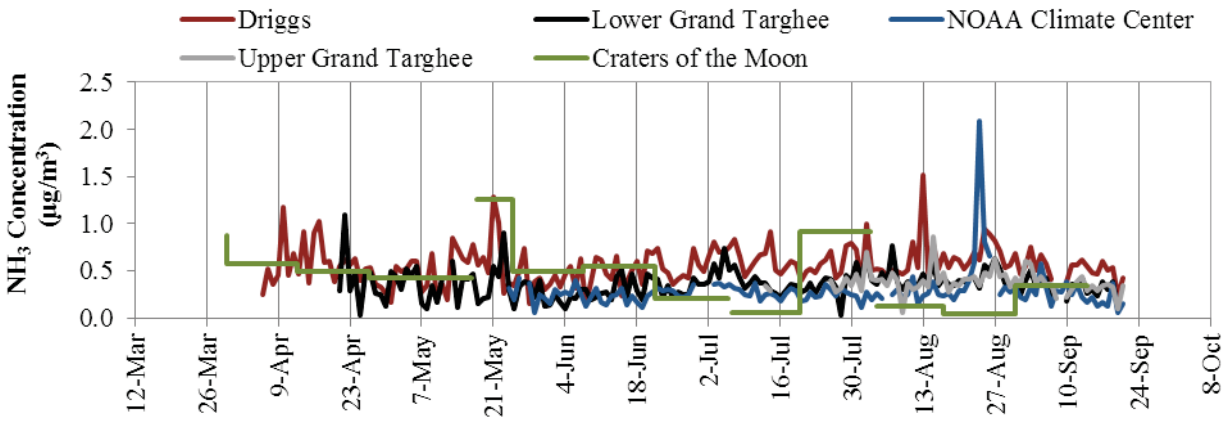

Figure 6. 24 hr altitude adjusted concentrations of gaseous ammonia (NH_3) from GrandTReNDS and NH_3 concentrations from the AMoN network site at Craters of the Moon.

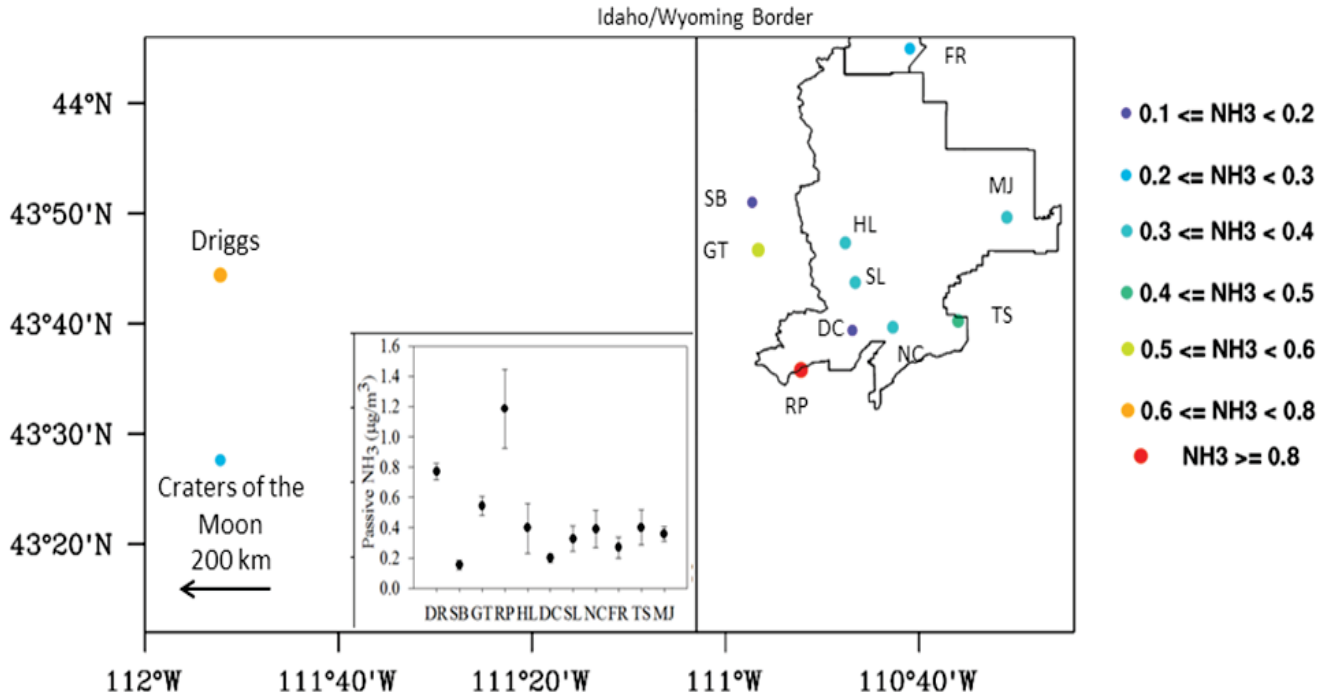

Figure 7. Spatial distribution of NH_3 from July to September 2011 from bi-weekly passive samplers deployed during GrandTReNDS. Data from Craters of the Moon are from NADP AMoN network weekly passive samplers. The color of each circle represents the average concentration at each sampling site. In the inset, sites are plotted according to longitude, west to east, and the error bars represent the standard deviation of concentrations during the study period at each site. The high concentrations at RP are believed to result from local emissions.

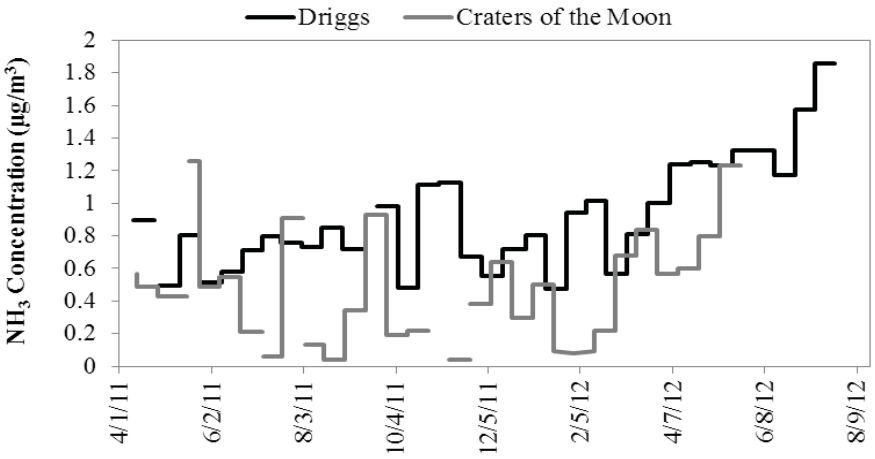

Figure 8. Ammonia concentrations measured in Driggs, ID using passive samplers from April 2011 –July 2012 along with ammonia concentrations measured at the Craters of the Moon AMoN site.

A timeline of all continuous gas phase measurements during GrandTReNDS is shown in Figure 9. Measured NO_x concentrations were generally low, with a median value of 0.55 ppb for the entire study, indicative of a remote site. NO_y concentrations were higher, with a median value of 1.34 ppb throughout the study, again typical for a rural sampling location. Although NO_x and NO_y concentrations were generally low, there are some features which deserve further attention. First, there are spikes in both NO_x and NO_y on August 15-16 and September 2. These spikes are associated with biomass burning episodes and are discussed below. Also apparent in Figure 9a is an increase in NO_x relative to NO_y beginning September 7 and continuing to the end of the study. Low values of the NO_x/NO_y ratio are expected for remote areas, with increasing conversion of NO_x to NO_y downwind of sources. Prior to September 7, NO_x accounted for just 39% of NO_y; after the shift, NO_x/NO_y increased to 76%. Increased levels of NO_x relative to NO_y suggest a source of NO_x near the site. During this period, HYSPLIT back-trajectories show that airmasses reaching the site had passed through multiple areas in WY, ID and MT with active fires, as detected from MODIS. CO (Figure 9c), particulate potassium and particulate organic carbon were also elevated during this time period, all suggestive of regional biomass burning impacts on the site for the final two weeks of the study.

Median hourly values for NO, NO_2, NO_x, NO_y, and CN for the entire study period are shown in Figure 10. NO values had a broad daytime maximum that corresponded to increased temperatures, presumably due, in part, to NO_2 photolysis. However, there is not a corresponding minimum in NO_2 during the day. Instead, NO_2 concentrations also show a broad maximum, as do NO_x, NO_y and CN. The increase in all species is partially explained by the daily cycle in wind direction, also shown in Figure 10. During summer, synoptic scale flows in this region are typically weak, such that thermally driven winds frequently dominate circulation patterns. For our sampling site, this equates to up-valley flows from the southwest during the day, reversing direction at night. For our measurements, we observed the daytime southwesterly flow, and

during the evening and early morning hours we measured winds primarily from the southeast. The exact direction of the measured air flow was likely impacted by the complex topography at our measurement site. In any case, to the east (SE, E, or NE) lies a pristine region with few, if any, sources. Jackson, WY lies SE; however, our sampling site and Jackson were separated by the Teton Range, and so we were likely isolated from impacts from Jackson. In contrast, daytime southwesterly flow was likely impacted by emissions from Driggs, ~10 km away, as well as a series of towns further west along highway 20.

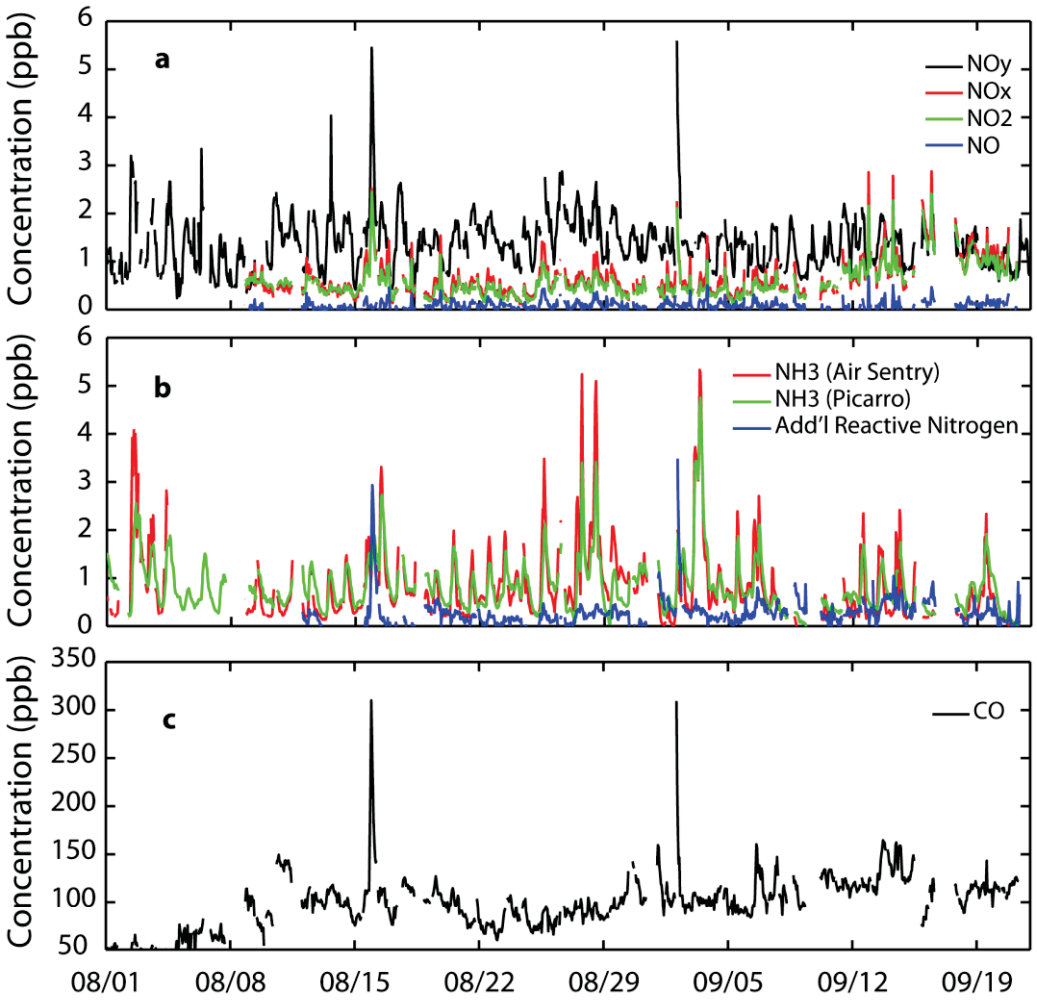

Figure 9. Observed concentrations of gas species. a) One hour averaged concentrations for NO_y, NO_x, NO_2 and NO, as determined from the Teledyne instruments. b) One hour averaged concentrations for ammonia from both the Air Sentry II and the Picarro instruments. Also shown is the additional reactive nitrogen measured using the Teledyne 201e, with ammonia and particulate nitrogen removed upstream and measured NO_x and HNO_3 subtracted. c) One hour averaged CO concentrations.

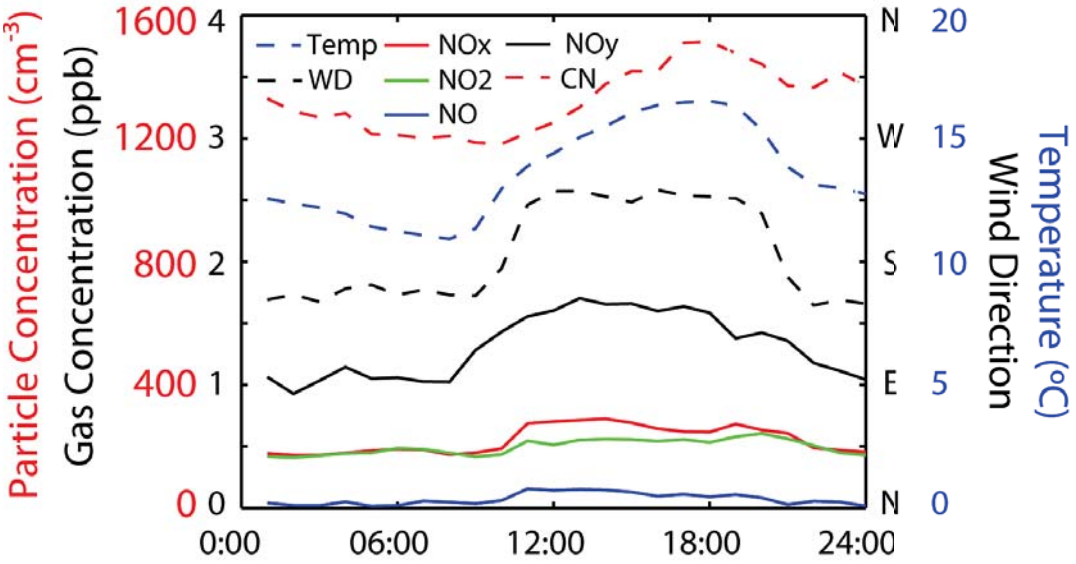

Figure 10. Daily cycle for NO, NO_2, NO_x, NO_y and CN for measurements made throughout the project. Median concentrations are given to remove biases due to spikes during biomass burning periods. Also shown are project average temperature and wind direction from the met station at the core site. Met data were not available at the site from 8/1-8/13 and 8/27-8/29.

A diel cycle in ammonia concentrations was also apparent in measurements at Grand Targhee (see Figure 11). Data are shown from the Picarro cavity ring down and Air Sentry II ion mobility ammonia analyzers. Both instruments show a clear increase in ammonia concentrations in the morning, peaking around noon, and then gradually decaying throughout the remainder of the day. This pattern is consistent with observed ammonia trends at Rocky Mountain National Park (RMNP) during the RoMANS campaign; however, the peak concentrations observed here were somewhat lower than those observed during RoMANS summer months. Despite the clear diel pattern in the GrandTReNDS data, results from RoMANS suggested that some of this variability may result from a sampling artifact, whereby ammonia adsorbs to surfaces in the inlet during the cold nighttime hours, and is then released when the sun rises and warms the inlet. To test this, for select periods we collected concurrent day-vs-night denuder samples, as denuders are not expected to suffer to the same extent from inlet artifacts. Results from these measurements are also shown in Figure 11. The good agreement between the URG and the Picarro (11b) and Air Sentry (11c) suggest that the diel cycle observed with the continuous instruments is real and not a sampling artifact. Analysis of changes in ammonia concentrations with wind direction indicate that median concentrations were 43% higher when winds came from the SW versus the SE, consistent with the location of large agricultural emissions west of the monitoring site.

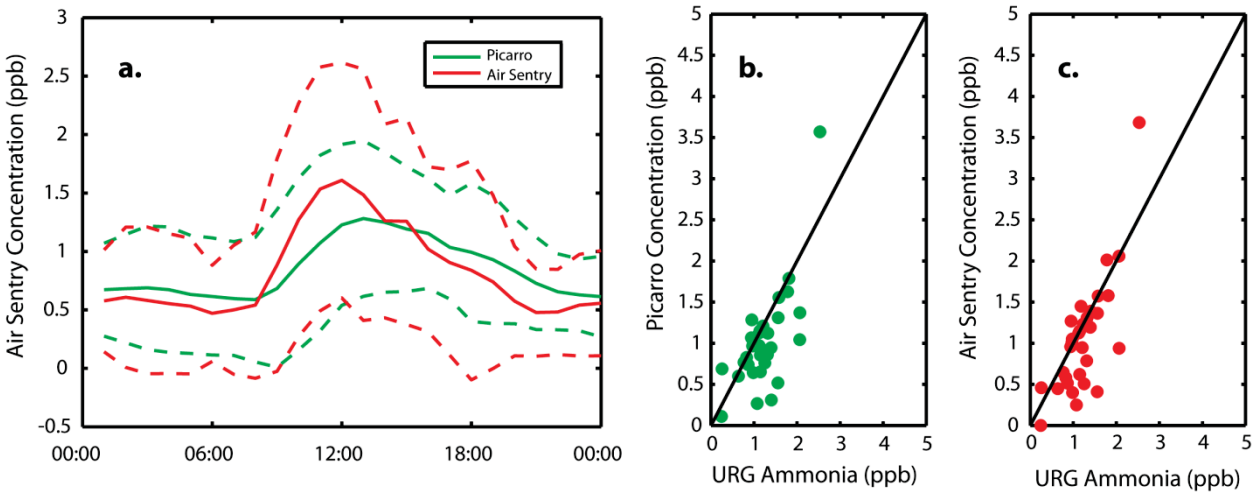

Figure 11. a.) Average daily ammonia concentrations throughout the study period from the Picarro and Air Sentry II instruments. Solid lines represent average values, while dashed lines designate ± 1 standard deviation. b.) Comparison of Picarro results with concurrent denuder measurements for sample periods aimed at capturing the diel cycle. c.) Comparison of Air Sentry II results with concurrent denuder measurements for sample periods aimed at capturing the diel cycle.

GrandTReNDS measurements were used to determine a nitrogen deposition budget for the GTNP region. Direct measurements of precipitation chemistry and volume were used to quantify wet deposition, while dry deposition is calculated from measured atmospheric concentrations and deposition velocities determined from the Clean Air Status and Trends Network (CASTNet) for sites in the region. In Figure 12 the percent contributions of each reactive nitrogen deposition pathway are shown for April to September at Driggs, Upper Grand Targhee, and NOAA Climate Center. Dry deposition of NH_3 and wet deposition of NH_4^+, NO_3^-, and ON together accounted for more than 90% of total quantified nitrogen deposition at the three intensive GrandTReNDS sites. At Driggs, to the west of GTNP, dry deposition of NH_3 was largest (39%) followed by wet deposition of NH_4^+ (33%), wet deposition of NO_3^- (15%), and wet deposition of organic nitrogen (8%). At NOAA Climate Center, on the eastern side of GTNP, dry deposition of NH_3 was also the largest deposition pathway (29%), followed by wet deposition of NH_4^+ (26%), wet deposition of organic nitrogen (19%), and wet deposition of NO_3^- (17%). The relative importance of the deposition pathway at Upper Grand Targhee was slightly different; wet deposition of NH_4^+ was most important (32%) followed by dry deposition of NH_3 (28%), wet deposition of NO_3^- (19%) and wet deposition of organic nitrogen (11%). Low atmospheric nitric acid concentrations resulted in its low contributions to nitrogen deposition at all three sites. $PM_{2.5}$ nitrate and ammonium deposition contributions were low because of low fine particle deposition velocities. The similarity in deposition amount for ammonium wet deposition and ammonia dry deposition contrasts with results from other studies and mountain locations where wet deposition typically is greater than dry deposition.

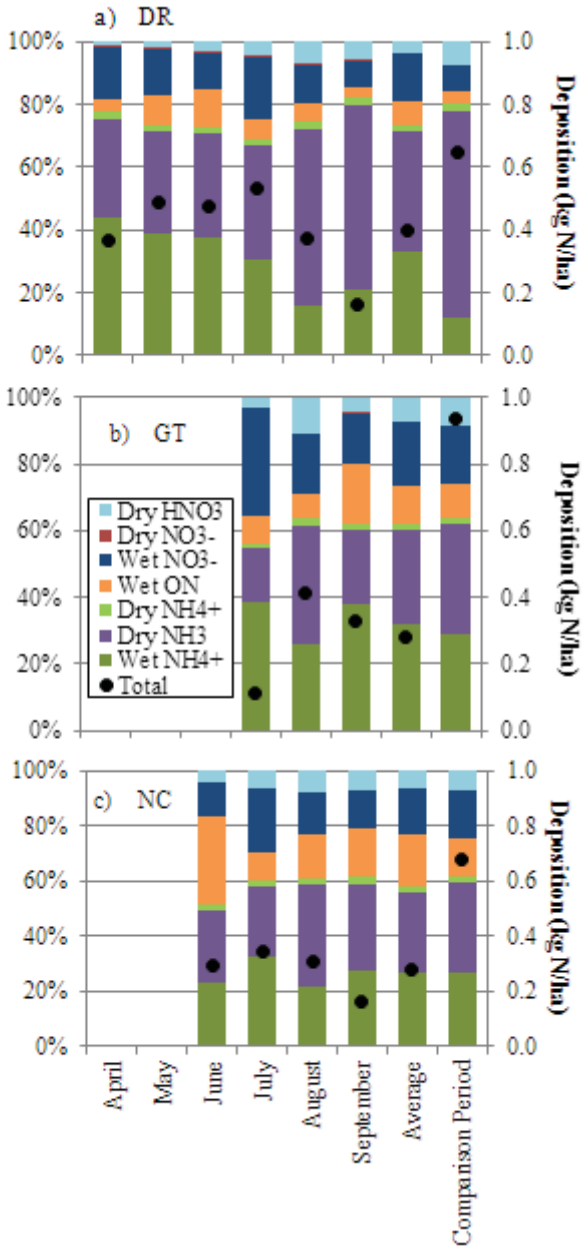

Figure 12. The monthly contributions of each nitrogen deposition pathway to total nitrogen deposition at a) Driggs, b) Grand Targhee, and c) NOAA Climate Center. The study average for each site and the overlapping comparison period are also included.

The relative contributions of reduced, oxidized, and organic nitrogen deposition changed across the three sites. At Driggs deposition of reduced nitrogen (wet NH_4^+, dry NH_3, and dry NH_4^+) contributed on average 73% to total quantified nitrogen deposition while at Upper Grand Targhee and NOAA Climate Center reduced nitrogen contributed 62% and 58%, respectively. This trend is consistent with the location of the largest ammonia sources west of the study region. While large NO_x sources are located to the east of the study region, the spatial trend in oxidized nitrogen deposition contributions was not as clear as for reduced nitrogen. The oxidized nitrogen deposition contribution was substantially higher at NOAA Climate Center (23%) than at Driggs (11%), but the Upper Grand Targhee contribution (27%) slightly exceeded the value at the NOAA Climate Center. The contribution of wet organic nitrogen deposition to total quantified nitrogen deposition increased from west to east, contributing 8%, 11%, and 18% at Driggs, Upper GrandTarghee, and NOAA Climate Center. Given the dominance of reduced nitrogen to the total nitrogen deposition budget, of course, spatial trends in relative contributions of the other forms of nitrogens partly reflect the spatial trend in reduced nitrogen deposition. NH_3 sources dominate the spatial trend of nitrogen deposition and atmospheric concentrations even on the east side of the Teton Range.

Monthly/seasonal changes in the relative importance of the deposition pathways corresponded to changes in precipitation amount. The example at Driggs is particularly striking (Figure 12a). At Driggs, a larger fraction of wet deposition (~40%) was observed in early spring when there was

more precipitation while dry deposition of ammonia was more important later in the study period, corresponding to a decrease in precipitation.

Dry deposition of particulate organic nitrogen (PON) was also determined using concentrations of water-soluble $PM_{2.5}$ organic nitrogen measured from weekly high volume filters at Upper Grand Targhee. Weekly dry deposition of PON ranged from 0.004-0.01 kg N/ha accounting for approximately 0.8 % of total measured nitrogen deposition at this site. In comparison dry deposition of NH_4^+ was 1.8% of total measured nitrogen deposition at the site and dry deposition of NO_3^- accounted for 0.2%. Contributions from water insoluble PON might increase the importance of PON somewhat but low deposition velocities for fine particles will limit the relative size of this nitrogen deposition pathway. Dry deposition of organic nitrogen gases was not included in these deposition budgets. However, the high wet deposited organic nitrogen and low concentrations of soluble particulate organic nitrogen suggest that dry deposition of organic nitrogen gases could be an important nitrogen deposition pathway.

Most important for understanding the impacts on the ecosystems and the relationship between deposition totals and critical load is the deposition flux. In Table 3 the flux of nitrogen per week was calculated from the deposition totals for each site. Included in this table is dry deposition of particulate organic nitrogen (PON), which was only sampled at Upper Grand Targhee, as well as deposition fluxes from RMNP from 2009 and 2010. Data from RMNP are included to provide a comparative measure of deposition since RMNP has been more extensively studied. While included in Table 1, Driggs is excluded in the following discussion since it is not representative of GTNP due to its proximity to ammonia source regions. Total measured nitrogen deposition rates were similar in GTNP and at the RMNP site. The deposition pathways had different relative contributions reflecting lower particulate and nitric acid concentrations and higher ammonia concentrations near GTNP. Upper Grand Targhee had the highest total measured nitrogen deposition for the period when all sites were operating. Upper Grand Targhee is just upwind of GTNP, suggesting high elevation lakes on the western side of GTNP may have similarly high deposition rates. Dry deposition rates tended to be similar at GTNP and RMNP for all pathways except dry deposition of NH_3 which was larger at GTNP.

To obtain a more complete annual nitrogen deposition budget estimate for GTNP, data from Rocky Mountain Regional Snowpack Chemistry Monitoring Study (http://co.water.usgs.gov/projects/RM_snowpack/index.html) from the 2010-2011 winter sampling were used. Deposition amounts from several sampling sites in the region, Garnet Canyon, Rendezvous Mountain, and Lewis Lake Divide, were averaged together to estimate winter inorganic nitrogen deposition. Average inorganic nitrogen deposition from these three sites, which includes both wet deposition and dry deposition accumulation in the winter snowpack, was 1.25 kg $N \cdot ha^{-1}$. Adding this amount to the NOAA Climate Center deposition budget from GrandTReNDS, we can better represent a full year of GTNP nitrogen deposition, though this will miss nitrogen deposition that occurred in the fall before snowfall began and in the spring after the snowpack sampling and before measurements started. In addition, the

organic nitrogen in the snow pack was not measured. Given these caveats,the annual GTNP nitrogen deposition at the NOAA Climate Center totals approximately 2.5 kg $N \cdot ha^{-1}$ from October 2010-September 2011. Adding the winter snowpack data to the Upper Grand Targhee budget yields total nitrogen deposition of 2.2 kg $N \cdot ha^{-1}$, but a larger portion of the year is missing measurements.

Table 1. Total deposition flux per week by pathway for each site where wet deposition samples were collected (kg N/ha/week). Deposition flux at RMNP was calculated from 2009 and 2010 datasets for the same dates of operation as the three GTNP sites (7/24-9/21).

		DR	GT	NC	RMNP 2009	RMNP 2010
Dry NH_3		0.032	0.024	0.017	0.014	0.0022
Wet NH_4^+		0.012	0.027	0.018	0.023	0.026
Wet ON		0.003	0.0096	0.0095	0.009	0.0038
Wet NO_3^-		0.009	0.016	0.012	0.013	0.023
Dry HNO_3		0.004	0.0061	0.0037	0.0041	0.0035
Dry NH_4^+		0.0014	0.0015	0.0013	0.0018	0.0013
Dry PON			0.0007		0.0008	0.0005
Dry NO_3		0.0002	0.0002	0.0002	0.0003	0.0002
Total N Deposition per week		0.061	0.085	0.061	0.065	0.061
Total N Deposition	4/6-9/21	2.38			2.34	2.12
	5/15-9/21	1.77		1.23	1.68	1.48
	7/24-9/21	0.62	0.90	0.62	0.65	0.61

Improved characterization of atmospheric reactive nitrogen in IMPROVE

Since 2010 CSU and NPS have been working with the IMPROVE (Interagency Monitoring of Protected Visual Environments) network to improve characterization of atmospheric concentrations of reduced nitrogen species. Gaseous ammonia and $PM_{2.5}$ ammonium are measured together as NH_x; collection is made on an acid-impregnated filter. Sampling is done on IMPROVE's normal 1-in-3 day schedule using an additional IMPROVE sampler module.

Before deploying the additional IMPROVE samplers in the field to collect NH_x, comparisons were conducted in March-April 2010 at Fort Collins, CO to examine measurement precision; accuracy was also tested against a reference URG denuder/filter-pack sampler in 2010 and again in 2012. Precision and accuracy findings were both good. The accuracy findings are shown in Figure 13. The deployment of IMPROVE NH_x samplers in the field started in June 2010. Surprising amounts of methylamine were found on many samples. After extensive field and lab

testing, it was determined that the methylamine resulted from a reaction between formaldehyde, produced by acid breakdown of the Delrin plastic used by IMPROVE for manufacture of filter cartridges and collected NH_x. NH_x sampling was suspended in October 2010 until new cartridges could be designed, tested for chemical inertness, and manufactured to resume sampling. Polypropylene was proven to successfully meet all manufacture and sampling requirements and IMPROVE NH_x sampling resumed starting from late April 2011 in a pilot network including 9 IMPROVE sites: Bondville, Illinois plus 8 sites in the Rocky Mountain region of the country. NH_x field blanks collected from April 2011 to January 2012 were similar across network sites with a low average airborne equivalent NH_x concentration of 0.030 $\mu g/m^3$. Co-located samplers installed at RMNP and Bondville demonstrated excellent field measurement precision as illustrated in Figure 14.

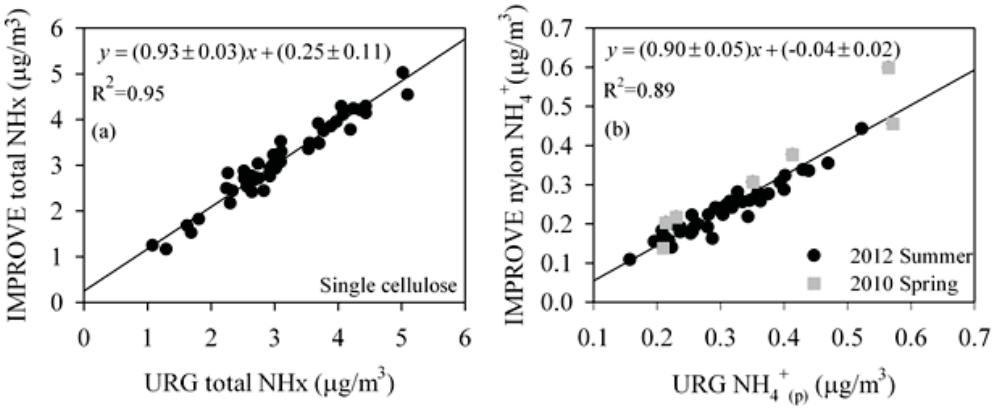

Figure 13. IMPROVE NH_x sampler comparison with the reference URG sampler. a) total NHx collected using IMPROVE single acid-coated cellulose filters; b) IMPROVE single nylon filter comparison with URG collected particulate NH_4^+.

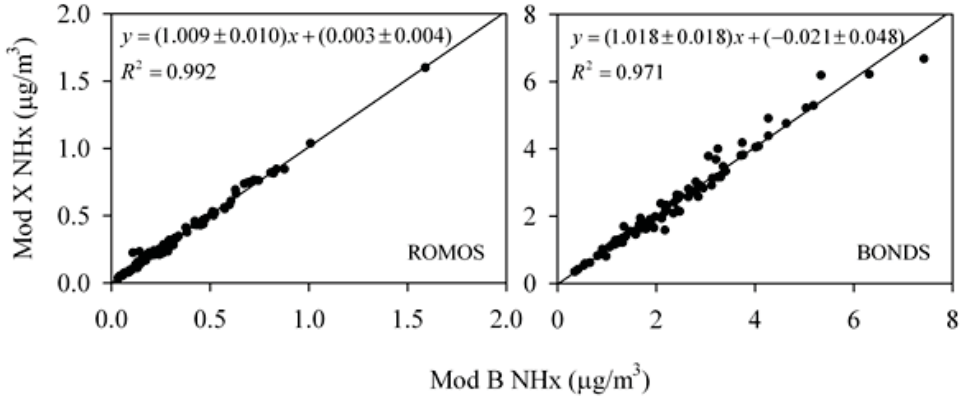

Figure 14. NH_x collected by collocated samplers at Rocky Mountain National Park and Bondville.

The network was operated from spring 2011 through summer 2012. Samples were prepared at CSU and analyzed by Research Triangle Institute. Monthly average concentrations for all IMPROVE NH_x sites from spring 2011 to summer 2012 are shown in Figure 15. Overall NH_x

concentrations measured during the study period were lowest at Yellowstone NP; concentrations were highest at Cedar Bluffs and Bondville, both areas expected to be impacted by agricultural emissions. A seasonal cycle was observed at all sites, with NH_x concentrations climbing from spring into early summer; a second late autumn peak was observed at Bondville and Cedar Bluffs. One particularly surprising finding was the high summer 2011 NH_x concentrations observed at Chiricahua. Concentrations here in June and July 2011 were comparable to those measured at Bondville and Cedar Bluffs. Some of the high concentration periods appear to be associated with wildfire emissions in the region. Summer 2012 Chiricahua NH_x concentrations were much lower.

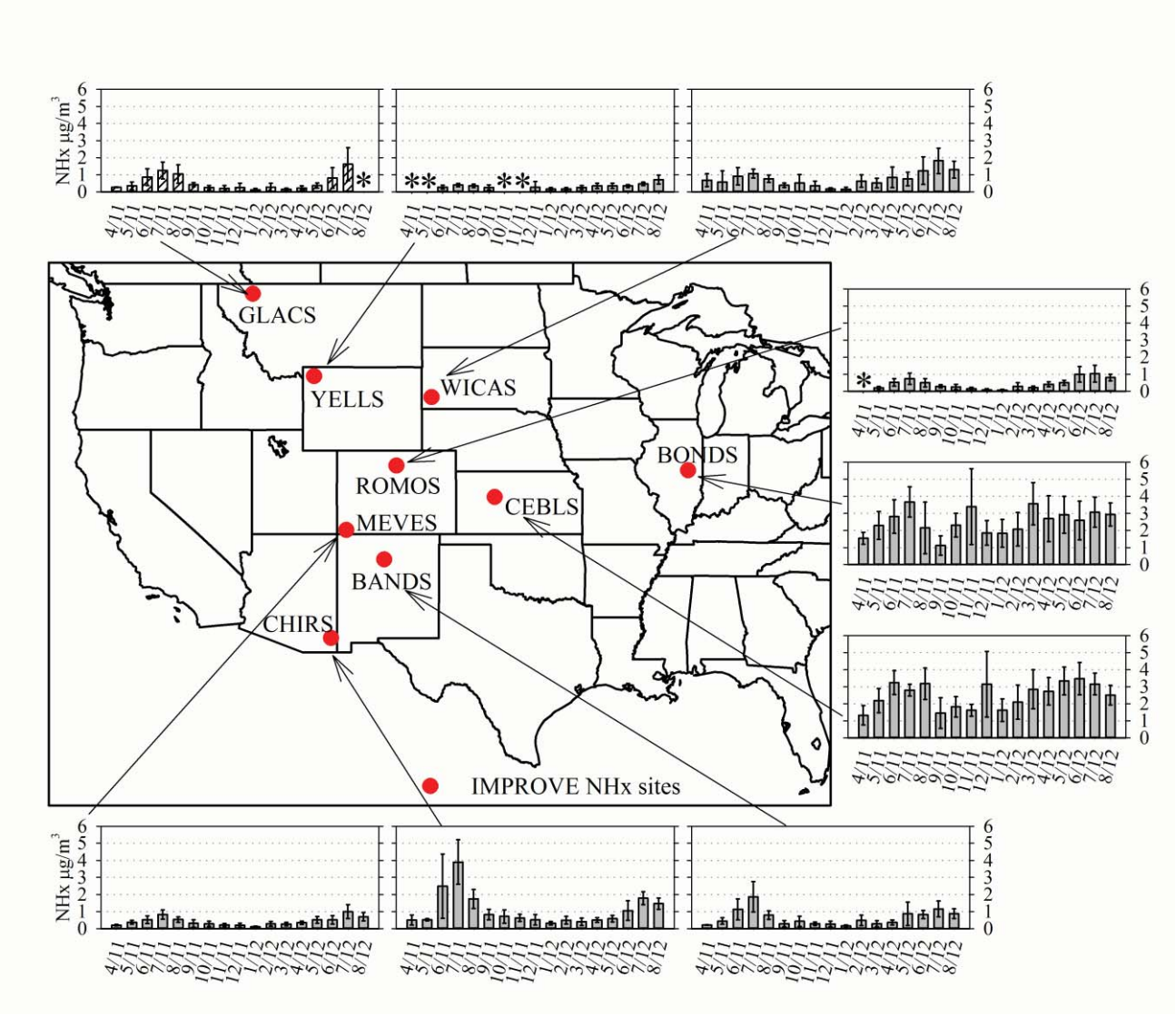

Figure 15. Monthly NH_x average concentrations ($\mu g/m^3$) measured from spring 2011 to summer 2012 at IMPROVE NH_x sites.

3. Chief Project Accomplishments

Here we briefly summarize several of the main accomplishments from this project.

- Analysis of findings from 2008-2010 reactive nitrogen species concentration and deposition flux measurements in RMNP. Publication of two journal manuscripts (Benedict et al., 2013a; Benedict et al., 2013b) examining gradients in pollutant concentrations in the RMNP region and across northern Colorado and seasonal and annual reactive nitrogen deposition budgets for RMNP.
- Measurements of organic nitrogen content and speciation in RoMANS precipitation and aerosol samples. Collaboration with USGS to determine organic N in snowpack samples.
- Collaboration with NPS/CIRA scientists on the analysis of spatial gradients in atmospheric ammonia concentrations in NE Colorado. Publication of a peer-reviewed journal article on this subject (Day et al., 2012).
- Collaboration with NPS/CIRA scientists on analysis and publication of findings re: ammonia source apportionment in RMNP (Malm et al., 2013).
- Completion of the GrandTReNDS study in Grand Teton National Park and the surrounding region. Field operations were conducted from April – September 2011 and included measurements at 12 field sites. Ammonia measurements at Driggs are ongoing.
- Analysis of denuder and filter samples from the GrandTReNDS study. Analysis of wet deposition samples from GrandTReNDS.
- Analysis of continuous instrument measurements of particle and gas phase composition during GrandTReNDS. Measurements included NO_x, NO_y, multiple methods for gaseous ammonia, measurement of particle composition by PILS-IC and Aerosol Mass Spectrometer (AMS), measurements of particle size distributions and particle number, and continuous meteorological observations.
- Preparation of two draft journal manuscripts (Prenni et al.; Benedict et al.) concerning observations of gaseous reactive nitrogen and reactive nitrogen deposition budgets for Grand Teton NP.
- Spring 2011-summer 2012 operation of the IMPROVE NH_x pilot network. Analysis of NH_x concentrations measured in the Rocky Mountain region by the network and preparation of a draft journal manuscript (Chen et al.)
- Analysis of aerosol mass spectrometer measurements of fine particle composition in RMNP and GTNP. Identification of key organic aerosol types using positive matrix factorization (PMF). Preparation of a draft manuscript reporting RMNP observations (Schurman et al.).
- Opportunistic sampling of fresh smoke plumes from summer 2012 wildfires west of Fort Collins to examine emissions of gas and particle phase oxidized, reduced and organic nitrogen.

- Presentations of project findings at several national and international meetings, including the annual meetings of the American Association for Aerosol Research, the Air and Waste Management Association, the American Geophysical Union, and the NADP annual meeting. Invited presentations to key stakeholder groups (e.g., EPA Regions 7 and 8 state agricultural commissioners). See full presentation list below.
- Maintenance and operation of the NPS Mobile Air Sampling Laboratory. During this project CSU researchers continued to maintain, improve, and operate the NPS Mobile Air Sampling Laboratory (MASL). The MASL was deployed during the initial part of this time period in GTNP in support of the GrandTReNDS study and later in North Dakota as part of a winter 2013 campaign in Theodore Roosevelt NP.

4. Project Deliverables

Deliverables for this project include submission of peer-reviewed journal articles, submission of a GrandTReNDS project dataset (provided to NPS researchers), and submission of this final report. Several peer-reviewed journal articles were published (Day et al., 2012; Heald et al., 2012; Benedict et al., 2013a; Benedict et al., 2013b) or accepted for publication (Malm et al., 2013) as part of this project.

Project peer-reviewed journal publications (published or in press)

1. Benedict, K.B., Kreidenweis, S.M., Schichtel, B., Malm, W.C., Carrico, C. and Collett, Jr., J. L. (2013a) A seasonal nitrogen deposition budget for Rocky Mountain National Park, *Ecol. Appl.*, in press.

2. Benedict, K.B., Day, D., Schwandner, F.M., Kreidenweis, S.M., Schichtel, B.A., Malm, W.C., and Collett, J.L. (2013b) Observations of atmospheric reactive nitrogen species in Rocky Mountain National Park and across northern Colorado. *Atmos. Environ.*, **64**, 66-76, doi:10.1016/j.atmosenv.2012.08.066.

3. Day, D.E., Chen, X., Gebhart, K.A., Carrico, C.M., Schwandner, F.M., Benedict, K.B., Schichtel, B.A., and Collett, Jr., J.L. (2012) Spatial and temporal variability of ammonia and other inorganic aerosol species. *Atmos. Environ.*, **61**, 490-498, dx.doi.org/10.1016/j.atmosenv.2012.06.045.

4. Heald, C. L., Collett, Jr., J.L., Lee, T., Benedict, K.B., Schwandner, F.M., Li, Y., Clarisse, L., Hurtmans, D. R., Van Damme, M., Clerbaux, C., Coheur, P.-F., Philip, S., Martin, R.V., and Pye, H.O.T. (2012) Atmospheric ammonia and particulate inorganic nitrogen over the United States, *Atmos. Chem. Phys.*,**12**,10295-10312,doi:10.5194/acp-12-10295-2012.

5. Malm, W. C., Schichtel, B. A., Barna, M. G., Gebhart, K. A., Rodriguez, M. A., Collett, Jr., J. L., Carrico, C. M., Benedict, K. B., Prenni, A. J., and Kreidenweis, S. M. (2013)

Aerosol species concentrations and source apportionment of ammonia at Rocky Mountain National Park. *J. Air Waste Mgmt. Assoc.*, in press.

Project presentations

Benedict, K., Y. Desyaterik, A. P. Sullivan, S. Kreidenweis, J. Collett et al. (2011) Speciation of organic nitrogen compounds in aerosol from Rocky Mountain National Park. Presented at the American Association for Aerosol Research 30th Annual Conference, Orlando, FL, Oct. 3-7 2011.

Benedict, K.B., D. Day, F.M. Schwandner, S.M. Kreidenweis, B.Schichtel, W. C. Malm, J.L. Collett, Jr. (2012) Transport and deposition of reactive nitrogen in Rocky Mountain National Park. Rocky Mountain National Park Research Conference March 28-29, 2012; Estes Park, CO.

Benedict, K.B., D. Day, F. M. Schwandner, S.M. Kreidenweis, B. Schichtel, W. C. Malm, J.L. Collett, Jr. (2012) Transport and deposition of reactive nitrogen in Rocky Mountain National Park. American Meteorological Society First Conference on Atmospheric Biogeosciences, May 29-June 1, 2012; Boston, MA.

Benedict, K.B., Y. Desyaterik, S.M. Kreidenweis, B.A. Schichtel and Jeffrey L. Collett, Jr. (2012) Organic Nitrogen Concentrations and Species in Aerosol and Precipitation Samples from the Rocky Mountains. 2012 Aerosol and Atmospheric Optics: Visibility & Air Pollution Specialty Conference, September 25-28, 2012; Whitefish, MT.

Chen, Xi, Derek Day, Bret Schichtel, William Malm, Jose Mojica, Chuck McDade, Eva Hardison, Sonia M. Kreidenweis, and Jeffrey L. Collett, Jr. (2012) A Pilot Monitoring Study of Atmospheric NHx at Selected IMPROVE sites. 2012 Aerosol and Atmospheric Optics: Visibility & Air Pollution Specialty Conference, September 25-28, 2012; Whitefish, MT.

Collett, Jr., J. L. (2012) Perspectives on pollution: nitrogen deposition in the Rocky Mountains and cloud chemistry in China. Invited seminar, Univ. of Toronto Department of Chemistry, Toronto, Canada, March 22, 2012.

Collett, Jr., J. L. (2012) Sources and sinks of reactive nitrogen in the Rocky Mountain region. Invited seminar, Swiss Federal Institute of Technology (ETH), Zurich, Switzerland, April 24, 2012.

Collett, Jr., J. L. (2012) Nitrogen deposition in Rocky Mountain National Park. Invited presentation at the AWMA Regional Meeting, Denver, CO, May 15, 2012.

Collett, Jr., J. L. (2012) An update on CSU nitrogen research. Invited presentation to the CDPHE Agriculture Subcommittee, Greeley, CO, May 16, 2012.

Collett, Jr., J. L. (2012) Sources and sinks of reactive nitrogen in the Rocky Mountain region. Invited seminar, Kanagawa University, Yokohama, Japan, Sept. 15, 2012.

Collett, Jr., J. L. (2012) Sources and sinks of reactive nitrogen in the Rocky Mountain region. Invited seminar, Waseda University, Tokyo, Japan, Sept. 15, 2012.

Collett, Jr., J. L. (2012) Reactive Nitrogen in the Rocky Mountain Region. Presented to the National Park Service Air Resources Division, Lakewood, CO, November, 2012.

Collett, J. (2012) Continuous PM speciation for air quality monitoring networks, 2012 Aerosol and Atmospheric Optics: Visibility & Air Pollution Specialty Conference, September 25-28, 2012; Whitefish, MT.

Collett, J. (2013) Nitrogen deposition and Rocky Mountain National Park. Presented to the 3rd Annual EPA Region 7/8 and State Department of Agriculture Meeting, Estes Park, Colorado, January 15, 2013.

Collett, Jr., J.L., Y. Li, T. Lee, D. Chen, K. Benedict, D. Day, S. Raja, F. M. Schwandner, C. M. Carrico, S. M. Kreidenweis, W. C. Malm, B. A. Schichtel, J. Ray, M. Tigges, S. Holcomb, C. Archuleta, L. Sherman, J. Molenar, H. J. Sewell, J. Mojica, and C. McDade (2011) Temporal and spatial variability in atmospheric ammonia concentrations in the western United States. Presented at the National Acid Deposition Program Annual Meeting, Providence, RI, Oct. 2011.

Collett, Jr., J.L., Y. Desyaterik, and Y. Sun (2012) Speciation of atmospheric "brown" carbon, Invited presentation, 2012 Aerosol and Atmospheric Optics: Visibility & Air Pollution Specialty Conference, September 25-28, 2012; Whitefish, MT.

Collett Jr., Jeffrey L., K. B. Benedict, C. M. Carrico, S. Raja, F. M. Schwandner, M. Schurman, D. Day, E. Levin, A. P. Sullivan, T. Lee, A. J. Prenni, S. M. Kreidenweis, W. C. Malm, and B. A. Schichtel (2012) Transport and deposition of reactive nitrogen species in Rocky Mountain National Park, presented at the American Meteorological Society Annual Meeting, New Orleans, LA, Jan. 23-26, 2012.

Collett, Jr., J.L., K.B. Benedict, T. Prenni, Y. Li, E. Levin, D. Day, T. Lee, Y. Desyaterik, M. Schurman, D. Chen, S. M. Kreidenweis, W. C. Malm, and B. A. Schichtel (2012) Initial Findings from GrandTReNDS: The Grand Teton Reactive Nitrogen Deposition Study. 2012 National Atmospheric Deposition Program Annual Meeting, October 3-4, 2012; Portland, ME.

Collett, Jeffrey L.; Katherine B. Benedict; Anthony J. Prenni; Derek Day; Yi Li; Ezra J. Levin; Amy P. Sullivan; Misha I. Schurman; Taehyoung Lee; Yury Desyaterik; Sonia M. Kreidenweis; Bret A. Schichtel (2012) GrandTReNDS: the Grand Teton Reactive Nitrogen Deposition Study, presented at the American Geophysical Union Fall Meeting, San Francisco, CA, Dec. 3-7, 2012.

Day, Derek E., William C. Malm, Katherine B. Benedict, Anthony J. Prenni, Ezra J.T. Levin, Amy P. Sullivan, Yi Li, Xi Chen, Yury Desyaterik, Misha Schurman, Jeffrey L. Collett Jr, and Bret A. Schichtel (2012) Nitrogen Deposition in the Grand Tetons: a Temporal and Spatial Perspective, presented at the 2012 Aerosol and Atmospheric Optics: Visibility & Air Pollution Specialty Conference, September 25-28, 2012; Whitefish, MT.

Desyaterik, Y., Y. Sun, G. McMeeking, A. Sullivan, S. Kreidenweis,and J. Collett (2011) Speciation of "brown" carbon in biomass burning aerosols. Presented at the American Association for Aerosol Research 30th Annual Conference, Orlando, FL, Oct. 3-7 2011

Desyaterik, Yury, Yele Sun, Katherine B. Benedict, Jeffrey L. Collett, Jr., Bret A. Schichtel, (2012), Organic nitrogen speciation in aerosols, precipitation and cloudwater, 244th ACS National Meeting, August 19-23, Philadelphia, PA.

Gebhart, Kristi A., Bret A. Schichtel, William C. Malm, Marco A. Rodriguez, Michael G. Barna, Katherine Benedict, and Jeffrey L. Collett, Jr. (2012) Spatial and temporal sensitivities in results of back-trajectory based receptor models as applied to the Rocky Mountain Atmospheric Nitrogen and Sulfur Study Part II (RoMANS II), 2012 Aerosol and Atmospheric Optics: Visibility & Air Pollution Specialty Conference, September 25-28, 2012; Whitefish, MT.

Malm, William C., Bret A. Schichtel, Michael G. Barna, Kristi A. Gebhart, Jeffrey L. Collett, Jr., Katherine B. Benedict, Anthony J. Prenni, Sonia M. Kreidenweis, Marco A. Rodriguez and Christian M.Carrico (2012) Source apportionment of ammonia at Rocky Mountain National Park using modeled conservative tracer releases, presented at the 2012 Aerosol and Atmospheric Optics: Visibility & Air Pollution Specialty Conference, September 25-28, 2012; Whitefish, MT.

Prenni, Anthony P., Katherine B. Benedict, Ezra J.T. Levin, Amy P. Sullivan, Yi Li, Xi Chen, Taehyoung Lee, Yury Desyaterik, Misha Schurman, Sonia M. Kreidenweis, Jeffrey L. Collett Jr., Derek Day, Bret Schichtel, and William C. Malm (2012) Measurements of Reactive Nitrogen in Grand Teton National Park, Extended Abstract #71, presented at the Aerosol and Atmospheric Optics / Visibility & Air Pollution Conference, Air & Waste Management Association, Whitefish, MT, 24-28 September.

Prenni, Anthony J.; Xi Chen; Arsineh Hecobian; Sonia M. Kreidenweis; Jeffrey L. Collett; Bret A. Schichtel (2012) Measurements of gas phase reactive nitrogen during two wildfires in Colorado, presented at the American Geophysical Union Fall Meeting, San Francisco, CA, Dec. 3-7, 2012.

Rodriguez, Marco A., Michael G. Barna, Kristi A. Gebhart, Bret A. Schichtel, William C. Malm, Jennifer L. Hand, Derek Day, Katherine Benedict, and Jeffrey L. Collett, Jr. (2012) Modeling the fate of atmospheric reduced nitrogen in the western United States during the Rocky Mountain Atmospheric Nitrogen and Sulfur Study Part II (RoMANS II), presented at the 2012 Aerosol and

Atmospheric Optics: Visibility & Air Pollution Specialty Conference, September 25-28, 2012; Whitefish, MT.

Schichtel, B., K. Beem, C. Carrico, E. Levin, D. Day, W. Malm, J. Collett, and S. Kreidenweis (2011) Seasonal nitrogen deposition budgets at Rocky Mountain National Park. Presented at the National Acid Deposition Program Annual Meeting, Providence, RI, Oct. 2011.

Schichtel, Bret A., Katie Benedict, Christian M. Carrico , Anthony Prenni, Ezra Levin, Derek Day, Doris Chen, John Ray, William C. Malm, Krisiti Gebhart, Mike Barna, Jeffrey L. Collett, and Sonia M. Kreidenweis (2012) Measuring total reactive N and its composition, presented at the NADP spring 2012 Total Deposition meeting, Portland, OR, April 23, 2012.

Schichtel, Bret A., Katie Benedict, Anthony J. Prenni, Michael G. Barna, Kristi A. Gebhart, Marco A. Rodriguez, Derek Day, Ezra Levin, Christian M. Carrico, William C. Malm, Jeffrey L. Collett, and Sonia M. Kreidenweis (2012) Reactive nitrogen composition and origin in the United States Rocky Mountains, presented at the 244th ACS National Meeting, August 19-23, Philadelphia, PA.

Schurman, M., T. Lee, Y. Sun, B. Schichtel, S. Kreidenweis, and J. Collett (2011) Investigating types and sources of organic aerosol in Rocky Mountain National Park using aerosol mass spectrometry, presented at the AGU Fall Meeting, San Francisco, CA, Dec. 2011.

Schurman, M., T. Lee, Y. Sun, B. Schichtel, S. Kreidenweis, and J. Collett (2012) Investigating types and sources of organic aerosol in the Rocky Mountains using aerosol mass spectrometry, presented at the AGU Fall Meeting, San Francisco, CA, Dec. 3-7, 2012

Sullivan, Amy P., S. M. Kreidenweis, B. A. Schichtel, and J. L. Collett Jr. (2012) Smoke marker ratios from controlled laboratory burns vs. prescribed burns and wildfires, presented at the American Meteorological Society Annual Meeting, New Orleans, LA, Jan. 23-26, 2012.